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IMPREGNATION PROCESS FOR CATALYSTS

THIS INVENTION relates to catalysts. It relates in particular to a process for preparing a catalyst precursor.

According to a first aspect of the invention, there is provided a process for preparing a catalyst precursor, which process comprises

subjecting, in an initial treatment stage, a slurry comprising a porous oxidic catalyst support or carrier, an active catalyst component or its precursor, and water, to treatment at elevated temperature and at sub-atmospheric pressure such that impregnation of the support or carrier with the active catalyst component or its precursor and partial drying of the impregnated support or carrier occurs, with the initial treatment stage not continuing beyond a point where the impregnated carrier or support has a loss on ignition ('LOI') which is less than 1,2 times its loss on ignition at incipient wetness ('LOI_{iw}');

thereafter, in a subsequent treatment stage, subjecting the partially dried impregnated support or carrier to treatment at elevated temperature and at sub-atmospheric pressure such that the temperature in the subsequent treatment stage exceeds that in the initial treatment stage and/or the sub-atmospheric pressure in the subsequent treatment stage is lower than that in the initial treatment stage, thereby to obtain more vigorous drying of the impregnated support or carrier in the subsequent treatment stage than in the initial treatment

stage, with a dried impregnated carrier or support thereby being produced; and

calcining the dried impregnated carrier or support, to obtain the catalyst precursor.

The resultant catalyst precursor is, in practice, subjected to reduction, in order to obtain a catalyst.

The porous oxidic catalyst support may, in particular, be in particulate form. In principle, any commercially available oxidic catalyst support can be used. Examples of catalyst supports that can be used are alumina (Al_2O_3) and titania (TiO_2). 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 1mℓ/g, preferably between 0,3 and 0,9mℓ/g. The average particle size may be between 1 and 500 micrometers, preferably between 10 and 250 micrometers, still more preferably between 45 and 200 micrometers. Alumina is preferred as the support, and the invention is described further hereunder with reference to alumina as the support.

While the active catalyst component can, at least in principle, be any known Fischer-Tropsch active component such as cobalt (Co), iron (Fe), nickel (Ni) or ruthenium (Ru); however, cobalt (Co) is preferred. In particular, a cobalt precursor can be used. Still more particularly, cobalt nitrate ($Co(NO_3)_2.6H_2O$) is preferably used.

From 1,18xy to 1,82xy kg $Co(NO_3)_2.6H_2O$ may initially be used in the initial treatment stage, where x is the BET pore volume of the alumina support in mℓ/g, and y is the mass of alumina support to be impregnated, in kg.

The process may include initially dissolving the $Co(NO_3)_2.6H_2O$ in the water, which is preferably distilled

water. Sufficient water may be used such that the volume of the solution is greater than $xy\ell$, and preferably is about $2xy\ell$.

In one version of the invention, this solution may be heated to a temperature between 60°C and 95°C, with the support then being added to the solution at atmospheric pressure, to form the slurry. The slurry may be mixed, preferably on a continuous basis, eg by means of an internal rotating screw in a conical vacuum drier in which the slurry is held.

In the initial treatment stage, vacuum may then gradually be applied to the slurry, preferably under continuous mixing, eg stirring, thereof, at a temperature between 60°C and 95°C, which may be the same as the temperature to which the solution is initially heated, or different therefrom. This constitutes the initial treatment of the slurry, and it is important that the initial treatment be effected in a gradual manner, ie excessive boiling of the slurry is to be avoided.

The sub-atmospheric pressure or vacuum that is applied during the initial treatment stage may be down to 20kPa(a), ie between atmospheric pressure and 20kPa(a). Typically, the vacuum may be about 20kPa(a) for a slurry temperature of 60°C, and about 83kPa(a) for a slurry temperature of 95°C.

The initial treatment stage is preferably continued until the loss on ignition ('LOI') of the impregnated alumina support is 1,2 times LOI_{iw}, ie 1,2 times the LOI at the point of incipient wetness ('iw'). Incipient wetness occurs when all the pores of the support are filled with liquid and there is no excess moisture, over and above the liquid required to fill the pores, present. Typically, the initial treatment time will be up to 3 hours or more.

Loss on ignition ('LOI') is defined as the mass % loss observed during complete calcination, ie during decomposition to Co_3O_4/Al_2O_3, experimentally to be determined as the mass % loss observed during calcination at 400°C, ie at a temperature sufficiently high to ensure quantitative decomposition of cobalt nitrate to Co_3O_4, but too low in order to effect the undesired formation of cobalt aluminates.

The LOI value at the state of incipient wetness, ie LOI_{iw}, can be expressed as a function of the pore volume of the support as well as the amount of catalyst active component to be impregnated. The pore volume of the support, prior to impregnation, is as stated hereinbefore, equal to x mℓ/g. The amount of $Co(NO_3)_2.6H_2O$ to be impregnated is M gram per gram of support material, and will fall within the range: 1,18x to 1,82x gram per gram support material. M is thus determined by the amount of $Co(NO_3)_2.6H_2O$ initially used. The LOI value at the state of incipient wetness can be calculated as follows:

$$LOI_{iw} = 100\ ((0,20M + x)/(0,475M + x + 1)) \quad \ldots\ldots\ldots (1)$$

This shows that the LOI at the state of incipient wetness is dependent on the pore volume of the support and the amount of $Co(NO_3)_2.6H_2O$ used for the catalyst preparation.

The gradual drying procedure until the LOI is 1,2 times LOI_{iw} ensures that about 83% of the cobalt nitrate is quantitatively drawn into the pores of the alumina support without the occurrence of localized saturation, which results in premature crystallization of cobalt nitrate.

At a moisture point somewhat above incipient wetness, ie when LOI of the impregnated alumina support is 1,2 times LOI_{iw}, aggressive evacuation, eg increased vacuum pump suction capacity when a vacuum pump is used, may be applied, in the subsequent treatment stage; at the same

time, it is ensured that the support temperature is controlled at between 60°C and 95°C. Thus, when a vacuum drier, in which the impregnated support is contained in the form of a bed, is used, an increased setting of the vacuum drier wall temperature is used, thereby ensuring that the bed temperature is controlled between 60°C and 95°C, under continuous mixing, eg stirring. This constitutes the subsequent treatment in which more forceful drying of the impregnated support takes place. Once the point where LOI = 1,2 times LOI_{1w} has been reached, the more forceful vacuum drying during the subsequent treatment stage preferably proceeds in an uninterrupted fashion, preferably at the conditions:

>60°C, but not higher than 95°C, and at the minimum pressure which is attainable, with this pressure being <20kPa(a)

Vacuum drying under these specific conditions should be maintained until a clearly defined maximum required LOI value is reached, which value depends on the need to store the dried material for a certain period of time before calcination can be executed, as hereinafter described, and this maximum required LOI value is smaller than, or equal to, 0,90 times LOI_{1w}.

The calcination of this dried impregnated support may be effected in a fluidized bed, or a rotary kiln, calciner at a temperature from 200°C to 300°C, preferably at about 250°C.

The process thus involves using a slurry, ie an excess of moisture, to achieve impregnation of the support; thereafter drying the impregnated support in a gradual manner during the initial treatment stage until 1,2 times LOI_{1w}; whereafter the more forceful drying of the subsequent treatment stage is effected until the maximum required LOI value is attained.

Sufficient cobalt nitrate may initially be used to obtain a cobalt loading between 5g Co/100g support and 70g Co/100g support, preferably between 20g Co/100g support and 40g Co/100g support, more preferably between 25g Co/100g support and 35g Co/100g support.

The maximum cobalt loading attainable in a single support impregnation step as hereinbefore described is as given in Table 1:

Table 1: Correlation between pore volume and maximum attainable cobalt loading

Pore volume of support (ie prior to the first impregnation step)	Maximum attainable cobalt loading
0,90 mℓ/g	32,4g Co/100gAl_2O_3
0,89 mℓ/g	32,0g Co/100gAl_2O_3
0,88 mℓ/g	31,7g Co/100gAl_2O_3
0,87 mℓ/g	31,3g Co/100gAl_2O_3
0,86 mℓ/g	31,0g Co/100gAl_2O_3
0,85 mℓ/g	30,6g Co/100gAl_2O_3
0,84 mℓ/g	30,2g Co/100gAl_2O_3
0,83 mℓ/g	29,9g Co/100gAl_2O_3
0,82 mℓ/g	29,5g Co/100gAl_2O_3
0,81 mℓ/g	29,2g Co/100gAl_2O_3
0,80 mℓ/g	28,8g Co/100gAl_2O_3

The optimum cobalt loading is defined as the maximum cobalt loading at which the cobalt utilization is still optimum. In the case of the Fischer-Tropsch application of a Co/Al_2O_3 catalyst, it was determined that a direct proportionality between cobalt loading and catalyst productivity existed up to a cobalt loading of 30g Co/100gAl_2O_3, for a Al_2O_3 support material with a pore volume of about 0,5mℓ/g, and an average pore diameter of 12 nanometer.

