(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
08 November 2018 (08.11.2018)

WIPO | PCT

(10) **International Publication Number**
WO 2018/202638 A1

(51) **International Patent Classification:**
B01J 23/89 (2006.01) ***B01J 37/16*** (2006.01)
C07C 29/17 (2006.01) ***B01J 37/18*** (2006.01)
B01J 37/02 (2006.01)

(21) **International Application Number:**
PCT/EP2018/061067

(22) **International Filing Date:**
01 May 2018 (01.05.2018)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
17168888.0 01 May 2017 (01.05.2017) EP

(71) **Applicant: DSM IP ASSETS B.V.** [NL/NL]; Het Overloon 1, 6411 TE Heerlen (NL).

(72) **Inventors: BONRATH, Werner**; c/o DSM Nutritional Products Ltd, Patent Department, Wurmisweg 576, 4303 Kaiseraugst (CH). **GOY, Roman**; c/o DSM Nutritional Products Ltd, Patent Department, Wurmisweg 576, 4303 Kaiseraugst (CH). **MEDLOCK, Jonathan, Alan**; c/o DSM Nutritional Products Ltd, Patent Department, Wurmisweg 576, 4303 Kaiseraugst (CH).

(74) **Agent: KURT, Manfred**; DSM Nutritional Products Ltd, Patent Department, Wurmisweg 576, 4303 Kaiseraugst (CH).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

WO 2018/202638 A1

(54) Title: METAL POWDEROUS CATALYST FOR HYDROGENATION PROCESSES

(57) **Abstract:** The present invention relates to a metal powder catalyst and its use in the selective catalytic hydrogenation of organic starting materials comprising a carbon-carbon triple bond. The powder catalyst comprises a metal alloy carrier, wherein the metal alloy comprises (i) 55 weight-% (wt-%) - 80 wt-%, based on the total weight of the metal alloy, of Co, and (ii) 20 wt-% - 40 wt-%, based on the total weight of the metal alloy, of Cr, and (iii) 2 wt-% - 10 wt-%, based on the total weight of the metal alloy, of Mo, and wherein the said metal alloy is coated by a metal oxide layer and impregnated with Pd, and is characterized in that the metal oxide layer comprises CeO_2.

METAL POWDERDOUS CATALYST FOR HYDROGENATION PROCESSES

The present invention is related to a new metal powder catalytic system (catalyst), its production and its use in hydrogenation processes.

Powderous catalysts are well known and used in chemical reactions. Important types of such catalysts are i.e. the Lindlar catalysts.

The Lindlar catalyst is a heterogeneous catalyst which consists of palladium deposited on a calcium carbonate carrier which is also treated with various forms of lead.

Such catalysts are of such an importance that there is always a need for their improvement.

The goal of the present invention was to find a powderous catalyst with improved properties.

The powderous catalysts according to the present invention have a metal (or metal alloy) as carrier material, instead of a calcium carbonate carrier.

This metal alloy is coated by a metal oxide layer on which palladium (Pd) is deposited.

Furthermore the new catalyst according to the present invention is free from lead (Pb). This applies to all powderous catalytic systems, which are part of this patent application.

Therefore, the present invention relates to a powderous catalytic system (I) comprising

a metal alloy carrier comprising

(i) 55 weight-% (wt-%) – 80 wt-%, based on the total weight of the metal alloy, of Co, and

(ii) 20 wt-% – 40 wt-%, based on the total weight of the metal alloy, of Cr, and

(iii) 2 wt-% – 10 wt-%, based on the total weight of the metal alloy, of Mo, and

wherein the said metal alloy is coated by a metal oxide layer and impregnated with Pd-nanoparticles,
characterized in that the metal oxide layer comprises CeO_2.

It is obvious that all percentages always add up to 100.

Therefore, the present invention relates to a powderous catalytic system (I') consisting of
a metal alloy carrier consisting of

(i) 55 weight-% (wt-%) – 80 wt-%, based on the total weight of the metal alloy, of Co, and
(ii) 20 wt-% – 40 wt-%, based on the total weight of the metal alloy, of Cr, and
(iii) 2 wt-% – 10 wt-%, based on the total weight of the metal alloy, of Mo, and

wherein the said metal alloy is coated by a metal oxide layer and impregnated with Pd-nanoparticles,
characterized in that the metal oxide layer comprises CeO_2.

The catalytic system is in the form of a powder.

