

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
4 August 2005 (04.08.2005)

PCT

(10) International Publication Number
WO 2005/070537 A1

(51) International Patent Classification⁷: **B01J 23/72**,
37/08, C07C 29/154, B01J 23/745, 23/89

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(21) International Application Number:
PCT/NL2004/000051

(22) International Filing Date: 21 January 2004 (21.01.2004)

(25) Filing Language: English

(26) Publication Language: English

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

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), Euro-
pean (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR,
GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: CHROMIUM-FREE CATALYSTS OF METALIC CU AND AT LEAST ONE SECOND METAL

(57) Abstract: Described is a method for the preparation of a chromium-free catalyst comprising Cu and at least one second metal in metallic or oxidic form, comprising the steps of a) preparing a final solution comprising ions of Cu and of at least one second metal, said final solution additionally comprising ions of a complexing agent and having a pH of above 5; b) contacting said final solution with inert carrier to form a final solution/carrier combination; c) optionally, drying the final solution/carrier combination; d) calcining the final solution/carrier combination obtained in step c) or d) to yield Cu and the at least one second metal in oxidic form; and e) reducing at least part of the thus obtained oxidic Cu on the carrier. Further, a catalyst obtainable by the said method as well as uses thereof are described.



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CHROMIUM-FREE CATALYSTS OF METALLIC CU AND AT LEAST ONE SECOND METAL

The present invention relates to a method for the preparation of a chromium-free catalyst comprising Cu and at least one second metal in metallic or oxidic form, a catalyst obtainable by such method and the use of said catalyst for the hydrogenation or hydrogenolysis of fatty acids and fatty esters to fatty alcohols and other esters or di-esters to their corresponding alcohols.

Copper containing catalysts are well known catalysts for the hydrogenation/hydrogenolysis of fatty acids and fatty esters to fatty alcohols. Fatty alcohols are used as intermediates for the production of surfactants, soaps and base oils, and additives for lubricants. Palm oil and palm kernel oil, for example, are commonly used as starting materials for the production of C₁₂-C₁₈ fatty alcohols.

However, severe conditions are especially required for the production of higher aliphatic alcohols. In industrially available processes, hydrogenation is carried out at temperatures of 200-300 °C, pressures of 200-300 bar and high H₂/substrate ratios usually in the presence of a copper chromium catalyst.

Cu-Cr catalysts are currently the commercially most successful catalysts employed for this process. These catalysts have adequate hydrogenation activity and adequate resistance to the fatty acids in the reaction mixture. However, these catalysts have one major drawback: like all catalysts they lose their activity with time, and as chromium compounds are toxic, they need to be handled prudently, and a great deal of labour and cost is spent in treating/recovering the waste catalyst. In addition, since many palm oil derived chemical intermediates have a final application in household products (soaps, detergents, cosmetics, etc.), chromium contamination of the product stream would have to be monitored.

In the art, there is a need for chromium-free Cu catalysts for the hydrogenation/hydrogenolysis of fatty acids and fatty esters, which are not toxic, and which are capable of performing under severe conditions,

i.e. high temperatures, pressures and/or H₂/substrate ratios, or, alternatively, are capable of performing the hydrogenation/hydrogenolysis with comparable conversion, selectivity, and yields under milder circumstances.

5 Several chromium-free Cu catalysts have been developed in the art, e.g. Cu-Zn catalysts (see e.g. US 5,475,159 and US 5,157,168), Cu-Fe catalysts (see e.g. US 4,278,567 and US 5,763,353) and catalysts containing only Cu as active metal (see e.g. US 5,403,962 and WO 97/34694). Generally, these chromium-free Cu catalysts have been
0 prepared by co-precipitation of the catalyst metal components, i.e. preparation of a solution containing the metal salts, optionally combined with a solution of an inert carrier metal precursor such as e.g. Al salts, or with inert carrier metal oxides of Al or Si, and reaction of the resultant solution or slurry with an alkaline aqueous
5 solution to obtain a precipitate of a mixture of metal hydroxides or oxides, after which the precipitate is washed and dried, followed by calcination.

Accordingly, these chromium-free Cu catalysts have the advantage that they do not comprise toxic Cr substances. Generally, however, the
0 chromium-free Cu catalysts obtained in the art thus far suffer in activity or selectivity in comparison with Cu-Cr catalysts, their acid resistance is low, or they are not able to withstand the harsh hydrogenation reaction conditions. It is thought that the co-precipitation has the drawback that separate metals precipitate at
5 different pH values such that at least part of the metals will not have intermixed at an atomic level, to result in the formation of distinct metal clusters at the catalyst surface.

An alternative preparation method for chromium-free Cu catalysts is disclosed in US 5,759,947. Said method comprises the preparation of
0 a solution containing the metal salts as above, whereto the complexing agent citric acid is added, followed by impregnation of spherical support therewith.

It has now surprisingly been found that upon impregnation with a solution comprising ions of a complexing agent, said solution having a
5 pH above 5, catalysts were obtained having an improved activity or selectivity, or relatively high activity, selectivity, and yield at low

temperatures and pressures in comparison with the catalysts known in the art.

