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(54) Title of the Invention: **Fischer-tropsch synthesis**
Abstract Title: **Fischer-Tropsch catalyst with an alkaline earth metal content of less than 2000 ppm**

(57) A process for preparing a Fischer-Tropsch catalyst is characterised by a porous support material selected from alumina, titania, zirconia, zeolites, carbonaceous material and mixtures thereof, having an alkaline earth metal content of less than 1000 ppm. An example of the alkaline earth metal is calcium or magnesium. The support material is impregnated with cobalt source, such as cobalt nitrate, cobalt carbonate, cobalt (hexa)amine salt(s) and organic cobalt compounds, which contributes an additional alkaline earth metal content of less than 1000 ppm in the final catalyst. The impregnated support is calcined at a temperature of at least 200°C to yield a cobalt oxide catalyst with an alkaline earth metal content of less than 2000 ppm. Also disclosed is a catalyst prepared using the method and a process for producing hydrocarbons using the catalyst.

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

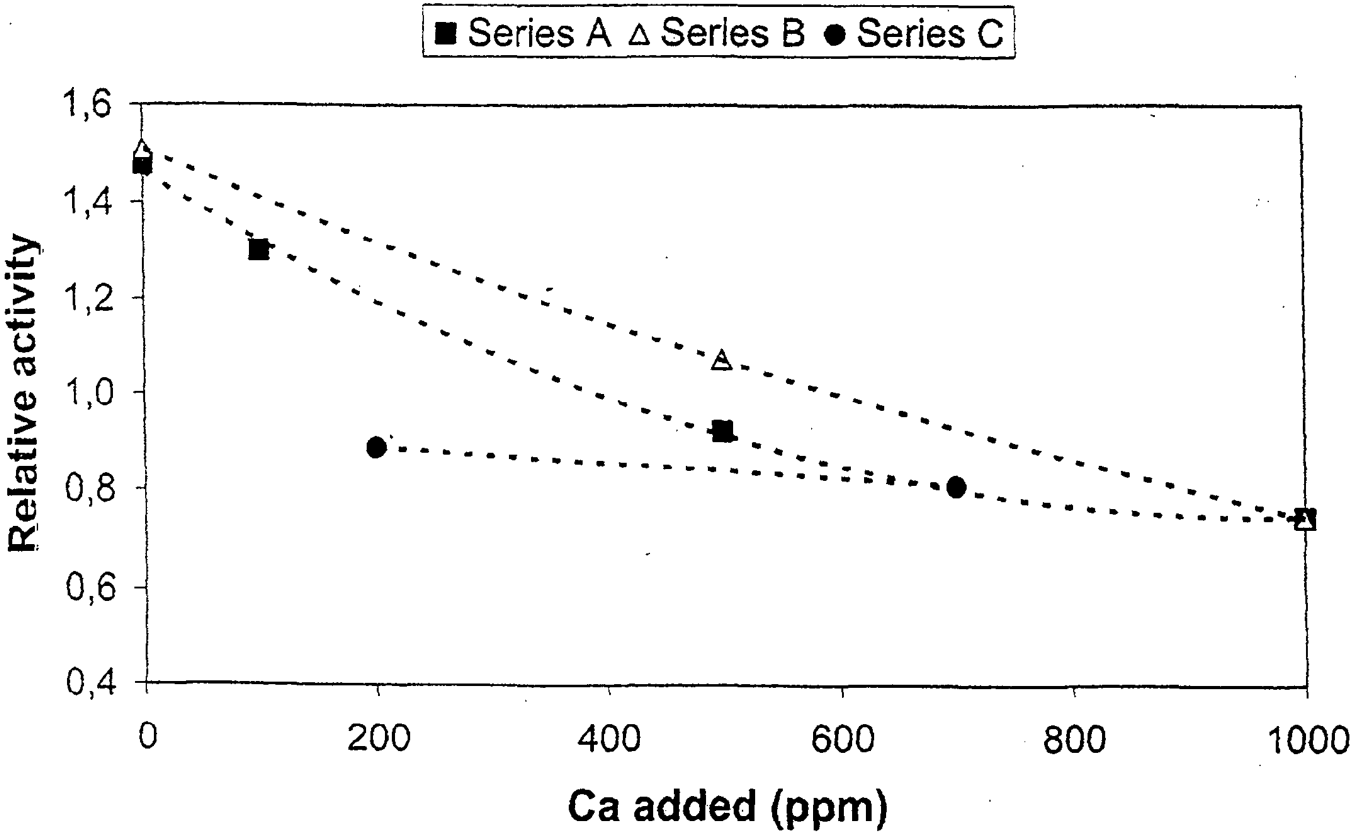

Figure 1. Relative activity vs. Ca amount for all catalysts.

FISCHER-TROPSCH SYNTHESIS

The Fischer-Tropsch (FT) reaction for conversion of synthesis gas, a mixture of CO and hydrogen, possibly also containing essentially inert components like CO_2, nitrogen and methane, is commercially operated over catalysts containing the active metals iron (Fe) or cobalt (Co). However, the iron catalysts exhibit a significant shift reaction, producing more hydrogen in addition to CO_2 from CO and steam. Therefore, the iron catalyst will be most suited for synthesis gas with low H_2/CO ratios (<1.2) e.g. from coal or other heavy hydrocarbon feedstock, where the ratio is considerably lower than the consumption ration of the FT reaction (2.0 - 2.1).

The present invention is concerned with Co-based catalysts, in particular, supported Co-based catalysts. A variety of products can be made by the FT-reaction, but from supported cobalt, the primary product is long-chain hydrocarbons that can be further upgraded to products like diesel fuel and petrochemical naphtha. By products can include olefins and oxygenates.

Normally, the active FT metal is dispersed on a solid, porous support. Thereby, a large portion of the Co is exposed as surface atoms where the reaction can take place. The support can be alumina, titania or silica, but generally speaking, other oxides like zirconia, magnesia, silica-alumina, various aluminates, zeolites as well as carbon, and mixtures thereof, have been used. Sometimes the support contains modifying components ingredients, e.g. of compounds of silicon, lanthanum, titanium and zirconium.