This new catalyst has numerous advantages:

- The catalyst is easy to recycle (and to remove) after the reaction. This can be done i.e. by filtration.
- The catalyst can be used more than once (re-usable).
- The catalyst is easy to produce.
- The catalyst is easy to handle.
- The hydrogenation can be carried out with or without any solvents.
- The catalyst is free from lead.
- The catalyst shows high selectivity and activity in hydrogenation reactions.

The metal alloys used as a carrier are known as cobalt/chromium/molybdenum alloy. Such alloys are available commercially, i.e. from EOS GmbH Germany (EOS

CobaltChrome MP1 ®), from Attenborough Dental UK (Megallium ®) and from International Nickel.

Such alloys are usually used in the field of dentistry. Especially, they are used in the production of dental prostheses.

The catalytic system is in the form of a powder.

Suitable metal alloys used in the present invention are cobalt/chromium/molybdenum alloy. Such alloys are available commercially, i.e. from EOS GmbH Germany (EOS CobaltChrome MP1 ®), from Attenborough Dental UK (Megallium ®) and from International Nickel.

Preferred metal alloys comprise

(i) 55 wt-% – 70 wt-%, based on the total weight of the metal alloy, of Co, and
(ii) 20 wt-% – 35 wt-%, based on the total weight of the metal alloy, of Cr, and
(iii) 4 wt-% – 10 wt-%, based on the total weight of the metal alloy, of Mo.

Further preferred metal alloys consist of

(i) 55 wt-% – 70 wt-%, based on the total weight of the metal alloy, of Co, and
(ii) 20 wt-% – 35 wt-%, based on the total weight of the metal alloy, of Cr, and
(iii) 4 wt-% – 10 wt-%, based on the total weight of the metal alloy, of Mo.

Therefore, the present invention relates to a powderous catalytic system (II) which is the powderous catalytic system (I), wherein the metal alloy carrier comprises

(i) 55 wt-% – 70 wt-%, based on the total weight of the metal alloy, of Co, and
(ii) 20 wt-% – 35 wt-%, based on the total weight of the metal alloy, of Cr, and

(iii) 4 wt-% – 10 wt-%, based on the total weight of the metal alloy, of Mo.

The metal alloy can comprise further metals, such as i.e. Cu, Fe, Ni, Mn, Si, Ti, Al and/or Nb.

Therefore, the present invention relates to a powderous catalytic system (II’) which is the powderous catalytic system (I), wherein the metal alloy carrier consists of

(i) 55 wt-% – 70 wt-%, based on the total weight of the metal alloy, of Co, and

(ii) 20 wt-% – 35 wt-%, based on the total weight of the metal alloy, of Cr, and

(iii) 4 wt-% – 10 wt-%, based on the total weight of the metal alloy, of Mo.

Therefore, the present invention also relates to a powderous catalytic system (III), which is a powderous catalytic system (I) or (II), wherein the alloy comprises further metals, such as i.e. Cu, Fe, Ni, Mn, Si, Ti, Al and/or Nb.

Furthermore the metal alloy can comprise carbon as well.

Therefore, the present invention also relates to a powderous catalytic system (IV), which is the catalytic system (I), (II) or (III), (wherein the metal alloy comprises at least one further metal chosen from the group consisting of Cu, Fe, Ni, Mn, Si, Ti, Al and Nb.

Therefore, the present invention also relates to a powderous catalytic system (V), which is the catalytic system (I), (II), (III) or (IV) wherein the metal alloy comprises carbon.

The metal oxide layer of the embodiment of the present invention (which comprises CeO_2), which coats the metal alloy, is non-acidic (preferably basic or amphoteric). Suitable non-acidic metal oxide layers can also comprise at least one further metal oxide wherein the metal is chosen from the group consisting of Zn, Cr, Mn, Mg, Cu and Al.

The metal alloy is preferably coated with a thin layer of metal oxide layer CeO_2 (0.5 - 3.5 μm thickness) and optionally at least one further metal oxide wherein the metal is chosen from the group consisting of Zn, Cr, Mn, Mg, Cu and Al.

Therefore the present invention also relates to a powderous catalytic system (VI), which is powderous catalytic system (I), (I'), (II), (II'), (III), (IV) or (V), wherein the metal alloy is coated with a thin layer of CeO_2 and optionally at least one further metal (Cr, Mn, Mg, Cu and/or Al) oxide.

