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(54) Benævnelse: **FREMSTILLING AF EN COBALTKATALYSATOR PÅ BASIS AF EN BÆRER INDEHOLDENDE EN BLANDET OXIDFASE INDEHOLDENDE COBALT OG/ELLER NIKKEL, FREMSTILLET VED ANVENDELSE AF EN DICARBOXYLSYRE MED MINDST TRE CARBONATOMER**

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Description

The invention relates to a method for preparing a catalyst containing an active cobalt phase, deposited on a support comprising alumina, silica or silica-alumina.

The present invention relates to the field of Fischer-Tropsch synthesis processes which make it possible to obtain a wide range of hydrocarbon cuts from the CO + H_2 mixture, commonly referred to as synthesis gas or syngas. The simplified stoichiometric equation (limited in the equation below to the formation of alkanes) of the Fischer-Tropsch synthesis is written:

$$n\ CO + (2n + 1)\ H_2 \rightarrow C_nH_{2n+2} + n\ H_2O$$

The catalysts used in Fischer-Tropsch synthesis are usually supported catalysts based on alumina, silica or silica-alumina or combinations of these supports, the active phase mainly consisting of iron (Fe) or cobalt (Co) optionally doped with a noble metal such as Pt, Rh or Ru.

The addition of an organic compound to Fischer-Tropsch catalysts to improve their activity has been recommended by those skilled in the art.

Many documents describe the use of various ranges of organic compounds as additives, such as nitrogen-containing organic compounds and/or oxygen-containing organic compounds.

In particular, Patents US 5 856 260 and US 5 856 261 respectively teach the introduction, during the preparation of the catalyst, of polyols of general formula $C_nH_{2n+2}O_x$, with n being an integer between 2 and approximately 6 and x being an integer between 2 and 11, or of sugars of mono- or disaccharide type, sucrose being particularly preferred.

Patent Application US 2005/0026776 teaches the use of chelating compounds of the following types: nitrilotriacetic acid (NTA), trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (CyDTA) or ethylenediaminetetraacetic acid (EDTA), or else of glycine, aspartic acid or citric acid for obtaining a catalyst with a reduced size of Co_3O_4 crystallites. Other documents teach the use of polyethers (WO 2014/092278 and WO 2015/183061), of glyoxylic acid (WO 2015/183059), of unsaturated dicarboxylic acids (US 2011/0028575) or else of polyfunctional carboxylic acids of formula $HOOC-(CRR^1)_n-COOH$ with $n \geq 1$ in the preparation of Fischer-Tropsch catalysts (WO 98/47618).

Patent Application US 2014/0353213 describes the use of lactams or cyclic esters of lactone type containing one oxygen atom in the ring (β-propiolactone, γ-butyrolactone, δ-valerolactone) or several oxygen atoms in the ring (propylene carbonate) in order to increase the activity of a catalyst of CoMo or NiMo type used in hydrodesulfurization of a diesel cut.

Document WO 2012/013866 discloses the use of a cyclic oligosaccharide, in particular cyclodextrin, as additive of a Fischer-Tropsch catalyst. This document also describes the use of a support based on silica-alumina optionally containing a spinel.

However, none of the documents relating to the additives describes a catalyst based on cobalt deposited on a support containing a mixed oxide phase containing cobalt and/or nickel prepared by means of a dicarboxylic acid chosen from malonic acid or succinic acid.

Whatever the compounds chosen, the modifications induced still do not make it possible to increase the performance qualities of the catalyst enough to render the process profitable. Furthermore, it is often very complicated to deploy them industrially since the methods are complex to implement.

Consequently, it appears essential, for catalyst manufacturers, to find new catalysts for the Fischer-Tropsch synthesis with improved performance qualities.

Summary

A subject-matter of the invention is a catalyst containing an active cobalt phase, deposited on a support comprising alumina, silica or silica-alumina, said support containing a mixed oxide phase containing cobalt and/or nickel, said catalyst being prepared by a process comprising at least:

a) a step of bringing a support comprising alumina, silica or silica-alumina into contact with at least one solution containing at least one precursor of cobalt and/or of nickel, then drying and calcining at a temperature between 700°C and 1200°C, so as to obtain a mixed oxide phase containing cobalt and/or nickel in the support, then carrying out
b) a step of bringing said support containing said mixed oxide phase into contact with at least one solution containing at least one precursor of cobalt,
c) a step of bringing said support containing said mixed oxide phase into contact with at least one dicarboxylic acid selected from malonic acid or succinic acid, steps b) and c) being able to be performed separately, in any order, or at the same time,
d) then carrying out a step of drying at a temperature below 200°C. This is because the Applicant Company has observed that the use of a dicarboxylic acid chosen from malonic acid or succinic acid as organic additive during the preparation of a catalyst containing an active cobalt phase, deposited on a support comprising alumina, silica or silica-alumina, said support also containing a mixed oxide phase containing cobalt and/or nickel, made it possible to obtain a catalyst for the Fischer-Tropsch synthesis displaying improved catalytic performance qualities.

This is because the catalyst obtained by the process of the invention displays increased activity and increased selectivity

relative to catalysts containing a mixed oxide phase containing cobalt and/or nickel in their support but prepared without additivation or relative to additive-containing catalysts with no mixed oxide phase containing cobalt and/or nickel in the support. The use of such an organic compound during the preparation of a cobalt-based catalyst containing a support containing a mixed oxide phase containing cobalt and/or nickel seems to have a synergistic effect on the activity and selectivity in a Fischer-Tropsch process.

Without being bound to any theory, it has been discovered that such a catalyst exhibits a dispersion of the cobalt which is substantially greater than that exhibited by catalysts prepared in the absence of such an organic compound. This results in the presence of a greater number of active sites for the catalysts prepared in the presence of at least one dicarboxylic acid chosen from malonic acid or succinic acid, even if this compound is at least partially removed afterwards by a drying and optionally a calcining.

According to one variant, the content of mixed oxide phase in the support is between 0.1% and 50% by weight relative to the weight of the support.

