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(54) Title: CATALYST MANUFACTURING METHOD

(57) Abstract: The invention relates to a process for preparing a catalyst, which process comprises: preparing a catalyst containing nickel and copper by a process comprising precipitation of a solution comprising nickel and copper salts; mixing the catalyst with an organic aliphatic acid comprising a carboxylic acid group (-CO₂H group); and subjecting the mixture to an elevated temperature which is equal to or higher than the decomposition temperature of the organic aliphatic acid resulting in a thermally treated material. Further, the invention relates to a catalyst obtainable by said process.



CATALYST MANUFACTURING METHOD

Field of the invention

The present invention relates to a process for preparing
5 a catalyst containing nickel and copper, and to a catalyst
obtainable by such process.

Background of the invention

It is known to use catalysts containing nickel and copper
in all kinds of processes, such as hydrogenation, reductive
10 amination and many other processes.

In catalyzed chemical processes in general, and more
specificly in the above-mentioned catalyzed processes, it is
desirable that the catalyst to be used has good mechanical
properties, for example a relatively high and uniform
15 crushing strength, specifically radial crushing strength, and
no fissures. In addition, it is desirable that the catalyst
has good catalytic properties in that the dispersion of the
catalytically active metal(s), such as nickel, is good and in
that the porosity of the catalyst is relatively high.
20 Further, it is desirable that the catalyst to be used has a
relatively large portion of pores having a relatively high
pore radius (e.g. greater than 50 nm). Still further, it is
desirable that the catalyst to be used has a large pore
volume.

25 It is an object of the present invention to provide a
process for preparing a catalyst containing nickel and copper
that results in a catalyst having one or more of the above-
described desired properties.

Summary of the invention

30 Surprisingly it was found that a catalyst having one or
more of the above-described desired mechanical and catalytic
properties can be prepared by a process wherein a catalyst

containing nickel and copper, said catalyst having been obtained by precipitation, is mixed with an organic aliphatic acid comprising a carboxylic acid group, and the obtained mixture is subjected to an elevated temperature which is equal to or higher than the decomposition temperature of the organic aliphatic acid.

Accordingly, the present invention relates to a process for preparing a catalyst, which process comprises:

preparing a catalyst containing nickel and copper by a process comprising precipitation of a solution comprising nickel and copper salts;

mixing the catalyst with an organic aliphatic acid comprising a carboxylic acid group ($-\text{CO}_2\text{H}$ group); and

subjecting the mixture to an elevated temperature which is equal to or higher than the decomposition temperature of the organic aliphatic acid resulting in a thermally treated material.

Further, the present invention relates to a catalyst obtainable by the above-mentioned process.

Detailed description of the invention

In the present invention, an organic aliphatic acid comprising a carboxylic acid group ($-\text{CO}_2\text{H}$ group) is mixed with a catalyst containing nickel and copper. Within the present specification, "aliphatic" means "non-aromatic".

Said organic aliphatic acid may have 1 to 15 carbon atoms, suitably 2 to 10 carbon atoms, more suitably 2 to 8 carbon atoms, including the carbon atoms from the carboxylic acid group or groups. Further, the organic aliphatic acid may be substituted with one or more substituents other than a carboxylic acid group. Suitable other substituents are hydroxyl ($-\text{OH}$) and keto ($=\text{O}$), preferably hydroxyl. The organic aliphatic acid may comprise 1 to 3 carboxylic acid groups, preferably 2 to 3 carboxylic acid groups, more

preferably 3 carboxylic acid groups. Still further, the organic aliphatic acid may contain one or more carbon-carbon double bonds.

In the present invention, the organic aliphatic acid may be an aliphatic saturated dicarboxylic acid, an aliphatic unsaturated dicarboxylic acid, an aliphatic hydroxycarboxylic acid or any combination thereof. Said aliphatic hydroxycarboxylic acid may comprise one or more carboxylic acid groups ($-\text{CO}_2\text{H}$) and one or more hydroxyl groups ($-\text{OH}$).

Suitable examples of aliphatic saturated dicarboxylic acids include oxalic acid, malonic acid, succinic acid, glutaric acid and adipic acid. Suitable examples of aliphatic unsaturated dicarboxylic acids include maleic acid and fumaric acid. Suitable examples of aliphatic hydroxycarboxylic acids include citric acid, tartaric acid and malic acid.

Further, it is preferred that the organic aliphatic acid is solid under the conditions when mixing the acid with the catalyst containing nickel and copper. This may be achieved by mixing at a temperature which lies below the melting point of the organic aliphatic acid.

Still further, it is preferred that the organic aliphatic acid has a relatively low decomposition temperature.

Preferably, the decomposition temperature of the organic aliphatic acid is of from 100 to 250 °C, more preferably 125 to 225 °C, most preferably 150 to 200 °C.

Preferably, the organic aliphatic acid is selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, fumaric acid, citric acid, tartaric acid and malic acid, or any combination thereof. Most preferably, the organic aliphatic acid is citric acid. Citric acid is 2-hydroxypropane-1,2,3-

tricarboxylic acid and has a decomposition temperature of 175 °C.

Before mixing said organic aliphatic acid with the catalyst containing nickel and copper, the latter catalyst is prepared by a process comprising precipitation of a solution comprising nickel and copper salts. The latter process comprising precipitation of a solution comprising nickel and copper salts, comprises:

preparing a solution comprising nickel and copper salts;

precipitating said solution resulting in a precipitate comprising nickel and copper;

recovering the precipitate thus obtained;

optionally washing the catalyst;

optionally drying the catalyst;

optionally calcining the catalyst; and

optionally grinding the catalyst.

