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(54) Title: PRASEODYMIUM CONTAINING COBALT CATALYSTS FOR THE FISCHER-TROPSCH PROCESS

(57) Abstract

The specification discloses a Fischer-Tropsch catalyst, a process for making the catalyst and a process for making liquid hydrocarbons using the catalyst. The catalyst comprises cobalt and praseodymium supported on a zeolite of the ZSM-5 family. A process for making the catalyst comprises impregnating the zeolite with a salt of praseodymium and a solution of a cobalt carbonyl in an organic solvent, evaporating the organic solvent and calcining the catalyst. Dimethyl ether is a suitable organic solvent. The process for making liquid hydrocarbons involves passing a synthesis gas over the catalyst at a temperature in the range from 200 °C to 300 °C.

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PRASEODYMIUM CONTAINING COBALT CATALYSTS FOR THE FISCHER-TROPSCH PROCESS

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 which are suitable for use as liquid fuels from a natural gas derived synthesis gas.

BACKGROUND

The Fischer-Tropsch process for hydrocarbon production is ell known and described in various texts such as "The Fischer-Tropsch and Related Synthesis" by H.H. Storch, N. Golumbic and R.B. Anderson (John Wiley and Sons, New York, 18951). 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 alcohols and olefins. This high n-alkane content is particularly desirable when a distillate product is targeted due to improved cetane numbers and smoke points.

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

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

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 production is being targeted from a natural gas derived synthesis gas, in light of points (i) to (v) above, cobalt catalysts would be preferred. Further improvement would result if methane selectivities could be further reduced.

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

$$W_n + N \quad ^{n-1}(1- \quad)^2$$

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 low carbon fractions are generally "higher 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 low olefins (especially ethylene) towards chain growth.

The type of hydrocarbon product produced is dependent on the Fischer-Tropsch active metal (as previously described), the nature of the support materials, and also operating conditions. The "classic" cobalt catalysts as described in Storch et al., which are supported on kieselguhr, produce predominantly n-alkanes. Similar products result form silica, alumina and silica-alumina supported cobalt catalysts. This high n-alkane content is desirable for wax and distillate production (as previously described), but not gasoline production as linear hydrocarbons have poor octane ratings.

When gasoline production is targeted, zeolite such as Zeolite Y and ZSM-5 can be used as supports, to produce enhanced levels of aromatics and/or branched hydrocarbons, which impart a higher octane rating to the product.

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-stabilised 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.

When production of both gasoline and distillate is targeted zeolite supported cobalt catalysts can be operated under conditions which limit the product to essentially the distillate range and produce a naphtha fraction with enhanced branching over that of the corresponding distillate fraction, as described in our Australian Patent Application no. 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). Th use of thoria (ThO_2), magnesia (mgO), beryllium oxide (BeO), alumina (Al_2O_3), uranium oxides (UO_2 and U_3O_8) and manganese (Mn) as such promoters for cobalt Fischer-Tropsch catalysts is well known, and has been described in Storch et al.

Australian Patent Application 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.

Other additives which give further improvements to the activity and selectivity of cobalt Fischer-Tropsch catalysts have also been identified.

One of these additives is chromium, which, as described in our co-pending Australian patent application

AU 62238/90, when added to cobalt supported on ZSM-5 type zeolite catalyst formulations promoted or unpromoted, gives catalysts of increased Fischer-Tropsch activity, reduced methane and increased liquid range hydrocarbon selectivities, whilst maintaining high levels of branching (and hence high octane number) in the naphthas produced.

Another identified additive is scandium, which is the subject of our co-pending international patent application number PCT/AU92/00457. When added to promoted or unpromoted supported cobalt catalyst compositions, scandium produces catalysts of increased Fischer-Tropsch activity which give an overall increased production of higher hydrocarbons.

For commercial operation, activity and selectivity to desired products must be maximised. This will minimise unwanted by-products and 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 minimising the number of stages in an overall process and by preferably alleviating the need for recycling, or otherwise reducing the amount of unconverted gas which needs to be recycled.