It is clear from Table 1 that an optimum cobalt loading of 30g Co/100gAl_2O_3 cannot be achieved on a Al_2O_3 support material with a pore volume of 0,5mℓ/g, in a single impregnation step. In order to achieve a cobalt loading of

30g Co/100gAl_2O_3 in a single impregnation step, an Al_2O_3 support material with a minimum pore volume of 0,84mℓ/g is required. In accordance with the invention, the calcined catalyst precursor obtained from the abovementioned initial or first impregnation step (ie 18,4g Co/100gAl_2O_3 in the case of a support material with a pore volume of 0,5mℓ/g), must be subjected to a further impregnation, drying and calcination in a second impregnation step. The second impregnation step may then comprise

subjecting, in an initial treatment stage, a slurry comprising the calcined material of the first impregnation step, an active catalyst component or its precursor, and water, to treatment at elevated temperature and at sub-atmospheric pressure such that impregnation of the calcined material with the active catalyst component or its precursor and partial drying of the impregnated material occurs, with the initial treatment stage not continuing beyond a point where the impregnated material has a LOI which is less than 1,2 times its LOI_{iw};

thereafter, in a subsequent treatment stage, subjecting the partially dried impregnated material to treatment at elevated temperature and at sub-atmospheric pressure such that the temperature in the subsequent treatment stage exceeds that in the initial treatment stage and/or the sub-atmospheric pressure in the subsequent treatment stage is lower than that in the initial treatment stage, thereby to obtain more vigorous drying of the impregnated material in the subsequent treatment stage than in the initial treatment stage, with a dried impregnated material thereby being produced; and

calcining the dried impregnated material, to obtain the catalyst precursor.

As also stated hereinbefore, the catalyst precursor is, in practice, reduced, to obtain a catalyst.

When a $Co(NO_3)_2.6H_2O$ precursor is used in the first impregnation step, then the same precursor is preferably used in the second impregnation step. The amount of $Co(NO_3)_2.6H_2O$ used during the second impregnation step may be from $1,18x_1y_1$ to $1,82x_1y_1$kg where x_1 is the BET pore volume of the calcined material from the first impregnation step, in mℓ/g, and y_1 is the mass of calcined material from the first impregnation step to be impregnated in the second impregnation step, in kg. This range of cobalt nitrate allows for a limited flexibility with respect to the cobalt loading of the resultant catalyst to be broadened by support tailoring. For example, when alumina is initially used as the support material, Table 2 provides the correlation between the pore volume of the starting alumina, ie x mℓ/g, and the empirically derived maximum attainable cobalt loading in a two-step impregnation procedure as hereinbefore described.

Table 2: Correlation between pore volume and maximum attainable cobalt loading

Pore volume of support (ie prior to the first impregnation step)	Maximum attainable cobalt loading
0,50	35,5g Co/100g Al_2O_3
0,49	34,7g Co/100g Al_2O_3
0,48	33,9g Co/100g Al_2O_3
0,47	33,1g Co/100g Al_2O_3
0,46	32,4g Co/100g Al_2O_3
0,45	31,6g Co/100g Al_2O_3
0,44	30,8g Co/100g Al_2O_3
0,43	30,1g Co/100g Al_2O_3
0,42	29,3g Co/100g Al_2O_3
0,41	28,6g Co/100g Al_2O_3
0,40	27,8g Co/100g Al_2O_3

For example, if the objective is a final catalyst having a cobalt loading of 30g Co/100g Al_2O_3, the starting alumina support must have a pore volume ≥0,43mℓ/g.

This amount of cobalt nitrate may initially be dissolved in water, which is preferably distilled water. Sufficient water may be used such that the volume of the solution is $>x_1y_1\ell$, preferably about $2x_1y_1\ell$. This solution may then be heated to a temperature between 60 and 95°C. To this solution, the final inventory of $y_1$kg of the first impregnation step material, ie the catalyst precursor of the first impregnation and calcination step, may be added at atmospheric pressure, whilst continuous mixing of the slurry is maintained, eg by means of an internal rotating screw in a conical vacuum drier.

In the initial treatment stage of the second impregnation step, vacuum may then gradually be applied to the slurry, preferably under continuous mixing, eg stirring, thereof, at a temperature between 60°C and 95°C, which may be the same as the temperature to which the solution is initially heated, or different therefrom. This constitutes the initial treatment stage of the slurry, and it is important that the initial treatment be effected in a gradual manner, ie excessive boiling of the slurry is to be avoided.

The initial treatment stage of the second impregnation step is preferably continued until the LOI of the impregnated material is reduced to a point where it is 1,2 times LOI_{1w}. Typically, the initial treatment time will be up to 3 hours or more.

The sub-atmospheric pressure or vacuum that is applied during the initial treatment stage may be down to 20kPa(a), ie between atmospheric pressure and 20kPa(a). Typically, the vacuum may be about 20kPa(a) for a slurry temperature of 60°C and about 83kPa(a) for a slurry temperature of 95°C.

As stated hereinbefore, this gradual drying procedure until the LOI is 1,2 times LOI_{1w} ensures that about 83% of the

cobalt nitrate is quantitatively drawn into the pores of the calcined material without the occurrence of localized saturation, which results in premature crystallization of cobalt nitrate. At a moisture point somewhat above incipient wetness, ie at the point where LOI is 1,2 times LOI_{iw}, aggressive evacuation, eg increased vacuum pump suction capacity when a vacuum pump is used, may be applied, in the subsequent treatment stage of the second impregnation step; at the same time, it is ensured that the support temperature is controlled at between 60°C and 95°C. Thus, when a vacuum drier, in which the impregnated material is contained in the form of a bed, is used, an increased setting of the vacuum drier wall temperature is used, thereby ensuring that the bed temperature is controlled between 60°C and 95°C, under continuous mixing, eg stirring. Preferably, maximum vacuum (<20kPa(a)) is applied, whilst simultaneously ensuring that the bed temperature does not drop below 60°C, under continuous mixing. This constitutes the subsequent treatment stage. Once the point where LOI = 1,2 times LOI_{iw} has been reached, vacuum drying during the subsequent treatment stage preferably proceeds in an uninterrupted fashion, preferably at the conditions:

>60°C, but not higher than 95°C, and at the minimum pressure which is attainable, with this pressure being <20kPa(a).

Vacuum drying under these specific conditions should be maintained until a clearly defined maximum LOI value is reached, which value depends on the need to store the dried material for a certain period of time before calcination can be executed, as hereinafter described, and this maximum required LOI value is smaller than, or equal to, 0,90 times LOI_{iw}.

The calcination of this dried impregnated material may be effected in a fluidized bed, or a rotary kiln, calciner at

a temperature from 200°C to 300°C, preferably at about 250°C.

During the first treatment stage of the first impregnation step and/or during the first treatment stage of the second impregnation step, a water soluble precursor salt of palladium (Pd) or platinum (Pt) may be added, as a dopant capable of enhancing the reducibility of the active component. The mass proportion of the palladium or platinum metal to the cobalt metal may be between 0,01:100 to 0,3:100.

It has hitherto generally be known to those skilled in the art that high drying rates during catalyst support impregnation and drying will result in catalysts with a homogeneous macroscopic distribution of the active component in the catalyst particles, ie an absence of an eggshell distribution.

Surprisingly, it has now been found that even if the macroscopic distribution of the active component is very homogeneous, controlling the drying rate of the slurry to a specified drying profile from the point of 1,2 times LOI_{iw} during the first and second impregnation steps, a catalyst with a more desired activity, is consistently obtained. The slope of the drying profile, ie the drying rate, at the point of incipient wetness should preferably be greater than (0,048 h^{-1}) LOI_{iw}. The slope of the drying profile is determined at the point of incipient wetness. This may be done by matching the experimental data to an empirical equation, eg y=a lnx+b, and calculating the derivative at the point of incipient wetness. After having determined a suitable equation to fit the experimental data, this type of equation should be used exclusively to calculate the drying rate, ie the tangent at the point of incipient wetness, for all drying profiles.

The impregnation and drying of the catalyst support in the sub-atmospheric environment, ie the initial and subsequent treatment stages of the first and second impregnation steps, can be performed in, for example, a conical vacuum drier with rotating screw or a tumbling vacuum drier, preferably a conical vacuum drier. The desired drying profile can be achieved by decreasing the sub-atmospheric pressure, by more efficient mixing, by increasing the temperature of the vacuum drier wall, or by the introduction of hot air during the subsequent treatment stage, but preferably is achieved by more efficient mixing.

It has also hitherto generally been known to those skilled in the art that the impregnated and dried material need not necessarily be calcined immediately after impregnation and drying thereof. A less desired catalyst activity has, however, been observed if storage occurred between the catalyst support impregnation/drying and product calcination.

Surprisingly, it has now been found that if the drying profile in accordance with the invention is met during the subsequent treatment stages, and drying is immediately continued under the sub-atmospheric pressure at temperatures between 60°C and 95°C to LOI values lower than $0,9LOI_{iw}$, the maximum allowable storage time at ambient conditions in a dry environment between the catalyst support impregnation/drying and the catalyst precursor calcination is a direct function of LOI_{unload}, ie the LOI at which the impregnated support drying, ie the subsequent treatment stage, was terminated and the dried impregnated material unloaded from the vacuum drying equipment. The maximum allowable storage time before calcination should preferably be less than $((-8,1/LOI_{iw})LOI_{unload}+26,2)$ hours, which thus results in a catalyst that has a more desired activity.