In the present invention, preferably one or more additional metals are present in the catalyst, in addition to the nickel (Ni) and copper (Cu). Said one or more additional metals are preferably selected from the group consisting of cobalt (Co), chromium (Cr), molybdenum (Mo), aluminium (Al), silicon (Si), manganese (Mn), tin (Sn), iron (Fe), lead (Pb), zirconium (Zr), bismuth (Bi), antimony (Sb), boron (B), rhenium (Re), rhodium (Rh), iridium (Ir), ruthenium (Ru), palladium (Pd) and platinum (Pt).

Preferably, the amount of nickel in the catalyst is of from 40 to 90 wt.%, more preferably 60 to 80 wt.%, , calculated as nickel metal and nickel oxide based on total weight of the catalyst.

Preferably, the amount of copper in the catalyst is of from 4 to 40 wt.%, more preferably 6 to 14 wt.%, , calculated as copper metal and copper oxide based on total weight of the catalyst.

If an additional metal is present, preferably, the amount of such additional metal in the catalyst is of from 0.01 to 50 wt.%, more preferably 0.1 to 30 wt.%, most preferably 1 to 20 wt.%, calculated as the oxide of the additional metal based on total weight of the catalyst.

The components of the catalyst, such as the above-mentioned metal oxides, are to be selected in an overall amount not to exceed 100 wt.%.

In the first step of the catalyst preparation, a solution comprising nickel and copper salts, preferably an aqueous solution, is prepared. In case the catalyst is to contain one or more additional metals, the solution should also comprise a salt of the additional metal.

The nickel salt may be a nitrate, sulfate, chloride or organic acid salt of nickel. Preferably, the nickel salt is nickel nitrate or an organic acid salt of nickel, most preferably nickel nitrate. A suitable organic acid salt of nickel is nickel acetate.

The copper salt may be a nitrate, sulfate, chloride or organic acid salt of copper. Preferably, the copper salt is copper nitrate or an organic acid salt of copper, most preferably copper nitrate. A suitable organic acid salt of copper is copper acetate.

If used, the salt of the additional metal may be a nitrate, sulfate, chloride or organic acid salt of the additional metal. Preferably, the salt of the additional metal is a nitrate of the additional metal or an organic acid salt of the additional metal, most preferably a nitrate of the additional metal. A suitable organic acid salt of the additional metal is an acetate of the additional metal.

The solution comprising the metal salts thus obtained should then be combined with a basic solution in order to effect precipitation of the solution comprising the metal

salts, resulting in a precipitate (in a slurry or dispersion) comprising at least nickel and copper.

Any basic solution effecting such precipitation may be used. Preferably, the basic solution is an aqueous solution.

5 Further, preferably, the basic solution comprises one or more bases selected from the group consisting of sodium hydroxide, sodium carbonate, sodium hydrogen carbonate, potassium hydroxide, potassium carbonate, potassium hydrogen carbonate, ammonium carbonate and ammonium hydrogen carbonate.

10 Preferably, sodium carbonate is used as the base in the basic solution. In addition to the base, the basic solution may comprise one or more of the above-mentioned metal salts.

The amount of base in said basic solution should be sufficient to allow for precipitation of all of the metal salts. This may be achieved by using such amount of base that a pH of 8 or greater, preferably a pH of 8.5 or greater, is achieved in the dispersion. Preferably, in the precipitation step, the combined solution comprising the base and the metal salts is heated, for example at 50 to 95 °C, preferably 70 to 95 °C.

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The solid (precipitate) in the dispersion or slurry resulting from combining the solution comprising the metal salts with a basic solution, can be recovered therefrom by filtration. The separated solid may be washed with water, preferably deionized, alkali metal free water, for example in order to remove substantially all alkali metal ions that originate from the basic solution. Possibly after drying the separated solid, for example at a temperature in the range of from 80 to 160 °C, suitably 100 to 140 °C, it may further be calcined in the presence of air, at a temperature in the range of from 200 to 800 °C, preferably 250 to 700 °C, more preferably 300 to 600 °C, most preferably 350 to 500 °C. Finally, the solid catalyst obtained may be grinded.

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In the present invention, the above-mentioned separated solid catalyst is to be mixed with the organic aliphatic acid. Preferably, the molar ratio of the total amount of nickel and copper in the catalyst (calculated as the metals Ni and Cu) to the amount of the acid is of from 10 to 120, more preferably 20 to 70, most preferably 30 to 60. Further, preferably, the molar ratio of the amount of copper (calculated as the metal Cu) in the catalyst to the amount of the acid is of from 0.1 to 10, more preferably 1 to 8, most preferably 1.5 to 6. Preferably, the mixing is carried out ambient temperature, for example at a temperature of from 15 to 40 °C, suitably 20 to 30 °C.

In addition, an auxiliary for making shaped catalyst bodies comprising tablets and extrudates may be mixed with the catalyst and the organic aliphatic acid. An example of such auxiliary is a binder, for example graphite. If such auxiliary is used, the amount used is preferably of from 0.1 to 10 wt.%, more preferably 1 to 5 wt.%, based on the total weight of the catalyst and the organic aliphatic acid.