Thus there is considerable incentive to even further increase the activity of cobalt based Fischer-Tropsch catalysts, whilst maintaining a low selectivity or further lowering the 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 suitable for use as liquid fuels from a natural gas derived synthesis gas by providing a cobalt based Fischer-Tropsch catalyst of enhanced activity which increases the overall production of higher hydrocarbons.

SUMMARY OF THE INVENTION

It has now been found that addition of praseodymium to cobalt supported on ZSM-5 type zeolite catalyst compositions, promoted or unpromoted, produces catalysts of increased Fischer-Tropsch activity, which give an overall increase in the production of higher hydrocarbons. These catalyst formulations re particularly advantageous in Fischer-Tropsch process which aim to produce hydrocarbons which are suitable for use as liquid fuels form natural gas derived synthesis gases.

Accordingly in a first aspect of the invention provides a Fischer-Tropsch catalysts comprising cobalt and praseodymium supported on a zeolite selected from the ZSM-5 family.

In a second aspect the invention provides a process for producing liquid hydrocarbons comprising passing a synthesis gas comprising carbon monoxide and hydrogen over a catalyst comprising cobalt and praseodymium supported on a zeolite selected from the ZSM-5 family.

In a third aspect the invention provides a process for preparing a Fischer-Tropsch catalyst which process comprises impregnating a zeolite selected from the ZSM-5 family with a salt of praseodymium and a solution of a cobalt carbonyl in an organic solvent, evaporating the solvent, and calcining the catalyst.

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 preferably 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 catalyst. This cobalt is an essential part of the catalyst composition, and is preferably present in an amount of 1 to 50 weight percent based on the total weight of the catalyst composition.

As liquid fuels are being targeted, gasoline or gasoline and distillate is the desired product. The production of a high octane number gasoline fraction requires an acidic support in the catalyst composition. Zeolite of reasonably high silica to alumina ratios, i.e. 10 or higher, fulfil this requirement. These zeolites are exemplified by the ZSM-5 family which include ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-38 and other similar materials. Particularly favoured are the small crystal variations of these ZSM-5 type zeolites, as described in our co-pending Australian patent application AU 44747/89, in which ZSM-5 type zeolites of 5 m or less, or more preferably 1 m or less, are used as supports to produce a highly branched, and hence high octane, liquid hydrocarbon product. The ZSM-5 type zeolite is preferably present in the formulation in an amount of from 10 to 98 percent of the catalyst.

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

Praseodymium is used as an additive to the catalyst formulation to achieve enhanced catalyst activity and higher hydrocarbon production. For the purposes of the invention praseodymium 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 praseodymium may be loaded onto the support by any of the methods known to those skilled in the art. These methods included:

(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 sith 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 use in synthesis gas conversion, the catalyst of the invention is 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 250-350°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. However, there are some limitations on the temperature range used if the catalyst of this invention is to be effective. In order for the zeolite to be effective in producing branched hydrocarbons the system must be at a temperature at which oligomerisation and isomerisation reactions can occur on the zeolite. This places a lower limit of 200°C on the reaction. As the temperature is increased undesirable side reactions begin to occur, including cracking, methanation, carbon deposition and the water gas shift. At high temperatures of 300°C and above, so much methane, carbon and carbon dioxide are produced that any benefits derived from the addition of the praseodymium to the catalyst formulation would note be realised. Preferably the reaction temperature is maintained in the range from 220 to 280°C and most preferably in the range from 220 to 260°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}.

The following comparative examples illustrate the preferred embodiments of the invention.

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

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

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

The above two resulting solutions were mixed, well stirred and made up to 45 l with water. The mixture was then charged to an autoclave and maintained at 100°C for 6 days, then 170°C for two days. The resulting product was filtered, washed and dried. It was then examined by X-ray diffraction and found to display the typical X-ray diffraction pattern of ZSM-5.

Prior to use in the following preparations calcined at 550°C, washed twice with 1 M 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 0.5 M hydrochloric acid, dried and calcined at 550°C.

