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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 impregnation of a support, wherein the impregnation solution comprises an organic aliphatic acid comprising a carboxylic acid group (-CO_2 H group); and subjecting the catalyst 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 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 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 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. 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.

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

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 impregnation of a support wherein the impregnation solution comprises an organic aliphatic acid comprising a carboxylic acid group (-CO_2H group), 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 impregnation of a support, wherein the impregnation solution comprises an organic aliphatic acid comprising a carboxylic acid group (-CO_2H group); and

subjecting the catalyst 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, the impregnation solution comprises an organic aliphatic acid comprising a carboxylic acid group (-CO_2H group). 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 ore more substituents other than a carboxylic acid group. Suitable other substituents are hydroxyl (-OH) and keto (=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 ($-CO_2H$) and one or more hydroxyl groups (-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 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.

The catalyst containing nickel and copper is prepared by a process comprising impregnation of a support. Impregnation may be carried out one time or multiple times, as long as one of the impregnation solutions contains the above-mentioned

organic aliphatic acid. Preferably, in case multiple impregnations are carried out, the organic aliphatic acid is present in the impregnation solution used for the last impregnation.

Further, said impregnation solution(s) should contain a nickel salt or a copper salt or a nickel salt and a copper salt. In case the support already contains nickel, the impregnation solution(s) does/do not have to contain a nickel salt. In case the support already contains copper, the impregnation solution(s) does/do not have to contain a copper salt. Further, it is envisaged that a support is impregnated first with a solution comprising nickel and/or copper salts, followed by impregnation with a solution comprising the organic aliphatic acid. Preferably, said impregnation solution(s) is/are aqueous solutions such as aqueous solutions comprising metal nitrate and/or metal amine carbonate complexes.

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), 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 1 to 35 wt.%, more preferably 5 to 30 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 0.01 to 20 wt.%, more preferably 0.1 to 15 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, impregnation with one or more metal salts, including at least nickel and/or copper salts, and the organic aliphatic acid, is performed. In case the catalyst is to contain one or more additional metals, the impregnation solution should also comprise a salt of the additional metal.

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

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

If used, the salt of the additional metal may be a nitrate, sulfate, chloride, organic acid salt or amine carbonate complex of the additional metal. Preferably, the salt of the additional metal is a nitrate of the additional metal, an organic acid salt of the additional metal or an

amine carbonate complex of the additional metal, most preferably an amine carbonate complex of the additional metal. A suitable organic acid salt of the additional metal is an acetate of the additional metal.

The support to be impregnated, which support may have any shape, may be a support which comprises a material which is selected from the group consisting of alumina, silica, aluminium silicate, magnesia, titania, zirconia and mixtures thereof. Preferably, said support material is alumina, more preferably a transition alumina, such as gamma, eta, chi, kappa, theta and/or delta alumina, most preferably theta alumina.

After impregnation, the impregnated support may be dried, for example at a temperature in the range of from 80 to 160 °C, suitably 100 to 140 °C. After such drying, it may further be calcined in the presence of air, at a temperature in the range of from 175 to 900 °C, preferably 250 to 700 °C, more preferably 300 to 600 °C, most preferably 350 to 500 °C.

In the present invention, 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 organic aliphatic acid is of from 5 to 120, more preferably 10 to 70, most preferably 20 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.

In the present invention, the catalyst, after impregnation with 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 325 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, most preferably at least 325 °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, most preferably at most 500 °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 catalyst 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 (N_2), 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 600 °C, preferably 200 to 500 °C, more preferably 250 to 450 °C. Preferably, said temperature is at least 100 °C, more

preferably at least 200 °C, more preferably at least 250 °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 H_2 (hydrogen), the remainder consisting of one or more inert gases which may be selected from the group consisting of the noble gases and nitrogen (N_2), 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.

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 O_2 (oxygen), suitably 0.01 to 6 vol.% of O_2, more suitably 0.05 to 3 vol.% of O_2, the remainder consisting of one or more inert gases which may be selected from the group consisting of the noble gases and nitrogen (N_2), 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 wit a hydrogen stream at an elevated temperature (for example 250 °C), which step is called the catalyst activation step.