According to one variant, the mixed oxide phase comprises an aluminate of formula $CoAl_2O_4$ or $NiAl_2O_4$ in the case of a support based on alumina or on silica-alumina. According to one variant, the mixed oxide phase comprises a silicate of formula Co_2SiO_4 or Ni_2SiO_4 in the case of a support based on silica or on silica-alumina.

According to one variant, the silica content of said support is between 0.5% by weight and 30% by weight relative to the weight of the support before the formation of the mixed oxide phase when the support is a silica-alumina.

According to one variant, the molar ratio of the dicarboxylic acid chosen from malonic acid or succinic acid introduced during

step c) relative to the cobalt element introduced in step b) is between 0.01 and 2.0 mol/mol.

According to one variant, the content of cobalt element introduced during step b) as active phase is between 2% and 40% by weight expressed as cobalt metal element relative to the total weight of the catalyst.

According to one variant, the catalyst further comprises an element chosen from groups VIIIB, IA, IB, IIA, IIB, IIIA, IIIB and VA.

According to one variant, the catalyst further contains an organic compound other than the dicarboxylic acid comprising at least three carbon atoms, said organic compound containing oxygen and/or nitrogen.

According to one variant, the organic compound is selected from a compound comprising one or more chemical functions selected from a carboxylic, alcohol, ether, aldehyde, ketone, ester, carbonate, amine, nitrile, imide, oxime, urea and amide function.

According to one variant, after the drying step d), a calcining step e) is carried out at a temperature of between 200°C and 550°C in an inert atmosphere or in an oxygen-containing atmosphere.

According to one variant, the catalyst obtained in the drying step d) or obtained in the calcining step e) is reduced at a temperature of between 200°C and 500°C.

Subsequently, the groups of chemical elements are given according to the CAS classification (CRC Handbook of Chemistry and Physics, published by CRC Press, editor-in-chief D.R. Lide, 81st edition, 2000-2001). For example, group VIII according to the CAS classification corresponds to the metals of columns 8, 9 and 10 according to the new IUPAC classification.

The textural and structural properties of the support and of the catalyst described below are determined by the characterization methods known to a person skilled in the art. The total pore volume and the pore distribution are determined in the present invention by nitrogen porosimetry as described in the work "Adsorption by Powders and Porous Solids. Principles, Methodology and Applications", written by F. Rouquérol, J. Rouquérol and K. Sing, Academic Press, 1999. The term "specific surface" is understood to mean the BET specific surface (S_{BET} in m^2/g) determined by nitrogen adsorption in accordance with Standard ASTM D 3663-78 established from the Brunauer-Emmett-Teller method described in the journal "The Journal of the American Chemical Society", 1938, 60, 309.

Detailed description of the invention

The various steps of the process according to the invention will be described in detail hereinafter:

Step a) Formation of the mixed oxide phase containing cobalt and/or nickel

The objective of step a) is the formation of a mixed oxide phase containing cobalt and/or nickel in a support comprising alumina, silica or silica-alumina by bringing into contact with a solution containing at least one precursor of cobalt and/or of nickel, followed by a drying and a high-temperature calcining.

It is known that the presence of a mixed oxide phase containing cobalt and/or nickel in a support of alumina, silica or silica-alumina type makes it possible to improve the resistance to the phenomenon of chemical and mechanical attrition in a Fischer-Tropsch process, and therefore to stabilize the support.

The formation of the mixed oxide phase in the support, often referred to as step of stabilization of the support, may be carried out by any method known to a person skilled in the art.

It is generally carried out by introducing cobalt and/or nickel in the form of a salt precursor, for example of nitrate type, over the initial support containing alumina, silica or silica-alumina. By calcining at very high temperature, the mixed oxide phase containing cobalt and/or nickel is formed and stabilizes the whole of the support. The cobalt and/or nickel contained in the mixed oxide phase cannot be reduced during the final activation of the Fischer-Tropsch catalyst (reduction). The cobalt and/or nickel contained in the mixed oxide phase does not therefore constitute the active phase of the catalyst.

According to step a), a step of bringing a support comprising alumina, silica or silica-alumina into contact with at least one solution containing at least one precursor of cobalt and/or of nickel is carried out, then drying and calcining are carried out at a temperature between 700°C and 1200°C, so as to obtain a mixed oxide phase containing cobalt and/or nickel in the support.

More particularly, the contacting step a) can be carried out by impregnation, preferably dry impregnation, of a support comprising alumina, silica or silica-alumina, preformed or in powder form, with at least one aqueous solution containing the precursor of cobalt and/or of nickel, followed by a drying and a calcining at a temperature of between 700°C and 1200°C.

The cobalt is brought into contact with the support by means of any precursor of cobalt which is soluble in the aqueous phase. Preferably, the precursor of cobalt is introduced in aqueous solution, preferably in nitrate, carbonate, acetate or chloride form, in the form of complexes formed with acetylacetonates, or in the form of any other inorganic derivative soluble in aqueous solution, which is brought into contact with said support. The precursor of cobalt advantageously used is cobalt nitrate or cobalt acetate.

The nickel is brought into contact with the support by means of any precursor of nickel which is soluble in the aqueous phase.

Preferably, said precursor of nickel is introduced in aqueous solution, for example in nitrate, carbonate, acetate, chloride, hydroxide, hydroxycarbonate or oxalate form, in the form of complexes formed with acetylacetonates, or in the form of any other inorganic derivative soluble in aqueous solution, which is brought into contact with said support. The precursor of nickel advantageously used is nickel nitrate, nickel chloride, nickel acetate or nickel hydroxycarbonate.

The total content of cobalt and/or of nickel is advantageously between 1% and 20% by weight and preferably between 2% and 10% by weight relative to the weight of the final support.

The drying is advantageously carried out at a temperature of between 60°C and 200°C, preferably for a period of time ranging from 30 minutes to three hours.