Examples 2 to 6: Preparation of ZSM-5 Supported Catalysts Using Cobalt Carbonyl as the Cobalt Source Catalysts

The ZSM-5 zeolite MA21 was impregnated with appropriate amounts of cobalt carbonyl and chromium, scandium or thorium nitrates (where appropriate) dissolved in dimethyl ether, so as to make the desired catalyst formulations. An aqueous praseodymium nitrate solution (3.9% Pr) was used as the praseodymium source. 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:

2.	FT672	75Co:1000 MA21
3.	FT675	75Co:5Th:1000 MA21
4.	FT673	75Co:5Cr:1000 MA21

5. FT674 75Co:5Sc:1000 MA21
6. FT680 75Co:5Pr:1000 MA21

Examples 7-14: Preparation of ZSM-5 Supported Catalysts Using Cobalt Nitrate as the Cobalt Source

The ZSM-5 zeolite MA21 was impregnated with the appropriate amounts of aqueous solutions of cobalt and praseodymium, chromium, scandium and/or thorium nitrates as appropriate. The impregnated zeolites were stirred under vacuum for 30 minutes, dried in a microwave oven, and then 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:

7. FT643 75Co 1000 MA21
8. FT636 75Co:5Pr:1000 MA21
9. FT637 75Co:5Th:1000 MA21
10. FT695 75Co:5Pr:5Th:1000 MA21
11. FT647 75Co:5Cr:1000 MA21
12. FT697 75Co:5Pr:5Cr:1000 MA21
13. FT646 75Co:5Sc:1000 MA21
14. FT696 75Co:5Pr:5Sc:1000 MA21

Examples 15-22 Preparation of Catalysts Not supported on ZSM-5 Type Zeolites

Commercially obtained mordenite (Norton Z-900H), zeolite Y (Linde LZ-Y82), kieselguhr (Ajax Labchem) and silica (Matrex 84160) were impregnated with appropriate amounts of aqueous solutions of cobalt nitrate, and praseodymium 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 four hours. The resulting catalysts, identified by their "FT" code names, and their desired compositions in parts by weight were as follows:

15. FT662 75Co:1000 mordenite

16.	FT690	75Co:5Pr:1000 mordenite
17.	FT664	75Co:1000 zeolite Y
18.	FT691	75Co:5Pr:1000 zeolite Y
19.	FT666	75Co:1000 keiselguhr
20.	FT692	75Co:5Pr:1000 keiselguhr
21.	FT639	75Co:1000 silica
22.	FT693	75Co:5Pr:1000 silica

The catalysts of Example Nos. 2-22 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 350°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 three 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 rate 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, hydrocarbons containing two to five carbon atoms and hydrocarbons containing six or more carbon atoms (the liquid plus wax range), respectively. The C_2+ production represents the mg of carbon from the carbon monoxide feed which ends up as C_2+ hydrocarbons per g of catalyst per hour of running time (averaged over the whole run). The liquid plus wax production represents the number of grams of hydrocarbons containing 6 or more carbon atoms produced from every cubic metre of synthesis gas feed. 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-Tropsch Catalysts With and Without Praseodymium in Their Formulations

(2:1 H_2:CO Synthesis Gas, 240°C, 2MPa, GHSV = $1000hr^{-1}$)