Therefore the present invention also relates to a powderous catalytic system (VI'), which is powderous catalytic system (VI), wherein the layer of metal oxide has a thickness of 0.5 - 3.5 μm.

The coating of the metal alloy is done by commonly known processes, such as i.e. dip-coating.

Usually the catalytic system (catalyst) of the present invention comprises between 0.1 wt-% and 50 wt-%, based on the total weight of the catalyst, of CeO_2, preferably between 0.1 wt-% and 30 wt-%, more preferably between 0.5 wt-% and 5 wt-% and most preferably between 0.5 wt-% and 2 wt-%.

Therefore the present invention also relates to a powderous catalytic system (VII), which is powderous catalytic system (I), (I') (II), (II'), (III), (IV), (V), (VI) or (VI'), wherein the catalyst comprises between 0.1 wt-% and 50 wt-%, based on the total weight of the catalytic system, of CeO_2 (preferably between 0.1 wt-% and 30 wt-%, more preferably between 0.5 wt-% and 10 wt-% and most preferably between 0.5 wt-% and 2 wt-%).

In a preferred embodiment of the present invention the non-acidic metal oxide layers comprises CeO_2 and at least one further metal oxide wherein the metal is chosen from the group consisting of Zn, Cr, Mn, Mg, Cu and Al.

In a more preferred embodiment of the present the non-acidic metal oxide layer comprises CeO_2 and Al_2O_3.
In an also more preferred embodiment of the present the non-acidic metal oxide layer comprises CeO_2 and ZnO.

Therefore the present invention also relates to a powderous catalytic system (VIII), which is powderous catalytic system (I), (I') (II), (II'), (III), (IV), (V), (VI), (VI') or (VII), wherein the non-acidic metal oxide layer comprises CeO_2 and Al_2O_3.

Therefore the present invention also relates to a powderous catalytic system (IX), which is powderous catalytic system I), (I') (II), (II'), (III), (IV), (V), (VI), (VI') or (VII), wherein the non-acidic metal oxide layer comprises CeO_2 and ZnO.

When a mixture of CeO_2 and Al_2O_3 is used then it is preferred that the ratio of CeO_2 : Al_2O_3 is from 2:1 to 1:2 (preferably 1:1).

When a mixture of CeO_2 and ZnO is used then it is preferred that the ratio of CeO_2 : ZnO is from 2:1 to 1:2 (preferably 1:1).

When using mixture of metal oxides the total content of the metal oxide will not exceed 50 wt-%, based on the total weight of the catalytic system.

Therefore the present invention also relates to a powderous catalytic system (VIII'), which is the powderous catalytic system (VIII), wherein the ratio of CeO_2 : Al_2O_3 is from 2:1 to 1:2 (preferably 1:1).

Therefore the present invention also relates to a powderous catalytic system (VIII"), which is the powderous catalytic system (VIII) or (VIII'), wherein the catalyst comprises between 0.1 wt-% and 50 wt-%, based on the total weight of the catalytic system, of metal oxides (preferably between 0.1 wt-% and 30 wt-%, more preferably between 0.5 wt-% and 10 wt-% and most preferably between 0.5 wt-% and 2 wt-%).

Therefore the present invention also relates to a powderous catalytic system (IX’), which is the powderous catalytic system (IX), wherein the ratio of CeO_2 : ZnO is from 2:1 to 1:2 (preferably 1:1).

Therefore the present invention also relates to a powderous catalytic system (IX”), which is the powderous catalytic system (IX) or (IX’), wherein the catalyst comprises between 0.1 wt-% and 50 wt-%, based on the total weight of the catalytic system, of metal oxides (preferably between 0.1 wt-% and 30 wt-%, more preferably between 0.5 wt-% and 10 wt-% and most preferably between 0.5 wt-% and 2 wt-%).

The coated metal alloys are then impregnated by Pd-nanoparticles. The nanoparticles are synthesized by commonly known methods, i.e. by using $PdCl_2$ as a precursor, which is then reduced by hydrogen.
It is also possible to use a process, wherein metal alloys are impregnated by the Pd-nanoparticles by a process, which comprises a sonication step. The sonication is the act of applying sound energy to agitate particles in a sample. Ultrasonic frequencies (>20 kHz) are usually used, leading to the process also being known as ultrasonication or ultra-sonication.
It is usually applied using an ultrasonic bath or an ultrasonic probe.
Such a process comprises usually (and preferably) the following steps:
(a) preparing an aqueous solution of Pd-salt optionally adding a polyethylene glycol
(b) heating the solution of step (a) and subjecting the solution to sonication
(c) adding a reducing agent, preferably a solution of formate, to the Pd solution
(d) adding the metal oxide powder
(e) the suspension which is obtained in step (d) is filtrated and dried

In the following the steps of the process wherein a sonication step is involved is discussed in more details below:
Step (a)
The Pd salt is dissolved in water (or aqueous solvent, which means that water is mixed at least one other solvent).

