



(86) Date de dépôt PCT/PCT Filing Date: 2008/05/05
(87) Date publication PCT/PCT Publication Date: 2008/11/13
(45) Date de délivrance/Issue Date: 2014/10/07
(85) Entrée phase nationale/National Entry: 2009/10/23
(86) N° demande PCT/PCT Application No.: IB 2008/051724
(87) N° publication PCT/PCT Publication No.: 2008/135940
(30) Priorité/Priority: 2007/05/04 (ZA2007/03621)

(51) Cl.Int./Int.Cl. *B01J 37/18* (2006.01),
B01J 23/75 (2006.01), *C10G 2/00* (2006.01)

(72) Inventeurs/Inventors:
VISAGIE, JACOBUS LUCAS, ZA;
BOTHIA, JAN MATTHEUS, ZA;
KOORTZEN, JOHANNES GERHARDUS, ZA;
DATT, MICHAEL STEVEN, ZA;
BOHMER, ALTA, ZA;
VAN DE LOOSDRECHT, JAN, ZA;
SAIB, ABDOL MUTHALIB, ZA

(73) Propriétaire/Owner:
SASOL TECHNOLOGY (PROPRIETARY) LIMITED, ZA

(74) Agent: SMART & BIGGAR

(54) Titre : CATALYSEURS
(54) Title: CATALYSTS

(57) Abrégé/Abstract:

A process for producing a supported cobalt-based Fischer-Tropsch synthesis catalyst includes, in a first activation stage, treating a particulate catalyst precursor with a reducing gas, at a heating rate, HR1, until the precursor has reached a temperature, T₁, where 80°C ≤ T₁ ≤ 180°C, to obtain a partially treated precursor. In a second activation stage, the partially treated precursor is treated with a reducing gas, at an average heating rate, HR2, with x step increments, where 0 < HR2 < HR1, for a time, t₁, where t₁ is from 0.1 to 20 hours, to obtain a partially reduced precursor. Thereafter, in a third activation stage, the partially reduced precursor is treated with a reducing gas, at a heating rate, HR3, where HR3 > HR2 until the partially reduced precursor reaches a temperature, T₂. The partially reduced precursor is maintained at T₂ for a time, t₂, where t₂ is from 0 to 20 hours, to obtain an activated catalyst.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 November 2008 (13.11.2008)

PCT

(10) International Publication Number
WO 2008/135940 A3

(51) International Patent Classification:

C10G 2/00 (2006.01) **B01J 37/18** (2006.01)
B01J 23/75 (2006.01)

(21) International Application Number:

PCT/IB2008/051724

(22) International Filing Date: 5 May 2008 (05.05.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

2007/03621 4 May 2007 (04.05.2007) ZA

(71) Applicant (for all designated States except US): **SASOL TECHNOLOGY (PROPRIETARY) LIMITED** [ZA/ZA]; 1 Sturdee Avenue, Rosebank, 2196 Johannesburg (ZA).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **VISAGIE, Jacobus, Lucas** [ZA/ZA]; 23 Donkin Street, 1947 Sasolburg (ZA). **BOTHA, Jan, Mattheus** [ZA/ZA]; 38 Billingham Street, 1947 Sasolburg (ZA). **KOORTZEN, Johannes, Gerhardus** [ZA/ZA]; 13 Ruben Street, 1947 Sasolburg (ZA). **DATT, Michael, Steven** [ZA/ZA]; 402 Headingley Jacobs Avenue, Illovo, 2196 Johannesburg (ZA). **BOHMER, Alta** [ZA/ZA]; 28 Aqua Street, 1932 Deneyville (ZA). **VAN DE LOOSDRECHT, Jan** [NL/ZA]; Boschenvaal Riverfront Lodges, 25, Barrage Road, 1947 Sasolburg (ZA). **SAIB, Abdool, Muthalib** [ZA/ZA]; 120 Kaldins Villa, Emfuleni Golf Estate, 1911 Vanderbijlpark (ZA).