Instead of, in the first and/or the second step, heating the solution of cobalt nitrate in water to the temperature between 60°C and 95°C and then adding the particulate support thereto, the support may be added to the solution at ambient temperature, whereafter the temperature of the slurry is increased to a minimum of 60°C and a maximum of 95°C prior to evacuation to a vacuum of $\geq$20kPa(a). During the initial treatment, the temperature may then be increased slowly, to ensure that the gradual treatment, ie without excessive boiling of the slurry, is effected. Once the stage described by LOI = 1,2 times LOI_{iw} has been reached, more vigorous treatment is effected by aiming for a slurry temperature $\geq$60°C, preferably 95°C, whilst applying maximum allowable suction capacity affordable by the vacuum pump, effecting a drying rate in excess of $(0,048h^{-1})$ LOI_{iw}.

The catalyst obtained is particularly suitable for use as a Fischer-Tropsch catalyst to catalyze the Fischer-Tropsch reaction of a synthesis gas, comprising hydrogen and carbon monoxide, to produce Fischer-Tropsch products.

The invention will now be described in more detail with reference to the accompanying drawings as well as the following non-limiting examples.

In the drawings,

FIGURE 1 shows a plot of the drying rate at the point of incipient wetness against LOI_{iw} for some of the catalysts of the Examples described hereinafter;

FIGURE 2 shows a plot of storage time vs LOI on unloading, again in respect of some of the catalysts of the Examples;

FIGURES 3a and 3b show drying profiles of the catalysts of Examples 1, 2 and 3 during the first and second Co impregnation and drying steps respectively; and

FIGURES 4a and 4b show the drying profiles of the catalysts of Examples 1 and 4 during the first and second Co impregnation and drying steps respectively.

In the Examples, all the catalysts were prepared in an identical manner as regards their impregnation and calcination. However, in the different examples the drying mechanism and storage time between the drying and calcination were varied, in order to ascertain the optimum values thereof.

EXAMPLE 1

An alumina supported cobalt catalyst precursor was prepared according to the process of the invention. A solution of 17,4 kg of $Co(NO_3)_2.6H_2O$, 9,6g of $(NH_3)_4Pt(NO_3)_2$, and 11 kg of distilled water was mixed with 20,0kg of a gamma alumina support (Puralox SCCa 5/150, pore volume of 0,48mℓ/g, from Condea Chemie GmbH of Uberseering 40, 22297 Hamburg, Germany) by adding the support to the solution. In a first impregnation step, 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 vacuum of 20kPa(a) was applied. During the first 3 hours of drying, ie during an initial treatment stage, the temperature was increased slowly and reached 95°C after 3 hours. The LOI_{iw} was calculated by using Equation 1, and applying 0,48 (mℓ/g) for x and 0,87(g $Co(NO_3)_2.6H_2O$ per gram alumina) for M. This gives a LOI_{iw} of 35%. The LOI values of samples of the impregnated material were determined by calcining a sample, taken from the vacuum drier during the impregnation/drying stage, at 400°C in air for 10 minutes. At 400°C all cobalt nitrates will decompose, without forming cobalt aluminate, and resulting in Co_3O_4/Al_2O_3. The LOI after 3 hours was 42,1%, ie $1,20LOI_{iw}$. Thereafter, ie during a subsequent treatment stage, the drying was performed more aggressively, ie the pressure was decreased to 7kPa(a). After 6 hours, as determined from the start of the initial

treatment stage, the LOI was found to be 30,7%, ie $0,88LOI_{1w}$. After reaching a LOI value of 25,7%, ie $0,73LOI_{1w}$, the subsequent treatment stage was terminated and the dried impregnated support was calcined immediately at 250°C. To obtain a catalyst with a cobalt loading of 30g $Co/100gAl_2O_3$, a second impregnation step was performed. A solution of 9,4kg of $Co(NO_3)_2.6H_2O$, 15,7g of $(NH_3)_4Pt(NO_3)_2$, and 15,1kg of distilled water was mixed with 20,0kg of the calcined material from the first impregnation step, by adding the calcined material to the solution. The temperature of this slurry was increased to 60°C after which a vacuum of 20kPa was applied. The LOI_{1w} can again be calculated by using Equation 1, and applying 0,36(mℓ/g) (measured) for x_1 and 0,47(g $Co(NO_3)_2.6H_2O$ per gram alumina) for M. This results in a LOI_{1w} of 29%. During the first 3 hours of drying, ie during an initial treatment stage of the second impregnation step, the temperature was increased slowly and reached 95°C after 3 hours. The LOI after 3 hours was 37,0%, ie $1,28LOI_{1w}$. Thereafter, ie during a subsequent treatment stage of the second impregnation step, the drying was performed more aggressively, ie the pressure was decreased to 7kPa(a). After 6 hours, as determined from the start of the initial treatment stage of the second impregnation step, the LOI was 26,8%, ie $0,92LOI_{1w}$. After reaching a LOI value of 20,5%, ie $0,71LOI_{1w}$, this subsequent treatment stage was terminated and the resultant dried impregnated material was calcined immediately at 250°C, to obtain a catalyst precursor.

EXAMPLE 2

A catalyst precursor was prepared according to Example 1 except that the dried impregnated material was stored in a dry environment at ambient temperature for 48 hours after each impregnation step, before calcination thereof.

EXAMPLE 3

A catalyst precursor was prepared according to Example 1 except that the dried impregnated material was stored in a dry environment at ambient temperature for 15 hours after each subsequent impregnation step, before calcination thereof.

The drying profiles of the catalyst precursors in Examples 1 to 3 are shown in Figures 3a and 3b. The calculated slopes, ie the drying rates, are presented in Table 3, and are shown in Figure 1 as a function of the LOI_{iw}.

Table 3: The tangent of the drying profile at the point of incipient wetness. The inscription 'Example X/1' means: Example X, after impregnation step 1.

Catalyst Precursor	Slope (m%/h)
Example 1/1	3,25
Example 2/1	4,18
Example 3/1	2,40
Example 4/1	0,51
Example 1/2	2,79
Example 2/2	1,95
Example 3/2	2,59
Example 4/2	1,11

Between 10 and 30 grams catalyst, ie properly externally reduced catalyst precursors of Examples 1 to 3, ranging between 38 and 150 micron, were suspended in 300mℓ molten wax and loaded in a CSTR with an internal volume of 500mℓ. The feed gas consisted of hydrogen and carbon monoxide in a H_2/CO molar ratio from 1,5/1 to 2,3/1. This reactor was electrically heated and sufficiently high stirrer speeds were employed so as to eliminate any gas-liquid mass transfer limitations. The feed flow was controlled by means of Brooks mass flow controllers, and space velocities ranging from 2 to 4 $m^3_n/(h.kg$ catalyst) were used. GC analyses of the permanent gases as well as the volatile

overhead hydrocarbons were used in order to characterize the product spectra.

All catalyst precursors were reduced prior to synthesis in a tubular reactor at a pure hydrogen space velocity of $2500h^{-1}$ and atmospheric pressure. The temperature was increased from room temperature to 350°C to 425°C at a rate of 1°C/min, after which isothermal conditions were maintained for 6 to 16 hours.

Fischer-Tropsch slurry phase synthesis performance results are shown in Table 4.

Table 4: Fischer-Tropsch slurry phase synthesis results

	Example 1	Example 2	Example 3
run analysis	233$	242$	265$
Synthesis conditions			
Calcined catalyst mass (g)	22,1	21,1	20,7
Reactor temperature (°C)	221	222	220
Reactor pressure (bar)	20,5	20,0	20,3
Time on stream (h)	15,5	15,0	15,3
Feed gas composition:			
H_2 (vol%)	54,6	54,1	55,5
CO (vol%)	28,5	28,4	27,5
CO_2 (vol%)	0,58	0,56	0,50
Syngas (H_2 + CO) space velocity (m^3_n/kg cat/h)	2,5	2,4	2,4
Reactor partial pressures			
H_2 (bar)	4,0	4,9	3,9
CO (bar)	2,4	2,9	2,3
H_2O (bar)	6,2	5,1	6,1
CO_2 (bar)	0,4	0,3	0,3
Synthesis performance			
Conversion: % syngas	76,0	67,7	76,8
Relative intrinsic specific Fischer-Tropsch activity	1,00	0,75	1,04
% C-atom CH_4 selectivity	3,3	4,8	3,4
% CO of total amount of CO converted to CO_2	3,7	2,3	3,9

Having applied a reported cobalt based Fischer-Tropsch kinetic equation, such as:

$$r_{FT} = (k_{FT}P_{H2}P_{CO}) / (1+KP_{CO})^2$$

the Arrhenius derived pre-exponential factor of k_{FT} was estimated for each of the reported runs. The relative intrinsic specific Fischer-Tropsch activity is defined as (pre-exponential factor of catalyst z)/(pre-exponential

factor of catalyst of Example 1/2), in which catalyst z can be the catalyst of Example 2/2, 3/2, or 4/2.