In the present invention, the mixture thus obtained, comprising the catalyst and the organic aliphatic acid, is subjected to an elevated temperature which is equal to or higher than the decomposition temperature of the organic aliphatic acid, resulting in a thermally treated material. Preferably, the temperature during this thermal treatment step is of from 175 to 900 °C, preferably of from 250 to 700 °C, more preferably of from 300 to 600 °C, most preferably of from 350 to 500 °C. Preferably, the temperature during this thermal treatment step is at least 175 °C, more preferably at least 200 °C, more preferably at least 225 °C, more preferably at least 250 °C, more preferably at least 275 °C, more preferably at least 300 °C, more preferably at least 325 °C, more preferably at least 350 °C, most preferably at least

375 °C. Further, the temperature during this thermal treatment step may be at most 1000 °C, preferably at most 900 °C, more preferably at most 800 °C, more preferably at most 700 °C, more preferably at most 650 °C, more preferably at most 600 °C, more preferably at most 550 °C, more preferably at most 500 °C, most preferably at most 475 °C. Most preferably, the temperature during this thermal treatment step is equal to or higher than the decomposition temperature of the organic aliphatic acid and lower than any one of the above-mentioned maximum temperatures. The duration of said thermal treatment step is not essential and may be of from 1 to 15 hours.

The above-mentioned thermal treatment step is preferably performed in an inert atmosphere. Suitably, during said thermal treatment step, the mixture of the catalyst and the organic aliphatic acid is subjected to a stream containing one or more inert gases which may be selected from the group consisting of the noble gases and nitrogen (N₂), preferably nitrogen. Preferably, said stream substantially consists of nitrogen (100 vol.% of nitrogen). A suitable noble gas is argon.

Subsequent to the above-mentioned thermal treatment step, the thermally treated material may be subjected to a stream containing hydrogen, preferably at an elevated temperature, resulting in a reduced, thermally treated material. Preferably, the thermally treated material is subjected to the stream containing hydrogen at a temperature of from 100 to 500 °C, preferably 200 to 400 °C. Preferably, said temperature is at least 100 °C, more preferably at least 200 °C, more preferably at least 300 °C, most preferably at least 350 °C. Further, preferably, said temperature is at most 600 °C, more preferably at most 500 °C, more preferably at most 450 °C, most preferably at most 400 °C. The stream containing

hydrogen may comprise of from 50 to 100 vol.% of H₂ (hydrogen), the remainder consisting of one or more inert gases which may be selected from the group consisting of the noble gases and nitrogen (N₂), preferably nitrogen. A suitable noble gas is argon. Preferably, the stream containing hydrogen substantially consists of hydrogen (100 vol.% of hydrogen). Hydrogen is a reducing agent. Therefore, contacting said hydrogen with the metal oxides from the catalyst results in metal reduction and production of water.

Preferably, the above-mentioned thermal treatment step, which is carried out in the presence of the organic aliphatic acid, results in partial reduction of the metals from the catalyst.

The extent of such partial reduction, of for example nickel, can be assessed by calculating the percentage of the nickel metal content of the catalyst after said thermal treatment step, wherein in addition to said organic aliphatic acid no stream containing hydrogen is used, on the basis of the nickel metal content of the catalyst after the above-mentioned optional reduction step wherein a stream containing hydrogen is used and the metal is further reduced. In the present invention, said percentage may be of from 5 to 50%, suitably 10 to 40%, more suitably 15 to 30%.

Further, the extent of such partial reduction resulting from thermal treatment in the presence of the organic aliphatic acid, of for example nickel, can be assessed by calculating the percentage of the nickel metal surface area of the catalyst after said thermal treatment step, wherein in addition to said organic aliphatic acid no stream containing hydrogen is used, on the basis of the nickel metal surface area of the catalyst after the above-mentioned optional reduction step wherein a stream containing hydrogen is used and the metal is further reduced. In the present invention,

said percentage may be of from 5 to 40%, suitably 10 to 30%, more suitably 15 to 25%.

An additional advantage of such partial reduction during the above-mentioned thermal treatment step, is that the above-mentioned optional reduction step wherein a stream containing hydrogen is used, can be shortened resulting in lowering of total production costs.

Further, after subjecting the thermally treated material to a stream containing hydrogen, the reduced, thermally treated material may be subjected to a stream containing oxygen. The stream containing oxygen may comprise of from 0.001 to 10 vol.% of O₂ (oxygen), suitably 0.01 to 6 vol.% of O₂, more suitably 0.05 to 3 vol.% of O₂, the remainder consisting of one or more inert gases which may be selected from the group consisting of the noble gases and nitrogen (N₂), preferably nitrogen. A suitable noble gas is argon. Further, preferably, the temperature during this treatment with oxygen is preferably at most 100 °C, more preferably at most 80 °C, most preferably of from 25 to 80 °C. Oxygen is a passivating agent. Therefore, contacting said oxygen with the metal from the catalyst results in metal oxidation and thus production of metal oxide. Suitably, after such passivation, an outer surface layer of metal oxide on the catalyst is obtained, the catalyst core still comprising non-oxidized metal. In general, before catalytic use of the catalyst, said metal oxide layer is removed by treatment with a hydrogen stream at an elevated temperature (for example 180 °C), which step is called the catalyst activation step.

In the present invention, before subjecting the mixture comprising the catalyst and the organic aliphatic acid to an elevated temperature which is equal to or higher than the decomposition temperature of the organic aliphatic acid, in the thermal treatment step, said mixture is preferably first

shaped. For example, said mixture may be shaped into a tablet form.

In a preferred embodiment for preparing the catalyst of the present invention, the catalyst preparation process
5 comprises:

preparing a catalyst containing nickel and copper by a process comprising precipitation of a solution comprising nickel and copper salts;

10 mixing the catalyst with an organic aliphatic acid comprising a carboxylic acid group ($-\text{CO}_2\text{H}$ group);

optionally shaping the mixture;

15 subjecting the mixture to an elevated temperature which is equal to or higher than the decomposition temperature of the organic aliphatic acid resulting in a thermally treated material;

subjecting the thermally treated material to a stream containing hydrogen; and

subjecting the reduced, thermally treated material to a stream containing oxygen.