To enhance the catalyst performance, e.g. by facilitating reduction of cobalt oxide to cobalt metal prior to the FT synthesis, it is common to add different promoters, and rhenium, ruthenium, platinum, iridium and other transition metals can all be beneficial. Alternatively, the promoter may be alkali metals or alkaline earth metals. It has been discovered that certain amounts of alkali metals (K, Na, Cs, Rb, Li, Cs) have a significant impact on the catalytic performance of cobalt supported catalysts. US 4880763 (Eri et al) reported that addition of an alkali to the catalyst serves to increase the average molecular weight of the product, as shown by an increase in the Schulz-Flory α value. However, the activity decreased as the alkali content increased. Thus, for any particular situation, there is an optimum alkali level that balances the desired average product molecular weight and catalyst activity. In WO2006/010936 A1, Rytter and Eri described the effect of Na on cobalt catalysts. A clear, negative effect on the activity was discovered in the range 0 to 500 ppm.

Luo and Davis (Fischer-Tropsch synthesis: Group II alkali-earth metal promoted catalysts, Appl. Catal. A 246 (2003) 171) compared the effect of alkaline earth metals, among them calcium, on the Fischer-Tropsch synthesis performance over an iron-based catalyst in a continuous stirred tank reactor (CSTR). They found that the addition of calcium as a promoter has a negative effect on the activities of both Fischer-Tropsch synthesis and the water-gas shift reaction. However Ca generated a higher FTS alpha value (chain growth probability) than the un-promoted catalysts.

An FT catalyst is operated in an industrial process in which synthesis gas (syngas; a gas mixture of H_2 and CO which possibly also can contain other gases e.g. CO_2, CH_4, light hydrocarbons, steam, N_2 etc.) is converted to hydrocarbons by the FT-process. Syngas can be prepared in a number of ways such as autothermal reforming (ATR), methane steam reforming (MSR) sometimes called tubular reforming, partial oxidation (POx), catalytic partial oxidation (CPO) and gasification. The latter is primarily used for other feeds than natural gas, typically coal or biomass. Combinations and optimisations of these processes are also possible, as in combined reforming, heat exchanged reforming, compact reforming and gas heated reforming.

Following syngas generation, frequently the gas is cooled down in a waste heat boiler (WHB), also called process gas cooler, and further energy can be extracted from the gas by using a superheater to enhance the temperature in generated steam. Before the gas enters the FT-reactor, the gas may be cleaned of impurities like ammonia and sulphur and various carbonyl compounds using guard beds. Both in the syngas generation and in the cleaning process, refractory or ceramic materials are frequently employed. These can consist of mixtures of various metal oxides. It has now been discovered that great care must be taken as to the composition of these materials.

In Catalyst Handbook (Catalyst Handbook, 2nd edition., M.V. Twigg, editor, Wolfe Publishing, London 1989), poisoning by impurities is described on pages 77-81. However, the effect of calcium is not described and sodium only in relation to hydrocracking catalysts. Furthermore, carryover of materials from the syngas or gas cleaning sections is not described. It has now been discovered that great care must be taken to avoid such carryover. Carryover through the syngas can be enhanced by the presence of steam. Certain materials used in syngas generation have been described by R. Stevens and U. R. Desai, Qatar Fertilizer Company, in the proceedings of Nitrogen + Syngas 2008 conference conducted in Moscow, 20-23 April 2008. These include alumina lumps used in the upper part of the secondary reformer (ATR) that contain 0.7 wt% NaO, use of sodium aluminate, NaAl11O18 and a ceramic lining (donuts) that contains 17 wt% CaO.

It is generally an object of the present invention to provide an improved supported cobalt-based F-T catalyst. Further, it is an object of the present invention to avoid contamination of the catalyst during operation in an XTL plant, XTL being GTL (Gas to liquids), BTL (biomass to liquids) or CTL (coal to liquids). Contamination will lead to reduced catalytic performance, in particularly lower activity, resulting in need to replace the catalyst earlier than otherwise necessary.

According to one aspect of the invention, there is provided a process for the preparation of a catalyst for a Fischer-Tropsch synthesis reaction, which comprises the following steps:

taking an initial porous support material selected from alumina, titania, zirconia, zeolites, carbonaceous material and mixtures thereof having an alkaline earth metal content of less than 1000 ppm;

impregnating the initial support material with a source of cobalt which contributes an additional alkaline earth metal content of less than 1000 ppm in the final catalyst; and

heat treating the impregnated support material at a temperature of at least 200°C to yield a cobalt oxide catalyst;

whereby the final catalyst has an alkaline earth metal content of less then 2000 ppm.

The preparation of a cobalt catalyst involves impregnation of a support with a solution of a cobalt precursor, both of which may be a source of impurities. Water is a common choice as solvent. Water commonly contains significant amounts of minerals such as calcium, magnesium, and sodium. Controlling these elements is often necessary to meet the requirements of medical, pharmacology, chemical and industrial applications. Methods include distillation, filtration, water softening, reverse osmosis, ultrafiltration, molecular stripping, deionisation, and carbon treatment.

In general, the invention is directed to the use of a Fischer-Tropsch catalyst in such a way that it is not exposed to unwanted components such as alkali and alkaline earth metals.

As has been shown the catalyst should contain between 10 and 2000 ppm of alkaline earth or alkali metal, preferably between 20 and 1000 ppm, more preferably between 20 and 400 ppm. It is therefore important that the feed gas contains a correspondingly low content of these metals. A simplified calculation can be performed assuming an average operation of 10 000 hours (i.e. total of 20 000 hours between catalyst replacements), a productivity of 1.0 kg hydrocarbon product per kg catalyst per hour, and that all alkali or alkaline earth metals is picked up by the FT-catalyst. This surprisingly means that the alkali or alkaline earth content in the syngas feed should be as low as 100 ppb by weight (relative to kg CO in syngas) to yield below 2000 ppm on the catalyst. In other words, the syngas, frequently referred to as make-up gas in operations with a recycle of unconverted gas, should contain between 0.1 and 100 ppb, preferably between 0.5 and 50 ppb, more preferably between 0.5 and 20 ppb of alkali or alkaline earth as an average.