The more desired relative intrinsic Fischer-Tropsch activity is $\geq$ 0,93, and subsequently the less desired relative intrinsic Fischer-Tropsch activity is < 0,93.

EXAMPLE 4

A catalyst precursor was prepared according to Example 1 except that there was no stirring during the first and second impregnation steps.

The drying profiles of Examples 1 and 4 can be seen in Figures 4a and 4b. The calculated slopes are given in Table 3, and shown, as function of the LOI_{1w}, in Figure 1.

After preparation and calcination, the catalyst precursors were reduced and the Fischer-Tropsch synthesis of the resultant catalysts determined, according to the procedures described hereinbefore. The Fischer-Tropsch synthesis results of these catalysts are given in Table 5.

Table 5: Fischer-Tropsch slurry phase synthesis results

	Example 1	Example 4
run analysis	233$	243$
Synthesis conditions		
Calcined catalyst mass (g)	22,1	21,7
Reactor temperature (°C)	221	222
Reactor pressure (bar)	20,5	19,8
Time on stream (h)	15,5	15,5
Feed gas composition:		
H_2 (vol%)	54,6	54,4
CO (vol%)	28,5	28,0
CO_2 (vol%)	0,58	0,50
Syngas (H_2 + CO) space velocity (m^3_n/kg cat/h)	2,5	2,4
Reactor partial pressures		
H_2 (bar)	4,0	10,0
CO (bar)	2,4	5,0
H_2O (bar)	6,2	0,8
CO_2 (bar)	0,4	0,1
Synthesis performance		
Conversion: % syngas	76,0	12,9
Relative intrinsic specific Fischer-Tropsch activity	1,00	0,11
% C-atom CH_4 selectivity	3,3	12,7
% CO of total amount of CO converted to CO_2	3,7	1,2

EXAMPLE 5

A catalyst precursor was prepared according to Example 1, except that the dried impregnated material was unloaded during the first impregnation step at an LOI of 31%, ie $0,89LOI_{iw}$. After unloading, the dried impregnated material was calcined immediately at 250°C. During the second impregnation step, the dried impregnated material was unloaded at a LOI of 26%, ie $0,90LOI_{iw}$. After unloading,

the dried impregnated material was calcined immediately at 250°C.

EXAMPLE 6

An alumina supported cobalt catalyst precursor was prepared according to the process of the invention. A solution of 221,13kg of $Co(NO_3)_2.6H_2O$, 121,5g of $(NH_3)_4Pt(NO_3)_2$, and 180,91kg of distilled water was mixed with 270,0kg of a gamma alumina support (Condea SCCa 5/150, pore volume of 0,45mℓ/g, from Condea Chemie GmbH of Uberseering 40, 22297 Hamburg, Germany) by adding the support to the solution. In a first impregnation step, the slurry was added to a conical vacuum drier and continuously mixed. The temperature of this slurry was increased to 60°C and a vacuum of 20kPa was applied. During the first 3 hours of drying, ie during an initial treatment stage, the temperature was increased slowly and reached 95°C after 3 hours. The LOI_{1w} can be calculated by using equation 1, and applying 0,45 (mℓ/g) for x and 0,82 (g $Co(NO_3)_2.6H_2O$ per gram alumina) for M. This results in a LOI_{1w} of 33%. The LOI value was determined as described in Example 1. The LOI after 3 hours was 41,8%, ie $1,28LOI_{1w}$. Thereafter, during a subsequent treatment stage, the pressure was decreased to 12kPa(a) and after 8 hours, as determined from the start of the initial treatment stage, the LOI was found to be 30,5%, ie $0,9LOI_{1w}$. The dried impregnated material was calcined at 250°C after a 1 hour waiting time between terminating the subsequent treatment stage and starting the calcination stage. To obtain a catalyst precursor with a cobalt loading of 30g CO/100g Al_2O_3, a second impregnation step was performed. A solution of 171,24kg of $Co(NO_3)_2.6H_2O$, 269,2g of $(NH_3)_4Pt(NO_3)_2$, and 240,1kg of distilled water was mixed with 330kg of the calcined material from the first impregnation step, by adding the calcined material to the solution. The temperature of this slurry was increased to 60°C and a vacuum of 20kPa was applied. The LOI_{1w} can again be calculated by using

Equation 1, and applying 0,35 (mℓ/g) for x and 0,52 (g $Co(NO_3)_2.6H_2O$ per gram alumina) for M. This results in a LOI_{iw} of 28%. During the first 3 hours of drying, ie during an initial treatment stage of the second impregnation step, the temperature was increased slowly and reached 95°C after 3 hours. The LOI after 3 hours was 38,5%, ie 1,38 LOI_{iw}. Thereafter, during a subsequent treatment stage of the second impregnation step, the pressure was decreased to 12kPa(a), and after 7 hours, as determined from the start of the initial treatment stage of the second impregnation step, the LOI was found to be 25,0%, ie 0,89LOI_{iw}. The dried impregnated material was calcined at 250°C after a 1 hour waiting time between terminating the subsequent treatment stage and starting the calcination.

EXAMPLE 7

A catalyst precursor was prepared according to Example 1 except that the dried impregnated material was stored in a dry environment at ambient temperature for 26 hours after the subsequent treatment stage of the second impregnation step, before calcination thereof.

EXAMPLE 8

An alumina supported cobalt catalyst precursor was prepared according to the process of the invention. A solution of 17,4kg of $Co(NO_3)_2.6H_2O$, 9,6g of $(NH_3)_4Pt(NO_3)_2$, and 11kg of distilled water was mixed with 20,0kg of a gamma alumina support (Condea SCCa 5/150, pore volume of 0,48mℓ/g, from Condea Chemie GmbH of Uberseering 40, 22297 Hamburg, Germany) by adding the support to the solution. In a first impregnation step, the slurry was added to a conical vacuum drier and continuously mixed. The temperature of this slurry was increased to 60°C and a vacuum of 20kPa was applied. During the first 3 hours of drying, ie during an initial treatment stage, the temperature was increased slowly and reached 95°C after 3 hours. The LOI_{iw} can be calculated by using Equation 1, and applying 0,48 (mℓ/g)

for x and 0,87 (g $Co(NO_3)_2.6H_2O$ per gram alumina) for M. This results in a LOI_{1w} of 35%. The LOI after 3 hours was 42,1%, ie $1,20LOI_{1w}$. Thereafter, during a subsequent treatment stage, the pressure was decreased to 7 kPa(a), and after 7 hours, as determined from the start of the initial treatment stage the LOI was found to be 29,5%, ie $0,84LOI_{1w}$. The dried impregnated material was calcined immediately at 250°C. To obtain a catalyst precursor with a cobalt loading of 30g Co/100g Al_2O_3, a second impregnation step was performed. A solution of 9,4kg of $Co(NO_3)_2.6H_2O$, 15,7g of $(NH_3)_4Pt(NO_3)_2$, and 15,1kg of distilled water was mixed with 20,0kg of calcined material from the first impregnation step, by adding the calcined material to the solution. The temperature of this slurry was increased to 60°C and a vacuum of 20kPa was applied. The LOI_{1w} can again be calculated by using Equation 1, and applying 0,36 (ml/g) for x and 0,47 (g $Co(NO_3)_2.6H_2O$ per gram alumina) for M. This results in a LOI_{1w} of 29%. During the first 3 hours of drying, ie during an initial treatment stage of the second impregnation step, the temperature was increased slowly and reached 95°C after 3 hours. The LOI after 3 hours was 37,0%, ie $1,28LOI_{1w}$. Thereafter, during a subsequent treatment stage of the second impregnation step, the pressure was decreased to 7kPa(a), and after 7 hours, as determined from the start of the initial treatment stage of the second impregnation step, the LOI was found to be 25,0%, ie $0,86LOI_{1w}$. The impregnated and dried material was then stored in a dry environment at ambient temperature for 6 hours before calcination thereof.

EXAMPLE 9

A catalyst precursor was prepared according to Example 8 except that the dried impregnated material was stored in a dry environment at ambient temperature for 35 hours after the subsequent treatment stage of the second impregnation step, before calcination thereof.

EXAMPLE 10

A catalyst precursor was prepared according to Example 8 except that the dried impregnated material was stored in a dry environment at ambient temperature for 16 hours after the subsequent treatment stage of the second impregnation step, and before calcination thereof.

EXAMPLE 11

A catalyst precursor was prepared according to Example 8 except that the dried impregnated material was stored in a dry environment at ambient temperature for 22 hours after the subsequent treatment stage of the second impregnation step, and before calcination thereof.

After preparation and calcination, the catalyst precursors of Examples 6 to 11 were reduced to obtain catalysts, and the Fischer-Tropsch intrinsic activity of these catalysts determined, according to the procedures described hereinbefore. The Fischer-Tropsch synthesis results of these catalysts are given in Tables 6 and 7.