Any commonly known and used Pd-salt can be used. Suitable salts are PdCl2 or Na2PdCl4. It can be one Pd-salt as well as a mixture of two or more Pd-salts. Furthermore, it is of an advantage to add at least one surfactant to the solution. Suitable are i.e. polyethylene glycol (PEG), polyvinylpyrrolidones (PVP) or glucosamides.

Step (b)

The solution of step is usually heated up to elevated temperature. Usually not to a higher temperature as the boiling point of the solvent (or solvent mixture used). Usually it is heated up to a temperature of between 30 – 80°C.

The sonication is usually carried out at a frequency of 30 – 50 kHz.

The duration of the sonication step is usually at least 10 minutes, preferred more than 20 (suitable and preferred range is 30 – 120 minutes). The maximal length of the duration of the sonication step is not critical.

The sonication step can be carried out by using an ultrasonic bath or an immersion probe. Or even a combination of both methods is possible.

Step (c)

To the solution of step (b) a reducing agent is added. Usually it is a sodium formate solution. But also, other formate salts (or mixtures of formate salts) could be used. Optionally (instead of or additionally), it is also possible to add H2-gas, L-ascorbic acid, and/or formic acid.

Step (d)

To the solution of step (c) the metal oxide powder (or a mixture of metal oxide powders) are added. Usually the reaction mixture is stirred.

Step (e)

Finally, the suspension of step (d) is filtered and the obtained doped metal oxide powder is usually washed and dried.

Usually the Pd-nanoparticles, which are on the non-acidic metal oxide layer, have an average particle size of between 0.5 and 20 nm, preferably of between 2 and 15 nm, more preferably of between 5 and 12 nm. (The average particle size can be measured by electron microscopy methods).

Therefore the present invention also relates to a powderous catalytic system (X), which is powderous catalytic system (I), (I') (II), (II'), (III), (IV), (V), (VI), (VI'), (VII), (VIII), (IX), (X), (XI), (XI'), (XI''), (XII), (XII') or (XII''), wherein the Pd-nanoparticles have an average particle size of between 0.5 and 20 nm (preferably of between 2 and 15 nm, more preferably of between 5 and 12 nm).

The catalyst according to present invention comprises between 0.001 wt-% and 5 wt-%, based on the total weight of the catalyst, of the Pd- nanoparticles, preferably between 0.01 wt-% and 2 wt-% more preferably between 0.05 wt-% and 1 wt-%.

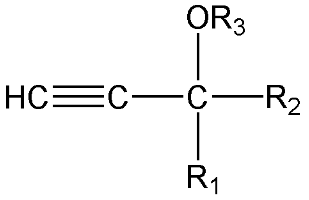
Therefore the present invention also relates to a powderous catalytic system (XIV), which is the powderous catalytic system (I), (I') (II), (II'), (III), (IV), (V), (VI), (VI'), (VII), (VIII), (IX), (X), (XI), (XI'), (XII), (XII') or (XIII), wherein the catalyst comprises between 0.001 wt-% and 5 wt-%, based on the total weight of the catalyst, of the Pd- nanoparticles (preferably between 0.01 wt-% and 2 wt-% more preferably between 0.05 wt-% and 1 wt-%).

The catalyst is usually activated before the use. The activation is done by using well known processes, such thermal activation under H_2.

The catalyst of the present invention is used in selective catalytic hydrogenation of organic starting material, especially of organic starting material comprising a carbon-carbon triple bond, more especially of alkynol compounds.

Therefore the present invention also relates to the use of a powderous catalytic system (catalyst) (I), (I') (II), (II'), (III), (IV), (V), (VI), (VI'), (VII), (VIII), (VIII'), (VIII''), (IX), (IX') or (IX'') in selective catalytic hydrogenation of organic starting material, especially of organic starting material comprising a carbon-carbon triple bond, more especially of alkynol compounds.