Such alkali or alkaline earth metal poisoning often takes place as a malfunction or upset in the operation, showing as a steep decline in catalyst activity over a shorter period of time, e.g. 10-1000 hours. Therefore, the alkali or alkaline earth metal content over such a period with enhanced poisoning should be kept in the range 5 ppb and 100 ppm, preferably between 10 ppb and 50 ppm, more preferably between 10 ppb and 20 ppm. Further, strict control of alkali and alkaline earth material should be in place during selection of any ceramic lining, reformer catalyst and guard bed materials, in addition to the content in process water and make-up water.

By controlling the levels of alkali and alkaline earth metals, an improved performance is achieved. The alkaline earth metals are those in Group 2 of the Periodic Table of the Elements and the invention is particularly concerned with calcium and magnesium, as well as sodium and potassium of Group 1.

Preferably, the heat treating step is a calcination step at a temperature in the range 200 to 600°C. The support material may be selected from alumina, silica, titania, zicinia, magnesia and zeolites and zeolite like materials, carbon in a variety of forms including carbon nanofibers and tubes, and mixtures and reaction products thereof, in any amorphous or crystallographic form, and optionally modified. The alumina may be γ-alumina, any transition alumina, α-alumina, boehmite, aluminium hydroxide or mixtures thereof.

The most preferred method of preparing alumina for the support is the alkoxide route, since it provides a high degree of purity. The precipitation method may also be adopted and if so, the precipitated alumina should be washed with excess water several times to remove various impurities, such as alkali metals, alkali earth metals and sulphates. The water used should have a level of impurities including those mentioned of no more than 20 ppm. After washing, the alumina is preferably dried and optimally calcined at a temperature in the range 200 to 600°C.

Preferably, the initial alumina support material includes a stabiliser which preferably comprises lanthanum.

The impregnation step may comprise melt impregnation, ion-exchange, deposition/precipitation or more preferably, incipient wetness impregnation. In the case of the incipient wetness method, the solvent may be an organic solvent or more preferably water. There may be more than one impregnation step.

It has been found, surprisingly, that some alkaline-earth metals affect the Fischer-Tropsch synthesis using cobalt catalyst in an adverse manner. In particular, amounts of 100 ppm (mg/l) Ca using incipient wetness impregnation has a clear negative effect on the activity of the catalyst. Larger amounts of calcium (200-1000 ppm) have a very strong detrimental effect. These quantities are not unusual for many raw (tap) water sources. For instance, hard water contains from 80 - 120 ppm Ca.

Where water is used in the impregnations and any other process steps of the present invention, the water may be treated in some way such as those indicated to ensure the stipulated limits of alkaline earth metal. Preferably, the water is distilled or de-ionised water.

Preferably, the impregnation step comprises an incipient wetness treatment in which an aqueous solution of cobalt metal is mixed with the modified alumina support material until the pores are filled and the impregnated support material is then dried, prior to calcination. Preferably the amount of aqueous solution used in the impregnation is 0.2-2 times larger then the measured pore volume of the catalyst support.

Preferably, the method includes additionally impregnating or co-impregnating the initial alumina support material with a promoter. Preferably, the promoter comprises platinum or rhenium. The preferred range of platinum promoter is between 0.001 and 0.5 wt%, preferably between 0.01 and 0.1 wt%. For Re, the preferred range is between 0.01 and 5 wt%, preferably between 0.1 and 1.0 wt%.

Preferably, where the promoter is rhenium the source of rhenium is preferably selected from perrhenic acid ($HReO_4$), ammonium perrhenate, rhenium halide(s) and rhenium carbonyl(s).

The source of cobalt may be selected from cobalt nitrate ($Co(NO_3)_2$), cobalt carbonate(s), cobalt (hexa) amine salt(s) and organic cobalt compounds. After the calcination step, the alumina-supported catalyst material is preferably activated.

Preferably, the impregnated support is dried at a temperature in the range 80 to 120°C. The subsequent calcination is preferably carried out at a temperature in the range 200 to 600°C.

After the calcination step, the alumina-supported catalyst material is preferably activated.

The activation step may comprise reduction of a substantial portion of the catalytically active metal compound present to the metal, and may be carried out by treating the catalyst material with a reducing gas, such as hydrogen and/or carbon monoxide, optionally mixed with an inert gas. The reduction may be carried out at an activation temperature of 250 to 500°C, preferably in the range of 300 to 450°C.

Prior to impregnating the support with a source of cobalt, the support material may be modified. This may be accomplished by first impregnating the support material with a source of divalent metal capable of forming a spinel compound (general formula $(X)(Y)_2O_4$, where X and Y are cations) with the support material.

Adding a di-valent metal compound to alumina followed by heat treatment can yield a spinel compound that then will constitute part of or the entire support. The divalent-metal can comprise cobalt, nickel, magnesium or zinc, but also other spinel forming elements can be used. The heat treatment can be at temperatures up to 900°C to give the spinel, but for certain purposes temperatures between 900 and 1400°C, typically 950-1250°C are advantageous.

The divalent metal is preferably therefore zinc, cobalt, magnesium or nickel and suitable sources may include corresponding nitrates. The divalent metal is preferably deployed in one or more impregnation steps using a suitable solvent, which may be an organic solvent, or more preferably, water.

As with the subsequent cobalt impregnation step previously described, the solvent preferably has an alkaline earth metal content of less than 20 ppm, and is preferably distilled or de-ionised water. The source of divalent metal preferably yields an additional alkaline earth metal content in the cobalt oxide catalyst of less than 500 ppm, preferably less than 300 ppm, more preferably less than 100 ppm.