Table 6: Fischer-Tropsch slurry phase synthesis results

	Example 6	Example 7	Example 8
Run analysis	196F	233F	237F
Synthesis conditions			
Calcined catalyst mass (g)	20,7	21,9	18,4
Reactor temperature (°C)	220	221	221
Reactor pressure (bar)	20,2	20,2	19,9
Time on stream (h)	15,0	15,0	15,0
Feed gas composition:			
H_2 (vol%)	53,7	53,9	55,2
CO (vol%)	27,8	27,7	26,4
CO_2 (vol%)	0,47	0,54	0,53
Syngas (H_2 + CO) space velocity (m^3_n/kg cat/h)	4,1	4,0	4,2
Reactor partial pressures			
H_2 (bar)	6,2	6,5	6,5
CO (bar)	3,2	3,4	3,1
H_2O (bar)	4,2	3,9	3,9
CO_2 (bar)	0,2	0,2	0,2
Synthesis performance			
Conversion: % syngas	57,4	54,9	56,2
Relative intrinsic specific Fischer-Tropsch activity	1,00	0,90	0,93
% C-atom CH_4 selectivity	1,6	4,7	5,9
Absolute WGS reaction rate (mol CO converted to CO_2/(g cat.s))	$1,7\times10^{-7}$	$1,7\times10^{-7}$	$1,6\times10^{-7}$
Absolute FT reaction rate (mol CO converted to HC/(g cat.s)	$9,76\times10^{-6}$	$9,16\times10^{-6}$	$9,81\times10^{-6}$

Table 7: Fischer-Tropsch slurry phase synthesis results

	Example 9	Example 10	Example 11
Run analysis	224F	229F	239F
Synthesis conditions			
Calcined catalyst mass (g)	20,2	20,3	17,1
Reactor temperature (°C)	221	220	221
Reactor pressure (bar)	20,2	20,0	20,0
Time on stream (h)	15,0	15,0	15,0
Feed gas composition:			
H_2 (vol%)	54,6	53,8	52,7
CO (vol%)	26,8	27,2	27,6
CO_2 (vol%)	0,61	0,36	0,56
Syngas (H_2 + CO) space velocity (m^3_n/kg cat/h)	4,1	3,9	4,1
Reactor partial pressures			
H_2 (bar)	6,5	7,2	6,0
CO (bar)	3,2	3,6	3,0
H_2O (bar)	3,9	3,2	4,2
CO_2 (bar)	0,2	0,2	0,2
Synthesis performance			
Conversion: % syngas	55,6	47,6	57,4
Relative intrinsic specific Fischer-Tropsch activity	0,86	0,71	0,93
% C-atom CH_4 selectivity	5,0	8,3	6,7
Absolute WGS reaction rate (mol CO converted to CO_2/(g cat.s))	$1,3x10^{-7}$	$1,3x10^{-7}$	$1,4x10^{-7}$
Absolute FT reaction rate (mol CO converted to HC/(g cat.s)	$9,44x10^{-6}$	$7,67x10^{-6}$	$9,61x10^{-6}$
% CO of total amount of CO converted to CO_2	1,4	1,7	1,4

Fischer-Tropsch synthesis is the conversion of synthesis gas to higher hydrocarbons, eg petrol, diesel, wax. Synthesis gas, ie a gas mixture with hydrogen and carbon monoxide as the main components, can be produced from

natural gas by processes well known to those skilled in the art, for example autothermal reforming or partial oxidation of natural gas. The Fischer-Tropsch synthesis process can be performed by using iron, nickel, cobalt, or ruthenium based catalysts. The catalysts can be used in fixed, slurry, and fluidized bed Fischer-Tropsch applications. It is known that supported cobalt based slurry phase Fischer-Tropsch catalysts produce a wax product. This wax product can be used as such, or it can, for example, be hydrocracked to petrol and diesel by processes known in the art.

It has hitherto generally been held by persons skilled in the art that, in supported catalysts for Fischer-Tropsch synthesis, only the catalyst composition is important for catalyst performance, and that any catalyst support impregnation method can be used, ie that the catalyst preparation procedure is not critical.

However, a serious problem encountered with catalysts made according to known methods is that the catalyst do not show the same activity in a micro CSTR reactor if the impregnated material was not dried with the same efficiency or if there was a waiting period between the drying of the impregnated material and the calcination thereof.

The Applicant has thus surprisingly found that by optimizing the drying procedure through ensuring that a particular drying profile is met during impregnation and drying and that, if a waiting period was required, the impregnated material is further dried to a set specification and the dried material is calcined within a set period of time, uniform catalysts of acceptable activities can be prepared.

The present invention thus involves the optimization of a drying procedure for the preparation of a catalyst

precursor from which can be obtained a catalyst with excellent Fischer-Tropsch synthesis behaviour and resulting in high activity. More particularly, this invention provides efficient drying of the impregnated material during catalyst precursor preparation, and once dried, the excellent properties of the catalyst introduced during drying are maintained until the calcination thereof.

CLAIMS

1. A process for preparing a catalyst precursor, which process comprises

subjecting, in an initial treatment stage, a slurry comprising a porous oxidic catalyst support or carrier, an active catalyst component or its precursor, and water, to treatment at elevated temperature and at sub-atmospheric pressure such that impregnation of the support or carrier with the active catalyst component or its precursor and partial drying of the impregnated support or carrier occurs, with the initial treatment stage not continuing beyond a point where the impregnated carrier or support has a loss on ignition ('LOI') which is less than 1,2 times its loss on ignition at incipient wetness ('LOI_{iw}');

thereafter, in a subsequent treatment stage, subjecting the partially dried impregnated support or carrier to treatment at elevated temperature and at sub-atmospheric pressure such that the temperature in the subsequent treatment stage exceeds that in the initial treatment stage and/or the sub-atmospheric pressure in the subsequent treatment stage is lower than that in the initial treatment stage, thereby to obtain more vigorous drying of the impregnated support or carrier in the subsequent treatment stage than in the initial treatment stage, with a dried impregnated carrier or support thereby being produced; and

calcining the dried impregnated carrier or support, to obtain the catalyst precursor.

2. A process according to Claim 1, wherein the porous oxidic catalyst support is particulate alumina which has an average pore diameter between 8 and 50 nanometers, a pore volume between 0,1 and 1mℓ/g, and an average particle size between 1 and 500 micrometers, and wherein

cobalt nitrate, $Co(NO_3)_2.6H_2O$, is used as an active catalyst component precursor.

3. A process according to Claim 2, wherein from 1,18xy to 1,82xy kg $Co(NO_3)_2.6H_2O$ is used in the initial treatment stage, where x is the BET pore volume of the alumina support in mℓ/g, and y is the mass of alumina support to be impregnated, in kg.

4. A process according to Claim 3, which includes initially dissolving the $Co(NO_3)_2.6H_2O$ in the water, with sufficient water being used such that the volume of the solution is >xyℓ; heating the solution to a temperature between 60°C and 95°C; adding the support to the solution at atmospheric pressure, to form the slurry, and continuously mixing the slurry.

5. A process according to any one of Claims 2 to 4 inclusive wherein, in the initial treatment stage, vacuum is gradually applied to the slurry, under continuous mixing thereof, with the elevated temperature being from 60°C to 95°C, and with the sub-atmospheric pressure or vacuum that is applied during the initial treatment stage being down to 20kPa(a).

6. A process according to Claim 5, wherein the initial treatment stage is continued until the loss on ignition ('LOI') of the impregnated alumina support is 1,2 times LOI_{iw}.

7. A process according to Claim 6 wherein, when the LOI of the impregnated alumina support is 1,2 times LOI_{iw}, increased evacuation is applied, in the subsequent treatment stage, while ensuring that the support temperature is controlled between 60°C and 95°C, under continuous mixing, so that more forceful drying of the

impregnated support takes place during the subsequent treatment stage.

8. A process according to Claim 7, wherein the more forceful vacuum drying during the subsequent treatment stage proceeds in an uninterrupted fashion, at the conditions:

>60°C, but not higher than 95°C, and at the minimum pressure which is attainable, with this pressure being <20kPa(a),

with the vacuum drying under these conditions being maintained until a clearly defined maximum LOI value is reached, with this maximum LOI value being smaller than, or equal to, 0,90 times LOI_{iw}.

9. A process according to Claim 7 or Claim 8 which includes, during the subsequent treatment stage, controlling the drying rate of the slurry by controlling the sub-atmospheric pressure, by controlling or adjusting the degree of mixing, by controlling or adjusting the treatment temperature and/or by introducing hot air into the slurry.

10. A process according to Claim 9 wherein, during the subsequent treatment stage, the drying rate is controlled such that, at the point of incipient wetness, the drying rate is greater than $(0,048h^{-1})$ LOI_{iw}.

11. A process according to Claim 9 or Claim 10, which includes storing the dried impregnated carrier or support from the subsequent treatment stage at ambient conditions in a dry environment before calcination thereof, with the storage time being less than $((-8,1/LOI_{iw})LOI_{unload}+26,2)$ hours, where LOI_{unload} is the LOI at which the subsequent treatment stage is terminated.

12. A process according to any one of Claims 2 to 11 inclusive, wherein the calcination of the dried impregnated support is effected in a fluidized bed calciner, or in a rotary kiln calciner, at a temperature from 200°C to 300°C.

13. A process according to any one of Claims 2 to 12 inclusive, wherein sufficient cobalt nitrate is initially used to obtain a cobalt loading between 5g Co/100g support and 70g Co/100g support.