(74) Agents: **KOTZE, Gavin, Salomon et al.**; Adams & Adams, Adams & Adams, Place, 1140 Prospect Street, Hatfield, PO Box 1014, 0001 Pretoria (ZA).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(88) Date of publication of the international search report:

12 March 2009

(54) Title: CATALYSTS

(57) Abstract: A process for producing a supported cobalt-based Fischer-Tropsch synthesis catalyst includes, in a first activation stage, treating a particulate catalyst precursor with a reducing gas, at a heating rate, HR1, until the precursor has reached a temperature, T₁, where 80°C ≤ T₁ ≤ 180°C, to obtain a partially treated precursor. In a second activation stage, the partially treated precursor is treated with a reducing gas, at an average heating rate, HR2, with x step increments, where 0 < HR2 < HR1, for a time, t₁, where t₁ is from 0.1 to 20 hours, to obtain a partially reduced precursor. Thereafter, in a third activation stage, the partially reduced precursor is treated with a reducing gas, at a heating rate, HR3, where HR3 > HR2 until the partially reduced precursor reaches a temperature, T₂. The partially reduced precursor is maintained at T₂ for a time, t₂, where t₂ is from 0 to 20 hours, to obtain an activated catalyst.

WO 2008/135940 A3

CATALYSTS

5

THIS INVENTION relates to catalysts. In particular, the invention relates to a process for activating a catalyst precursor, to obtain a supported cobalt-based Fischer-Tropsch synthesis catalyst, and to a catalyst obtained from the
10 process.

As regards supported cobalt-based Fischer-Tropsch synthesis catalysts, it is well-known that precursors of such catalysts are prepared using a metal precursor and a particulate support. The catalyst precursor preparation
15 involves a number of different catalyst preparation steps. The catalyst precursor is then, in an activation process or step, reduced by using a reducing gas such as hydrogen, to obtain an active Fischer-Tropsch synthesis catalyst.

20 In known activation processes, ie involving reduction of the catalyst precursor in a flowing hydrogen or hydrogen containing gas stream at elevated temperatures, for supported cobalt-based Fischer-Tropsch synthesis catalyst precursors that the Applicant is aware of, hydrogen reduction is carried out at a temperature in the range 250°C to 500°C, and preferably at low pressures
25 and high linear gas velocities to minimize vapour pressure of any product water which enhances sintering of the reduced metal. It is well known that manipulation of the reduction of cobalt oxide to cobalt metal in different ways influences activity and selectivity of the resultant Fischer-Tropsch synthesis catalyst. In particular, US 4605679 discloses that the activity of a cobalt
30 catalyst can be increased by reduction in hydrogen, then re-oxidising the catalyst followed by re-reduction in hydrogen. In US 5292705, it is shown that hydrogen reduction in the presence of hydrocarbon liquids enhances the initial Fischer-Tropsch synthesis performance of the catalyst. US 5585316 claims that the selectivity of heavier Fischer-Tropsch products is increased if the

catalyst is first oxidised and then reduced with carbon monoxide. .
EP 1444040 discloses a two stage reduction step with pure hydrogen with a
catalyst precursor in which all reducible cobalt oxide species combined can be
described by the formula-unit CoO_aH_b (where: $a \geq 1.7$ and $b > 0$), resulting in a
5 more economical reduction process without sacrificing Fischer-Tropsch
synthesis catalyst activity.

An object of the present invention is to provide a supported cobalt-based
Fischer-Tropsch synthesis catalyst having a higher hydrocarbon synthesis
10 activity. Such a catalyst can be obtained with the process of the present
invention.

According to the invention, there is provided a process for producing a
supported cobalt-based Fischer-Tropsch synthesis catalyst, which process
15 includes

in a first activation stage, treating a particulate supported cobalt-based
Fischer-Tropsch synthesis catalyst precursor comprising a catalyst support
impregnated with cobalt and containing cobalt oxide, with a hydrogen-
containing reducing gas or a nitrogen-containing gas, at a first heating rate,
20 HR1, until the precursor has reached a temperature, T_1 , where
 $80^\circ\text{C} \leq T_1 \leq 180^\circ\text{C}$, to obtain a partially treated catalyst precursor;