After impregnation with the divalent metal, the support material is dried, washed (if required) and calcined in one or several steps up to 600°C, to decompose the source of a divalent metal essentially to form a divalent metal oxide, or a compound thereof. Thereafter, a high temperature calcination may be carried out at a temperature in the range 600 to 900°C to form the spinel. If a particularly high strength support is required, the last calcination may be carried out at an even higher temperature, in the range of 900 to 1400°C, preferably 950 to 1250°C.

This treatment with the divalent metal produces a modified support material which can then be impregnated with cobalt, as previously described. This high temperature treatment will reduce the porosity of the support to give a modified support with a surface area of below 80 m^2/g, typically 30-70 m^2/g, as well as a pore volume below 0.5 ml/g, typically between 0.15 and 0.4 ml/g. Although a high surface area is advantageous for maximizing the cobalt loading and dispersion and a high pore volume facilitates impregnation, the obtained values are perfectly acceptable in light of the much increased physical and chemical robustness of the modified support compared to the initial support.

It is also desirable to minimise the presence of alkali metals in the final catalyst, the alkali metals being those in Group 1 of the Periodic Table of the Elements. Preferably, therefore, the support material has an alkali metal content of less than 200 ppm, and any water used in the processing has an alkali metal content of less than 50 ppm, whereby the final catalyst has an alkali metal content of less than 250 ppm.

The invention also extends to a catalyst material made in accordance with the process of the invention.

The invention also extends to the use of such a catalyst in an F-T synthesis reaction, for example, carried out in a slurry bubble column reactor. In such a case, H_2 and CO are supplied to a slurry in the reactor, the slurry comprising the catalyst in suspension in a liquid including the reaction products of the H_2 and CO, the catalyst being maintained in suspension in the slurry at least partly by the motion of the gas supplied to the slurry.

The invention also extends to a process for the production of hydrocarbons which comprises subjecting H_2 and CO gases to a Fischer-Tropsch synthesis reaction in a reactor in the presence of a catalyst made by a process according to the invention. Preferably, the reaction is a three-phase reaction in which the reactants are gaseous, the product is at least partially liquid and the catalyst is solid, and in which the reaction is carried out in a slurry bubble column reactor. In such a case, the H_2 and CO may be supplied to a slurry in the reactor, the slurry comprising the catalyst in suspension in a liquid including the reaction products of the H_2 and CO, the catalyst being maintained in suspension in the slurry at least partly by the motion of the gas supplied to the slurry.

In such a process, make-up synthesis gas, comprising H_2 and CO, from a syngas generator is generally introduced into the system. Preferably, the make-up synthesis gas contains less than 100 ppb of an alkaline earth metal or alkali metal, for example, between 0.1 and and 100 ppb, preferably between 0.5 and 50, more preferably between 0.5 and 20 ppb, of an alkaline earth metal or alkali metal. The alkaline earth metal may be calcium and the alkali metal may be sodium.

Preferably, the make-up synthesis gas is passed through a guard bed of materials arranged to absorb components of alkali and alkaline earth metals from the synthesis gas stream, before the synthesis gas is subjected to a Fischer-Tropsch synthesis reaction.

Typically, the reaction temperature is in the range 190 - 250°C, preferably, in the range 200 - 230°C. Typically, the reaction pressure is in the range 10 - 60 bar, preferably, the range 15 to 30 bar.

Typically, the H_2/CO ratio of the gases supplied to the Fischer-Tropsch synthesis reactor is in the range 1.1 to 2.2, preferably, in the range 1.5 to 1.95. Typically, the superficial gas velocity in the reactor is in the range 5 to 60 cm/s, preferably, in the range 20 to 40 cm/s.

The product of the Fischer-Tropsch synthesis reaction may subsequently be subjected to post-processing. The post-processing may comprise de-waxing, hydro-isomerisation, hydro-cracking and combinations of these.

The invention may be carried into practice in various ways and will now be illustrated in the following non-limiting examples.

Catalyst preparation

For all series of catalyst, high purity chemicals and solvents were used in the preparation.

Series A

The catalysts of series A contain a normal amount of 20 wt% Co, 0.5 wt% Re and 0-1000 ppm Ca, as calculated assuming reduced catalysts with complete reduction of cobalt. The actual metal loading as determined by XRF or ICP may vary by up to 10%, e.g. for a catalyst with nominal loading of 20 wt%, the actual amount of cobalt can vary between 18 and 22 wt% of the total reduced catalyst weight. The catalysts were prepared by one-step incipient wetness co-impregnation of a γ-Al_2O_3 support (BET surface area = 182 m^2/g, pore volume = 0.73 cm^3/g) with aqueous solutions of cobalt nitrate hexahydrate, perrhenic acid and calcium nitrate tetrahydrate.

The freshly prepared catalysts were dried for 3 h at a temperature of 110°C. During drying, the catalysts were stirred every 15 min during the first hour and every 30 min during the next two hours. After impregnation and drying, the samples were calcined at 300°C for 16 h.

Series B

The catalysts of series B contain a nominal amount of 20 wt% Co, 0.5 wt% Re and 0-1000 ppm Ca, as calculated assuming reduced catalysts with complete reduction of cobalt.

The supports were prepared by one-step incipient wetness impregnation of a γ-Al_2O_3 support (BET surface area = 182 m^2/g, pore volume 0.73cm^3/g) with aqueous solutions of calcium nitrate tetrahydrate. The supports were dried for 3 h at 110°C. During drying, the supports were stirred every 15 min during the first hours and every 30 min during the next two hours. After impregnation and drying, the modified supports were calcined at 900°C for 10 h.

The catalysts were prepared by one-step incipient wetness co-impregnation of the Ca-containing supports (BET surface area = 107 m^2/g, pore volume = 0.68 cm^3/g) with aqueous solutions of cobalt nitrate hexahydrate and perrhenic acid. The catalysts were dried in the same manner as for series A. The catalysts were finally calcined at 300°C for 16 h.