The calcining is carried out at a temperature of between 700°C and 1200°C, preferably of between 850°C and 1200°C and in a preferred way of between 850°C and 900°C, generally for a period of time of between one hour and 24 hours and preferably of between 2 hours and 5 hours. The calcining is generally carried out under an oxidizing atmosphere, for example in air, or in oxygen-depleted air; it can also be carried out at least partly under nitrogen. It makes it possible to convert the precursors of cobalt and/or of nickel and the alumina and/or silica into the mixed oxide phase containing cobalt and/or nickel. According to one variant, the calcining can also be carried out in two steps, said calcining being advantageously carried out at a temperature of between 300°C and 600°C in air for a period of time of between half an hour and three hours, and then at a temperature of between 700°C and 1200°C, preferably of between 850°C and 1200°C and in a preferred way between 850°C and 900°C, generally for a period of time of between one hour and 24 hours and preferably of between 2 hours and 5 hours.

The support comprises alumina, silica or silica-alumina.

When the support comprises alumina, it contains more than 50% by weight of alumina relative to the weight of the support before the formation of the mixed oxide phase and, preferably, it contains only alumina. The alumina can be present in a crystallographic form of gamma-, delta-, theta- or alpha-alumina type, taken alone or as a mixture.

In another preferred case, the support comprises silica. In this case, it contains more than 50% by weight of silica relative to the weight of the support before the formation of the mixed oxide phase and, preferably, it contains only silica. Sources of silicon are well known to a person skilled in the art.

In another preferred case, the support comprises a silica-alumina. A support comprising a silica-alumina is understood to mean a support in which the silicon and the aluminium are in the form of agglomerates of silica or of alumina respectively, of amorphous aluminosilicate or any other mixed phase containing silicon and aluminium, it being understood that the support is not mesostructured. Preferably, the alumina and the silica are present in the form of a mixture of oxides SiO_2-Al_2O_3. The silica content in the silica-alumina support varies from 0.5% by weight to 30% by weight, preferably from 1% by weight to 25% by weight and more preferably still from 1.5% to 20% by weight relative to the weight of the support before the formation of the mixed oxide phase.

According to a preferred variant, the support consists of alumina, silica or silica-alumina and particularly preferably the support consists of silica-alumina.

The support also contains a mixed oxide phase containing cobalt and/or nickel. Mixed oxide phase containing cobalt and/or nickel is understood to mean a phase in which cobalt and/or of nickel cations are combined with the oxide ions O^{2-} of the alumina and/or silica support, thus forming a mixed phase containing aluminates and/or silicates containing cobalt and/or nickel. The mixed oxide phase can be in amorphous form or in crystalline

form. When the support is based on alumina, the mixed oxide phase can comprise an aluminate of formula $CoAl_2O_4$ or $NiAl_2O_4$, in amorphous or crystalline form, for example in spinel form.

When the support is based on silica, the mixed oxide phase can comprise a silicate of formula Co_2SiO_4 or Ni_2SiO_4 (cobalt orthosilicate or nickel orthosilicate), in amorphous or crystalline form.

When the support is based on silica-alumina, the mixed oxide phase can comprise an aluminate of formula $CoAl_2O_4$ or $NiAl_2O_4$, in amorphous or crystalline form, for example in spinel form, and/or a silicate of formula Co_2SiO_4 or Ni_2SiO_4, in amorphous or crystalline form.

Generally, the content of the mixed oxide phase in the support is between 0.1% and 50% by weight relative to the weight of the support, preferably between 0.5% and 30% by weight and more preferably between 1% and 20% by weight.

The presence of a mixed oxide phase in the catalyst is measured by temperature-programmed reduction (or TPR), such as, for example, described in Oil & Gas Science and Technology, Rev. IFP, Vol. 64 (2009), No. 1, pp. 11-12. According to this technique, the catalyst is heated under a stream of a reducing agent, for example under a stream of molecular hydrogen. The measurement of the molecular hydrogen consumed as a function of the temperature gives quantitative information regarding the reducibility of the entities present. The presence of a mixed oxide phase in the catalyst is thus expressed by a consumption of molecular hydrogen at a temperature of greater than approximately 800°C.

The support can exhibit a morphology in the form of beads, extrudates (for example of trilobe or quadrilobe shape) or pellets, in particular when said catalyst is employed in a reactor operating as a fixed bed, or exhibit a morphology in the form of a powder of variable particle size, in particular when

said catalyst is employed in a reactor of bubble-column (or "slurry bubble-column") type. The size of the grains of the catalyst can be between a few microns and a few hundred microns. For a "slurry" reactor use, the size of the particles of the catalyst is preferentially between 10 microns and 500 microns, preferably between 10 microns and 300 microns, very preferably between 20 and 200 microns and more preferably still between 30 and 160 microns.

The specific surface of the support containing the mixed oxide phase is generally between 50 m^2/g and 500 m^2/g, preferably between 100 m^2/g and 300 m^2/g, more preferably between 150 m^2/g and 250 m^2/g. The pore volume of said support is generally between 0.3 ml/g and 1.2 ml/g and preferably between 0.4 ml/g and 1 ml/g.

Thus, at the end of said step a), said support comprising alumina, silica or silica-alumina additionally comprises a mixed oxide phase containing cobalt and/or nickel.

Steps b) and c): Introduction of the active phase and of the dicarboxylic acid chosen from malonic acid or succinic acid

After the formation of the mixed oxide phase, the following steps are carried out in the preparation of the catalyst:
b) a step of bringing said support containing said mixed oxide phase into contact with at least one solution containing at least one precursor of cobalt,
c) a step of bringing said support containing said mixed oxide phase into contact with at least one dicarboxylic acid selected from malonic acid or succinic acid, steps b) and c) being able to be performed separately, in any order, or at the same time.