Therefore, it was an object of the present invention to prepare novel chromium-free Cu catalysts that had improved activity or selectivity, or preferably combinations thereof. It was also an object of the present invention to prepare such catalysts that were capable of catalysing the hydrogenation under milder conditions in comparison with conventional Cu-Cr catalysts.

Thus, the invention relates to a novel method for the preparation of a chromium-free catalyst comprising Cu and at least one second metal in metallic or oxidic form, comprising the steps of:

- a) preparing a final solution comprising ions of Cu and the at least one second metal, said final solution additionally comprising ions of a complexing agent and having a pH of above 5;
- b) contacting said final solution with inert carrier to form a final solution/carrier combination;
- c) optionally, drying the final solution/carrier combination;
- d) calcining the final solution/carrier combination obtained in step c) or d) to yield Cu and the at least one second metal in oxidic form; and
- e) reducing at least part of the thus obtained oxidic Cu on the carrier.

It was found that the chromium-free Cu catalysts thus obtained showed promising activity and selectivity, particularly in the hydrogenation and hydrogenolysis of methyl acetate and other palm oil derived fatty esters and fatty acids.

Without wishing to be bound by theory, it is thought that the pH of the final solution is important for keeping all metals present in a uniform solution such that the metals are fully intermixed at an atomic level and no distinct metal clusters are formed at the catalyst surface.

As used herein, with the term "at least one second metal" is meant that in addition to Cu at least one second metal is provided in the catalyst; however, it is also possible that the catalyst comprises two, three, four, etc. different metals in addition to the Cu. Preferably,

In a preferred embodiment, step a) comprises the step of preparing said final solution by combining at least a first solution comprising ions of Cu with at least a second solution comprising ions of at least one second metal. Thus, the pH of the solutions can be controlled separately and precipitation of the metals can be avoided. It is preferred that the said first and second solutions are compatible. With "compatible" as herein used, it is meant that no precipitation of separate metals occurs upon combining of the first and second solutions. Said first solution may be prepared from any Cu salt, and a complexing agent, such as e.g. citric acid, and adjustment of the pH to above 5, or may alternatively be prepared by dissolution of the salt of the Cu and the complexing agent, preferably in a basic solution such as ammonia, and, if required, adjustment of the pH to above 5. Similarly, said second solution may be prepared from any salt of the at least one second metal, followed by the addition of complexing agent, such as e.g. citric acid, and adjustment of the pH to above 5, or may alternatively be prepared by dissolution of the salt of the at least one second metal and the complexing agent, preferably in a basic solution such as ammonia, and, if required, adjustment of the pH to above 5. Any first solution, regardless of the preparation method thereof, can be combined with any second solution, regardless of the preparation method thereof, to obtain the final solution, as long as the first and second solution are compatible. In case metal citrate is used to prepare the solutions, it is preferred that these are dissolved in ammonia.

Preferably, the first solution and the second solution both comprise ions of the complexing agent in a similar concentration, and are thus in this regard compatible. With "a similar concentration" as herein used, it is meant that the concentration differs at most by a factor 2, preferably at most by a factor 1.6, more preferably at most by a factor 1.3.

Moreover, it is preferred that both the first and the second solution have a pH above 5, such that precipitation of the Cu or the at least one second metal due to pH differences can be avoided. It is most preferred that the first and second solution have a similar pH. With "a similar pH" as herein used, it is meant that the pH difference between

the first and second solution is at most 1.5, preferably at most 1.0, more preferably at most 0.5.

In one embodiment, said chromium-free catalyst further comprises at least one third metal, said third metal being chosen from Pd, Pt, Ru and Rh. The at least one third metal can be considered as promoter metal.

Said third metal can be added to the final solution, or to the above first and second solutions. Further, a third metal can be provided in a third solution, that preferably is compatible with the above first and second solution, preferably both with regard to pH and concentration of ions of the complexing agent. Thus, it is preferred that the third solution comprises ions of the complexing agent in a similar concentration as the first and the second solution. Moreover, it is preferred that the third solution has a pH of above 5, and preferably a pH that is similar to the pH of the first and second solutions.

However, it is also possible that the calcined final solution/carrier combination of step d) is impregnated with a solution comprising the at least one third metal, followed by another round of calcination. This is particularly suitable for the incorporation of the noble metal promoters.

It is preferred that the pH of the final solution is above 6, as it was found that under these circumstances best catalysts were obtained. In case the final solution is prepared from a first and second and optionally a third solution, it is preferred that the pH of the first, second and third solution is above 6.

It is preferred that the concentration of Cu ions in the final solution is in the range of 0.001-0.3 g/mL, more preferably of 0.005-0.15 g/mL. Preferably, the amount of Cu ions in the final solution is such that a catalyst is obtained comprising 1-50 %wt, more preferably 10-30 %wt, and most preferably 15-25 %wt Cu. It was found that excellent catalysts were obtained using such amounts of Cu.