in a second activation stage, treating the partially treated catalyst
precursor with a hydrogen-containing reducing gas, at a second average
heating rate, HR2, with x step increments, where x is an integer and is greater
25 than 1, and where $0 < \text{HR2} < \text{HR1}$, for a time, t_1 , where t_1 is from 0.1 to 20
hours, to obtain a partially reduced catalyst precursor; and thereafter

in a third activation stage, treating the partially reduced catalyst
precursor with a hydrogen-containing reducing gas, at a third heating rate,
HR3, where $\text{HR3} > \text{HR2}$ until the partially reduced catalyst precursor reaches a
30 temperature, T_2 , and maintaining the partially reduced catalyst precursor at T_2
for a time, t_2 , where t_2 is from 0 to 20 hours, to obtain an activated supported
cobalt-based Fischer-Tropsch synthesis catalyst.

Within the context of this invention, the average heating rate HR2 is defined as the sum of the heating rates for each step increment divided by the number of step increments, where a step increment is defined as an increase in the heating rate, x is the number of step increments, and $x > 1$.

5

It was surprisingly found that a supported cobalt-based Fischer-Tropsch synthesis catalyst having high intrinsic activity was obtained when the catalyst precursor was subjected to the reduction or activation procedure of the invention.

10

The treatments in the first, second and third activation stages may, at least in principle, be effected by using any suitable contacting configuration of the catalyst precursor with the reducing gas, such as a fluidized bed of the catalyst precursor particles, with the reducing gas acting as the fluidizing medium; a fixed bed of the catalyst precursor particles through which the reducing gas passes; or the like. However, a fluidized bed configuration is preferred.

15

The first activation stage commences when the catalyst precursor is first subjected to treatment with the hydrogen-containing reducing gas or the nitrogen-containing gas with the immediate application of the first heating rate HR1. The gas in the first activation stage will have a gas space velocity, SV1. Preferably, $1 \leq SV1 \leq 35 \text{ m}^3_{\text{n}}/\text{kg red. Co/h}$; more preferably, $3 \leq SV1 \leq 15 \text{ m}^3_{\text{n}}/\text{kg red. Co/h}$. By 'red.Co' or 'reducible cobalt' is meant the cobalt that can be reduced during normal reduction, eg if the catalyst or catalyst precursor contains 20mass% cobalt and 50% of the cobalt can be reduced, then the amount of reducible cobalt is 0.1g/g catalyst or catalyst precursor. The first activation stage continues until the precursor attains the temperature T_1 .

20

25

30

Preferably, $0.5^\circ\text{C/min} \leq HR1 \leq 10^\circ\text{C/min}$; more preferably, $1^\circ\text{C/min} \leq HR1 \leq 2^\circ\text{C/min}$.

In the first activation stage, T_1 may be $\geq 90^\circ\text{C}$. In one embodiment of the invention, $120^\circ\text{C} \leq T_1 \leq 150^\circ\text{C}$. This embodiment will typically apply to precursors obtained by forming a slurry of a particulate catalyst support, a cobalt compound as an active component precursor, and water; subjecting the catalyst support to impregnation with the cobalt compound; drying the
5 impregnated catalyst support; and calcining the impregnated support.

The second activation stage thus commences when the precursor has attained the temperature T_1 , and endures for the time t_1 as hereinbefore
10 described. As regards the second activation stage treatment time t_1 , more preferably $1 \leq t_1 \leq 10$ hours, typically $2 \leq t_1 \leq 6$ hours.

In the second activation stage, at least two heating ramps are employed. Thus, at least two heating ramps in which the precursor is heated from the
15 temperature T_1 to a temperature T_H where $T_H > T_1$ and $T_H < 200^\circ\text{C}$, are employed over treatment time t_1 . Thus, when two heating ramps are employed, $x=2$; when three heating ramps are employed, $x=3$; etc. The heating rates in the heating ramps will thus differ. For example, if the heating rate in a first heating ramp is $1^\circ\text{C}/\text{min}$, then the heating rate in a second
20 heating ramp can be $2^\circ\text{C}/\text{min}$. Still further, the precursor can, if desired, be held for some time at the temperature attained at the end of a heating ramp, before commencing the next heating ramp.