20 The above-described preferences for each of the above steps also apply to the corresponding step in said preferred embodiment of the present catalyst preparation process. Further, the order in which said steps in the preferred embodiment are given is the order in which they should be
25 carried out in said embodiment.

Unless indicated otherwise, catalyst properties mentioned in this specification may be measured by standard measuring techniques, such as ISO. The following specific measuring techniques may be employed in the context of the invention.

30 The nickel content (wt.% Ni) in the catalysts of the present invention may be determined by complexometric titration with murexide as indicator. Before measurements the

catalyst samples are dissolved in sulphuric acid (25 wt.%) by using a microwave treatment.

The nickel metal content of the catalysts of the present invention may be determined by using a volumetric method.

5 After pre-treatment (reduction) of the reduced and passivated catalyst samples for 1 hour at 180 °C in a hydrogen stream (which is similar to the above-mentioned catalyst activation step), the catalysts are treated with hydrochloric acid and the generated hydrogen is measured. The nickel metal content
10 (wt.%) is then calculated by using the following formula:

$$273 * 2.62 * a * b/10 * 760 * (273+T) * E$$

wherein: a = air pressure (Torr); b = measured gas volume (ml); T = temperature (°C); E = catalyst weight (g).

The catalyst composition (in terms of the metal oxides)
15 may be determined by X-ray fluorescence analysis, specifically the analysis method "S4 Explorer" from Bruker AXS.

The crushing strength, specifically radial crushing strength, may be determined by using the tablets crushing
20 strength tester TBH 30, supplied by ERWEKA GmbH, D-63150 Heusenstamm, Germany. The tablets are exposed between two plates, one of which is flexible. The force recorded at tablet fracture is the crushing strength in Newton. For each measurement 20 tablets are used.

25 The nickel metal surface area may be determined by using the CO-pulse ("CO") chemisorption method. After pre-treatment (reduction) of the reduced and passivated catalyst samples for 1 hour at 180 °C in a hydrogen stream (which is similar to the above-mentioned catalyst activation step), the samples
30 are cooled in hydrogen and subsequently loaded with CO-pulses at 0° C for saturation of the metal surface with CO. The carrier gas is hydrogen (2 l/h). These measurements are made with the device "TPDRO 1100" from Thermo Finnigan.

Pore volume may be calculated from the envelope density by using mercury and absolute density values by using helium for the same sample (according to "Analytical Methods in Fine Particle Technology", Micromeritics 1997, p. 11, P.A. Webb and C. Orr).

Pore size distribution may be determined according to "Analytical Methods in Fine Particle Technology", Micromeritics 1997, Chapter 4: "Pore structure by Mercury Intrusion Porosimetry", p. 155, P.A. Webb and C. Orr, using "Autopore IV 9500" device from Micromeritics (Contact Angle: 141.3 degrees, Hg surface Tension: 480.5 dynes/cm). Prior to the pore volume and distribution measurements, all samples are pre-treated for 2 hours at 100 °C in air.

The invention is further illustrated by the following Examples.

Examples

Example 1

3.5 kg sodium carbonate (Na_2CO_3) were dissolved in 40 l deionized water under stirring in a vessel. Then 9.6 l of an aqueous waterglass solution containing 250 g silicon (Si) were added and the solution was heated to 90 °C. Then 24 l of an aqueous metal nitrate solution, containing 1750 g nickel (Ni) and 146 g copper (Cu), were added dropwise over a period of 2 hours. Said metal nitrate solution was previously made by dissolving nickel nitrate and copper nitrate in water. Then the resulting slurry comprising the precipitate containing the metals Ni, Cu, Si and Na, was stirred at 90 °C for 2 hours. Then the pH was measured, which was 8.5-9. Then the slurry was filtered thereby recovering said precipitate. The resulting filter cake (precipitate) was washed with deionized water until a Na_2O content lower than 0.3 wt.%, for the residue resulting from annealing a small portion of the filter cake at 800 °C, was reached. Then the filter cake was

dried at 120 °C for 15 hours and subsequently calcined at 400 °C for 2 hours. Then the resulting material was grinded into a powder.

Example 1.1 (invention)

The powder obtained in Example 1 was mixed with 3 wt.% of graphite (based on total amount of powder) and with 108 g citric acid. The added amount of citric acid was such that the molar ratio of nickel and copper (calculated as Ni and Cu) in the powder to the added amount of citric acid was 57, and the molar ratio of copper (calculated as Cu) to the citric acid was 4.1. These data are also shown in Table 1. The resulting powder mixture was shaped into 3x3 mm tablets.

The catalyst tablets were charged into a furnace. First the tablets were heated at 450 °C for 2 hours in a pure nitrogen stream (100 vol.% of nitrogen; GHSV (gas hourly space velocity) = 2,000 v/vh).

In Table 1, some properties are shown for the catalyst as measured after the above-described thermal treatment but before the below described reduction (with hydrogen gas containing stream) and passivation. These properties are nickel metal content and nickel metal surface area. From the values for these properties, it can be seen that in the intermediate catalyst, a part of the nickel oxide had already been reduced to nickel metal during the above-described thermal treatment.

Then the temperature was decreased to 350 °C and the nitrogen stream was replaced by a hydrogen stream. After the nitrogen was completely replaced by hydrogen, the temperature was increased to 400 °C. At this temperature, the catalyst was treated (reduced) in a pure hydrogen stream (100 vol.% of hydrogen; GHSV = 2,000 v/vh) for 5 hours.