The concentration of ions of the complexing agent in the final solution preferably is in the range of 0.001-1.5 g/mL, more preferably of 0.15-0.5 g/mL. Most preferably, the amount of ions of the complexing agent in the final solution is such that the molar ratio of metal to

(Sigma-Aldrich). When the solution had reached pH 7, water was added to obtain 250 mL solution. A second solution was prepared in a similar fashion using 50.0 g iron nitrate nonahydrate (Sigma-Aldrich) and 26.0 g citric acid monohydrate. To a sample of 1 g silica (Aerosil 300, Degussa) was added 3.97 mL of the Cu solution and 2.21 mL of the Fe solution, after which the slurry was stirred for five minutes. The slurry was then dried at 120 °C for 12 h and calcined at 450 °C for 2 h. Finally, the catalyst precursor was crushed to a powder. The catalyst composition was 20 g Cu-Fe per 100 g catalyst with a Cu to Fe at/at ratio of 3:1.

Comparative example 1A Preparation of a Cu-Fe on silica catalyst

A first solution was prepared by dissolving 50.0 g copper nitrate trihydrate in water to obtain 250 mL solution. A second solution was prepared by dissolving 50.0 g iron nitrate nonahydrate in water to obtain 250 mL solution. Aliquots of 3.97 mL of the Cu solution and 2.21 mL of the second solution were mixed and diluted with water to obtain 25 mL of a third solution. To this solution was added 1 g of silica powder (Aerosil 300). While stirring, an ammonia solution (2 mol/L) was added to the thus obtained slurry at a rate of 0.2 mL/min. After reaching a pH of 9, a precipitate had formed, which was washed with water. After drying (2 h at 120 °C) and calcination (2 h at 450 °C) a catalyst precursor was obtained with a composition of 20 g Cu-Fe per 100 g catalyst with a Cu to Fe at/at ratio of 3:1.

Comparative example 1B Preparation of a Cu-Fe on silica catalyst

A catalyst was prepared in the same manner as described in Comparative Example 1A, except that a 0.2 M ammonia solution was used for the precipitation reaction.

Comparative example 2 Preparation of a Cu-Cr-Ba-Mn-Si catalyst (Example 1 of US 5,124,491, Henkel, 1992)

A first solution was prepared by dissolving 48.25 g CrO₃ in 265 g water, which was heated to 60 °C. Next, 97 g 28-30% ammonia was added. The addition of ammonia changed the colour of the solution from orange to light orange-brown, and the pH increased from <1 to 7.9. A second

solution was prepared by dissolving 2.50 g Ba-nitrate, 102.84 g Cu-nitrate, and 8.67 g Mn-nitrate in 265 g water. A clear blue solution was obtained, which was heated to 60 °C. To this solution was added 1.83 g of a 40% silica sol (Ludox AS-40, Sigma-Aldrich). The second
5 solution was added to the Cr solution through a funnel in about 20 minutes, upon which the Cr solution turned dark green. After adding all of the solution, the Cr-Cu-Mn-Ba solution remained dark green, and the pH was 7. After cooling the solution, a brown precipitate had formed. The solution + precipitate was poured over a filter (glass, P2) to
.0 separate the dark green solution from the precipitate. The precipitate was washed six times with 250 mL water. After the last washing, the precipitate was transferred to a dish, dried and calcined (heat to 105 °C (2 °C/min), heat at 105 °C (12 h), heat to 500 °C (2 °C/min), heat at 500 °C (2 h), cool). A dark brown catalyst precursor was obtained
.5 with a composition of 38.5% Cu, 28.3% Cr, 4.6% Ba, 3.5% Mn, 0.8% Si.

Example 2A Preparation of a Cu-Zn on magnesia catalyst

A first solution was prepared by dissolving 49.1 g copper citrate Pfaltz and Bauer) in 104.2 g 30% ammonia. A second solution was
20 prepared by dissolving 50.4 g zinc citrate dihydrate (Sigma-Aldrich) in 102.8 g 30% ammonia. To a sample of 1 g magnesia (E-10, DSP) was added 1.00 mL of the Cu solution and 1.87 mL of the Zn solution, after which the slurry was stirred for five minutes. The slurry was then dried at 120 °C for 12 h and calcined at 450 °C for 2 h. Finally, the catalyst
25 precursor was crushed to a powder. The catalyst composition was 20 g Cu-Zn per 100 g catalyst with a Cu to Zn at/at ratio of 1:1.

Example 2B Preparation of a Cu-Zn-Co on magnesia catalyst

Copper and zinc citrate solutions were prepared as in Example 2A.
30 A third solution was prepared by dissolving 10.5 g cobalt citrate (STREM) in 104.1 g 30% ammonia. To a sample of 1 g magnesia (E-10, DSP) was added 1.51 mL of the Cu solution, 0.63 mL of the Zn solution, and 0.135 mL of the Co solution, after which the slurry was stirred for five minutes. The slurry was then dried at 120 °C for 12 h and calcined
35 at 450 °C for 2 h. Finally, the catalyst precursor was crushed to a

powder. The catalyst composition was 20 g Cu-Zn-Co per 100 g catalyst with a Cu to Zn to Co at/at ratio of 3:1:0.04.