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

preparing a catalyst containing nickel and copper by a process comprising impregnation of a support, wherein the impregnation solution comprises an organic aliphatic acid comprising a carboxylic acid group (-CO_2H group);

subjecting the catalyst 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.

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 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.

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. After pre-treatment (reduction) of the reduced and passivated catalyst samples for 1 hour at 250 °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 (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) 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 extrudate crushing strength tester Dillon Quantrol™ TC^2, supplied by company Dillon. The extrudates are exposed between two plates, one of which is flexible. The force recorded at extrudate fracture is the crushing strength. The measured value is related to the extrudate length (N/mm length). For each measurement 20 extrudates are used.

The nickel metal surface area may be determined by using the CO-pulse ("CO") and/or H_2 chemisorption method. In both said methods, after pre-treatment (reduction) of the reduced and passivated catalyst samples for 1 hour at 250 °C in a hydrogen stream (which is similar to the above-mentioned catalyst activation step), the samples are cooled in hydrogen. In the CO chemisorption method, the cooled samples are 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. The H_2 chemisorption method is a volumetric process by means of ASAP 2010 of Micromeritics ("Analytical Methods in Fine Particle Technology", Micromeritics 1997, page 227, P.A. Webb and C. Orr).

Ni crystallite size and crystallite size distribution are determined by X-ray diffraction (XRD), based on the Scherrer relationship. The processing of the data was carried out with RAYFLEX software from SEIFERT FPM. The ICDD database (PDF-2 Release 2004) was used for the identification of the phase structures. The X-ray diffractometer used was a XRD7 from Rich. Seifert Co. The scattering curve sections were recorded perpendicularly to the (220) lattice plane from the interference line spreading under the following conditions:

Generator data	34 kV/30 mA
Goniometer	XRD7
Radiation	Cu-K alpha
Filter	Ni
Angular range	2 theta = 70.0- 83.0°
Step width	delta = 0.05°
Count time	10 sec

Conclusions on the modality (mono Gauss-line profile or bimodal Gauss-line profile) of the Ni-(220) line profile were obtained by use of the peak fit program PF4 from Jandel

Corporation. Before the XRD measurements all catalyst samples were reduced for 1 hour at 250 °C in a hydrogen stream.

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

200 g of a theta-Al_2O_3 support, in the form of 1.3 mm trilobes having a BET surface area of 145 m^2/g and a total pore volume of 0.9 cm^3/g, were impregnated by spraying with 195 ml of an aqueous solution containing Ni and Cu salts (according to 110% of the water pore volume). The latter impregnation solution was obtained by dissolving 350 g of nickel hydroxy carbonate (containing 40 wt.% of Ni) and 25 g of copper hydroxy carbonate (containing 55 wt.% of Cu) in a mixture of 230 g of ammonium carbonate with 600 g of an aqueous ammonium hydroxide solution (containing 25 wt.% of NH_3). The impregnation solution contained 127 g Ni/l solution and 12 g Cu/l solution.

After said impregnation, the impregnated support was dried in air at 120 °C for 12 hours and then calcined in air at 350 °C for 4 hours.

Then said impregnation, drying and calcination procedure was repeated for a second time.

Then said impregnation procedure was repeated for a third time, with the proviso that the impregnation solution used for this third impregnation also contained citric acid. The added amount of citric acid was such that the molar ratio of nickel and copper (calculated as Ni and Cu) to the added amount of citric acid was 30, and the molar ratio of copper (calculated as Cu) to the citric acid was 4.3. These data are also shown in Table 1.

After said third impregnation, the impregnated support is dried in air at 120 °C for 12 hours.

Then the dried intermediate catalyst was charged into a furnace, heated to 350 °C and treated at this temperature for 4 hours in a pure nitrogen stream (100 vol.% of nitrogen; GHSV (gas hourly space velocity) = 2,000 v/vh).