The third activation stage commences once the time t_1 has elapsed. The precursor thus, at the commencement of the third activation stage, will be at
25 the temperature T_H . The third activation stage treatment is thus continued until the temperature in the third treatment stage, ie the temperature of the activated Fischer-Tropsch catalyst, reaches T_2 . Preferably, $300^\circ\text{C} \leq T_2 \leq 600^\circ\text{C}$. More preferably, T_2 may be in the range of 300°C to 500°C , with a typical
30 value of T_2 being in the range of 300°C to 450°C . The catalyst can be maintained at T_2 for 0-20 hours (ie t_2), preferably $0 < t_2 \leq 20$ hours, more preferably $1 \leq t_2 \leq 10$ hours, typically $2 \leq t_2 \leq 6$ hours.

The gas will also, in the second activation stage, have a space velocity, hereinafter referred to as SV2, and will also, in the third activation stage, have a space velocity, hereinafter referred to as SV3.

- 5 In one embodiment of the invention, SV1, SV2 and/or SV3 may be constant during the treatments in their respective activation stages. For example, the relationship of the space velocities in the various stages may be $SV1=SV2=SV3$. However, in another embodiment of the invention, SV1, SV2 and SV3 may vary during the respective activation stages.

10

In the first activation stage, a hydrogen-containing reducing gas is preferably used, and the gas used in the three activation stages may have the same composition. By 'hydrogen-containing reducing gas' is meant a hydrogen containing gas mixture comprising $10\text{vol}\% < H_2 \leq 100\text{vol}\%$, more preferably

- 15 $>90\text{vol}\% H_2$ and $<10 \text{ vol}\%$ inerts, most preferably $>97 \text{ vol}\% H_2$ and $<3\text{vol}\%$ inerts. The inerts could be any combination of Ar, He, NH_3 and H_2O , with the preferred dew point of the hydrogen-containing reducing gas being $\leq 4^\circ\text{C}$, more preferably $\leq -30^\circ\text{C}$.

- 20 In the first activation stage, a nitrogen-containing gas can instead be used. By 'nitrogen-containing gas' is meant a gas mixture comprising $>90\text{vol}\% N_2$ and $<10\text{vol}\%$ other components with the other components being any combination of Ar, He, and H_2O . The preferred dew point of the nitrogen-containing gas is $\leq 4^\circ\text{C}$, more preferably $\leq -30^\circ\text{C}$. This nitrogen containing gas does not contain
25 any hydrogen (ie hydrogen=0vol%).

The treatments in the first, second and third activation stages may be effected at the same or different pressures, and may each be effected at about atmospheric pressure, preferably at between 0.6 and 1.3 bar(a).

30

The particulate supported cobalt-based Fischer-Tropsch synthesis ('FTS') catalyst precursor may be any suitable catalyst precursor requiring activation or reduction to obtain an active Fischer-Tropsch catalyst, and may be that obtained during preparation of a fresh catalyst or from a regenerated catalyst.

69738-21

6

Thus, it may be that obtained during preparation of a fresh catalyst, ie obtained by forming a slurry of a particulate catalyst support, a cobalt compound as an active component precursor, and water; subjecting the catalyst support to impregnation with the cobalt compound; drying the impregnated catalyst support; and calcining the impregnated support, to obtain the catalyst precursor, which contains cobalt oxide. The catalyst precursor thus obtained must, however, then still be activated or reduced prior to using it for catalyzing a Fischer-Tropsch reaction, and this reduction or activation is effected in accordance with the method of the present invention. The resultant catalyst is thus an activated Fischer-Tropsch catalyst.

The regenerated catalyst precursor can be that obtained by regenerating a spent cobalt Fischer-Tropsch catalyst, that was used in a FTS process for a period of time, by means of any suitable regeneration process, which results in an oxidized catalyst precursor containing supported cobalt oxide.