After cooling down to 50 °C, using a stream containing nitrogen of ambient temperature, a catalyst passivation was

carried out in a stream containing nitrogen and air (GHSV = 2,000 v/vh). The oxygen concentration in the first used gas stream was 0.1 vol.%. Once the temperature started to decrease, the oxygen concentration was increased step by step, to 0.2, 0.5, 1 and 2 vol.%. The oxygen concentration in all streams was chosen such that the catalyst temperature did not exceed 80 °C.

Properties for the catalyst after said reduction and passivation are also shown in Table 1.

10 Example 1.2 (comparative)

The procedure of Example 1.1 was followed, with the proviso that in the treatment step carried out at 450 °C, an air stream (100 vol.% of air) was used instead of the pure nitrogen stream.

15 Example 1.3 (comparative)

The procedure of Example 1.1 was followed, with the proviso that no citric acid was added. Further in deviation from the procedure of Example 1.1, the catalyst tablets (containing the catalyst powder and graphite) charged into the furnace were heated in a stream containing nitrogen and 2 vol.% of hydrogen (GHSV = 2,000 v/vh) up to a temperature of 250 °C. Once the temperature started to decrease, the hydrogen concentration was increased step by step, up to 100 vol.% of hydrogen. After the nitrogen was completely replaced by hydrogen, the temperature was maintained at 250 °C for 2 hours. Then the temperature was increased to 400 °C, at which temperature the catalyst was further treated (reduced) in the pure hydrogen stream for an additional 5 hours. After cooling down to 50 °C, using a stream containing nitrogen of ambient temperature, a catalyst passivation was carried out in the same way as in Example 1.1.

30 Example 2

5.4 kg sodium carbonate (Na_2CO_3) were dissolved in 40 l deionized water under stirring in a vessel and the solution was heated to 90 °C. Then 24 l of an aqueous metal nitrate solution, containing 1750 g nickel (Ni), 146 g copper (Cu) and 284 g aluminium (Al), were added dropwise over a period of 2 hours. Said metal nitrate solution was previously made by dissolving nickel nitrate, copper nitrate and aluminium nitrate in water. Then the resulting slurry comprising the precipitate containing the metals Ni, Cu, Al and Na, was stirred at 90 °C for 2 hours. Then the pH was measured, which was 8.5-9. Then the slurry was filtered thereby recovering said precipitate. The resulting filter cake (precipitate) was washed with deionized water until a Na_2O content lower than 0.3 wt.%, for the residue resulting from annealing a small portion of the filter cake at 800 °C, was reached. Then the filter cake was dried at 120 °C for 15 hours and subsequently calcined at 400 °C for 2 hours. Then the resulting material was grinded into a powder.

Example 2.1 (invention)

The powder obtained in Example 2 was mixed with 3 wt.% of graphite (based on total amount of powder) and with 162 g citric acid. The added amount of citric acid was such that the molar ratio of nickel and copper (calculated as Ni and Cu) in the powder to the added amount of citric acid was 38, and the molar ratio of copper (calculated as Cu) to the citric acid was 2.7. These data are also shown in Table 2. The resulting powder mixture was shaped into 3x3 mm tablets.

The catalyst tablets were charged into a furnace. First the tablets were heated at 400 °C for 2 hours in a pure nitrogen stream (100 vol.% of nitrogen; GHSV (gas hourly space velocity) = 2,000 v/vh).

In Table 2, some properties are shown for the catalyst as measured after the above-described thermal treatment but

before the below-described reduction (with hydrogen gas containing stream) and passivation. These properties are nickel metal content and nickel metal surface area. From the values for these properties, it can be seen that in the intermediate catalyst, a part of the nickel oxide had already been reduced to nickel metal during the above-described thermal treatment.

Then the temperature was decreased to 350 °C and the nitrogen stream was replaced by a hydrogen stream. After the nitrogen was completely replaced by hydrogen, the temperature was increased to 380 °C. At this temperature, the catalyst was treated (reduced) in a pure hydrogen stream (100 vol.% of hydrogen; GHSV = 2,000 v/vh) for 5 hours.

After cooling down to 50 °C, using a stream containing nitrogen of ambient temperature, a catalyst passivation was carried out in the same way as in Example 1.1.

Properties for the catalyst after said reduction and passivation are also shown in Table 2.

Example 2.2 (comparative)

The procedure of Example 2.1 was followed, with the proviso that in the treatment step carried out at 400 °C, an air stream (100 vol.% of air) was used instead of the pure nitrogen stream.

Example 2.3 (comparative)

The procedure of Example 2.1 was followed, with the proviso that no citric acid was added. Further in deviation from the procedure of Example 2.1, the catalyst tablets (containing the catalyst powder and graphite) charged into the furnace were heated in a stream containing nitrogen and 2 vol.% of hydrogen (GHSV = 2,000 v/vh) up to a temperature of 250 °C. Once the temperature started to decrease, the hydrogen concentration was increased step by step, up to 100 vol.% of hydrogen. After the nitrogen was completely replaced

by hydrogen, the temperature was maintained at 250 °C for 2 hours. Then the temperature was increased to 380 °C, at which temperature the catalyst was further treated (reduced) in the pure hydrogen stream for an additional 5 hours. After cooling
5 down to 50 °C, using a stream containing nitrogen of ambient temperature, a catalyst passivation was carried out in the same way as in Example 1.1.