Step b) of bringing said support into contact with at least one solution containing at least one precursor of cobalt can be carried out by any method well known to a person skilled in the art. Said step b) is preferentially carried out by impregnation of the support by at least one solution containing at least one

precursor of cobalt. In particular, said step b) can be carried out by dry impregnation, by excess impregnation, or else by deposition-precipitation (as described in Patents US 5 874 381 and US 6 534 436) according to methods well known to a person skilled in the art. Preferably, said step b) is carried out by dry impregnation, which consists in bringing the support of the catalyst into contact with a solution containing at least one precursor of cobalt, the volume of which is equal to the pore volume of the support to be impregnated. This solution contains the precursor of cobalt at the desired concentration.

The cobalt is brought into contact with said support by means of any precursor of cobalt which is soluble in the aqueous phase or in the organic phase. When it is introduced in organic solution, said precursor of cobalt is, for example, cobalt acetate. Preferably, said precursor of cobalt is introduced in aqueous solution, for example in nitrate, carbonate, acetate or chloride form, in the form of complexes formed with acetylacetonates, or in the form of any other inorganic derivative soluble in aqueous solution, which is brought into contact with said support. Use is advantageously made, as precursor of cobalt, of cobalt nitrate or cobalt acetate.

The content of cobalt element is of between 2% and 40% by weight, preferably between 5% and 30% by weight and more preferably between 10% and 25% by weight expressed as cobalt metal element relative to the total weight of the catalyst.

The catalyst can advantageously comprise in addition at least one element chosen from an element from groups VIIIB, IA, IB, IIA, IIB, IIIA, IIIB and/or VA.

The preferred optional elements from group VIIIB are platinum, ruthenium and rhodium. The preferred elements from group IA are sodium and potassium. The preferred elements from group IB are silver and gold. The preferred elements from group IIA are manganese and calcium. The preferred element from group IIB is zinc. The preferred elements from group IIIA are boron and

indium. The preferred elements from group IIIB are lanthanum and cerium. The preferred element from group VA is phosphorus.

The content of optional element from groups VIIIB, IA, IB, IIA, IIB, IIIA, IIIB and/or VA is between 50 ppm and 20% by weight, preferably between 100 ppm and 15% by weight and more preferably between 100 ppm and 10% by weight expressed as element relative to the total weight of the catalyst.

According to one variant, when the catalyst contains an additional element or several additional elements from groups VIIIB, IA, IB, IIA, IIB, IIIA, IIIB and/or VA, this or these elements can be either initially present on the support before the preparation of the catalyst or introduced at any point of the preparation and by any method known to a person skilled in the art.

The organic compound employed for carrying out said step c) is brought into contact with said support by impregnation, in particular by dry impregnation or excess impregnation, preferentially by dry impregnation. Said organic compound is preferentially impregnated on said support after dissolution in aqueous solution.

Said dicarboxylic acid is malonic acid or succinic acid.

The molar ratio of the dicarboxylic acid chosen from malonic acid or succinic acid introduced during step c) relative to the cobalt element introduced in step b) is between 0.01 and 2.0 mol/mol, preferably between 0.05 and 1.0.

In addition to the dicarboxylic acid chosen from malonic acid or succinic acid, the catalyst can comprise another organic compound or a group of organic compounds known for their role of additives. The function of the additives is to increase the catalytic activity relative to catalysts not treated with additives. More particularly, the catalyst can additionally

comprise one or more oxygen-containing and/or nitrogen-containing organic compounds.

Generally, the organic compound is selected from a compound comprising one or more chemical functions selected from a carboxylic, alcohol, ether, aldehyde, ketone, ester, carbonate, amine, nitrile, imide, oxime, urea and amide function. The oxygen-containing organic compound can be one or more chosen from the compounds comprising one or more chemical functions chosen from a carboxylic, alcohol, ether, aldehyde, ketone, ester or carbonate function. By way of example, the oxygen-containing organic compound can be one or more chosen from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, a polyethylene glycol (with a molecular weight of between 200 and 1500 g/mol), propylene glycol, 2-butoxyethanol, 2-(2-butoxyethoxy)ethanol, 2-(2-methoxyethoxy)ethanol, triethylene glycol dimethyl ether, glycerol, acetophenone, 2,4-pentanedione, pentanone, acetic acid, malic acid, oxalic acid, gluconic acid, tartaric acid, citric acid, succinic acid, γ-ketovaleric acid, γ-valerolactone, 4-hydroxyvaleric acid, 2-pentenoic acid, 3-pentenoic acid, 4-pentenoic acid, a di(C_1-C_4)alkyl succinate, methyl acetoacetate, dibenzofuran, a crown ether, orthophthalic acid, glucose and propylene carbonate.

The nitrogen-containing organic compound can be one or more chosen from the compounds comprising one or more chemical functions chosen from an amine or nitrile function. By way of example, the nitrogen-containing organic compound can be one or more chosen from the group consisting of ethylenediamine, diethylenetriamine, hexamethylenediamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, acetonitrile, octylamine, guanidine and a carbazole.

The oxygen-containing and nitrogen-containing organic compound can be one or more chosen from the compounds comprising one or more chemical functions chosen from a carboxylic, alcohol, ether, aldehyde, ketone, ester, carbonate, amine, nitrile,

imide, oxime, urea and amide function. By way of example, the oxygen-containing and nitrogen-containing organic compound can be one or more chosen from the group consisting of 1,2-cyclohexanediaminetetraacetic acid, monoethanolamine (MEA), N-methylpyrrolidone, dimethylformamide, ethylenediaminetetraacetic acid (EDTA), alanine, glycine, nitrilotriacetic acid (NTA), N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DPTA), tetramethylurea, glutamic acid, dimethylglyoxime, bicine and tricine, or else a lactam.

The total molar ratio of oxygen-containing and/or nitrogen-containing organic compound(s) other than the dicarboxylic acid chosen from malonic acid or succinic acid relative to the cobalt element introduced in step b) is between 0.01 and 2 mol/mol, preferably between 0.1 and 2 mol/mol, in a preferred way between 0.2 and 1.5 mol/mol, calculated on the basis of the components introduced in the impregnation solution(s).

When the catalyst also contains an organic compound other than the dicarboxylic acid chosen from malonic acid or succinic acid, this organic compound can be either initially present on the support before the preparation of the catalyst or be incorporated in the catalyst at any point during the preparation and by any method known to a person skilled in the art.