Series C

The catalysts of series C contain a nominal amount of 20 wt% Co and 0.5 wt% Re, as calculated assuming reduced catalysts with complete reduction of cobalt. In addition, the catalysts contained 200 or 700 ppm of Ca originating from the alumina production process.

The catalysts were prepared by one-step incipient wetness co-impregnation of the Ca-containing supports (BET surface area = 107 m^2/g, pore volume = 0.68 cm^3/g) with aqueous solutions of cobalt nitrate hexahydrate and perrhenic acid. The supports were dried for 3 h at 110°C. During drying, the supports were stirred every 15 min during the first hour and every 30 min during the next two hours. The catalysts were finally calcined at 300°C for 16 h.

Series D

The catalysts of series D contain a normal amount of 20 wt% Co, 0.5 wt% Re and 0 or 500 ppm Ca, as calculated assuming reduced catalysts with complete reduction of cobalt. The catalysts were prepared by one-step incipient wetness co-impregnation of SiO_2 support with aqueous solutions of cobalt nitrate hexahydrate, perrhenic acid and calcium nitrate tetahydrate. The procedures were as for series A regarding impregnation, drying and calcination.

Series E

The catalysts of series E contain a normal amount of 12 wt% Co, 0.3 wt% Re and 0 or 400 ppm Ca or Mg, as calculated assuming reduced catalysts with complete reduction of cobalt. The catalyst support was in all cases essentially Ni-spinel prepared by one-step incipient wetness impregnation of nickel nitrate hydrate on the initial γ–alumina support followed by drying and calcination at a hold temperature in the range 400-500°C giving a support in nickel oxide on alumina form. This oxide support was subsequently exposed to high temperature treatment at 1000-1200°C for 10-30 min. in a rotary calciner giving a modified support, and one analysis shows a content of 29 ppm Ca and 18 ppm Mg, small amounts that come in addition to the 400 ppm introduced later by impregnation. The modified support has a pore volume of 0.23 ml/g and a surface area of 50 m^2/g.

The catalyst was prepared by co-impregnation of cobalt and rhenium salts in aqueous solution on to the modified support followed by drying and calcination giving a catalyst in oxide form. Ca or Mg then was deliberately added to this oxide catalyst by aqueous incipient wetness impregnation of the nitrate salts followed by drying for 3 h at 110°C. During drying, the supports were stirred every 15 min during the first hour and every 30 min during the next two hours. The Mg or Ca doped catalysts were finally calcined at 300°C for 16 h.

Hydrogen chemisorption

Hydrogen adsorption isotherms were recorded on a Micromeritics ASAP 2010 unit at 40°C. The samples were reduced *in situ* in flowing hydrogen at 350°C for 16 h. The temperature was increased by 1K/min from ambient to350°C. An adsorption isotherm was recorded in the pressure interval 20 to 510 mmHg. The amount of chemisorbed hydrogen was calculated by extrapolating the linear part of the isotherm to zero pressure. In order to calculate the cobalt surface area, it was assumed that two cobalt sites were covered by one hydrogen molecule and that the area of one cobalt atom is $6.62 - 10^{-22}$ m^2.

Catalyst testing

The fixed bed testing was performed in a laboratory unit with four parallel fixed-bed reactors. 1 g of catalyst particles in a size fraction between 53 and 90 microns was mixed with 20 g of inert SiC. Reduction was performed *in situ* at 350°C for 16 h in hydrogen before a mixture of hydrogen and CO at ratio 2:1 was added. After 20 h on stream at 210°C and 20 bar total pressure, the space velocity was adjusted to give an estimated conversion level of CO between 45 and 50% after 100 h. It is very important to perform selectivity, as well as activity, comparisons at the same level of conversion, as the level of steam generated in the reaction has a profound influence on the catalyst performance.

Results

Series A

The Fischer-Tropsch synthesis performance of the catalyst of series A is given in Table 1. In this case, Ca was deliberately added to the catalysts and the results are compared to the situation in which no calcium is added. It is clear that the relative activity decreases strongly with increasing calcium amount. Addition of 1000 ppm (0.1 wt%) Ca decreases the activity by 50%. However, the cobalt surface area (m^2/g catalyst) measured *ex situ* of all catalysts is, within experimental error, similar. Ca does not only affect the relative activity of the catalysts, but also the C_{5+} selectivity; as shown in Table 1, addition of Ca decreases the C_{5+} selectivity. Thus, Ca affects both the activity and selectivity in an unfavourable manner.

Table 1. Properties and catalytic data of the catalysts of series A. All contain 20 wt% Co, 0.5 wt% Re, and 0-1000 ppm Ca. Ca was co impregnated with cobalt and rhenium.

Catalyst	**Calcium amount (ppm)**	**Cobalt Surface area (m^2/g)**	**Relative activity**	**Relative C_{5+} selectivity**
A1	0	12.4	1.48	0.929
A2	100		1.30	0.914
A3	500		0.92	0.918
A4	1000	13.2	0.75	0.910

As described above, the calcium can originate from impurities in the make-up syngas, and clearly deposition of such an impurity will have a negative effect on catalyst performance. In Table 2, it is assumed that operation is over 10 000 h (i.e. total of 20 000 hours between catalyst replacements), that productivity is of 1.0 kg HC/per kg catalysts, and that all of the calcium present in the syngas is picked up by the catalyst. As shown in Table 2, a concentration of 50 ppb Ca in the syngas decreases the activity by 50%.

Table 2. Properties and catalytic data of the catalysts of series A. simulating calcium being picked-up from the syngas. All contain 20 wt% Co, 0.5 wt% Re.