Example 3

4.5 kg sodium carbonate (Na_2CO_3) were dissolved in 40 l deionized water under stirring in a vessel. Then 4.8 l of an aqueous waterglass solution containing 125 g silicon (Si) were added and the solution was heated to 90 °C. Then 24 l of an aqueous metal nitrate solution, containing 1750 g nickel (Ni), 146 g copper (Cu) and 142 g aluminium (Al), were added dropwise over a period of 2 hours. Said metal nitrate solution was previously made by dissolving nickel nitrate, copper nitrate and aluminium nitrate in water. Then the resulting slurry comprising the precipitate containing the metals Ni, Cu, Al, Si and Na, was stirred at 90 °C for 2 hours. Then the pH was measured, which was 8.5–9. Then the slurry was filtered thereby recovering said precipitate. The resulting filter cake (precipitate) was washed with deionized water until a Na_2O content lower than 0.3 wt.%, for the residue resulting from annealing a small portion of the filter cake at 800 °C, was reached. Then the filter cake was dried at 120 °C for 15 hours and subsequently calcined at 400 °C for 2 hours. Then the resulting material was grinded into a powder.

Example 3.1 (invention)

10 The powder obtained in Example 3 was mixed with 3 wt.% of graphite (based on total amount of powder) and with 120 g citric acid. The added amount of citric acid was such that the molar ratio of nickel and copper (calculated as Ni and

Cu) in the powder to the added amount of citric acid was 51, and the molar ratio of copper (calculated as Cu) to the citric acid was 3.7. These data are also shown in Table 3. The resulting powder mixture was shaped into 3x3 mm tablets.

5 The catalyst tablets were charged into a furnace. First the tablets were heated at 400 °C for 2 hours in a pure nitrogen stream (100 vol.% of nitrogen; GHSV (gas hourly space velocity) = 2,000 v/vh).

10 In Table 3, some properties are shown for the catalyst as measured after the above-described thermal treatment but before the below-described reduction (with hydrogen gas containing stream) and passivation. These properties are nickel metal content and nickel metal surface area. From the values for these properties, it can be seen that in the
15 intermediate catalyst, a part of the nickel oxide had already been reduced to nickel metal during the above-described thermal treatment.

20 Then the temperature was decreased to 350 °C and the nitrogen stream was replaced by a hydrogen stream. After the nitrogen was completely replaced by hydrogen, the temperature was increased to 400 °C. At this temperature, the catalyst was treated (reduced) in a pure hydrogen stream (100 vol.% of hydrogen; GHSV = 2,000 v/vh) for 5 hours.

25 After cooling down to 50 °C, using a stream containing nitrogen of ambient temperature, a catalyst passivation was carried out in the same way as in Example 1.1.

Properties for the catalyst after said reduction and passivation are also shown in Table 3.

Example 3.2 (comparative)

30 The procedure of Example 3.1 was followed, with the proviso that in the treatment step carried out at 400 °C, an air stream (100 vol.% of air) was used instead of the pure nitrogen stream.

Example 3.3 (comparative)

The procedure of Example 3.1 was followed, with the proviso that no citric acid was added. Further in deviation from the procedure of Example 3.1, the catalyst tablets
5 (containing the catalyst powder and graphite) charged into the furnace were heated in a stream containing nitrogen and 2 vol.% of hydrogen (GHSV = 2,000 v/vh) up to a temperature of 250 °C. Once the temperature started to decrease, the hydrogen concentration was increased step by step, up to 100
10 vol.% of hydrogen. After the nitrogen was completely replaced by hydrogen, the temperature was maintained at 250 °C for 2 hours. Then the temperature was increased to 400 °C, at which temperature the catalyst was further treated (reduced) in the pure hydrogen stream for an additional 5 hours. After cooling
15 down to 50 °C, using a stream containing nitrogen of ambient temperature, a catalyst passivation was carried out in the same way as in Example 1.1.

Discussion of experimental results

Upon comparing the results for the catalysts of the
20 invention (Examples 1.1, 2.1 and 3.1) with those for the comparative catalysts (Examples 1.2, 1.3, 2.2, 2.3, 3.2 and 3.3) as shown in Tables 1-3, it appears that the radial crushing strength for the catalysts of the invention is advantageously higher. In Tables 1-3, the radial crushing
25 strengths for the intermediate catalyst tablets (before thermal treatment, reduction and passivation) are also shown. Further, it was found for the catalysts of Examples 1.1, 2.1 and 3.1 (invention) that the radial crushing strength was advantageously more uniform (that is to say, over 20
30 measurements of 20 tablets): compare the maximums and minimums for the radial crushing strength in Tables 1-3. Still further, in the tablets of Examples 1.1, 2.1 and 3.1

(invention) no fissures could be detected, whereas fissures were detected in the tablets of the Comparative Examples.

Apart from showing better mechanical properties for the catalysts of Examples 1.1, 2.1 and 3.1 (invention), as
5 discussed above, Tables 1-3 also show that the catalysts of the invention advantageously had a better nickel metal dispersion than the catalysts of the Comparative Examples. This is indicated by the higher nickel metal surface area for Examples 1.1, 2.1 and 3.1 (invention) in Tables 1-3. Further,
10 the catalysts of the invention advantageously had a higher (or similar) porosity than the catalysts of the Comparative Examples. This is indicated in Tables 1-3 by a higher (or similar) pore volume for the catalysts of the invention (Examples 1.1, 2.1 and 3.1). Finally, advantageously, the
15 portion of pores having pore radius > 50 nm (macropores) for Examples 1.1, 2.1 and 3.1 (invention) was larger than (or similar to) that for the Comparative Examples.