Catalyst (Example No.)	Catalyst Composition	% CO Conversion (Averaged after 30 hours on stream)	C Selectivity (wt%)				Liquid plus wax production (g/m^3 of feed)
			CH_4	CO_2	C_2-C_5	Liquid plus wax (>C_5)	
2	75Co:1000 MA21 (ZSM-5)	49.8	10.0	0.1	5.6	84.4	87.4
3	75Co:5Th:1000 MA21 (ZSM-5)	70.0	7.6	1.0	4.2	87.2	126.6
4	75Co:5Cr:1000 MA21 (ZSM-5)	74.2	7.1	1.3	3.9	87.7	135.2
5	75Co:5Sc:1000 MA21 (ZSM-5)	71.0	7.7	1.0	4.7	87.2	128.6
6	75Co:5Pr:1000 MA21 (ZSM-5)	82.3	9.0	2.1	4.3	84.6	144.6
7	75Co:1000 MA21 (ZSM-5)	51.8	9.3	0.7	7.5	82.5	88.7
8	75Co:5Pr:1000 MA21 (ZSM-5)	56.8	8.9	1.1	7.3	82.7	97.5
9	75Co:5Th:1000 MA21 (ZSM-5)	62.4	12.0	1.1	7.5	79.4	103.0
10	75Co:5Pr:5Th:1000 MA21 (ZSM-5)	65.7	11.6	1.4	7.8	79.2	108.0
11	75Co:5Cr:1000 MA21 (ZSM-5)	59.7	8.9	1.0	5.9	84.2	104.4
12	75Co:5Pr:5Cr:1000 MA21 (ZSM-5)	67.4	9.9	2.0	6.6	81.5	114.1
13	75Co:5Sc:1000 MA21 (ZSM-5)	60.3	8.0	1.1	6.2	84.7	106.0
14	75Co:5Pr:5Sc:1000 MA21 (ZSM-5)	66.8	10.3	1.4	6.3	82.0	113.7
15	75Co:1000 mordenite	17.8	10.4	0.1	6.8	82.7	30.6
16	75Co:5Pr:1000 mordenite	6.1	13.9	0.0	4.5	82.1	10.3
17	75Co:1000 zeolite Y	8.1	11.6	0.0	5.7	82.7	14.0
18	75Co:5Pr:1000 zeolite Y	8.2	12.0	0.0	7.9	80.1	13.6
19	75Co:1000 kieselguhr	18.2	8.7	0.0	7.9	83.4	31.5
20	75Co:5Pr:1000 kieselguhr	12.8	9.4	0.0	16.7	73.9	19.6
21	75Co:1000 silica	45.2	8.9	4.8	5.6	80.7	75.8
22	75Co:5Pr:1000 silica	18.1	4.6	0.0	12.3	83.1	31.3

The results presented in the Table clearly illustrate one aspect of the invention (i.e. the provision of a cobalt based Fischer-Tropsch catalyst of enhances activity which increases the overall production of higher hydrocarbons).

The first series of catalysts, examples 2-6, which were prepared using cobalt carbonyl as the cobalt source, show the effect of known promoters/additives, as well as praseodymium on cobalt/ZSM-5 catalyst formulations. It can be seen that the effect of additional thorium, chromium, scandium and praseodymium has been to significantly improve activity (as methane selectivity and increasing selectivity to liquid and wax range hydrocarbons). The improvement in activity by the addition of praseodymium was much greater than by the addition of either thorium, chromium or scandium. The effect of this increase in activity and selectivity improvement was to significantly increase the production of liquid and was range hydrocarbons (as measured by the g of hydrocarbons produced/m^3 of synthesis gas feed).

The second series of catalysts, examples 7-14, were prepared using cobalt nitrate as the cobalt source. Once again the addition of thorium, chromium, scandium and praseodymium was found in all instances to increase catalyst activity. However, for this series of catalysts praseodymium was less effective than the other three additives. But when praseodymium was added to catalysts already promoted with thorium, chromium or scandium, even further improvement in activity was obtained, resulting in greater production of liquid and wax range hydrocarbons.

The third series of catalyst, examples 15-22, examines other support materials including mordenite, zeolite Y, kieselguhr and silica. From the results presented it can be seen that praseodymium is not an effective additive for such supported catalysts, and for the improved higher capacity catalyst of our invention to result, a ZSM-5 type zeolite is required as a support material.

The other aspect of the invention is the provision of an improved process for the production of hydrocarbons suitable for use as liquid fuels.

The suitability of the product from a catalyst of our invention is illustrated in Table 2, which presents the results of a gas chromatographic investigation of the liquid hydrocarbon product from the catalyst Example 6(i.e. 75Co: 5Pr:1000 MA21 prepared using cobalt carbonyl).

From the simulated distillation given in this Table, it can be seen that the hydrocarbon distribution is very desirable for liquid fuel production with only 8.1% wt of the product boiling higher than the distillate range (62.6% of the product falls into the gasoline boiling range, 11.8% into the aviation fuel boiling range and 17.5% into the distillate boiling range.

The proportions of identified n-alkenes and unidentified compounds in the fuel fractions gives us an indication of the degree of hydrocarbon branching into the product. It can be seen that the proportions of n-alkenes in the product is low especially in the lower fuel fractions. There are also very few n-alkanes in the product. It is known from NMR experiments that there are negligible amounts of aromatics in the product. It can thus be deduced that a high degree of branching is present and the naphthas would be of a much higher octane rating than standard Fischer-Tropsch naphthas consisting predominantly of n-alkanes.