Any commercially available pre-shaped porous oxide catalyst support, such as alumina (Al_2O_3), silica (SiO_2), titania (TiO_2), magnesia (MgO), $\text{SiO}_2\text{-Al}_2\text{O}_3$ and zinc oxide (ZnO), may be used. The support preferably has an average pore diameter between 8 and 50 nanometers, more preferably between 10 and 15 nanometers. The support pore volume may be between 0.1 and 1.5ml/g, preferably between 0.3 and 0.9ml/g.

The support may be a protected modified catalyst support, containing, for example, silicon as modifying component, as generally described in EP Application No. 99906328.2 (European Publication No. 1058580).

More specifically, the protected modified catalyst support may be that obtained by contacting a silicon precursor, eg an organic silicon compound such as tetra ethoxy silane ('TEOS') or tetra methoxy silane ('TMOS'), with the catalyst support, eg by means of impregnation, precipitation or chemical vapour deposition, to obtain a silicon-containing modified catalyst support; and calcining the silicon-containing modified catalyst support, eg in a rotary

69738-21

7

calciner, at a temperature from 100°C to 800°C, preferably from 450°C to 550°C, and for a period of from 1 minute to 12 hours, preferably from 0.5 hour to 4 hours.

- 5 The cobalt loading can be between 5gCo/100g support and 70gCo/100g support, preferably between 20gCo/100g support and 55gCo/100g support.

The cobalt salt may, in particular, be cobalt nitrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

- 10 The impregnation of the catalyst support may, in principle, be effected by any known method or procedure such as incipient wetness impregnation or slurry impregnation. Thus, the impregnation may generally be effected in the manner described in US 6455462 or in US 5733839.
- 15 More specifically, impregnation may be effected by subjecting, at elevated temperature, a slurry comprising the particulate catalyst support, water, and the cobalt salt to a sub-atmospheric pressure environment, which may be down to 5kPa(a), preferably between atmospheric pressure and 10kPa(a); drying the impregnated carrier at elevated temperature and under a sub-
- 20 atmospheric pressure environment, which may be as hereinbefore described. Still more specifically, the impregnation may be effected by subjecting the slurry, in an initial treatment stage, to treatment at elevated temperature and under a sub-atmospheric pressure environment as hereinbefore described to impregnate the support with the cobalt salt and to dry the impregnated support
- 25 partially, and thereafter, in a subsequent treatment stage, subjecting the partially dried impregnated support to treatment of elevated temperature and under a sub-atmospheric pressure environment as hereinbefore described, such that the temperature in the subsequent treatment stage exceeds that in the initial treatment stage and/or the sub-atmospheric pressure in the
- 30 subsequent treatment stage is lower than that in the initial treatment stage, thereby to obtain more vigorous drying of the impregnated support in the subsequent treatment stage than in the initial treatment stage, to obtain a dried impregnated support.

69738-21

8

The impregnation may include subjecting the support to two or more impregnation steps, to obtain a desired cobalt loading. Each impregnation step may then include an initial and a subsequent treatment stage as hereinbefore described.

5

The process may then include, in each of the impregnation steps, controlling the drying rate of the slurry to a specified drying profile.

The support impregnation may thus involve a 2-step slurry phase
10 impregnation process, which is dependent on a desired cobalt loading requirement and the pore volume of the catalyst support.

The support impregnation and drying may typically be effected in a conical vacuum drier with a rotating screw or in a tumbling vacuum drier.

15

During the cobalt impregnation steps, a water soluble precursor salt of platinum (Pt), palladium (Pd), ruthenium (Ru), rhenium (Re) or mixtures thereof, may be added, as a dopant capable of enhancing the reducibility of the active component.

20

Calcination of the impregnated and dried material may be done using any method, known to those skilled in the art, for example in a fluidized bed, or a rotary kiln, calciner at 200-400°C. It may, in particular, be effected as described in PCT Patent Application WO 01/39882.

25

The invention extends also to an activated Fischer-Tropsch catalyst, when obtained by the process of the first aspect of the invention.

The activated Fischer-Tropsch catalyst can be used in a process for
30 producing hydrocarbons, which includes contacting a synthesis gas

comprising hydrogen (H_2) and carbon monoxide (CO) at an elevated temperature between 180°C and 250°C and an elevated pressure between 10 and 40 bar with an activated Fischer-Tropsch catalyst as hereinbefore described, using a Fischer-Tropsch reaction of the hydrogen with the carbon
5 monoxide.