14. A process according to any one of Claims 2 to 13 inclusive wherein, in order to obtain an increased cobalt loading of the alumina support, the calcined material is subjected to further impregnation, drying and calcination in a second impregnation step, with the initial treatment stage, the subsequent treatment stage, and the calcination thus constituting a first impregnation step.

15. A process according to Claim 14, wherein the second impregnation step comprises

subjecting, in an initial treatment stage, a slurry comprising the calcined material of the first impregnation step; cobalt as an active catalyst component, or a precursor thereof; and water, to treatment at elevated temperature and at sub-atmospheric pressure such that impregnation of the calcined material with the active catalyst component or its precursor and partial drying of the impregnated material occurs, with the initial treatment stage not continuing beyond a point where the impregnated material has a LOI which is less than 1,2 times its LOI_{1w};

thereafter, in a subsequent treatment stage, subjecting the partially dried impregnated material to treatment at elevated temperature and at sub-atmospheric pressure such that the temperature in the subsequent treatment stage exceeds that in the initial treatment stage and/or the sub-atmospheric pressure in the subsequent treatment stage is lower than that in the initial treatment

stage, thereby to obtain more vigorous drying of the impregnated material in the subsequent treatment stage than in the initial treatment stage, with a dried impregnated material thereby being produced; and

calcining the dried impregnated material, to obtain the catalyst precursor.

16. A process according to Claim 15, wherein cobalt nitrate, $Co(NO_3)_2.6H_2O$, is used as an active catalyst component precursor in the second impregnation step, and wherein from $1,18x_1y_1$ to $1,82x_1y_1$kg $Co(NO_3)_2.6H_2O$ is used in the initial treatment stage of the second impregnation step where x_1 is the BET pore volume of the calcined material from the first impregnation step, in $m\ell/g$, and y_1 is the mass of calcined material from the first impregnation step to be impregnated in the second impregnation step, in kg, with the proviso that the amount of $Co(NO_3)_2.6H_2O$ used in the second impregnation step, is adjusted in the event that the maximum amount of $Co(NO_3)_2.6H_2O$, as determined by the formula $1,82x_1y_1$, results in a desired cobalt loading of the catalyst precursor being exceeded.

17. A process according to Claim 16, which includes, in the second impregnation step, initially dissolving the $Co(NO_3)_2.6H_2O$ in water, with sufficient water being used such that the volume of the solution is $>x_1y_1\ell$; heating the solution to a temperature between 60 and 95°C; adding the final inventory of $y_1$kg of the calcined material from the first impregnation step to this solution at atmospheric pressure, to form the slurry; and continuously mixing the slurry.

18. A process according to Claim 16 or Claim 17 wherein, in the initial treatment stage of the second impregnation step, vacuum is gradually applied to the slurry, under continuous mixing thereof, with the elevated temperature being from 60°C to 95°C, and with the sub-

atmospheric pressure or vacuum that is applied during the initial treatment stage being down to 20kPa(a).

19. A process according to Claim 18, wherein the initial treatment stage of the second impregnation step is continued until the loss on ignition ('LOI') of the impregnated material is 1,2 times LOI_{iw}.

20. A process according to Claim 19 wherein, when the LOI of the impregnated material is 1,2 times LOI_{iw}, increased evacuation is applied, in the subsequent treatment stage of the second impregnation step, while ensuring that the partially dried impregnation material temperature is controlled between 60°C and 95°C, under continuous mixing, so that more forceful drying of the impregnated material takes place during the subsequent treatment stage.

21. A process according to Claim 20, wherein the more forceful vacuum drying during the subsequent treatment stage proceeds in an uninterrupted fashion, at the conditions:

>60°C, but not higher than 95°C, and at the minimum pressure which is attainable, with this pressure being <20kPa(a),

with vacuum drying under these conditions being maintained until a clearly defined maximum LOI value is reached, with this maximum LOI value being smaller than, or equal to, 0,90 times LOI_{iw}.

22. A process according to Claim 20 or Claim 21 which includes, during the subsequent treatment stage, controlling the drying rate of the slurry by controlling the sub-atmospheric pressure, by controlling or adjusting the degree of mixing, by controlling or adjusting the treatment temperature and/or by introducing hot air into the slurry.

23. A process according to Claim 22 wherein, during the subsequent treatment stage, the drying rate is controlled such that, at the point of incipient wetness, the drying rate is greater than $(0,048h^{-1})$ LOI_{iw}.

24. A process according to Claim 22 or Claim 23, which includes storing the dried impregnated carrier or support from the subsequent treatment stage at ambient conditions in a dry environment before calcination thereof, with the storage time being less than $((-8,1/LOI_{iw})LOI_{unload}+26,2)$ hours, where LOI_{unload} is the LOI at which the subsequent treatment stage is terminated.

25. A process according to any one of Claims 16 to 24 inclusive, wherein the calcination of the dried impregnated material is effected in a fluidized bed calciner, or in a rotary kiln calciner, at a temperature from 200°C to 300°C.

26. A process according to any one of Claims 2 to 25 inclusive wherein, during the first treatment stage of the first impregnation step and/or during the first treatment stage of the second impregnation step, a water soluble precursor salt of palladium, Pd, or platinum, Pt, is added, as a dopant capable of enhancing the reducibility of the active component, with the mass proportion of the palladium or the platinum metal to the cobalt metal being between 0,01:100 to 0,3:100.

27. A process according to Claim 2, wherein from 1,18xy to 1,82xy kg $Co(NO_3)_2.6H_2O$ is used in the initial treatment stage, where x is the BET pore volume of the alumina support in mℓ/g, and y is the mass of alumina support to be impregnated, in kg and which includes initially dissolving the $Co(NO_3)_2.6H_2O$ in the water, with sufficient water being used such that the volume of the solution is >xyℓ; adding the support to the solution at ambient temperature to form the slurry, and thereafter

heating the slurry to the elevated temperature which is from 60°C to 95°C, with the sub-atmospheric pressure or vacuum that is applied during the initial treatment stage being down to 20kPa(a).

28. A process for preparing a catalyst precursor, which process comprises

subjecting, in an initial treatment stage, a slurry comprising a porous oxidic catalyst support or carrier, an active catalyst component or its precursor, and water, to treatment at an elevated temperature T_1 and at a sub-atmospheric pressure P_1 such that impregnation of the support or carrier with the active catalyst component or its precursor and partial drying of the impregnated support or carrier occurs, with the initial treatment stage not continuing beyond a point where the impregnated carrier or support has a loss on ignition ('LOI') which is less than 1,2 times its loss on ignition at incipient wetness ('LOI_{iw}');

thereafter, in a subsequent treatment stage, subjecting the partially dried impregnated support or carrier to treatment at an elevated temperature T_2 and at a sub-atmospheric pressure P_2 such that $T_2 > T_1$ and/or $P_2 < P_1$, thereby to obtain more vigorous drying of the impregnated support or carrier in the subsequent treatment stage than in the initial treatment stage, with a dried impregnated carrier or support thereby being produced; and

calcining the dried impregnated carrier or support, to obtain the catalyst precursor.

29. A process according to Claim 28, wherein the porous oxidic catalyst support is particulate alumina which has an average pore diameter between 8 and 50 nanometers, a pore volume between 0,1 and 1mℓ/g, and an average particle size between 1 and 500 micrometers, and wherein cobalt nitrate, $Co(NO_3)_2.6H_2O$, is used as an active catalyst component precursor.

30. A process according to Claim 29, wherein from 1,18xy to 1,82xy kg $Co(NO_3)_2.6H_2O$ is used in the initial treatment stage, where x is the BET pore volume of the alumina support in mℓ/g, and y is the mass of alumina support to be impregnated, in kg.

31. A process according to Claim 30, which includes initially dissolving the $Co(NO_3)_2.6H_2O$ in the water, with sufficient water being used such that the volume of the solution is >xyℓ; heating the solution to a temperature between 60°C and 95°C; adding the support to the solution at atmospheric pressure, to form the slurry, and continuously mixing the slurry.

32. A process according to any one of Claims 29 to 31 inclusive wherein, in the initial treatment stage, vacuum is gradually applied to the slurry, under continuous mixing thereof, with $60°C \leq T_1 \leq 95°C$. and with atmospheric pressure $> P_1 \geq 20kPa(a)$.

33. A process according to Claim 32, wherein the initial treatment stage is continued until the loss on ignition ('LOI') of the impregnated alumina support is 1,2 times LOI_{iw}.

34. A process according to Claim 33 wherein, when the LOI of the impregnated alumina support is 1,2 times LOI_{iw}, increased evacuation is applied in the subsequent treatment stage so that $P_2 < P_1$, while ensuring that the support temperature is controlled between 60°C and 95°C, under continuous mixing, so that more forceful drying of the impregnated support takes place during the subsequent treatment stage.

35. A process according to Claim 34, wherein the more forceful vacuum drying during the subsequent treatment

stage proceeds in an uninterrupted fashion, at the conditions:

$60°C < T_2 \leq 95°C$, and at the minimum pressure P_2 which is attainable, with $P_2 < 20kPa(a)$,

with the vacuum drying under these conditions being maintained until a clearly defined maximum LOI value is reached, with this maximum LOI value being smaller than, or equal to, 0,90 times LOI_{iw}.