Example 2C Preparation of a Cu-Zn-Co on magnesia catalyst

5 Solutions of copper, zinc, and cobalt nitrates, with equimolar amounts of citric acid, and their pH adjusted to pH 7 with 30% ammonia, were prepared as described in Example 1. To a sample of 1 g magnesia (E-10, DSP) was added 3.75 mL of the Cu solution, 1.52 mL of the Zn solution, and 0.121 mL of the Co solution, after which the slurry was
0 stirred for five minutes. The slurry was then dried at 120 °C for 12 h and calcined at 450 °C for 2 h. Finally, the catalyst precursor was crushed to a powder. The catalyst composition was 20 g Cu-Zn-Co per 100 g catalyst with a Cu to Zn to Co at/at ratio of 3:1:0.04.

Example 3 Preparation of a Cu-Zn on zirconia catalyst

5 Copper citrate and zinc citrate solutions were prepared as in Example 2. To a sample of 1 g zirconia powder (NNC100, Daiichi) was added 1.52 mL of the Cu solution, 0.94 mL of the Zn solution, after which the slurry was stirred for five minutes. The slurry was then
0 dried at 120 °C for 12 h and calcined at 450 °C for 2 h. Finally, the catalyst precursor was crushed to a powder. The catalyst composition was 20 g Cu-Zn per 100 g catalyst with a Cu to Zn ratio of 3:1.

Example 4 Preparation of a Cu-Fe-Co on titania catalyst

5 A copper citrate solution was prepared as in Example 2. A second solution was prepared by dissolving 50.3 g iron citrate dihydrate (Sigma-Aldrich) in 102.3 g 30% ammonia. A third solution was prepared by dissolving 10.5 g cobalt citrate (STREM) in 104.1 g 30% ammonia. To a sample of 1 g titania powder (P25, Degussa) was added 1.51 mL of the
0 Cu solution, 0.94 mL of the Zn solution, and 0.142 mL of the Co solution, after which the slurry was stirred for five minutes. The slurry was then dried at 120 °C for 12 h and calcined at 450 °C for 2 h. Finally, the catalyst precursor was crushed to a powder. The catalyst composition was 20 g Cu-Fe-Co per 100 g catalyst with a Cu to
5 Fe to Co at/at ratio of 3:1:0.4.

Example 5A Preparation of a Cu-Zn-Ni on magnesia catalyst

Copper citrate and zinc citrate solutions were prepared as in Example 2. A third solution was prepared by dissolving 10.1 g nickel citrate (Alfa Aesar) in 108.1 g 30% ammonia. To a sample of 1 g magnesia (E-10, DSP) was added 1.51 mL of the Cu solution, 0.63 mL of the Zn solution, and 0.11 mL of the Ni solution, after which the slurry was stirred for five minutes. The slurry was then dried at 120 °C for 12 h and calcined at 450 °C for 2 h. Finally, the catalyst precursor was crushed to a powder. The catalyst composition was 20 g Cu-Zn-Ni per 100 g catalyst with a Cu to Zn to Ni at/at ratio of 3:1:0.4.

Example 5B Preparation of a Cu-Zn-Ni on zirconia catalyst

A catalyst was prepared analogous to Example 5A, except that zirconia was used as a carrier. The catalyst composition was 20 g Cu-Zn-Ni per 100 g catalyst with a Cu to Zn to Ni at/at ratio of 3:1:0.4.

Example 6 Preparation of a Cu-Fe-Ni on silica catalyst

Solutions of copper, iron, and nickel nitrates, with equimolar amounts of citric acid, and their pH adjusted to pH 7 with 30% ammonia, were prepared as described in Example 1. These solutions were mixed in amounts to obtain a Cu-Fe-Ni solution of which 1.1 mL was impregnated on 1 g silica (Grace Davison, Davicat® SI 1351) to obtain a final catalyst composition of 10.3 %wt of total metal loading, with a Cu to Fe atomic ratio of 3:1, and 0.1 %at/at Ni relative to Cu and Fe. The impregnated support was homogenized and the catalyst precursor thus obtained was dried at 120 °C for 2 h and calcined at 450 °C for 2 h in air.

Example 7 Preparation of a Cu-Zn on silica catalyst

Solutions (0.3 g salt/mL solution) of copper and zinc nitrates, with equimolar amounts of citric acid, and their pH adjusted to pH 7 with 30% ammonia, were prepared as described in Example 1. The solutions were mixed in amounts to obtain a Cu-Zn solution of which 2.5 mL was impregnated on 1 g silica (PQ, CS 2050) to obtain a final catalyst composition of 27.8 %wt of total metal loading, with a Cu to Zn atomic ratio of 3:1. The impregnated support was homogenized and the

catalyst precursor thus obtained was dried at 120 °C for 2 h and calcined at 450 °C for 2 h in air. To obtain the 27.8 %wt metals loading, the support was twice impregnated, with a drying/calcination step in between.

5

Example 8 Preparation of a Cu-Zn on silica catalyst

Copper citrate and zinc citrate solutions were prepared as in Example 2. To a sample of 1 g silica (Aerosil 300) was added 1.52 mL of the Cu solution, and 0.64 mL of the Zn solution, after which the slurry
0 was stirred for five minutes. The slurry was then dried at 120 °C for 12 h and calcined at 450 °C for 2 h. The catalyst precursor was crushed to a powder. The catalyst composition was 20 g Cu-Zn per 100 g catalyst with a Cu to Zn at/at ratio of 3:1.