The invention will now be described in more detail with reference to the following non-limiting example.

10 EXAMPLE 1

A particulate supported cobalt-based Fischer-Tropsch synthesis catalyst precursor, which, on activation, produces a 30g Co/0.075Pt/1.5Si/100g Al_2O_3 proprietary slurry phase Fischer-Tropsch synthesis catalyst of the Applicant, and which is fully described in WO 01/39882, was investigated.

15

A representative batch of this pre-reduced catalyst precursor was specifically prepared as follows: Puralox SCCa 2/150, pore volume of 0.48ml/g, from SASOL Germany GmbH of Uberseering 40, 22297 Hamburg, Germany was modified with silicon such that the final silicon level was 2.5 Si atoms/nm² of
20 support. TEOS (tetra ethoxy silane) was added to ethanol, alumina (1l ethanol/kg alumina) was added to this solution, and the resultant mixture stirred at 60 °C for 30 minutes. Subsequently the solvent was removed under vacuum with a jacket temperature of the drier equipment of 95 °C. The dried modified support was then calcined at 500 °C for 2 hours. A solution of 17.4kg
25 of $Co(NO_3)_2 \cdot 6H_2O$, 9.6g of $(NH_3)_4Pt(NO_3)_2$, and 11kg of distilled water was mixed with 20.0kg of the above mentioned silica modified gamma alumina support by adding the support to the solution. The slurry was added to a conical vacuum drier and continuously mixed. The temperature of this slurry was increased to 60°C after which a pressure of 20kPa(a) was applied.
30 During the first 3 hours of the drying step, the temperature was increased slowly and reached 95°C after 3 hours. After 3 hours the pressure was decreased to 3-15kPa(a), and a drying rate of 2.5m%/h at the point of incipient wetness was used. The complete impregnation and drying step took 9 hours, after which the impregnated and dried catalyst support was

immediately and directly loaded into a fluidised bed calciner. The temperature of the dried impregnated catalyst support was about 75°C at the time of loading into the calciner. The loading took about 1 to 2 minutes, and the temperature inside the calciner remained at its set point of about 75°C. The

5 dried impregnated catalyst support was heated from 75°C to 250°C, using a heating rate of 0.5°C/min and an air space velocity of 1.0 m³_n/kg Co(NO₃)₂.6H₂O/h, and kept at 250°C for 6 hours. To obtain a catalyst with a cobalt loading of 30gCo/100gAl₂O₃, a second impregnation/drying/calcination step was performed. A solution of 9.4kg of Co(NO₃)₂.6H₂O, 15.7g of

10 (NH₃)₄Pt(NO₃)₂, and 15.1kg of distilled water was mixed with 20.0kg of the catalyst precursor from the first impregnation and calcination, by adding the catalyst precursor to the solution. The slurry was added to a conical vacuum drier and continuously mixed. The temperature of this slurry was increased to 60°C after which a pressure of 20kPa(a) was applied. During the first 3 hours

15 of the drying step, the temperature was increased slowly and reached 95°C after 3 hours. After 3 hours the pressure was decreased to 3-15kPa(a), and a drying rate of 2.5m%/h at the point of incipient wetness was used. The complete impregnation and drying step took 9 hours, after which the treated catalyst support was immediately and directly loaded into the fluidised bed

20 calciner. The temperature of the dried impregnated catalyst support was about 75°C at the time of loading into the calciner. The loading took about 1 to 2 minutes, and the temperature inside the calciner remained at its set point of about 75°C. The dried impregnated catalyst was heated from 75°C to 250°C, using a heating rate of 0.5°C/min and an air space velocity of 1.0

25 m³_n/kg Co(NO₃)₂.6H₂O/h, and kept at 250°C for 6 hours. A supported cobalt catalyst precursor on an alumina support was thus obtained.