TABLE 2: Results of Gas Chromatographic Analysis of Liquid Hydrocarbon Product from Catalyst Example 6 75Co:5Pr:1000 MA21) Operating Conditions: 240°C, 02MPa, GHSV 1000 hr^{-1}, 2:1 H_2:CO synthesis gas

	FUEL FRACTION				
	Light Gasoline C_4-C_9	Heavy Gasoline C_{10}-C_{11}	Aviation Fuel C_{12}-C_{13}	Distillate C_{14}-C_{18}	Heavy C_{19}-C_{29}
Simulated Distillation (wt%)	47.7	14.9	11.8	17.5	8.1
Proportions of identified n-alkanes	0.17	0.18	0.18	0.19	0.23
Proportions of identified n-alkenes	0.19	0.13	0.13	0.10	0.0
Proporations of unidentified compounds	0.63	0.69	0.69	0.71	0.77

Table 3 shows the results of operation of a catalyst of our invention under different temperatures, pressure and space velocities as per our invention. It can be seen that by appropriate selection of these parameters within the ranges claimed, very high yields of liquid and wax range hydrocarbons (>100g/m^3 synthesis gas feed) can be obtained.

TABLE 3: Carbon Monoxide Conversion, Product Selectivities and Higher Hydrocarbon Production for Catalyst FT680 (75Co:5Pr:1000 MA21) Under Different Operating Conditions

(Example No.)	Operating Conditions	% CO Conversion (Averaged after 30 hours on stream)	C Selectivity (wt%)				Liquid plus wax production (g/m^3 of feed)
			CH_4	CO_2	C_2-C_5	Liquid Plus wax (>C_5)	
23	220°C, 2MPa, GHSV 250hr^{-1}	81.7	5.4	2.5	3.56	88.5	150
24	220°C, 2MPa, GHSV 500hr^{-1}	61.9	9.1	1.0	6.4	83.5	107
25	220°C, 2MPa, GHSV 1000hr^{-1}	35.5	8.6	0.0	11.8	79.6	59
26	240°C, 2MPa, GHSV 250hr^{-1}	90.5	6.8	13.4	4.6	75.2	141
27	240°C, 2MPa, GHSV 500hr^{-1}	91.1	5.3	5.8	4.2	84.7	160
28	240°C, 2MPa, GHSV 1000hr^{-1}	87.9	5.3	4.5	5.0	85.2	160
29	240°C, 1MPa, GHSV 1000hr^{-1}	85.7	5.8	4.6	8.3	81.3	145
30	240°C, 1.5MPa, GHSV 1000hr^{-1}	90.6	5.1	5.5	5.8	83.6	157
31	240°C, 2.5MPa, GHSV 1000hr^{-1}	80.6	6.7	4.1	8.1	81.1	136
32	240°C, 3.0MPa, GHSV 1000hr^{-1}	71.5	7.8	2.7	6.5	83.0	123
33	240°C, 3.5MPa, GHSV 1000hr^{-1}	71.0	8.6	4.1	8.3	79.0	117
34	260°C, 2MPa, GHSV 250hr^{-1}	98.7	7.2	16.8	5.4	70.6	145
35	260°C, 2MPa, GHSV 500hr^{-1}	99.5	6.8	14.0	4.4	74.8	155
36	260 C, 2.5MPa, GHSV 1000hr-1	96.7	6.8	10.5	4.5	78.2	157
37	280°C, 2MPa, GHSV 500hr^{-1}	99.9	9.3	18.5	6.5	65.7	136
38	280°C, 2MPa, GHSV 1000hr^{-1}	99.9	10.4	19.0	6.6	64.0	132

CLAIMS

1. A Fisher Tropsch catalyst comprising cobalt and praseodymium supported on a zeolite selected from the ZSM-5 family.

2. A Fischer Tropsch catalyst according to claim 1 wherein cobalt comprises from 1 to 50% by weight of the catalyst.

3. A Fischer Tropsch catalyst according to claim 1 or claim 2 wherein the zeolite is selected from a group consisting of ZSM-5, ZSM-11, ZSM-12, ZSM-35 and ZSM-38.