Preferably the present invention relates to a process of reacting a compound of formula (I)



$$HC\equiv C-\overset{\displaystyle OR_3}{\underset{\displaystyle R_1}{C}}-R_2$$

(I)

,

wherein

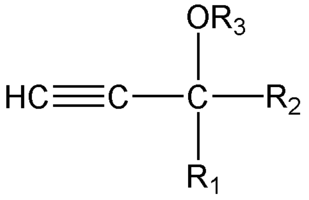
R_1 is linear or branched C_1-C_{35} alkyl or linear or branched C_5-C_{35} alkenyl moiety, wherein the C chain can be substituted, and

R_2 is linear or branched C_1-C_4 alkyl, wherein the C chain can be substituted,

R_3 is H or $-C(CO)C_1$-C_4alkyl,

with hydrogen in the presence of a catalyst (I), (I') (II), (II'), (III), (IV), (V), (VI), (VI'), (VII), (VIII), (VIII'), (VIII"), (IX), (IX') or (IX").

Therefore the present invention relates to a process (P) of reacting a compound of formula (I)



$$HC\equiv C-\overset{\displaystyle OR_3}{\underset{\displaystyle R_1}{C}}-R_2$$

(I)

,

wherein

R_1 is linear or branched C_1-C_{35} alkyl or linear or branched C_5-C_{35} alkenyl moiety, wherein the C chain can be substituted, and

R_2 is linear or branched C_1-C_4 alkyl, wherein the C chain can be substituted,

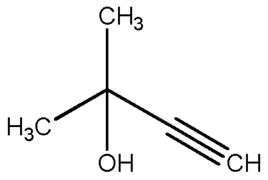
R_3 is H or $-C(CO)C_1$-C_4alkyl,

with hydrogen in the presence of a catalyst (I), (I') (II), (II'), (III), (IV), (V), (VI), (VI'), (VII), (VIII), (VIII'), (VIII"), (IX), (IX') or (IX").

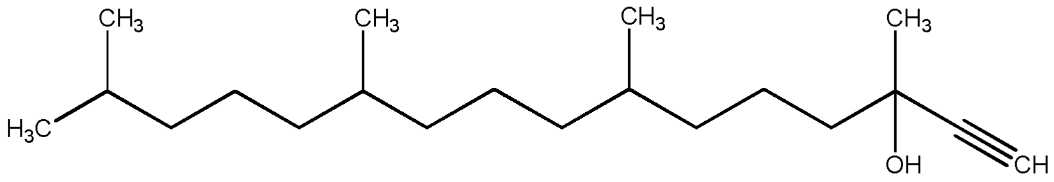
Hydrogen is usually used in the form of H_2 gas.

Therefore the present invention relates to a process (P1), which process (P), wherein hydrogen is usually used in the form of H_2 gas.

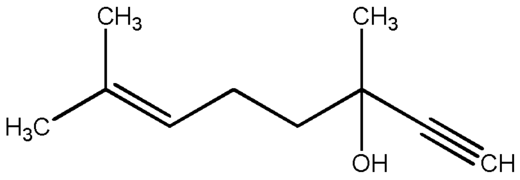
Preferred compounds of formula (I) are the following:



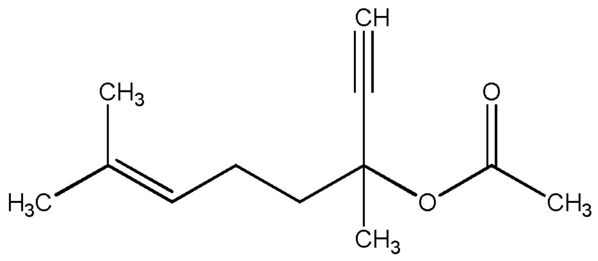
,



,

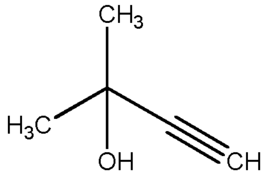


, and

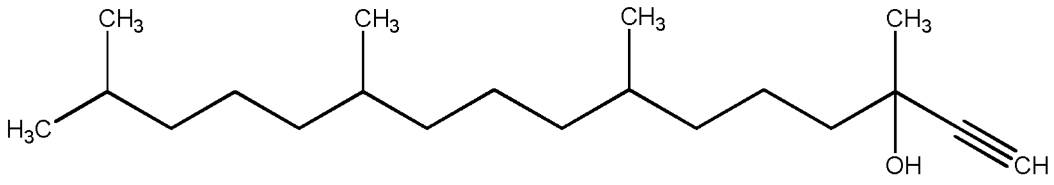


.