Then 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 final catalyst are also shown in Table 1.

Comparative Example 1

The procedure of Example 1 was followed, with the proviso that in the step of treating the dried intermediate catalyst at 350 °C, an air stream (100 vol.% of air) was used instead of the pure nitrogen stream.

Comparative Example 2

The procedure of Example 1 was followed, with the proviso that no citric acid was added to the impregnation solution used in the third impregnation. Further in deviation from the procedure of Example 1, after drying following the third impregnation, the dried intermediate catalyst was calcined in air at 350°C for 4 hours. Subsequently, the calcined intermediate catalyst was 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 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.

Example 2

200 g of a dried and calcined Ni/Al_2O_3 catalyst precursor (commercial name KL 6662 TL 1.3, available at CRI Catalyst Leuna GmbH), which contained 23 wt.% of Ni and which was in the form of 1.3 mm trilobes, were impregnated by spraying with 128 ml of an aqueous solution containing a Cu salt

(according to 110% of the water pore volume). The latter impregnation solution was obtained by dissolving 90 g of copper hydroxy carbonate (containing 55 wt.% of Cu) in a mixture of 250 g of ammonium carbonate with 900 g of an aqueous ammonium hydroxide solution (containing 25 wt.% of NH_3). The impregnation solution contained 32 g Cu/l solution and in addition it contained citric acid. The added amount of citric acid was such that the molar ratio of nickel and copper (calculated as Ni and Cu) to the added amount of citric acid was 20, and the molar ratio of copper (calculated as Cu) to the citric acid was 2.6. These data are also shown in Table 2.

The procedure that was performed after said impregnation, was the same procedure that was performed after the third impregnation in Example 1.

Properties for the final catalyst are also shown in Table 2.

Comparative Example 3

The procedure of Example 2 was followed, with the proviso that in the step of treating the dried intermediate catalyst at 350 °C, an air stream (100 vol.% of air) was used instead of the pure nitrogen stream.

Comparative Example 4

The procedure of Example 2 was followed, with the proviso that no citric acid was added to the impregnation solution used in the third impregnation. Further in deviation from the procedure of Example 2, after drying following the third impregnation, the dried intermediate catalyst was calcined in air at 350°C for 4 hours. Subsequently, the calcined intermediate catalyst was 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 increased to 400 °C, at which temperature the catalyst was further treated (reduced) in the pure hydrogen stream for an additional 6 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.

Discussion of experimental results

Upon comparing the results for the catalyst of Example 1 (invention) with those for the catalysts of Comparative Examples 1 and 2 and upon comparing the results for the catalyst of Example 2 (invention) with those for the catalysts of Comparative Examples 3 and 4, as shown in Tables 1 and 2, respectively, it appears that the radial crushing strength for the catalysts of the invention is advantageously higher.

Apart from showing better mechanical properties for the catalysts of the invention, as discussed above, Tables 1 and 2 also show that the catalysts of the invention advantageously had a better nickel metal dispersion. This is indicated for Examples 1 and 2 in Tables 1 and 2 by a higher nickel metal surface area, both by CO chemisorption and by H_2 chemisorption, and by a lower nickel crystallite size.

Such better mechanical strength and better nickel metal dispersion 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 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

	Ex. 1	Comp. Ex. 1	Comp. Ex. 2
Citric acid added?	Yes	Yes	No
Molar ratio Ni and Cu to citric acid (calculated as Ni and Cu metals)	30	30	n.a.
Molar ratio Cu to citric acid (calculated as Cu metal)	4.3	4.3	n.a.
Gas in thermal treatment of dried or calcined intermediate catalyst before (complete) reduction	N_2	air	N_2+H_2
Composition and further properties of final catalyst, wt. % based on total weight of catalyst			
Nickel (calculated as Ni metal and NiO)	24	24	24
Copper (calculated as Cu metal and CuO)	2.3	2.3	2.3
Alumina (calculated as Al_2O_3)	73.7	73.7	73.7
Total	100	100	100
Radial crushing strength (N/mm)	14.0	13.6	13.5
Nickel metal content (wt.%), after reduction (250 °C; H_2; 1 hour)	18.6	19.0	19.0
Nickel metal surface area (m^2/g), after reduction (250 °C; H_2; 1 hour), by CO chemisorption	18.9	13.4	12.4
Nickel metal surface area (m^2/g), after reduction (250 °C; H_2; 1 hour), by H_2 chemisorption	11.8	9.8	9.5
Nickel (crystallite size (nm), after reduction (250 °C; H_2; 1 hour)	2.4	3.2	3.2
Bulk density (kg/l)	0.80	0.80	0.82