Catalyst	**Ca amount in syngas (ppb)**	**Corresponding Ca amount in catalyst (ppm)**	**Relative activity**
A1	0	0	1.48
A2	5	100	1.30
A3	25	500	0.92
A4	50	1000	0.75

Series B

Table 3 shows the catalytic data of the catalysts of series B. For these catalysts, calcium was added to the support. After the γ-Al_2O_3 supports were impregnated with the calcium precursor solutions, the samples were dried and subsequently calcined at 1173 K for 10 h. Thus, most of the calcium is probably present as calcium aluminate. However, just as for the catalysts of series A, calcium is detrimental for the catalyst activity. The C_{5+} selectivity also decreases when Ca is added.

Table 3. Properties and catalytic data of the catalysts of series B. All contain 20 wt% Co, 0.5 wt% and 0-1000 ppm Ca. Ca was added to the support.

Catalyst	**Calcium amount (ppm)**	**Cobalt surface area (m^2/g)**	**Relative activity**	**Relative C_{5+} selectivity**
B1	0	12.6	1.51	0.930
B2	500		1.07	0.930
B3	1000		0.75	0.906

Series C

The calcium content of the catalysts of series C originates from the preparation process. Thus, no external Ca was added to these catalysts. Similar to series A and B, the activity and C_{5+} selectivity decreases with increasing calcium concentration (Table 4).

Table 4. Properties and catalytic data of the catalysts of series C. All contain 20 wt% Co, 0.5 wt% Re and 0-700 ppm Ca. Ca was inherent in the alumina at levels of 200 and 700 ppm and the results are compared with the case where no Ca was present in the alumina.

Catalyst	**Calcium amount (ppm)**	**Cobalt surface area (m^2/g)**	**Relative activity**	**Relative C_{5+} selectivity**
A1	0		1.48	0.929
C1	200		0.89	0.916
C2	700		0.81	0.897

Series D

The Fischer-Tropsch synthesis performance of the catalyst of series D is given in Table 5. Ca was deliberately added to the catalyst by co-impregnation with cobalt and rhenium on a silica support and the results are compared to the situation in which no calcium is added. Also for these catalysts, the relative activity decreases strongly with increasing calcium amount. Addition of Ca also lowered the C_{5+} selectivity. However, by comparing the results for 500 ppm Ca in Tables 1 and 5, it is surprising that alumina is more robust towards alkaline earth, in particular calcium, poisoning than silica. Alumina is therefore a more preferred support material than silica.

Table 5. Properties and catalytic data of the catalysts of series D. All contain 20 wt% Co, 0.5 wt% Re, and 0-500 ppm Ca. Ca was co impregnated with cobalt and rhenium on a silica support.

Catalyst	**Calcium amount (ppm)**	**Relative activity**	**Relative C_{5+} selectivity**
D1	0	1.36	0.957
D2	500	0.44	0.951

Series E

The Fischer-Tropsch synthesis performance of the catalysts of series E is given in Table 6. In this case the support essentially was Ni-spinel, and the catalyst was prepared by co-impregnation of cobalt and rhenium salts in aqueous solution followed by drying and calcination, giving a catalyst in oxide form. Ca or Mg then was deliberately added to this oxide catalyst by impregnation. Also for these catalysts, the relative activity decreases strongly with increasing calcium or magnesium amount, but to a lesser extent for magnesium.

Note that adding the impurity element to the catalyst closely resembles a situation where the impurity is introduced by make-up syngas, ref. Table 2 with 25 ppb calcium in syngas, and then picked-up by the catalyst.

Table 6. Properties and catalytic data of the catalysts of series D. All contain 12 wt% Co, 0.3 wt% Re, and 0-500 ppm Ca or Mg. The latter was impregnated on the oxide catalyst.

Catalyst	**Calcium or magnesium amount (ppm)**	**Relative activity**	**Relative C_{5+} selectivity**
E1	0	0.96	0.915
E2	400 (Ca)	0.49	0.894
E3	400 (Mg)	0.76	0.908

Claims

1. A process for the preparation of a catalyst for a Fischer-Tropsch synthesis reaction, which comprises the following steps:

taking an initial porous support material selected from alumina, titania, zirconia, zeolites, carbonaceous material and mixtures thereof, having an alkaline earth metal content of less than 1000 ppm;

impregnating the initial support material with a source of cobalt which contributes an additional alkaline earth metal content of less than 1000 ppm in the final catalyst; and

heat treating the impregnated support material at a temperature of at least 200°C to yield a cobalt oxide catalyst;

whereby the final catalyst has an alkaline earth metal content of less then 2000 ppm.

2. A process as claimed in Claim 1, in which the heat treating step is a calcination step at a temperature in the range 200 to 600°C.

3. A process as claimed in Claim 1 or Claim 2, in which, prior to the heat treating step, the impregnated support material is subjected to a drying step at a temperature of at least 100°C.

4. A process as claimed in any preceding Claim, in which the heat treating is conducted in a plurality of steps.

5. A process as claimed in any preceding claim, in which the support material is carbon in a variety of forms including carbon nanofibers and tubes, and mixtures and reaction products thereof, in any amorphous or

crystallographic form, and optionally modified or mixed with other support material(s) optionally also comprising binders.

6. A process as claimed in any of Claims 1 to 4, in which the support material is γ-alumina, any transition alumina, α-alumina, boehmite, aluminium hydroxide or mixtures thereof.

7. A process as claimed in any of Claims 1 to 4 or Claim 6, in which the support material is alumina and is prepared by the precipitation method or the alkoxide route.

8. A process as claimed in Claim 6 or Claim 7, in which the support material is γ-alumina, and is prepared by heating to a temperature in the range 400 to 800°C.

9. A process as claimed in any preceding claims, in which the initial support material has an alkaline earth metal content of less than 500 ppm.

10. A process as claimed in any of Claims 1 to 8, in which the initial support material has an alkaline earth metal content of between 5 and 1000 ppm, preferably between 10 and 500 ppm, more preferably between 10 and 200 ppm.

11. A process as claimed in any preceding Claim, in which the alkaline earth metal is calcium or magnesium.

12. A process as claimed in any preceding claim, in which a stabiliser is incorporated into the initial support material.