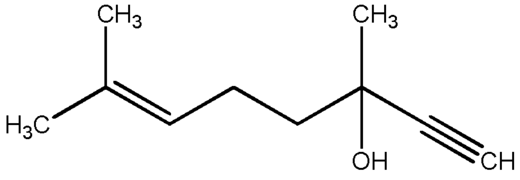
Therefore the present invention relates to a process (P2), which process (P) or (P1), wherein, the following compounds



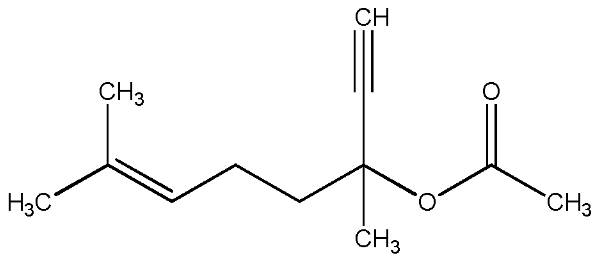
,



,



, and



.

are hydrogenated selectively.

The following examples serve to illustrate the invention. All percentages are related to weight and the temperatures are given in degree Celsius, if not otherwise stated.

Examples

Example 1: *Preparation of metal powder catalyst*

The *EOS CobaltChrome MP1* was heated at 450 °C for 3 h in air. For preparation of the primer solution, $Ce(NO_3)_3 \cdot 6H_2O$ (508 mmol) and 700 mL water were added to a beaker. The mixture was stirred until the salt was completely dissolved. The solution was heated to 90 °C and ZnO (508 mmol) was slowly added to the solution. The stirring was maintained at 90 °C and 65 % nitric acid was added dropwise until all ZnO was completely dissolved (final c_{HNO3} = 1 M). Afterwards the solution was cooled to room temperature and filtrated through a 0.45 μm membrane filter. The deposition of ZnO/CeO_2 was performed by adding thermally treated MP1 powder (10.0 g) to 25 mL of the precursor solution. This mixture was stirred at room temperature for 15 min. Afterwards the suspension was filtered *via* a 0.45 μm membrane filter and dried under vacuum at 40 °C for 2h followed by calcination at 450 °C for 1 h. This process was repeated until the desired number of primer layers had been deposited.

Sodium tetrachloropalladate(II) (0.48 mmol) was dissolved in 133 mL of Millipore water and PEG-MS40 (3.2 mmol) was added. The solution was heated to 60°C and sonication was started at this temperature. A fresh prepared solution of sodium formate (16 mM, 67 mL) were added. The solution was sonicated for further 60 minutes at this temperature and then cooled to room temperature followed by addition of the coated MP1 (10.0 g). The suspension was stirred at room temperature for 60 minutes followed by filtration *via* a 0.45 μm membrane filter. The residue was washed with water and dried under vacuum at 40 °C for 2 h. The catalyst was subjected to a temperature treatment at 300°C for 4 h (temperature ramp – 10°/min) under H_2-Ar flow (1:9; total flow rate - 450 ml/min).

Hydrogenation Examples

Selective Semi-Hydrogenation of an Alkyne to an Alkene

40.0 g of 2-methyl-3-butyne-2-ol (MBY) and the desired amount of metal powder catalyst were added to a 125 mL autoclave reactor. Isothermal conditions during the hydrogenation reaction (338 K) were maintained by a heating/cooling jacket. The reactor was equipped with a gas-entrainment stirrer. Pure hydrogen was supplied at the required value under nitrogen atmosphere. After purging with nitrogen, the reactor was purged with hydrogen and heated to the desired temperature. The pressure in the reactor (3.0 bar) was maintained during the experiments by supplying hydrogen from external reservoir. The reaction mixture was stirred with 1000 rpm. Liquid samples (200 µL) were periodically withdrawn from the reactor starting at a minimum conversion of 95% of MBY and analysed by gas-chromatography (HP 6890 series, GC-system). Selectivity is reported as amount of the desired semi-hydrogenation product (2-methyl-3-butene-2-ol (MBE)) compared to all reaction products.