Implementation of steps b) and c)

The process for preparing the catalyst, in particular steps b) and c), comprises several embodiments. They differ in particular in the moment of the introduction of the organic compound, which can be carried out either at the same time as the impregnation with cobalt of the active phase (co-impregnation), or after the impregnation with cobalt of the active phase (post-impregnation), or before the impregnation with cobalt of the active phase (pre-impregnation). In addition, it is possible to combine the embodiments.

A first embodiment consists in carrying out said steps b) and c) simultaneously so that said organic compound and at least said precursor of cobalt present in the active phase are co-impregnated onto said support (co-impregnation). Said first embodiment advantageously comprises the implementation of one or more steps b). In particular, one or more steps b) advantageously precede(s) and/or follow(s) said co-impregnation step. Said first embodiment can comprise several co-impregnation steps.

A second embodiment consists in carrying out said step b) prior to said step c) (post-impregnation). In accordance with said second embodiment, one or more steps b) of bringing into contact at least cobalt present in the active phase of the catalyst precede(s) said step c).

A third embodiment consists in carrying out said step c) prior to said step b) (pre-impregnation). Advantageously, said step c) is followed by several steps b).

When steps b) and c) are carried out separately (post-impregnation or pre-impregnation), a drying step is advantageously carried out between the impregnation steps. The intermediate drying step is carried out at a temperature of less than 200°C, advantageously of between 50°C and 180°C, preferably between 70°C and 150°C, very preferably between 75°C and 130°C, and optionally a maturation period was observed between the impregnation step and the intermediate drying step.

Each of the three embodiments described above can be carried out independently so that the catalyst is prepared either according to said first embodiment, or according to said second embodiment, or else according to said third embodiment. However, it can be advantageous to combine said first embodiment with said second embodiment or with said third embodiment: both the cobalt present in the active phase and the organic compound are deposited at least twice on the support of the catalyst, namely

at least once by co-impregnation and at least once by successive impregnation.

Advantageously, after each impregnation step, whether this is a step of impregnation with the cobalt or with the organic compound, the impregnated support is left to mature. Maturation makes it possible for the impregnation solution to homogeneously disperse within the support.

Any maturation step described in the present invention is advantageously carried out at atmospheric pressure, in a water-saturated atmosphere and at a temperature of between 17°C and 50°C, and preferably at ambient temperature. Generally, a maturation time of between ten minutes and forty-eight hours and preferably of between thirty minutes and five hours is sufficient. Longer periods of time are not ruled out but do not necessarily contribute an improvement.

Any impregnation solution described in the present invention can comprise any polar solvent known to a person skilled in the art. Said polar solvent used is advantageously chosen from the group formed by methanol, ethanol, water, phenol and cyclohexanol, taken alone or as a mixture. Said polar solvent can also advantageously be chosen from the group formed by propylene carbonate, DMSO (dimethyl sulfoxide), N-methylpyrrolidone (NMP) and sulfolane, taken alone or as a mixture. Preferably, a polar protic solvent is used. A list of the common polar solvents and also their dielectric constants can be found in the book *Solvents and Solvent Effects in Organic Chemistry*, C. Reichardt, Wiley-VCH, 3rd edition, 2003, pages 472-474. Very preferably, the solvent used is water or ethanol and particularly preferably the solvent is water. In one possible embodiment, the solvent can be absent from the impregnation solution.

When several impregnation steps are carried out, each impregnation step is preferably followed by an intermediate drying step at a temperature of less than 200°C, advantageously of between 50°C and 180°C, preferably between 70°C and 150°C,

very preferably between 75°C and 130°C, and optionally a maturation period was observed between the impregnation step and the intermediate drying step.

Drying step d)

In accordance with the drying step d) of the implementation for the preparation of the catalyst, prepared according to at least one embodiment described above, the drying is carried out at a temperature of less than 200°C, advantageously of between 50°C and 180°C, preferably between 70°C and 150°C, very preferably between 75°C and 130°C. The drying step is preferentially carried out over a period of time of between 1 and 4 hours, preferably in an inert atmosphere or in an oxygen-containing atmosphere.

The drying step can be carried out by any technique known to a person skilled in the art. It is advantageously carried out at atmospheric pressure or at reduced pressure. Preferably, this step is carried out at atmospheric pressure. It is advantageously carried out in a traversed bed using hot air or any other hot gas. Preferably, when the drying is carried out in a fixed bed, the gas used is either air or an inert gas, such as argon or nitrogen. Very preferably, the drying is carried out in a traversed bed in the presence of nitrogen and/or of air. Preferably, the drying step has a short duration of between 5 minutes and 4 hours, preferably between 30 minutes and 4 hours and very preferably between 1 hour and 3 hours.

According to a first variant, the drying is carried out so as to preferably retain at least 30% of the dicarboxylic acid chosen from malonic acid or succinic acid introduced during an impregnation step; preferably, this amount is greater than 50% and more preferably still greater than 70%, calculated on the basis of the carbon remaining on the catalyst. When an oxygen-containing and/or nitrogen-containing organic compound other than the dicarboxylic acid chosen from malonic acid or succinic acid is present, the drying step is carried out so as to retain

preferably at least 30%, preferably at least 50% and very preferably at least 70% of the amount introduced, calculated on the basis of the carbon remaining on the catalyst.

At the end of the drying step d), a dried catalyst is then obtained, which will be subjected to an activation step for the subsequent employment thereof in Fischer-Tropsch synthesis.

According to another variant, at the end of the drying step d), a calcining step e) is carried out at a temperature of between 200°C and 550°C, preferably of between 250°C and 500°C, in an inert atmosphere (nitrogen for example) or in an oxygen-containing atmosphere (air for example). The duration of this heat treatment is generally of between 0.5 hour and 16 hours, preferably between 1 hour and 5 hours. After this treatment, the cobalt of the active phase is thus in oxide form and the catalyst contains no more or very little organic compound introduced during the synthesis thereof. However the introduction of the organic compound during the preparation thereof has made it possible to increase the dispersion of the active phase, thus leading to a more active and/or more selective catalyst.