Example 8A Preparation of a Cu-Zn-Rh on silica catalyst

A Cu-Zn catalyst precursor was prepared equivalent to Example 8. A third solution was prepared by dissolving 0.1 g of a rhodium nitrate solution (14.7% Rh, Chempur) in 10 mL water. The Cu-Zn on silica catalyst precursor was impregnated with a solution 0.292 mL of the Rh
0 solution and sufficient additional water to reach incipient wetness. The wet powder was dried at 120 °C for 2 h and calcined at 450 °C for 2 h. The catalyst composition was 20 g Cu-Zn-Rh per 100 g catalyst with a Cu to Zn to Rh at/at ratio of 3:1:0.004.

Example 8B Preparation of a Cu-Zn-Ru on silica catalyst

A catalyst was prepared analogous to Example 8A, except that the catalyst precursor powder was impregnated with a solution of ruthenium nitrosyl (13.0% Ru, Chempur). The catalyst composition was 20 g Cu-Zn-Ru per 100 g catalyst with a Cu to Zn to Ru at/at ratio of 3:1:0.004.

0

Example 8C Preparation of a Cu-Zn-Pd on silica catalyst

A catalyst was prepared analogous to Example 8A, except that the catalyst precursor powder was impregnated with a solution of palladium nitrate (40.5% Pd, Chempur). The catalyst composition was 20 g Cu-Zn-Pd
5 per 100 g catalyst with a Cu to Zn to Pd at/at ratio of 3:1:0.004.

Example 8D Preparation of a Cu-Zn-Pt on silica catalyst

Solutions (0.5 g salt/mL solution) of copper and zinc nitrates, with equimolar amounts of citric acid, and their pH adjusted to pH 7 with 30% ammonia, were prepared as described in Example 1. To a sample
5 of 1 g silica (Aerosil 300, Degussa) was added 3.77 mL of the Cu solution and 1.55 mL of the Zn solution, after which the slurry was stirred for five minutes. The slurry was then dried at 120 °C for 12 h and calcined at 450 °C for 2 h. The catalyst precursor was crushed to a powder. A third solution was prepared by dissolving 0.1 g of a platinum
0 nitrate solution (58.2% Pt, Chempur) in 10 mL water. The Cu-Zn on silica catalyst precursor was impregnated with 0.139 mL Pt solution and sufficient additional water to reach incipient wetness. The wet powder was dried at 120 °C for 2 h and calcined at 450 °C for 2 h. The catalyst composition was 20 g Cu-Zn-Pt per 100 g catalyst with a Cu to
5 Zn to Pt at/at ratio of 3:1:0.004.

Example 9 Preparation of a Cu-Zn on zirconia catalyst

A catalyst was prepared analogous to Example 8. Instead of silica, zirconia powder was used (NNC100, Daiichi). The catalyst composition
0 was 20 g Cu-Zn per 100 g catalyst with a Cu to Zn at/at ratio of 1:1.

Example 9A Preparation of a Cu-Zn-Rh on zirconia catalyst

A catalyst was prepared analogous to Example 8A. Instead of silica, zirconia powder was used (NNC100, Daiichi). The catalyst
5 composition was 20 g Cu-Zn-Rh per 100 g catalyst with a Cu to Zn to Rh at/at ratio of 1:1:0.004.

Example 9B Preparation of a Cu-Zn-Ru on zirconia catalyst

A Cu-Zn catalyst precursor was prepared analogous to Example 8D.
0 Instead of silica, zirconia powder was used (NNC100, Daiichi). The Ru was added analogous to Example 8B. The catalyst composition was 20 g Cu-Zn-Ru per 100 g catalyst with a Cu to Zn to Ru at/at ratio of 3:1:0.004.

Example 9C Preparation of a Cu-Zn-Pd on zirconia catalyst

A catalyst was prepared analogous to Example 8C. Instead of silica, zirconia powder was used (NNC100, Daiichi). The catalyst composition was 20 g Cu-Zn-Pd per 100 g catalyst with a Cu to Zn to Pd at/at ratio of 1:1:0.004.

Example 9D Preparation of a Cu-Zn-Pt on zirconia catalyst

A catalyst was prepared analogous to Example 8D. Instead of silica, zirconia powder was used (NNC100, Daiichi). The catalyst composition was 20 g Cu-Zn-Pt per 100 g catalyst with a Cu to Zn to Pt at/at ratio of 1:1:0.004.

Example 10 Preparation of a Cu-Zn on magnesia catalyst

A Cu-Zn catalyst precursor was prepared analogous to Example 8D. Instead of silica, magnesia powder was used (E-10, DSP). The catalyst composition was 20 g Cu-Zn per 100 g catalyst with a Cu to Zn at/at ratio of 1:1.

Example 10A Preparation of a Cu-Zn-Rh on magnesia catalyst

A Cu-Zn catalyst precursor was prepared analogous to Example 8D. Instead of silica, magnesia powder was used (E-10, DSP). The Rh was added analogous to Example 8A. The catalyst composition was 20 g Cu-Zn-Rh per 100 g catalyst with a Cu to Zn to Rh at/at ratio of 1:1:0.004.