Tables 1a and 1b: *Test results of different oxide layers, Pd-Source, Pd-amount and Pd-reduction*

The catalysts prepared according to the process described in the example above and they were thermal activated as mentioned in the preparation procedure

Reaction conditions for a: 500 mg catalyst, 40.0 MBY, 1000 rpm, 3.0 bar H_2, 65°C.

Reaction conditions for b: 158 mg catalyst, 30.0 MBY, 1000 rpm, 3.0 bar H_2, 65°C.

Exp. 1 is a comparison example using an oxide layer known from the prior art.

Table 1a

Exp	Oxide Layer & Layer #	Pd-source (loading wt%)	Pd-reduction procedure
1a	Al_2O_3/ZnO (3)	$PdCl_2$ (0.50)	H_2 bubbling (25°C)
2b	CeO_2/ZnO (3)	Na_2PdCl_4 (0.50)	H_2 bubbling (25°C)
3b	CeO_2/ZnO (3)	Na_2PdCl_4 (0.5)	HCOONa, PEG, sonication (60°C)

Table 1b:

Exp	**Conv. (%)**	**Time (min)**	**Select. (%)**	**Activity (mmol/sg$_{Pd}$)**
1a	99.8	740	95.3	122.8
2b	99.9	122	95.6	317.1
3b	99.7	122	96.9	335.0

It can be seen that the new metal oxide powders show an improved activity as well as an improved selectivity.

[a] Conditions: 500 mg catalyst, 40.0 MBY, 1000 rpm, 3.0 bar H_2, 65°C.

[b] Conditions: 158 mg catalyst, 30.0 MBY, 1000 rpm, 3.0 bar H_2, 65°C.

The catalyst according to the present invention show improved properties when used in selective hydrogenation processes.

CLAIMS

1. Use of a powderous catalytic system which comprises a metal alloy carrier, wherein the metal alloy comprises

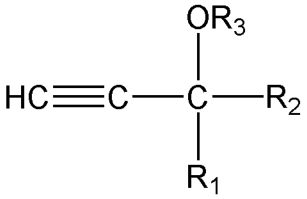
- (i) 55 weight-% (wt-%) – 80 wt-%, based on the total weight of the metal alloy, of Co, and
- (ii) 20 wt-% – 40 wt-%, based on the total weight of the metal alloy, of Cr, and
- (iii) 2 wt-% – 10 wt-%, based on the total weight of the metal alloy, of Mo, and

wherein the said metal alloy is coated by a metal oxide layer and impregnated with Pd,

characterized in that the metal oxide layer comprises CeO_2,

in selective catalytic hydrogenation with hydrogen of organic starting material comprising a carbon-carbon triple bond (preferably alkynol compounds).

2. Use according to claim 1, wherein the organic starting material comprising a carbon-carbon triple bond is a compound of formula (I)



$$HC{\equiv}C{-}C(OR_3)(R_1){-}R_2$$

(I)

,

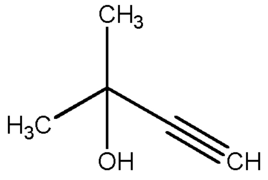
wherein

R_1 is linear or branched C_1-C_{35} alkyl or linear or branched C_5-C_{35} alkenyl moiety, wherein the C chain can be substituted, and

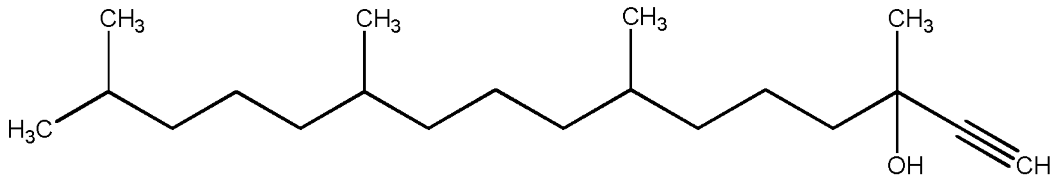
R_2 is linear or branched C_1-C_4 alkyl, wherein the C chain can be substituted, and

R_3 is H or $-C(CO)C_1$-C_4alkyl.