	Ex. 1	Comp. Ex. 1	Comp. Ex. 2
Catalyst surface area, BET (m^2/g)	150	154	149
Pore volume (cm^3/g)	0.50	0.49	0.49

Ex. = Example; Comp. = Comparative; n.a. = not applicable. In the description preceding the Examples, it is described how the above properties were determined.

Table 2

	Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Citric acid added?	Yes	Yes	No
Molar ratio Ni and Cu to citric acid (calculated as Ni and Cu metals)	20	20	n.a.
Molar ratio Cu to citric acid (calculated as Cu metal)	2.6	2.6	n.a.
Gas in thermal treatment of dried or calcined intermediate catalyst before (complete) reduction	N_2	air	N_2+H_2
Composition and further properties of final catalyst, wt. % based on total weight of catalyst			
Nickel (calculated as Ni metal and NiO)	23	23	23
Copper (calculated as Cu metal and CuO)	2	2	2
Alumina (calculated as Al_2O_3)	75	75	75
Total	100	100	100
Radial crushing strength (N/mm)	13.9	13.0	13.7

	Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Nickel metal content (wt.%), after reduction (250 °C; H_2; 1 hour)	19.5	19.2	18.8
Nickel metal surface area (m^2/g), after reduction (250 °C; H_2; 1 hour), by CO chemisorption	19.5	13.9	14.3
Nickel metal surface area (m^2/g), after reduction (250 °C; H_2; 1 hour), by H_2 chemisorption	12.5	9.4	9.7
Nickel (crystallite size (nm), after reduction (250 °C; H_2; 1 hour)	2.6	3.3	3.2
Bulk density (kg/l)	0.82	0.82	0.82
Catalyst surface area, BET (m^2/g)	155	155	153
Pore volume (cm^3/g)	0.52	0.50	0.49

Ex. = Example; Comp. = 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 impregnation of a support, wherein the impregnation solution comprises an organic aliphatic acid comprising a carboxylic acid group (-CO_2H group); and

subjecting the catalyst 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.

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, 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 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 copper, calculated as the metals Ni and Cu, in the catalyst to the amount of the organic aliphatic acid is of from 5 to 120.

7. Process according to any one of the preceding claims, wherein the molar ratio of the amount of copper, calculated 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.

9. Process according to claim 10, wherein the thermally treated material is subjected to a stream containing hydrogen at a temperature of from 100 to 600 °C, preferably 200 to 500 °C.

10. Process according to any one of the preceding claims, wherein the support comprises a material which is selected from the group consisting of alumina, silica, aluminium silicate, magnesia, titania, zirconia and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/053300

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J37/18 B01J23/72 B01J23/755 B01J35/00 B01J35/10
B01J37/02
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 2010/087312 A1 (SIJPKES ANDRE HARMEN [NL] ET AL) 8 April 2010 (2010-04-08) paragraph [0032] examples 5A,6	1-10
X	US 5 759 947 A (ZHOU HONGXING [CN]) 2 June 1998 (1998-06-02) examples 7-9	1-10
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	1-10
A	US 2008/076660 A1 (REYES CLEMENTINE [US] ET AL) 27 March 2008 (2008-03-27) the whole document	1-10

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

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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	Date of mailing of the international search report
5 May 2014	16/05/2014

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/EP2014/053300

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