13. A process as claimed in Claim 12, in which the stabiliser is lanthanum.

14. A process as claimed in any preceding claim, in which the impregnation step comprises an incipient wetness treatment.

15. A process as claimed in Claim 14, in which, in the incipient wetness treatment, an aqueous solution of a cobalt metal compound is mixed with the support material until the pores are filled and the impregnated support material is then dried, prior to calcination.

16. A process as claimed in Claim 15, in which the amount of aqueous solution used in the impregnation is 0.05-2 times larger than the measured pore volume of the catalyst support.

17. A process as claimed in any preceding claim, in which the source of cobalt is selected from cobalt nitrate ($Co(NO_3)_2$), cobalt carbonate(s), cobalt (hexa) amine salt(s) and organic cobalt compounds.

18. A process as claimed in any of Claims 15 to 17, in which the water used is distilled or de-ionised water.

19. A process as claimed in any preceding claim, which includes impregnating or co-impregnating the initial alumina support material with a promoter.

20. A process as claimed in Claim 19, in which the promoter comprises platinum or rhenium.

21. A process as claimed in Claim 20, in which the promoter in the oxide catalyst is platinum and represents between 0.001 and 0.5 wt%, preferably between 0.01 and 0.1 wt%.

22. A process as claimed in Claim 20, in which the promoter in the oxide catalyst is rhenium and represents between 0.01 and 5 wt%, preferably between 0.1 and 1.0 wt%.

23. A process as claimed in Claim 20, in which, where the promoter is rhenium and the source of rhenium is selected from perrhenic acid ($HReO_4$), ammonium perrhenate, rhenium halide and rhenium carbonyl(s).

24. A process as claimed in any of Claims 14 to 18, in which the impregnated support material is dried at a temperature in the range of 80 to 120°C.

25. A process as claimed in any of Claims 19 to 24, in which the steps of impregnating cobalt and the promoter yield an alkaline earth metal content of less than 1000 ppm in the cobalt oxide catalyst.

26. A process as claimed in any of Claims 19 to 25, in which the steps of impregnating cobalt and the promoter yield an alkaline earth metal content of between 5 and 1000 ppm, preferably between 10 and 500 ppm, more preferably between 10 and 200 ppm, in the cobalt oxide catalyst.

27. A process as claimed in any preceding claim, in which after the calcination step, the alumina-supported catalyst material is activated.

28. A process as claimed in Claim 27, in which the activation step comprises reduction of a substantial portion of the catalytically active metal compound present to the metal, and is carried out by treating the catalyst material with a reducing gas, such as hydrogen and/or carbon monoxide, optionally mixed with an inert gas.

29. A process as claimed in Claim 28, in which the reduction is carried out at an activation temperature of 250 to 500°C, preferably in the range of 300 to 450°C.

30. A process as claimed in any preceding claim, in which prior to impregnating the support with a source of cobalt, the support material is modified by treatment with a divalent metal which is capable of forming a spinel, in order to form a spinel with the support material.

31. A process as claimed in any preceding claim, in which the porous support material is modified by treatment with a divalent metal and prior to the cobalt impregnation step, the modified support material has a specific surface area below 80 m^2/g, preferably in the range 30 to $70m^2/g$.

32. A process as claimed in any preceding claim, in which the porous support material is modified by treatment with a divalent metal and prior to the cobalt impregnation step, the modified support material has a pore volume below 0.5 ml/g.

33. A process as claimed in any of Claims 30 to 32, in which the divalent metal is nickel or zinc or mixtures thereof.

34. A process as claimed in Claim 33, in which the source of nickel is nickel nitrate, and/or the source of zinc is zinc nitrate.

35. A process as claimed in Claims 30 to 34, in which the divalent metal is deployed in one or more impregnation steps using a solvent, yielding from the impregnation step an alkaline earth metal content of less than 500ppm in the cobalt oxide catalyst.

36. A process as claimed in Claim 35, in which the divalent metal is deployed in one or more impregnation steps using a solvent, yielding from the impregnation step an alkaline earth metal content between 5 and 500 ppm, preferably between 5 and 300 ppm, more preferably between 5 and 100 ppm, in the cobalt oxide catalyst.

37. A process as claimed in Claim 35 or Claim 36, in which the solvent is distilled or de-ionised water.

38. A process as claimed in any of Claims 35 to 37, in which the impregnation step comprises an incipient wetness treatment.

39. A process as claimed in any of Claims 35 to 37, in which the impregnation step comprises a precipitation/deposition step.

40. A process as claimed in any of Claims 30 to 40, in which the divalent metal is incorporated into the material of the support to form a spinel and thereby a modified support material.

41. A process as claimed in Claim 40, in which the support material is dispersed as a precursor suspension in a liquid vehicle, a source of a divalent

metal capable of forming a spinel compound with the support precursor is added to the liquid, and the support material precursor is then formed into porous solid particles incorporating the divalent metal source, to produce a modified support material.

42. A process as claimed in Claim 41, in which the solid particles are produced by spray drying.

43. A process as claimed in any of Claims 30 to 42, in which the support material incorporating the divalent metal is washed, dried and calcined at up to 600°C in order to decompose the source of the divalent metal compound to produce essentially the divalent metal oxide.

44. A process as claimed in Claim 43, in which the modified support material is subjected to a high temperature calcination at a temperature in the range 600 to 900°C to form a spinel compound.

45. A process as claimed in Claim 43 or Claim 44, in which the modified support material is subjected to a high temperature calcination at a temperature in the range 900 to 1400°C, preferably 950 to 1100°C, in order to strengthen the material.

46. A process as claimed in any of Claims 38 to 45, in which the process of forming a modified support material yields an alkaline earth metal content of less than 1000 ppm in the cobalt oxide catalyst

47. A process as claimed in Claim 46, in which the process of forming a modified support material yields an alkaline earth metal content of between 10

and 1000 ppm, preferably between 20 and 500 ppm, in the cobalt oxide catalyst.