36. A process according to Claim 34 or Claim 35 which includes, during the subsequent treatment stage, controlling the drying rate of the slurry by controlling the sub-atmospheric pressure P_2, by controlling or adjusting the degree of mixing, by controlling or adjusting the treatment temperature T_2 and/or by introducing hot air into the slurry.

37. A process according to Claim 36 wherein, during the subsequent treatment stage, the drying rate is controlled such that, at the point of incipient wetness, the drying rate is greater than $(0,048h^{-1})\ LOI_{iw}$.

38. A process according to Claim 36 or Claim 37, which includes storing the dried impregnated carrier or support from the subsequent treatment stage at ambient conditions in a dry environment before calcination thereof, with the storage time being less than $((-8,1/LOI_{iw})LOI_{unload}+26,2)$ hours, where LOI_{unload} is the LOI at which the subsequent treatment stage is terminated.

39. A process according to any one of Claims 29 to 38 inclusive, wherein the calcination of the dried impregnated support is effected in a fluidized bed calciner, or in a rotary kiln calciner, at a temperature from 200°C to 300°C.

40. A process according to any one of Claims 29 to 39 inclusive, wherein sufficient cobalt nitrate is initially

used to obtain a cobalt loading between 5g Co/100g support and 70g Co/100g support.

41. A process according to any one of Claims 29 to 40 inclusive wherein, in order to obtain an increased cobalt loading of the alumina support, the calcined material is subjected to further impregnation, drying and calcination in a second impregnation step, with the initial treatment stage, the subsequent treatment stage, and the calcination thus constituting a first impregnation step.

42. A process according to Claim 41, wherein the second impregnation step comprises

subjecting, in an initial treatment stage, a slurry comprising the calcined material of the first impregnation step; cobalt as an active catalyst component, or a precursor thereof; and water, to treatment at an elevated temperature T_1' and at a sub-atmospheric pressure P_1' such that impregnation of the calcined material with the active catalyst component or its precursor and partial drying of the impregnated material occurs, with the initial treatment stage not continuing beyond a point where the impregnated material has a LOI which is less than 1,2 times its LOI_{iw};

thereafter, in a subsequent treatment stage, subjecting the partially dried impregnated material to treatment at an elevated temperature T_2' and at a sub-atmospheric pressure P_2' such that $T_2' > T_1'$ and/or $P_2' < P_1'$, thereby to obtain more vigorous drying of the impregnated material in the subsequent treatment stage than in the initial treatment stage, with a dried impregnated material thereby being produced; and

calcining the dried impregnated material, to obtain the catalyst precursor.

43. A process according to Claim 42, wherein cobalt nitrate, $Co(NO_3)_2.6H_2O$, is used as an active catalyst component precursor in the second impregnation step, and

wherein from $1,18x_1y_1$ to $1,82x_1y_1$kg $Co(NO_3)_2.6H_2O$ is used in the initial treatment stage of the second impregnation step where x_1 is the BET pore volume of the calcined material from the first impregnation step, in $m\ell/g$, and y_1 is the mass of calcined material from the first impregnation step to be impregnated in the second impregnation step, in kg, with the proviso that the amount of $Co(NO_3)_2.6H_2O$ used in the second impregnation step, is adjusted in the event that the maximum amount of $Co(NO_3)_2.6H_2O$, as determined by the formula $1,82x_1y_1$, results in a desired cobalt loading of the catalyst precursor being exceeded.

44. A process according to Claim 43, which includes, in the second impregnation step, initially dissolving the $Co(NO_3)_2.6H_2O$ in water, with sufficient water being used such that the volume of the solution is $>x_1y_1\ell$; heating the solution to a temperature between 60 and 95°C; adding the final inventory of $y_1$kg of the calcined material from the first impregnation step to this solution at atmospheric pressure, to form the slurry; and continuously mixing the slurry.

45. A process according to Claim 43 or Claim 44 wherein, in the initial treatment stage of the second impregnation step, vacuum is gradually applied to the slurry, under continuous mixing thereof, with $60°C \leq T_1' \leq 95°C$, and with atmospheric pressure $> P_1' \geq 20kPa(a)$.

46. A process according to Claim 45, wherein the initial treatment stage of the second impregnation step is continued until the loss on ignition ('LOI') of the impregnated material is 1,2 times LOI_{iw}.

47. A process according to Claim 19 wherein, when the LOI of the impregnated material is 1,2 times LOI_{iw}, increased evacuation is applied in the subsequent treatment

stage of the second impregnation step so that $P_2' < P_1'$, while ensuring that the partially dried impregnation material temperature is controlled between 60°C and 95°C, under continuous mixing, so that more forceful drying of the impregnated material takes place during the subsequent treatment stage.

48. A process according to Claim 47, wherein the more forceful vacuum drying during the subsequent treatment stage proceeds in an uninterrupted fashion, at the conditions:

$60°C < T_2' \leq 95°C$, and at the minimum pressure P_2' which is attainable, with $P_2' < 20kPa(a)$,

with vacuum drying under these conditions being maintained until a clearly defined maximum LOI value is reached, with this maximum LOI value being smaller than, or equal to, 0,90 times LOI_{iw}.

49. A process according to Claim 47 or Claim 48 which includes, during the subsequent treatment stage, controlling the drying rate of the slurry by controlling the sub-atmospheric pressure P_2', by controlling or adjusting the degree of mixing, by controlling or adjusting the treatment temperature T_2' and/or by introducing hot air into the slurry.

50. A process according to Claim 49 wherein, during the subsequent treatment stage, the drying rate is controlled such that, at the point of incipient wetness, the drying rate is greater than $(0,048h^{-1})$ LOI_{iw}.

51. A process according to Claim 49 or Claim 50, which includes storing the dried impregnated carrier or support from the subsequent treatment stage at ambient conditions in a dry environment before calcination thereof, with the storage time being less than

$((-8,1/LOI_{iw})LOI_{unload}+26,2)$ hours, where LOI_{unload} is the LOI at which the subsequent treatment stage is terminated.

52. A process according to any one of Claims 43 to 51 inclusive, wherein the calcination of the dried impregnated material is effected in a fluidized bed calciner, or in a rotary kiln calciner, at a temperature from 200°C to 300°C.

53. A process according to any one of Claims 29 to 52 inclusive wherein, during the first treatment stage of the first impregnation step and/or during the first treatment stage of the second impregnation step, a water soluble precursor salt of palladium, Pd, or platinum, Pt, is added, as a dopant capable of enhancing the reducibility of the active component, with the mass proportion of the palladium or the platinum metal to the cobalt metal being between 0,01:100 to 0,3:100.

54. A process according to Claim 29, wherein from 1,18xy to 1,82xy kg $Co(NO_3)_2.6H_2O$ is used in the initial treatment stage, where x is the BET pore volume of the alumina support in mℓ/g, and y is the mass of alumina support to be impregnated, in kg and which includes initially dissolving the $Co(NO_3)_2.6H_2O$ in the water, with sufficient water being used such that the volume of the solution is >xyℓ; adding the support to the solution at ambient temperature to form the slurry, and thereafter heating the slurry to the elevated temperature which is from 60°C to 95°C, with the sub-atmospheric pressure or vacuum that is applied during the initial treatment stage being down to 20kPa(a).

55. A process for preparing a catalyst precursor, which process comprises

subjecting, in an initial treatment stage, a slurry comprising a porous oxidic catalyst support or carrier, an active catalyst component or its precursor, and water, to treatment at a temperature T_1 where $60°C \leq T_1 \leq 95°C$ and at a sub-atmospheric pressure P_1 where P_1 ranges from atmospheric pressure $> P_1 \geq 20kPa(a)$ when $T_1 = 60°C$ to atmospheric pressure $> P_1 \geq 83kPa(a)$ when $T_1 = 95°C$, such that impregnation of the support or carrier with the active catalyst component or its precursor and partial drying of the impregnated support or carrier occurs, with the initial treatment stage not continuing beyond a point where the impregnated carrier or support has a loss on ignition ('LOI') which is less than 1,2 times its loss on ignition at incipient wetness ('LOI_{iw}');

thereafter, in a subsequent treatment stage, subjecting the partially dried impregnated support or carrier to treatment at a temperature T_2 and at a sub-atmospheric pressure P_2 such that $60°C < T_2 \leq 95°C$ and $T_2 > T_1$ and/or $P_2 < 20kPa(a)$ and $P_2 < P_1$, thereby to obtain more vigorous drying of the impregnated support or carrier in the subsequent treatment stage than in the initial treatment stage, with a dried impregnated carrier or support thereby being produced; and

calcining the dried impregnated carrier or support, to obtain the catalyst precursor.

56. A process according to Claim 55, wherein the porous oxidic catalyst support is particulate alumina which has an average pore diameter between 8 and 50 nanometers, a pore volume between 0,1 and 1mℓ/g, and an average particle size between 1 and 500 micrometers, and wherein

cobalt nitrate, $Co(NO_3)_2.6H_2O$, is used as an active catalyst component precursor.