Activation (Reduction)

Prior to its use in the catalytic reactor and the implementation of the Fischer-Tropsch process, the dried catalyst obtained in step d) or the calcined catalyst obtained in step e) advantageously undergoes a reductive treatment, for example with pure or dilute hydrogen, at high temperature. This treatment makes it possible to activate said catalyst and to form particles of cobalt metal in the zero-valent state. The temperature of this reductive treatment is preferentially between 200°C and 500°C and the duration thereof is between 2 and 20 hours.

This reductive treatment is carried out either *in situ* (in the same reactor as the one where the Fischer-Tropsch reaction is carried out according to the process of the invention) or *ex situ* before being loaded into the reactor.

Fischer-Tropsch process

The Fischer-Tropsch process leads to the production of essentially linear and saturated C5+ hydrocarbons (having at least 5 carbon atoms per molecule). The hydrocarbons produced by the process are thus essentially paraffinic hydrocarbons, the fraction exhibiting the highest boiling points of which can be converted with a high yield into middle distillates (gas oil and kerosene cuts) by a hydroconversion process, such as catalytic hydrocracking and/or catalytic hydroisomerization.

The feedstock employed for the implementation of the process comprises synthesis gas. Synthesis gas is a mixture comprising in particular carbon monoxide and hydrogen exhibiting H_2/CO molar ratios which can vary in a ratio of 0.5 to 4 depending on the process by which it was obtained. The H_2/CO molar ratio of the synthesis gas is generally in the vicinity of 3 when the synthesis gas is obtained from the process for the steam reforming of hydrocarbons or of alcohol. The H_2/CO molar ratio of the synthesis gas is of the order of 1.5 to 2 when the synthesis gas is obtained from a partial oxidation process. The H_2/CO molar ratio of the synthesis gas is generally in the vicinity of 2.5 when it is obtained from a thermal reforming process. The H_2/CO molar ratio of the synthesis gas is generally in the vicinity of 1 when it is obtained from a process for the gasification and reforming of CO_2.

The catalyst used in the process for the synthesis of hydrocarbons can be employed in various types of reactors, for example fixed-bed, moving-bed, ebullated-bed or else three-phase fluidized-bed reactors. The employment of the catalyst in suspension in a three-phase fluidized reactor, preferentially of bubble column type, is preferred. In this preferred employment of the catalyst, said catalyst is divided in the form of a very fine powder, particularly of the order of a few tens of microns, this powder forming a suspension with the reaction

medium. This technology is also known under the terminology of "slurry" process by a person skilled in the art.

The process for the synthesis of hydrocarbons is carried out under a total pressure of between 0.1 and 15 MPa, preferably between 0.5 and 10 MPa, under a temperature of between 150°C and 350°C, preferably between 180°C and 270°C. The hourly space velocity is advantageously of between 100 and 20 000 volumes of synthesis gas per volume of catalyst and per hour (100 to 20 000 h^{-1}) and preferably between 400 and 10 000 volumes of synthesis gas per volume of catalyst and per hour (400 to 10 000 h^{-1}).

The examples which follow demonstrate the gains in performance qualities regarding the catalysts.

Examples

Example 1 (comparative): Catalyst A of formula Co/Al_2O_3.

A catalyst A comprising cobalt deposited on an alumina support is prepared by dry impregnation with an aqueous solution of cobalt nitrate so as to deposit, in two successive steps, of the order of 10% by weight of Co on a gamma-alumina powder (Puralox® SCCa 5/170, Sasol) with a mean particle size equal to 80 µm, with a specific surface of 165 m^2/g and with a pore volume, measured by nitrogen adsorption isotherm, of 0.4 ml/g.

After a first dry impregnation, the solid is dried in a traversed bed at 120°C for 3 h in air and then calcined at 400°C for 4 h in a traversed bed in a stream of air. The intermediate catalyst contains approximately 6% by weight of Co. It is subjected to a second step of dry impregnation using a cobalt nitrate solution. The solid obtained is dried in a traversed bed at 120°C for 3 h in air and then calcined at 400°C for 4 h in a traversed bed in a stream of air. The final catalyst A is obtained, which catalyst contains 10.5% by weight of Co (in Co_3O_4 oxide form).

Example 2 (comparative): Catalyst B of formula $Co/Al_2O_3.SiO_2$

A catalyst B comprising cobalt deposited on a silica-alumina support is prepared by dry impregnation with an aqueous solution of cobalt nitrate so as to deposit, in one step, approximately 10% by weight of Co on a silica-alumina initially containing 5% by weight of SiO_2 and having a specific surface of 180 m^2/g and a pore volume of 0.8 ml/g.

After the dry impregnation, the solid is dried in a traversed bed at 120°C for 3 h in air and then calcined at 400°C for 4 h in a traversed bed. The final catalyst B is obtained, which catalyst contains 9.9% by weight of Co (in Co_3O_4 oxide form).

Example 3 (comparative): Catalyst C of formula $Co/CoAl_2O_4$-$Al_2O_3.SiO_2$

A catalyst C comprising cobalt deposited on a support, based on a mixed oxide phase (in spinel form) included in a silica-alumina, is prepared by dry impregnation with an aqueous solution of cobalt nitrate so as to deposit, in one step, approximately 10% by weight of cobalt on the support.

The spinel present in the support of the catalyst C is a simple spinel formed of cobalt aluminate, which is included in a silica-alumina containing 5% by weight of SiO_2, and exhibiting a specific surface of 180 m^2/g and a pore volume of 0.8 ml/g. The preparation of the spinel included in the silica-alumina is carried out by dry impregnation with an aqueous solution of cobalt nitrate so as to introduce 5% by weight of Co into said silica-alumina. After drying at 120°C for 3 hours, the solid is calcined at 850°C for 4 hours in air. The support of the catalyst, denoted C', is formed of 5% by weight of cobalt in the form of cobalt aluminate (i.e. 15% by weight of spinel) in the silica-alumina.