48. A catalyst for a Fischer-Tropsch synthesis reaction made in accordance with a method as claimed in any preceding claim, and comprising a porous support material, an active cobalt content of 5 to 60 wt% expressed in terms of weight of the catalyst as a whole, assuming complete reduction of the cobalt to cobalt metal, and an alkaline earth metal content of less than 1000 ppm.

49. A catalyst as claimed in Claim 48, in which the support material is γ-alumina.

50. A catalyst as claimed in Claim 49, in which the support is γ-alumina, modified by the inclusion of an alumina spinel.

51. A catalyst as claimed in Claim 50, in which the spinel is a nickel alumina spinel.

52. A catalyst as claimed in any of Claims 48 to 51, further comprising lanthanum as a stabiliser.

53. A catalyst as claimed in Claim 52, in which the lanthanum content is up to 3 wt% based on the weight of the catalyst.

54. A catalyst as claimed in any of Claims 48 to 53, in which the cobalt content is 10 to 30 wt%.

55. A catalyst as claimed in any of Claims 48 to 54, further comprising a rhenium as a promoter.

56. A catalyst as claimed in Claim 55, in which the promoter content is 0.01 to 5 wt% based on the weight of the catalyst.

57. A catalyst as claimed in any of Claims 48 to 56, having a pore volume of at least 0.2ml/g.

58. A catalyst as claimed in any of Claims 48 to 57, having a specific surface area of at least 20 m^2/g.

59. A process for the production of hydrocarbons which comprises subjecting H_2 and CO gases to a Fischer-Tropsch synthesis reaction in a rector in the presence of a catalyst made by a process according to any of Claims 1 to 47.

60. A process as claimed in Claim 59, in which make-up synthesis gas comprising H_2 and CO is introduced to the synthesis reaction and the make-up synthesis gas contains less than 100 ppb of an alkaline earth metal or alkali metal.

61. A process as claimed in Claim 59 or Claim 60, in which the make-up synthesis gas contains between 0.1 and 100 ppb, preferably between 0.5 and 50, more preferably between 0.5 and 20 ppb, of an alkaline earth metal or alkali metal.

62. A process as claimed in Claim 60 or Claim 61, in which the alkaline earth metal is calcium.

63. A process as claimed in Claim 60 or Claim 61, in which the alkali metal is sodium.

64. A process as claimed in any of Claims 60 to 63, in which the make-up synthesis gas in passed through a guard bed of materials arranged to absorb components of alkali and alkaline earth metals from the synthesis gas stream, before the synthesis gas is subjected to a Fischer-Tropsch synthesis reaction.

65. A process as claimed in any of Claim 59 to 64, in which the reaction is a three-phase reaction in which the reactants are gaseous, the product is at least partially liquid and the catalyst is solid, and in which the reaction is carried out in a slurry bubble column reactor.

66. A process as claimed in Claim 65, in which the H_2 and CO are supplied to a slurry in the reactor, the slurry comprising the catalyst in suspension in a liquid including the reaction products of the H_2 and CO, the catalyst being maintained in suspension in the slurry at least partly by the motion of the gas supplied to the slurry.

67. A process as claimed in Claim 66, in which the reaction temperature is in the range 190 - 250°C preferably, in the range 200 - 230°C, and the reaction pressure is in the range 10 - 60 bar, preferably, the range 15 - 30 bar.

68. A process as claimed in any of Claims 59 to 67, in which the H_2/CO ration of the gases supplied to the Fischer-Tropsch synthesis reactor is in the range 1.1 to 2.2, preferably, in the range 1.5 to 1.95.

69. A process as claimed in any of Claims 59 to 68, in which the superficial gas velocity in the reactor is in the range 5 to 60 cm/s, preferably, in the range 20 to 40 cm/s.

70. A process as claimed in any of Claims 59 to 69, in which the product of the Fischer-Tropsch synthesis reaction is subsequently subjected to post-processing.

71. A process as claimed in Claim 70, in which the post-processing comprises de-waxing and/or hydro-isomerisation and/or hydro-cracking.

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Claims searched:	1-71	**Date of search:**	27 April 2010

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1-2, 6, 9-11, 17, 30, 46-48 at least.	GB1542634 A (ICI), see whole document, note particularly page 2 lines 10-42, the Examples (Catalyst A-H), teaching a cobalt catalyst suitable for a Fischer-Tropsch synthesis reaction and having a calcium content ranging from under 20 ppm to under 500 ppm.
X	1-2, 6, 9-11, 25, 27, 48, 59, 65-67 at least.	EP1632289 A1 (NIPPON STEEL CORP.), see para. [0001], [0011], [0016]-[0017], [0036], Catalysts A-F.
X	1-4, 6-11, 14-15, 17, 27-29, 31-32, 48-49, 57-58 at least.	WO2006/106357 A1 (JOHNSON MATTHEY), see abstract, page 1 lines 3-7, lines 30-37, page 2 lines 9-17, lines 23-36, page 4 lines 35-39, page 5 lines 1-31, line 38,page 6 lines 1-4, the Examples and the Claims.
X	1-2, 6-11, 48-49 at least.	WO2005/089934 A1 (SAINT-GOBAIN CERAMICS & PLASTICS), see abstract, para. [0001], [0009], [0011]-[0012], [0013], [0041], [0042], [0045], [0046], [0057], Examples 3, 4, Claims 19, 20, 21, 22.

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{X} :

Worldwide search of patent documents classified in the following areas of the IPC

B01J; C07C; C10G

The following online and other databases have been used in the preparation of this search report

ONLINE : EPODOC, WPI.

International Classification:

Subclass	Subgroup	Valid From
B01J	0023/75	01/01/2006
B01J	0021/04	01/01/2006
B01J	0021/10	01/01/2006
B01J	0035/10	01/01/2006
C07C	0001/04	01/01/2006
C10G	0002/00	01/01/2006