Such better mechanical strength, better nickel metal dispersion, higher porosity and larger portion of macropores
20 are advantageous in a chemical process wherein starting material is converted into a desired product, in terms of conversion and selectivity, which reaction is catalyzed by the catalyst of the present invention and in which reaction nickel is the or one of the catalytically active metals. For
25 example, the catalyst of the present invention may advantageously be used in a process for preparing amines by reacting alcohols, ketones and/or aldehydes with nitrogen compounds and with a reducing agent, such as hydrogen.

Table 1

Example	1.1	1.2 (*)	1.3 (*)
Citric acid added?	Yes	Yes	No
Molar ratio Ni and Cu to citric acid (calculated as Ni and Cu metals)	57	57	n.a.
Molar ratio Cu to citric acid (calculated as Cu metal)	4.1	4.1	n.a.
Radial crushing strength (N), before thermal treatment, reduction and passivation (average of 20 measurements of 20 tablets)	95	100	100
Gas in thermal treatment of catalyst tablets before (complete) reduction	N ₂	air	N ₂ +H ₂
<i>Properties of intermediate catalyst (after thermal treatment, before reduction in H₂ and passivation)</i>			
Nickel metal content (wt.%)	10.2	n.a.	n.a.
Percentage of nickel metal content for intermediate catalyst based on nickel metal content for final catalyst	20%	n.a.	n.a.
Nickel metal surface area (m ² /g), by CO chemisorption	4.0	n.a.	n.a.
Percentage of nickel metal surface area for intermediate catalyst based on nickel metal surface area for final catalyst	15%	n.a.	n.a.
<i>Composition and further properties of final catalyst (after reduction in H₂ and passivation), wt.% based on total weight of catalyst</i>			
Nickel (calculated as Ni metal and NiO)	60	60	60
Silicon (calculated as SiO ₂)	16	16	16

Example	1.1	1.2 (*)	1.3 (*)
Copper (calculated as Cu metal and CuO)	5	5	5
Sodium (calculated as Na ₂ O)	0.3	0.3	0.3
Oxygen	18.7	18.7	18.7
Total	100	100	100
Nickel metal content (wt.%), after reduction (180 °C; H ₂ ; 1 hour)	51.0	52.5	53.6
Nickel metal surface area (m ² /g), after reduction (180 °C; H ₂ ; 1 hour), by CO chemisorption	26.1	20.3	22.5
Bulk density (kg/l)	1.13	1.08	1.20
Radial crushing strength (N) (average of 20 measurements of 20 tablets)	55	35	42
Radial crushing strength, minimum (N)	40	13	20
Radial crushing strength, maximum (N)	70	71	68
Difference between maximum and minimum radial crushing strength (N)	30	58	48
Fissures?	No	Yes	Yes
Catalyst surface area, BET (m ² /g)	212	225	204
Pore volume (cm ³ /g)	0.35	0.34	0.30
Portion of pores having pore radius > 50 nm (wt.%)	17.1	17.2	10.3

(*) = Comparative; n.a. = not applicable. In the description preceding the Examples, it is described how the above properties were determined.

Table 2

Example	2.1	2.2 (*)	2.3 (*)
Citric acid added?	Yes	Yes	No
Molar ratio Ni and Cu to citric acid (calculated as Ni and Cu metals)	38	38	n.a.
Molar ratio Cu to citric acid (calculated as Cu metal)	2.7	2.7	n.a.
Radial crushing strength (N), before thermal treatment, reduction and passivation (average of 20 measurements of 20 tablets)	100	105	95
Gas in thermal treatment of catalyst tablets before (complete) reduction	N ₂	air	N ₂ +H ₂
<i>Properties of intermediate catalyst (after thermal treatment, before reduction in H₂ and passivation)</i>			
Nickel metal content (wt.%)	6.9	n.a.	n.a.
Percentage of nickel metal content for intermediate catalyst based on nickel metal content for final catalyst	20%	n.a.	n.a.
Nickel metal surface area (m ² /g), by CO chemisorption	3.4	n.a.	n.a.
Percentage of nickel metal surface area for intermediate catalyst based on nickel metal surface area for final catalyst	16%	n.a.	n.a.
<i>Composition and further properties of final catalyst (after reduction in H₂ and passivation), wt.% based on total weight of catalyst</i>			
Nickel (calculated as Ni metal and NiO)	60	60	60
Aluminium (calculated as Al ₂ O ₃)	16	16	16

Example	2.1	2.2 (*)	2.3 (*)
Copper (calculated as Cu metal and CuO)	5	5	5
Sodium (calculated as Na ₂ O)	0.3	0.3	0.3
Oxygen	19.7	19.7	19.7
Total	100	100	100
Nickel metal content (wt.%), after reduction (180 °C; H ₂ ; 1 hour)	34.3	36.4	35.8
Nickel metal surface area (m ² /g), after reduction (180 °C; H ₂ ; 1 hour), by CO chemisorption	21.0	16.3	17.9
Bulk density (kg/l)	0.93	0.89	1.00
Radial crushing strength (N) (average of 20 measurements of 20 tablets)	60	37	45
Radial crushing strength, minimum (N)	43	12	19
Radial crushing strength, maximum (N)	80	66	68
Difference between maximum and minimum radial crushing strength (N)	37	54	49
Fissures?	No	Yes	Yes
Catalyst surface area, BET (m ² /g)	164	150	164
Pore volume (cm ³ /g)	0.46	0.48	0.41
Portion of pores having pore radius > 50 nm (wt.%)	14.1	13.9	6.9

(*) = Comparative; n.a. = not applicable. In the description preceding the Examples, it is described how the above properties were determined.