The cobalt-based active phase is subsequently deposited on said support in one step, by dry impregnation, according to a protocol which is identical to that described for the preparation of the

catalyst B. The drying and calcining steps are also carried out under the same operating conditions as those of Example 2. The concentration of cobalt in the solution of cobalt nitrate, used for the successive impregnations, is chosen in order to obtain the catalyst C with the desired final Co content.

The final catalyst C exhibits a total content of cobalt of 15.7% by weight (the content of Co present in the spinel phase being included) and a content of cobalt in Co_3O_4 oxide form of 10.7% by weight.

Example 4 (comparative): Catalyst D of formula $Co/CoAl_2O_4$-$Al_2O_3.SiO_2$ containing acetic acid.

A catalyst D comprising cobalt and acetic acid which are deposited on a support, based on a spinel included in a silica-alumina, is prepared by dry impregnation with an aqueous solution of cobalt nitrate and then with a solution of acetic acid so as to deposit approximately 10% by weight of cobalt on the support.

The cobalt-based active phase is deposited on the support C' of Example 3 in one step, by dry impregnation with a solution containing cobalt nitrate. After the dry impregnation, the solid undergoes drying in a traversed bed at 120°C for 3 h in air.

In a second step, the acetic acid is deposited on the preceding solid in one step, by dry impregnation with a solution containing acetic acid (Sigma Aldrich@, > 99%) at a concentration which makes it possible to achieve an acetic acid:Co molar ratio of 0.2 on the final catalyst. After the dry impregnation, the solid undergoes a maturation in a water-saturated atmosphere for 9 hours at ambient temperature, is then dried in a traversed bed at 120°C for 3 h in air and is then treated in a traversed bed at 400°C for 4 h in nitrogen.

The final catalyst D exhibits a total content of cobalt of 14.6% by weight (the content of Co present in the spinel phase being

included) and a content of cobalt in Co_3O_4 oxide form of 9.6% by weight.

Example 5 (comparative): Catalyst E of formula $Co/CoAl_2O_4$-$Al_2O_3.SiO_2$ containing citric acid.

A catalyst E comprising cobalt and citric acid which are deposited on a support, based on a spinel included in a silica-alumina, is prepared by dry impregnation with an aqueous solution of cobalt nitrate and then with an aqueous solution of citric acid so as to deposit approximately 10% by weight of cobalt on the support.

The cobalt-based active phase is deposited on the support C' of Example 3 in one step, by dry impregnation with a solution containing cobalt nitrate. After the dry impregnation, the solid undergoes drying in a traversed bed at 120°C for 3 h in air.

In a second step, the citric acid is deposited on the preceding solid in one step, by dry impregnation with a solution containing citric acid (Sigma Aldrich@, > 99%) at a concentration which makes it possible to achieve a citric acid:Co molar ratio of 0.5 on the final catalyst. After the dry impregnation, the solid undergoes a maturation in a water-saturated atmosphere for 9 hours at ambient temperature, is then dried in a traversed bed at 120°C for 3 h in air and is then treated in a traversed bed at 400°C for 4 h in nitrogen.

The final catalyst E exhibits a total content of cobalt of 14.0% by weight (the content of Co present in the spinel phase being included) and a content of cobalt in Co_3O_4 oxide form of 9.0% by weight.

Example 6 (according to the invention): Catalyst F of formula $Co/CoAl_2O_4$-$Al_2O_3.SiO_2$ containing malonic acid.

A catalyst F comprising cobalt and malonic acid which are deposited on a support, based on a spinel included in a silica-

alumina, is prepared by dry impregnation with an aqueous solution of cobalt nitrate and then with an ethanolic solution of malonic acid so as to deposit approximately 10% by weight of cobalt on the support.

The cobalt-based active phase is deposited on the support C' of Example 3 in one step, by dry impregnation with a solution containing cobalt nitrate. After the dry impregnation, the solid undergoes drying in a traversed bed at 120°C for 3 h in air.

In a second step, the malonic acid is deposited on the preceding solid in one step, by dry impregnation with an ethanolic solution containing malonic acid (Sigma Aldrich@, > 98%) at a concentration which makes it possible to achieve a malonic acid:Co molar ratio of 0.2 on the final catalyst. After the dry impregnation, the solid undergoes a maturation in a water-saturated atmosphere for 9 hours at ambient temperature, is then dried in a traversed bed at 120°C for 3 h in air and is then treated in a traversed bed at 400°C for 4 h in nitrogen.

The final catalyst F exhibits a total content of cobalt of 15.1% by weight (the content of Co present in the spinel phase being included) and a content of cobalt in Co_3O_4 oxide form of 10.1% by weight.

Example 7 (according to the invention): Catalyst G of formula $Co/CoAl_2O_4-Al_2O_3.SiO_2$ containing succinic acid.

A catalyst H comprising cobalt and succinic acid which are deposited on a support, based on a spinel included in a silica-alumina, is prepared by dry impregnation with an aqueous solution of cobalt nitrate and then with an ethanolic solution of succinic acid so as to deposit approximately 10% by weight of cobalt on the support.

The cobalt-based active phase is deposited on the support C' of Example 3 in one step, by dry impregnation with a solution

containing cobalt nitrate. After the dry impregnation, the solid undergoes drying in a traversed bed at 120°C for 3 h in air.

In a second step, the succinic acid is deposited on the preceding solid in one step, by dry impregnation with an ethanolic solution containing succinic acid (Sigma Aldrich@, > 98%) at a concentration which makes it possible to achieve a succinic acid:Co molar ratio of 0.2 on the final catalyst. After the dry impregnation, the solid undergoes a maturation in a water-saturated atmosphere for 9 hours at ambient temperature, is then dried in a traversed bed at 120°C for 3 h in air and is then treated in a traversed bed at 400°C for 4 h in nitrogen.