57. A process according to Claim 56, wherein from 1,18xy to 1,82xy kg $Co(NO_3)_2.6H_2O$ is used in the initial treatment stage, where x is the BET pore volume of the alumina support in mℓ/g, and y is the mass of alumina support to be impregnated, in kg.

58. A process according to Claim 57, which includes initially dissolving the $Co(NO_3)_2.6H_2O$ in the water, with sufficient water being used such that the volume of the solution is >xyℓ; heating the solution to a temperature between 60°C and 95°C; adding the support to the solution at atmospheric pressure, to form the slurry, and continuously mixing the slurry.

59. A process according to any one of Claims 56 to 58 inclusive wherein, in the initial treatment stage, vacuum is gradually applied to the slurry, under continuous mixing thereof, with $60°C \leq T_1 \leq 95°C$, and with atmospheric pressure $> P_1 \geq 20kPa(a)$.

60. A process according to Claim 59, wherein the initial treatment stage is continued until the loss on ignition ('LOI') of the impregnated alumina support is 1,2 times LOI_{iw}.

61. A process according to Claim 60 wherein, when the LOI of the impregnated alumina support is 1,2 times LOI_{iw}, increased evacuation is applied in the subsequent treatment stage so that $P_2 < P_1$, while ensuring that the support temperature is controlled between 60°C and 95°C, under continuous mixing, so that more forceful drying of the impregnated support takes place during the subsequent treatment stage.

62. A process according to Claim 61, wherein the more forceful vacuum drying during the subsequent treatment stage proceeds in an uninterrupted fashion at the minimum pressure P_2 which is attainable, with the vacuum drying under these conditions being maintained until a clearly defined maximum LOI value is reached, with this maximum LOI value being smaller than, or equal to, 0,90 times LOI_{iw}.

63. A process according to Claim 61 or Claim 62 which includes, during the subsequent treatment stage, controlling the drying rate of the slurry by controlling the sub-atmospheric pressure P_2, by controlling or adjusting the degree of mixing, by controlling or adjusting the treatment temperature T_2 and/or by introducing hot air into the slurry.

64. A process according to Claim 63 wherein, during the subsequent treatment stage, the drying rate is controlled such that, at the point of incipient wetness, the drying rate is greater than $(0,048h^{-1})$ LOI_{iw}.

65. A process according to Claim 63 or Claim 64, which includes storing the dried impregnated carrier or support from the subsequent treatment stage at ambient conditions in a dry environment before calcination thereof, with the storage time being less than $((-8,1/LOI_{iw})LOI_{unload}+26,2)$ hours, where LOI_{unload} is the LOI at which the subsequent treatment stage is terminated.

66. A process according to any one of Claims 56 to 65 inclusive, wherein the calcination of the dried impregnated support is effected in a fluidized bed calciner, or in a rotary kiln calciner, at a temperature from 200°C to 300°C.

67. A process according to any one of Claims 56 to 66 inclusive, wherein sufficient cobalt nitrate is initially

used to obtain a cobalt loading between 5g Co/100g support and 70g Co/100g support.

68. A process according to any one of Claims 56 to 67 inclusive wherein, in order to obtain an increased cobalt loading of the alumina support, the calcined material is subjected to further impregnation, drying and calcination in a second impregnation step, with the initial treatment stage, the subsequent treatment stage, and the calcination thus constituting a first impregnation step.

69. A process according to Claim 68, wherein the second impregnation step comprises

subjecting, in an initial treatment stage, a slurry comprising the calcined material of the first impregnation step; cobalt as an active catalyst component, or a precursor thereof; and water, to treatment at a temperature T_1' where $60°C \leq T_1' \leq 95°C$ and at a sub-atmospheric pressure P_1' where P_1' ranges from atmospheric pressure $> P_1' \geq 20kPa(a)$ when $T_1' = 60°C$ to atmospheric pressure $> P_1' \geq 84kPa(a)$ when $T_1' = 95°C$, such that impregnation of the calcined material with the active catalyst component or its precursor and partial drying of the impregnated material occurs, with the initial treatment stage not continuing beyond a point where the impregnated material has a LOI which is less than 1,2 times its LOI_{iw};

thereafter, in a subsequent treatment stage, subjecting the partially dried impregnated material to treatment at a temperature T_2' and at a sub-atmospheric pressure P_2 such that $60°C < T_2' \leq 95°C$ and $T_2' > T_1'$ and/or $P_2' < 20kPa(a)$ and $P_2' < P_1'$, thereby to obtain more vigorous drying of the impregnated material in the subsequent treatment stage than in the initial treatment stage, with a dried impregnated material thereby being produced; and

calcining the dried impregnated material, to obtain the catalyst precursor.

70. A process according to Claim 69, wherein cobalt nitrate, $Co(NO_3)_2.6H_2O$, is used as an active catalyst component precursor in the second impregnation step, and wherein from $1,18x_1y_1$ to $1,82x_1y_1$kg $Co(NO_3)_2.6H_2O$ is used in the initial treatment stage of the second impregnation step where x_1 is the BET pore volume of the calcined material from the first impregnation step, in mℓ/g, and y_1 is the mass of calcined material from the first impregnation step to be impregnated in the second impregnation step, in kg, with the proviso that the amount of $Co(NO_3)_2.6H_2O$ used in the second impregnation step, is adjusted in the event that the maximum amount of $Co(NO_3)_2.6H_2O$, as determined by the formula $1,82x_1y_1$, results in a desired cobalt loading of the catalyst precursor being exceeded.

71. A process according to Claim 70, which includes, in the second impregnation step, initially dissolving the $Co(NO_3)_2.6H_2O$ in water, with sufficient water being used such that the volume of the solution is $>x_1y_1\ell$; heating the solution to a temperature between 60 and 95°C; adding the final inventory of $y_1$kg of the calcined material from the first impregnation step to this solution at atmospheric pressure, to form the slurry; and continuously mixing the slurry.

72. A process according to Claim 70 or Claim 71 wherein, in the initial treatment stage of the second impregnation step, vacuum is gradually applied to the slurry, under continuous mixing thereof, with $60°C \leq T_1' \leq 95°C$, and with atmospheric pressure $> P_1' \geq 20kPa(a)$.

73. A process according to Claim 72, wherein the initial treatment stage of the second impregnation step is continued until the loss on ignition ('LOI') of the impregnated material is 1,2 times LOI_{iw}.

74. A process according to Claim 73 wherein, when the LOI of the impregnated material is 1,2 times LOI_{iw}, increased evacuation is applied in the subsequent treatment stage of the second impregnation step so that $P_2' < P_1'$, while ensuring that the partially dried impregnation material temperature is controlled between 60°C and 95°C, under continuous mixing, so that more forceful drying of the impregnated material takes place during the subsequent treatment stage.

75. A process according to Claim 74, wherein the more forceful vacuum drying during the subsequent treatment stage proceeds in an uninterrupted fashion at the minimum pressure which is attainable, with vacuum drying under these conditions being maintained until a clearly defined maximum LOI value is reached, with this maximum LOI value being smaller than, or equal to, 0,90 times LOI_{iw}.

76. A process according to Claim 74 or Claim 75 which includes, during the subsequent treatment stage, controlling the drying rate of the slurry by controlling the sub-atmospheric pressure P_2', by controlling or adjusting the degree of mixing, by controlling or adjusting the treatment temperature T_2' and/or by introducing hot air into the slurry.

77. A process according to Claim 76 wherein, during the subsequent treatment stage, the drying rate is controlled such that, at the point of incipient wetness, the drying rate is greater than $(0,048h^{-1})$ LOI_{iw}.

78. A process according to Claim 76 or Claim 77, which includes storing the dried impregnated carrier or support from the subsequent treatment stage at ambient conditions in a dry environment before calcination thereof, with the storage time being less than

$((-8,1/LOI_{iw})LOI_{unload}+26,2)$ hours, where LOI_{unload} is the LOI at which the subsequent treatment stage is terminated.

79. A process according to any one of Claims 70 to 78 inclusive, wherein the calcination of the dried impregnated material is effected in a fluidized bed calciner, or in a rotary kiln calciner, at a temperature from 200°C to 300°C.

80. A process according to any one of Claims 56 to 79 inclusive wherein, during the first treatment stage of the first impregnation step and/or during the first treatment stage of the second impregnation step, a water soluble precursor salt of palladium, Pd, or platinum, Pt, is added, as a dopant capable of enhancing the reducibility of the active component, with the mass proportion of the palladium or the platinum metal to the cobalt metal being between 0,01:100 to 0,3:100.

81. A process according to Claim 56, wherein from 1,18xy to 1,82xy kg $Co(NO_3)_2.6H_2O$ is used in the initial treatment stage, where x is the BET pore volume of the alumina support in mℓ/g, and y is the mass of alumina support to be impregnated, in kg and which includes initially dissolving the $Co(NO_3)_2.6H_2O$ in the water, with sufficient water being used such that the volume of the solution is >xyℓ; adding the support to the solution at ambient temperature to form the slurry, and thereafter heating the slurry to the elevated temperature which is from 60°C to 95°C, with the sub-atmospheric pressure or vacuum that is applied during the initial treatment stage being down to 20kPa(a).