One sample of this precursor, identified as Precursor A, was subjected to a standard one-step reduction or activation procedure as follows:

30 In a fluidized bed (20mm internal diameter) reduction unit, the catalyst precursor A was reduced, at atmospheric pressure, utilizing an undiluted H₂ reducing gas (100vol% H₂) as total feed gas at a space velocity of 13.7 m³_n per kilogram reducible cobalt per hour, whilst applying the following

temperature program: heat from 25°C to 425°C at 1°C/min, and hold isothermally at 425°C for 16 hours.

Precursor A was thus thereby transformed into comparative Catalyst A.

5 Another sample of this precursor, identified as Precursor B, was subjected to the following 3 stage reduction procedure (Table 1):

- (i) in a first activation stage, the sample was heated from 25°C to 120°C at a first heating rate of 1°C/min using pure 100% hydrogen;
- (ii) in a second activation stage, sample B was held at 120°C for 3 hours,
10 then at 130°C for a further 3 hours, and thereafter at 140°C for yet a further 3 hours;
- (iii) in a third activation stage, the sample was heated from 140°C to 425°C at a heating rate of 1°C/min and using the same space velocity as in the first and second activation stages; the temperature was held at
15 425°C for 4 hours.

This reduction procedure was also carried out in the fluidized bed reduction unit hereinbefore described, and the same undiluted H₂ reducing gas (100vol% H₂) was used in all three activation stages. During all three stages
20 a space velocity of 13.7m_n³/kg reducible cobalt/hour was used, while using the pure 100 % hydrogen.

Thus, Precursor B was subjected to a 3-stage reduction/activation procedure in accordance with the invention, to obtain Catalyst B which is thus in
25 accordance with the invention.

During reduction, precursors A and B were thus transformed into Fischer-Tropsch synthesis ('FTS') Catalysts A and B respectively. These catalysts were evaluated in a laboratory scale reactor under realistic FTS conditions
30 (230°C, 17.5 bar_g pressure, H₂:CO inlet ratio of 1.9:1, inlet contains 15% inerts (hence 85% of inlet is H₂ and CO), synthesis gas space velocity of 7000ml/g/h and at synthesis gas conversions of between 50 and 65%).

Table 1: Summary of the FTS runs of Example 1

Catalysts	Stage 2 conditions	Run	RIAF after 15 hours on line relative to sample A
A	-	198£	1.00
B	3 hour steps at 120°C, 130°C and 140°C	CB034	1.10

RIAF = Relative Intrinsic Fischer-Tropsch Tropsch synthesis Activity
 5 Factor

From Table 1(RIAF data) it is clear that the activity of the 3-stage reduced catalyst B (run CB034) is significantly higher than that of the standard reduced catalyst A (run 198£) after 1 day online.

10

The Relative Intrinsic Fischer-Tropsch synthesis Activity Factor ('RIAF_x') of a supported cobalt slurry phase catalyst, of which the pre-reduction catalyst precursor has been prepared in strict accordance with a prescribed catalyst preparation procedure X, ie catalyst precursor X, is defined as:

15
$$\text{RIAF}_x = [A_{xi}/A_x] \dots\dots\dots (1)$$

where:

- a) A_{xi} is the Arrhenius pre-exponential factor of catalyst precursor X, activated according to an arbitrary reduction procedure
- b) A_x is the Arrhenius pre-exponential factor of catalyst precursor X,
 20 estimated from the 15 hours on stream slurry-phase Continuous Stirred Tank Reactor (CSTR) Fischer-Tropsch synthesis performance under realistic conditions, and having utilized the standard one-step reduction procedure:

Fluidized bed (20mm internal diameter) reduction of 15±5g catalyst precursor A (ie pre-reduction catalyst mass), at atmospheric pressure
 25 utilizing an undiluted H₂ reducing gas (purity of 5.0) as total feed at a space

velocity of 13700ml_n per gram reducible cobalt per hour, whilst applying the following temperature program: heat from 25°C to 425°C at 1°C/min, and hold isothermally at 425°C for 16 hours.