Example 10B Preparation of a Cu-Zn-Ru on magnesia catalyst

A catalyst was prepared analogous to Example 8B. Instead of silica, magnesia powder was used (E-10, DSP). The catalyst composition was 20 g Cu-Zn-Ru per 100 g catalyst with a Cu to Zn to Ru at/at ratio of 3:1:0.004.

Example 10C Preparation of a Cu-Zn-Pd on magnesia catalyst

A catalyst was prepared analogous to Example 8C. Instead of silica, magnesia powder was used (E-10, DSP). The catalyst composition was 20 g Cu-Zn-Pd per 100 g catalyst with a Cu to Zn to Pd at/at ratio of 1:1:0.004.

Example 10D Preparation of a Cu-Zn-Pt on magnesia catalyst

A catalyst was prepared analogous to Example 8D. Instead of silica, magnesia powder was used (E-10, DSP). The catalyst composition
5 was 20 g Cu-Zn-Pt per 100 g catalyst with a Cu to Zn to Pt at/at ratio of 1:1:0.004.

Examples 11 Preparation of Cu-Fe on silica catalyst

A catalyst was prepared analogous to Example 8A, using a Cu
0 citrate solution (as in Example 2) and an iron citrate solution (as in Example 4). The catalyst compositions were 20 g Cu-Fe per 100 g catalyst with a Cu to Fe at/at ratio of 1:1.

Examples 11A - 11D Preparation of Cu-Fe-(Rh, Ru, Pd, or Pt) on silica
5 catalysts

Catalysts were prepared analogous to Example 8A, using a Cu
citrate solution (as in Example 2) and an iron citrate solution (as in
Example 4). The catalyst compositions were 20 g Cu-Fe-(Rh, Ru, Pd, or
Pt) per 100 g catalyst with a Cu to Fe to (Rh, Ru, Pd, or Pt) at/at
0 ratio of 1:1:0.004.

Examples 12 Preparation of a Cu-Fe on silica catalyst

A catalyst was prepared analogous to Example 8D, using a Cu
nitrate solution and an iron nitrate solution (as used in Example 6).
5 The catalyst compositions were 20 g Cu-Fe per 100 g catalyst with a Cu
to Fe at/at ratio of 1:1.

Examples 12A - 12D Preparation of Cu-Fe-(Rh, Ru, Pd, or Pt) on silica
catalysts

0 Catalysts were prepared analogous to Example 8D, using a Cu
nitrate solution and an iron nitrate solution (as used in Example 6).
The catalyst compositions were 20 g Cu-Fe-(Rh, Ru, Pd, or Pt) per 100 g
catalyst with a Cu to Fe to (Rh, Ru, Pd, or Pt) at/at ratio of
1:1:0.004.

Example 13 Catalyst testing procedure

5 A catalyst sample of 0.25 g (as prepared by the methods described in Examples 1-12) was reduced under a hydrogen flow for 2 h at a temperature of 350 °C. The reduced catalyst was transferred to a reactor and suspended in 25 mL methyl laurate. The reaction mixture was stirred at 750 rpm under 100 bar hydrogen and at 250 °C for 4 h. After cooling, the reaction mixture was analysed by GC. The results of the GC analysis are listed in Tables 1-3.

Table 1 Test results of (promoted) Cu-(Fe or Zn) catalysts

CAT	CATALYST COMPOSITION											PREC	CONV	Selectivity			
	M1	%wt	M2	%wt	M3	%wt	M4	%wt	S	Ialc				IL	Lac	DD	
											(%)	(%)	(%)	(%)			
Ex.1	Cu	15	Fe	5					sill	A	55.3	83.9	15.8	0.0	0.2		
Ex.2A	Cu	10	Zn	10					mag	B	41.6	44.9	51.9	3.0	0.0		
Ex.2B	Cu	15	Zn	5	Co	0.2			mag	B	45.7	46.9	48.2	4.8	0.0		
Ex.2C	Cu	15	Zn	5	Co	0.2			mag	A	60.8	59.8	37.4	2.6	0.0		
Ex.3	Cu	15	Zn	5					zir	B	45.7	64.3	25.8	9.8	0.0		
Ex.4	Cu	15	Fe	5	Co	0.2			tit	B	46.6	73.0	26.8	0.1	0.0		
Ex.5A	Cu	15	Zn	5	Ni	0.2			mag	B	39.4	35.7	61.9	2.2	0.0		
Ex.5B	Cu	15	Zn	5	Ni	0.2			zir	B	55.9	82.9	16.6	0.4	0.0		
Ex.6	Cu	8.0	Fe	2.3	Ni	0.01			sil2	A	35.3	82.3	17.2	0.3	0.0		
Ex.7	Cu	20.7	Zn	7.1					sil3	A	57.7	72.0	27.9	0.0	0.0		
Comp. Ex.1	Cu	15	Fe	5					sill	C	50.0	50.0	10.0	2.0	0.0		
Comp. Ex.2	Cu	38.5	Cr	28.3	Ba	4.6	Mn	3.5			18.0	80.8	17.4	1.8	0.0		