4. A Fischer Tropsch catalyst according to claim 1 wherein the zeolite comprises from 10 to 98 per cent by weight of the catalyst.

5. A Fischer Tropsch catalyst according to claim 1 wherein the zeolite has a crystal size of 5 micron or less.

6. A Fischer Tropsch catalyst according to claim 1 wherein the zeolite has a crystal size of 1 micron or less.

7. A Fischer Tropsch catalyst according to Claim 1 wherein praseodymium comprises from 0.01 to 25 per cent by weight of the catalyst.

8. A Fischer Tropsch catalyst according to Claim 1 wherein praseodymium comprises from 0.05 to 5 per cent by weight of the catalyst.

9. A Fischer Tropsch catalyst according to Claim 1 wherein the catalyst includes from 0.01 to 25 per cent by weight of a promoter.

10. A Fischer Tropsch catalyst according to Claim 1 wherein the catalyst includes from 0.05 to 5 per cent by weight of a promoter.

11. A catalyst according to Claim 9 or Claim 10 wherein the promoter is selected from a group consisting of thoria, magnesia, beryllium oxide, alumina, uranium oxides, manganese, chromium and scandium.

12. A process for producing liquid hydrocarbons, the process comprising passing a synthesis gas containing a substantial proportion of carbon monoxide and hydrogen over a Fischer Tropsch catalyst according to any one of claims 1 to 11.

13. A process according to Claim 12 wherein the synthesis gas has a hydrogen to carbon monoxide molar ratio in a range from 1 to 3.

14. A process according to Claim 12 or Claim 13 wherein the synthesis gas is passed over the Fischer Tropsch catalyst at a temperature in a range from 220°C to 280°C.

15. A process according to Claim 12 or Claim 13 wherein the synthesis gas is passed over the Fischer Tropsch catalyst at a temperature in a range from 220°C to 260°C.

16. A process for preparing a Fischer Tropsch catalyst according to any one of claims 1 to 11, the process comprising impregnating the zeolite with a solution of a cobalt carbonyl and a salt of praseodymium in an organic solvent, evaporating the organic solvent and calcining the catalyst.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU93/00067

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.^{5} B01J 29/34, 29/36, C07C 1/04

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 : B01J 29/34, 29/36, C07C 1/04

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)
CHEMICAL ABSTRACTS : (CO or COBALT) and (ZSM: or PENTASIL or MFI:) and (PR or PRAESEODYMIUM or RARE EARTH or LANTHANIDE)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	EP,A, 434063 (TOYOTA JIDOSHA KABUSHIKI KAISHA) 26 June 1990 (26.06.90) See claims, example 17.	1-3,7-11
A	AU,A, 36377/84 (COMPAGNIE FRANCAIS DE RAFFINAGE) 12 June 1986 (12.06.86) See claims.	1-16
A	US,A, 4605680 (BEUTHER et al) 12 August 1986 (12.08.86) See abstract, claims and col. 2 lines 24-38.	1-16

☒ 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 25 May 1993 (25.05.93)	Date of mailing of the international search report 28 MAY 1993 (28.05.93)
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.J. BROXAM Telephone No. (06) 2832133

INTERNATIONAL SEARCH REPORT

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	**Citation of document, with indication, where appropriate of the relevant passages**	**Relevant to Claim No.**
A	AU,A, 44747/89 (THE BROKEN HILL PROPRIETARY COMPANY LIMITED) 31 May 1990 (31.05.90) See claims.	1-16
A	US,A, 4842720 (MOOREHEAD) 27 June 1989 (27.06.89) See claim 1.	1-16
A	DE,A, 4219690 (INSTITUT FRANCAIS DU PETROLE) 24 December 1992 (24.12.92) See claims.	1-16

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU93/00067

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		
EP 434063	AU 68281/90 JP 3196842	CA 2032799 JP 4040239	JP 3193139 JP 4215846
AU 36377/84	EP 148048 ZA 8409560	FR 2556237	JP 60139342
AU 44747/89	CA 2003394 US 5104902	GB 2225255	NZ 231449
US 4842720	US 4828813	US 4776946	US 4782166
DE 4219690	FR 2677992	GB 2258414	NL 9201084

END OF ANNEX