- c) The pre-exponential factor A, ie applicable to both A_{xi} and A_x, is defined
 5 from the generally accepted cobalt-based Fischer-Tropsch empirical kinetic expression:

$$r_{FT} = [Ae^{(-E_a/RT)}P_{H_2}P_{CO}]/[1+KP_{CO}]^2 \dots\dots\dots (2)$$

Thus:

10 $A = [r_{FT} (1+KP_{CO})^2]/[e^{(-E_a/RT)}P_{H_2}P_{CO}] \dots\dots\dots (3)$

where:

r_{FT} is expressed in terms of the number of moles of CO converted into Fischer-Tropsch synthesis products per unit time per unit mass of the
 15 catalyst precursor in its pre-reduction state.

- d) x is any catalyst precursor.

69738-21

14

CLAIMS:

1. A process for producing a supported cobalt-based Fischer-Tropsch synthesis catalyst, which process includes

in a first activation stage, treating a particulate supported cobalt-based Fischer-Tropsch synthesis catalyst precursor comprising a catalyst support impregnated with cobalt and containing cobalt oxide, with a hydrogen-containing reducing gas or a nitrogen-containing gas, at a first heating rate, HR1, until the precursor has reached a temperature, T_1 , where $80^{\circ}\text{C} \leq T_1 \leq 180^{\circ}\text{C}$, to obtain a partially treated catalyst precursor;

in a second activation stage, treating the partially treated catalyst precursor with a hydrogen-containing reducing gas, at a second average heating rate, HR2, with x step increments, where x is an integer and is greater than 1, and where $0 < \text{HR2} < \text{HR1}$, for a time, t_1 , where t_1 is from 0.1 to 20 hours, to obtain a partially reduced catalyst precursor; and thereafter

in a third activation stage, treating the partially reduced catalyst precursor with a hydrogen-containing reducing gas, at a third heating rate, HR3, where $\text{HR3} > \text{HR2}$ until the partially reduced catalyst precursor reaches a temperature, T_2 , and maintaining the partially reduced catalyst precursor at T_2 for a time, t_2 , where $0 < t_2 \leq 20$ hours, to obtain an activated supported cobalt-based Fischer-Tropsch synthesis catalyst.

2. A process according to Claim 1 wherein, in the first activation stage, $0.5^{\circ}\text{C}/\text{min} \leq \text{HR1} \leq 10^{\circ}\text{C}/\text{min}$.

3. A process according to Claim 2 wherein, in the first activation stage, $1^{\circ}\text{C}/\text{min} \leq \text{HR1} \leq 2^{\circ}\text{C}/\text{min}$.

4. A process according to any one of Claims 1 to 3 inclusive wherein, in the second activation stage, $1 \leq t_1 \leq 10$ hours.

5. A process according to Claim 4 wherein, in the second activation stage, $2 \leq t_1 \leq 6$ hours.

6. A process according to any one of Claims 1 to 5 inclusive wherein, in the second activation stage, the precursor is heated from the temperature T_1 to a temperature T_H where $T_H > T_1$ and $T_H < 200^\circ\text{C}$.

5

7. A process according to any one of Claims 1 to 6 inclusive wherein, in the third activation stage, $300^\circ\text{C} \leq T_2 \leq 600^\circ\text{C}$.

8. A process according to any one of Claims 1 to 7 inclusive
10 wherein, in the third activation stage, $1 \leq t_2 \leq 10$ hours.

9. A process according to any one of Claims 1 to 8 inclusive, wherein the space velocity of the gas is constant during the treatments in the first, second and third stages.

15

10. A process according to any one of Claims 1 to 9 inclusive, wherein the treatments in the first, second and third activation stages are each effected at a pressure between 0.6 and 1.3 bar(a).

20 11. A process according to any one of Claims 1 to 10 inclusive, wherein a hydrogen-containing reducing gas is used in the first activation stage, with the hydrogen-containing reducing gas in each of the activation stages comprising $>90\text{vol}\% \text{H}_2$ and $<10\text{vol}\%$ inerts.

25 12. A process according to Claim 1, wherein the hydrogen-containing gas in each of the activation stages comprised $>97\text{vol}\% \text{H}_2$ and $<3\text{vol}\%$ inerts.