Test conditions: 250 °C, 100 bar hydrogen, 4 h, 750 rpm, 25 mL methyl laurate feed
Metal precursor (PREC): A = metal nitrate + equimolar citric acid + ammonia (pH 7); B = metal citrate in 30% ammonia; C = metal nitrate.
Abbreviations used: CAT = catalyst; M1 = metal 1, etc.; S = support; CONV = percent conversion of lauric methyl ester; Lalc = lauryl alcohol; LL = lauryl laurate; Lac = lauric acid; DD = dodecane
Supports: sil1 = Aerosil 300 (Degussa); sil2 = Davicat® SI 1351 (Grace Davison); sil3 = CS 2050 (PQ) mag = E-10 (DSP); zir = NNC100 (Daichi); tit = P25 (Degussa)

Table 2 Test results of unpromoted and noble metal promoted Cu-Zn catalysts

CAT	CATALYST COMPOSITION									Selectivity			
	M1	%wt	M2	%wt	M3	%wt	S	PREC		CONV	Ialc	IL	Iac
									(%)	(%)	(%)	(%)	(%)
Ex. 8	Cu	15	Zn	5			sill	B	69.9	83.7	16.1	0.1	0.0
Ex. 8A	Cu	15	Zn	5	Rh	0.03	sill	B	57.8	79.9	19.8	0.1	0.0
Ex. 8B	Cu	15	Zn	5	Ru	0.03	sill	B	55.5	82.3	17.2	0.3	0.0
Ex. 8C	Cu	15	Zn	5	Pd	0.03	sill	B	46.6	82.6	17.1	0.2	0.0
Ex. 8D	Cu	15	Zn	5	Pt	0.06	sill	A	50.5	76.8	23.1	0.0	0.0
Ex. 9	Cu	10	Zn	10			zir	B	38.1	72.9	25.8	1.1	0.0
Ex. 9A	Cu	10	Zn	10	Rh	0.03	zir	B	55.5	78.8	20.5	0.5	0.0
Ex. 9B	Cu	15	Zn	5	Ru	0.03	zir	A	53.0	79.9	19.7	0.3	0.0
Ex. 9C	Cu	10	Zn	10	Pd	0.03	zir	B	47.4	81.3	17.0	1.6	0.0
Ex. 9D	Cu	10	Zn	10	Pt	0.06	zir	A	55.6	83.7	15.8	0.4	0.0
Ex. 10	Cu	10	Zn	10			mag	A	48.7	58.1	39.8	1.9	0.0
Ex. 10A	Cu	10	Zn	10	Rh	0.03	mag	A	47.3	48.3	50.4	1.1	0.0
Ex. 10B	Cu	15	Zn	5	Ru	0.03	mag	B	41.1	44.0	53.2	2.6	0.0
Ex. 10C	Cu	15	Zn	5	Pd	0.03	mag	B	43.9	44.4	50.8	4.6	0.0
Ex. 10D	Cu	10	Zn	10	Pt	0.06	mag	A	44.5	50.4	48.1	1.4	0.0

See Table 1 for abbreviations and test conditions.

Table 3 Test results of unpromoted and noble metal promoted Cu-Fe catalysts

CAT	CATALYST COMPOSITION							Selectivity					
	M1	%wt	M2	%wt	M3	%wt	S	PREC	CONV	Ialc	LL	Lac	DD
									(%)	(%)	(%)	(%)	(%)
Ex.11	Cu	10	Fe	10			sill	B	37.9	74.8	24.9	0.1	0.0
Ex.11A	Cu	10	Fe	10	Rh	0.03	sill	B	38.6	66.3	33.1	0.0	0.0
Ex.11B	Cu	10	Fe	10	Ru	0.03	sill	B	39.8	77.7	22.0	0.2	0.0
Ex.11C	Cu	10	Fe	10	Pd	0.03	sill	B	38.9	76.0	23.5	0.4	0.0
Ex.11D	Cu	10	Fe	10	Pt	0.06	sill	B	37.0	66.3	33.1	0.5	0.0
Ex.12	Cu	10	Fe	10			sill	A	56.4	79.6	20.3	0.0	0.0
Ex.12A	Cu	10	Fe	10	Rh	0.03	sill	A	55.4	80.9	19.0	0.0	0.0
Ex.12B	Cu	10	Fe	10	Ru	0.03	sill	A	52.1	78.5	21.0	0.3	0.0
Ex.12C	Cu	10	Fe	10	Pd	0.03	sill	A	48.2	80.3	19.6	0.0	0.0
Ex.12D	Cu	10	Fe	10	Pt	0.06	sill	A	51.9	80.5	19.4	0.0	0.0

See Table 1 for abbreviations and test conditions.

C L A I M S

1. Method for the preparation of a chromium-free catalyst comprising Cu and at least one second metal in metallic or oxidic form, comprising the steps of:
 - a) preparing a final solution comprising ions of Cu and of at least one second metal, said final solution additionally comprising ions of an organic complexing agent and having a pH of above 5;
 - b) contacting said final solution with inert carrier to form a final solution/carrier combination;
 - c) optionally, drying the final solution/carrier combination;
 - d) calcining the final solution/carrier combination obtained in step c) or d) to yield Cu and the at least one second metal in oxidic form; and
 - e) reducing at least part of the thus obtained oxidic Cu on the carrier.
2. Method according to claim 1, wherein the organic complexing agent is chosen from citric acid, lactic acid, and EDTA.
3. Method according to any of claims 1 or 2, step a) comprising the step of preparing said final solution by combining at least a first solution comprising ions of Cu with at least a second solution comprising ions of at least one second metal.
4. Method according to claim 3, wherein the first and second solutions both comprise ions of the complexing agent in a similar concentration.
5. Method according to any of claims 3 or 4, wherein both the first solution and the second solution have a pH of above 5.
6. Method according to claim 5, wherein the first and the second solution have a similar pH.