The final catalyst G exhibits a total content of cobalt of 14.8% by weight (the content of Co present in the spinel phase being included) and a content of cobalt in Co_3O_4 oxide form of 9.8% by weight.

Example 8 (according to the invention): Catalyst H of formula $Co/CoAl_2O_4-Al_2O_3.SiO_2$ containing succinic acid.

The catalyst H is prepared in a similar way to the catalyst G except that it does not undergo a heat treatment in nitrogen at 400°C at the end of preparation.

Example 9: Catalytic performance qualities of the catalysts A to H in Fischer-Tropsch reaction

The catalysts A, B, C, D, E, F, G and H, before being tested in Fischer-Tropsch synthesis, are reduced *in situ* under a stream of pure hydrogen at 400°C for 16 hours. The Fischer-Tropsch synthesis reaction is carried out in a tubular reactor of fixed bed type which operates continuously.

Each of the catalysts is in powder form with a diameter of between 40 and 150 microns.

The test conditions are as follows:

- Temperature = 216°C
- Total pressure = 2 MPa
- Hourly space velocity (HSV) = 4100 $Sl/h^{-1}/kg_{catalyst}$
- H_2/CO molar ratio = 2/1

The results, expressed in terms of activity (conversion of the CO in %) and of selectivity (percentage by weight of C_8^+ hydrocarbons over all of the products formed), appear in Table 1.

Table 1: Catalytic performance qualities of each catalyst

Catalyst	Conversion of the CO at 70 h under reaction stream (%)	C_8^+ selectivity at 70 h under reaction stream (% by weight)
A (comparative)	27.5	57.1
B (comparative)	38.1	65.9
C (comparative)	44.7	68.0
D (comparative)	35.3	62.0
E (comparative)	41.3	56.1
F (invention)	51.3	70.1
G (invention)	53.5	70.5
H (invention)	53.2	70.6

The results appearing in Table 1 demonstrate that the catalysts according to the invention are more active and/or more selective than the known catalysts of the prior art.

Patentkrav

1. Fremgangsmåde til fremstilling af en katalysator, der indeholder en aktiv fase af cobalt, som er pålagt på en bærer, der omfatter aluminiumoxid, silica eller silica-aluminiumoxid, hvilken bærer indeholder en blandet oxidfase, der indeholder cobalt og/eller nikkel, hvilken fremgangsmåde som minimum omfatter følgende:
a) et trin, hvorunder en bærer, der omfatter aluminiumoxid, silica eller silica-aluminiumoxid, bringes i kontakt med mindst én opløsning, der indeholder mindst én cobalt- og/eller nikkelforløber, hvorefter der udføres tørring og kalcinering ved en temperatur på mellem 700 °C og 1200 °C, hvorved der opnås en blandet oxidfase, der indeholder cobalt og/eller nikkel i bæreren,
derefter udføres
b) et trin, hvorunder bæreren indeholdende den blandede oxidfase bringes i kontakt med mindst én opløsning, der indeholder mindst én cobaltforløber
c) et trin, hvorunder bæreren indeholdende den blandede oxidfase bringes i kontakt med mindst én dicarboxylsyre, der er valgt blandt maleinsyre eller ravsyre,
idet trin b) og c) kan udføres særskilt, i vilkårlig rækkefølge eller samtidigt
d) derefter udføres et tørretrin ved en temperatur på under 200 °C.

2. Fremgangsmåde til fremstilling af en katalysator ifølge krav 1, hvorved indholdet af blandet oxidfase i bæreren ligger mellem 0,1 og 50 vægt-% i forhold til bærerens vægt.

3. Fremgangsmåde til fremstilling af en katalysator ifølge et af kravene 1 eller 2, hvorved den blandede oxidfase omfatter et aluminat med formlen $CoAl_2O_4$ eller $NiAl_2O_4$, når der er tale om en bærer på basis af aluminiumoxid- eller silica-aluminiumoxid.

4. Fremgangsmåde til fremstilling af en katalysator ifølge et af kravene 1 til 3, hvorved indholdet af silica i bæreren ligger

mellem 0,5 vægt-% og 30 vægt-% i forhold til bærerens vægt forud for dannelsen af den blandede oxidfase, når bæreren er af typen silica-aluminiumoxid.

5. Fremgangsmåde til fremstilling af en katalysator ifølge et af kravene 1 til 4, hvorved molforholdet mellem den dicarboxylsyre med mindst tre carbonatomer, der føres ind under trin c), og det cobaltelement, der føres ind i trin b), ligger mellem 0,01 og 2,0 mol/mol.

6. Fremgangsmåde til fremstilling af en katalysator ifølge et af kravene 1 til 5, hvorved indholdet af det cobaltelement, der føres ind under trin b) som aktiv fase, ligger mellem 2 vægt-% og 40 vægt-%, udtrykt som cobaltmetal i forhold til katalysatorens samlede vægt.

7. Fremgangsmåde til fremstilling af en katalysator ifølge et af kravene 1 til 6, hvorved katalysatoren desuden indeholder en anden organisk forbindelse end dicarboxylsyren med mindst tre carbonatomer, hvilken organisk forbindelse indeholder oxygen og/eller nitrogen.

8. Fremgangsmåde til fremstilling af en katalysator ifølge krav 7, hvorved den organiske forbindelse er valgt blandt en forbindelse, der omfatter én eller flere kemiske grupper, som er valgt blandt en gruppe af typen carboxyl, alkohol, ether, aldehyd, keton, ester, carbonat, amin, nitril, imid, oxim, urea og amid.

9. Fremgangsmåde til fremstilling af en katalysator ifølge et af kravene 1 til 8, hvorved der efter tørringstrinnet d) udføres et kalcineringstrin e) ved en temperatur på mellem 200 °C og 550 °C under en inert atmosfære eller under en oxygenholdig atmosfære.

10. Fremgangsmåde til fremstilling af en katalysator ifølge et af kravene 1 til 9, hvorved den katalysator, der opnås i

tørringstrinnet d) eller i calcineringstrinnet e), reduceres ved en temperatur på mellem 200 °C og 500 °C.