Table 3

Example	3.1	3.2 (*)	3.3 (*)
Citric acid added?	Yes	Yes	No
Molar ratio Ni and Cu to citric acid (calculated as Ni and Cu metals)	51	51	n.a.
Molar ratio Cu to citric acid (calculated as Cu metal)	3.7	3.7	n.a.
Radial crushing strength (N), before thermal treatment, reduction and passivation (average of 20 measurements of 20 tablets)	100	110	105
Gas in thermal treatment of catalyst tablets before (complete) reduction	N ₂	air	N ₂ +H ₂
<i>Properties of intermediate catalyst (after thermal treatment, before reduction in H₂ and passivation)</i>			
Nickel metal content (wt.%)	7.5	n.a.	n.a.
Percentage of nickel metal content for intermediate catalyst based on nickel metal content for final catalyst	17%	n.a.	n.a.
Nickel metal surface area (m ² /g), by CO chemisorption	3.8	n.a.	n.a.
Percentage of nickel metal surface area for intermediate catalyst based on nickel metal surface area for final catalyst	16%	n.a.	n.a.
<i>Composition and further properties of final catalyst (after reduction in H₂ and passivation), wt.% based on total weight of catalyst</i>			
Nickel (calculated as Ni metal and NiO)	60	60	60
Silicon (calculated as SiO ₂)	8	8	8

Example	3.1	3.2 (*)	3.3 (*)
Aluminium (calculated as Al_2O_3)	8	8	8
Copper (calculated as Cu metal and CuO)	5	5	5
Sodium (calculated as Na_2O)	0.3	0.3	0.3
Oxygen	19.7	19.7	19.7
Total	100	100	100
Nickel metal content (wt.%), after reduction (180 °C; H_2 ; 1 hour)	43.9	45.4	43.6
Nickel metal surface area (m^2/g), after reduction (180 °C; H_2 ; 1 hour), by CO chemisorption	24.0	20.5	21.2
Bulk density (kg/l)	0.90	0.89	0.97
Radial crushing strength (N) (average of 20 measurements of 20 tablets)	64	38	42
Radial crushing strength, minimum (N)	48	18	24
Radial crushing strength, maximum (N)	75	65	59
Difference between maximum and minimum radial crushing strength (N)	27	47	35
Fissures?	No	Yes	Yes
Catalyst surface area, BET (m^2/g)	211	205	210
Pore volume (cm^3/g)	0.44	0.43	0.37
Portion of pores having pore radius > 50 nm (wt.%)	15.1	16.9	10.3

(*) = Comparative; n.a. = not applicable. In the description preceding the Examples, it is described how the above properties were determined.

C L A I M S

1. Process for preparing a catalyst, which process comprises:

preparing a catalyst containing nickel and copper by a process comprising precipitation of a solution comprising
5 nickel and copper salts;

mixing the catalyst with an organic aliphatic acid comprising a carboxylic acid group ($-\text{CO}_2\text{H}$ group); and

subjecting the mixture to an elevated temperature which is equal to or higher than the decomposition temperature of
10 the organic aliphatic acid resulting in a thermally treated material.

2. Process according to claim 1, wherein the thermal treatment step is performed in an inert atmosphere.

3. Process according to any one of the preceding claims,
15 wherein the organic aliphatic acid has 1 to 15 carbon atoms including the carbon atoms from the carboxylic acid group or groups.

4. Process according to any one of the preceding claims, wherein the organic aliphatic acid comprises 1 to 3
20 carboxylic acid groups.

5. Process according to any one of the preceding claims, wherein the elevated temperature is of from 175 to 900 °C.

6. Process according to any one of the preceding claims, wherein the molar ratio of the total amount of nickel and
25 copper, calculated as the metals Ni and Cu, in the catalyst to the amount of the organic aliphatic acid is of from 10 to 120.

7. Process according to any one of the preceding claims, wherein the molar ratio of the amount of copper, calculated
30 as the metal Cu, in the catalyst to the amount of the organic aliphatic acid is of from 0.1 to 10.

8. Process according to any one of the preceding claims, wherein the thermally treated material is subjected to a stream containing hydrogen.

5 9. Process according to claim 8, wherein the thermally treated material is subjected to a stream containing hydrogen at a temperature of from 100 to 500 °C, preferably 200 to 400 °C.

10 10. Process according to any one of the preceding claims, wherein before the thermal treatment step, the mixture comprising the catalyst and the organic aliphatic acid is shaped.

11. Process according to claim 10, wherein the mixture is shaped into a tablet form.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/053301

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J37/18 B01J23/72 B01J23/755 B01J35/00 B01J35/10
B01J37/02 B01J37/03 B01J37/00

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 669 906 A (KOBERSTEIN EDGAR ET AL) 13 June 1972 (1972-06-13) column 3, line 24 - column 4, line 18 example 3	1-11
X	US 2010/087312 A1 (SIJPKES ANDRE HARMEN [NL] ET AL) 8 April 2010 (2010-04-08) paragraph [0032] examples 5A,6	1-11
X	US 5 759 947 A (ZHOU HONGXING [CN]) 2 June 1998 (1998-06-02) examples 7-9	1-11
A	WO 2008/043060 A2 (RES TRIANGLE INST [US]; SUBRAMANI VELU [US]; GANGWAL SANTOSH K [US]; N) 10 April 2008 (2008-04-10) the whole document	1-11
	-/--	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

5 May 2014

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2008/076660 A1 (REYES CLEMENTINE [US] ET AL) 27 March 2008 (2008-03-27) the whole document -----	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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