7. Method according to any of the preceding claims, wherein said chromium-free catalyst further comprises at least one third metal.
8. Method according to any of the preceding claims, wherein the pH of the final solution is above 6.
9. Method according to any of the preceding claims, wherein the concentration of Cu ions in the final solution is in the range of 0.001-0.3, more preferably of 0.005-0.15 g Cu/mL.
10. Method according to any of the preceding claims, wherein the amount of Cu ions in the final solution is such that a catalyst is obtained comprising 1-50 %wt, more preferably 10 to 30 %wt, and most preferably 15 - 25 %wt Cu.
11. Method according to any of the preceding claims, wherein the concentration of ions of the complexing agent in the final solution is in the range of 0.001-1.5, more preferably of 0.15-0.5 g/mL.
12. Method according to any of the preceding claims, wherein the amount of ions of the complexing agent in the final solution is such that the molar ratio of metal to complexing agent is in the range of 0.1 to 5, more preferably 0.5 to 2, and most preferably 0.75-1.25.
13. Method according to any of the preceding claims, wherein the concentration of ions of the at least one second metal in the final solution is in the range of 0.001-0.3, preferably in the range of 0.005-0.15 g/mL.
14. Method according to any of the preceding claims, wherein the amount of ions of the at least one second metal in the final solution is such that catalyst is obtained with an atomic ratio of Cu to the at least one second metal in the range of 0.01-10, more preferably in the range of 0.1-5, and most preferably in the range of 0.3-3.0.

15. Method according to any of the claims 7-14, wherein the concentration of ions of the at least one third metal in the final solution is in the range of 0.0001-0.03, preferably in the range of 0.0005-0.015 g/mL.
16. Method according to any of the claims 7-15, wherein the amount of the at least one third metal is such that catalyst is obtained with an atomic ratio of the at least one third metal to Cu in the range of 0.001-0.05, more preferably in the range of 0.001-0.01.
17. Method according to any of the preceding claims, comprising an additional step g) of pulverising the obtained catalyst.
18. Method according to any of the preceding claims, wherein the at least one second metal is chosen from one or more of Fe, Zn, Co, Ni, or a combination thereof.
19. Method according to any of the preceding claims, wherein the at least one third metal is chosen from one or more of Pd, Ru, Pt, Rh, or a combination of two or more thereof.
20. Method according to any of the preceding claims, wherein the inert carrier is chosen from alumina, silica, silica-alumina, titania, magnesia, zirconia, zinc oxide, or any combination thereof.
21. Method according to any of the preceding claims, wherein the inert carrier is present in an amount of 50-95 %wt.
22. Chromium-free catalyst comprising Cu and at least one second metal obtainable by a method according to any of the preceding claims.
23. Chromium-free catalyst according to claim 22, said catalyst comprising at least 5 %wt Cu and having an atomic ratio of Cu to the at least one second metal of 0.1-10.

24. Chromium-free Cu-Zn catalyst supported on silica, zirconia, or magnesia according to any of claims 22 or 23, comprising 5-50 %wt, preferably 10-30 %wt (Cu + Zn) and having a Cu to Zn ratio of 0.1-10 at/at, preferably 0.5-5 at/at, more preferably 1-4 at/at.
25. Chromium-free Cu-Zn catalyst according to claim 24, further comprising as at least one second metal Co or Ni, or a combination thereof.
26. Chromium-free Cu-Zn catalyst according to any of claims 24 or 25, further comprising at least one third metal chosen from Rh, Ru, Pd and Pt, or combinations of two or more thereof.
27. Chromium-free Cu-Zn catalyst according to claim 26 having a ratio of (Cu + Zn) to the at least one third metal of 0.0001-0.5 at/at, preferably of 0.001-0.01 at/at.
28. Chromium-free Cu-Fe catalyst supported on silica, zirconia, or magnesia according to any of claims 22 or 23, comprising 5-50 %wt, preferably 10-30 %wt (Cu + Fe) and having a Cu to Fe ratio of 0.1-10 at/at, preferably 0.5-5 at/at, more preferably 1-4 at/at.
29. Chromium-free Cu-Fe catalyst according to claim 28, further comprising as at least one second metal Co or Ni, or a combination thereof.
30. Chromium-free Cu-Fe catalyst according to any of claims 28 or 29, further comprising at least one third metal chosen from Rh, Ru, Pd and Pt, or combinations of two or more thereof.
31. Chromium-free Cu-Fe catalyst according to claim 30 having a ratio of (Cu + Fe) to the at least one third metal of 0.0001-0.5 at/at, preferably of 0.001-0.01 at/at.
32. Use of chromium-free catalyst according to any of claims 22-31 for the hydrogenation of fatty acids, fatty esters, esters and diesters to fatty alcohols, alcohols and dialcohols, respectively.