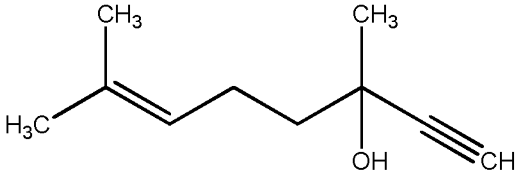
3. Use according to claim 1 or claim 2, wherein the organic starting material comprising a carbon-carbon triple bond is any compound of the following formulae



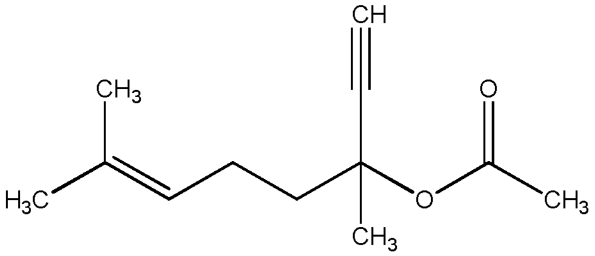
,



,



, and



.

4. Use according to anyone of the preceeding claims, wherein hydrogen is used in the form of H_2 gas.

5. Use according to anyone of the preceeding claims, wherein the metal alloy carrier comprises

(i) 55 wt-% – 70 wt-%, based on the total weight of the metal alloy, of Co, and

(ii) 20 wt-% – 35 wt-%, based on the total weight of the metal alloy, of Cr, and

(iii) 4 wt-% – 10 wt-%, based on the total weight of the metal alloy, of Mo.

6. Use according to anyone of the preceeding claims, wherein the metal alloy comprises at least one further metal chosen from the group consisting of Cu, Fe, Ni, Mn, Si, Ti, Al and Nb.

7. Use according to anyone of the preceeding claims, wherein the metal alloy comprises carbon.

8. Use according to anyone of the preceeding claims, wherein the metal alloy is coated with a layer of CeO_2 and optionally at least one further metal (Cr, Mn, Mg, Cu and/or Al) oxide.

9. Powderous catalytic system which comprises a metal alloy carrier, wherein the metal alloy comprises

- (i) 55 weight-% (wt-%) – 80 wt-%, based on the total weight of the metal alloy, of Co, and
- (ii) 20 wt-% – 40 wt-%, based on the total weight of the metal alloy, of Cr, and
- (iii) 2 wt-% – 10 wt-%, based on the total weight of the metal alloy, of Mo, and

wherein the said metal alloy is coated by a metal oxide layer and impregnated with Pd,

characterized in that the metal oxide layer comprises CeO_2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/061067

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J23/89 C07C29/17 B01J37/02 B01J37/16 B01J37/18
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 C07C

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, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2015/025267 A1 (BONRATH WERNER [CH] ET AL) 22 January 2015 (2015-01-22) claims; examples paragraphs [0019] - [0029] -----	1-9
Y	WO 2015/044410 A1 (DSM IP ASSETS BV [NL]) 2 April 2015 (2015-04-02) examples ----- -/--	1-9

☒ 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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"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 7 August 2018	Date of mailing of the international search report 14/08/2018
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Besselmann, Sonja

3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/061067

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	ABDELHAMID BENSALEM ET AL: "Palladium-ceria catalysts: Metal-support interactions and reactivity of palladium in selective hydrogenation of but-1-yne", REACTION KINETICS AND CATALYSIS LETTERS, vol. 60, no. 1, 30 March 1997 (1997-03-30), pages 71-77, XP055164932, ISSN: 0133-1736, DOI: 10.1007/BF02477692 abstract table 2 page 72, lines 1-5 page 76, lines 1-6 -----	1-9
Y	US 2015/105580 A1 (BONRATH WERNER [CH]) 16 April 2015 (2015-04-16) paragraph [0011]; examples; tables -----	1-9
A	US 2006/217579 A1 (BAILEY STEPHEN [GB]) 28 September 2006 (2006-09-28) claims; examples -----	1-9

3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2018/061067

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2015025267 A1	22-01-2015	CN 104136114 A	05-11-2014
		EP 2817092 A1	31-12-2014
		JP 6232672 B2	22-11-2017
		JP 2015513457 A	14-05-2015
		KR 20140134299 A	21-11-2014
		US 2015025267 A1	22-01-2015
		WO 2013124393 A1	29-08-2013
WO 2015044410 A1	02-04-2015	CN 105579421 A	11-05-2016
		CN 105612137 A	25-05-2016
		EP 3052459 A1	10-08-2016
		EP 3052460 A1	10-08-2016
		WO 2015044410 A1	02-04-2015
		WO 2015044411 A1	02-04-2015
US 2015105580 A1	16-04-2015	CN 104245112 A	24-12-2014
		EP 2864032 A1	29-04-2015
		JP 6238211 B2	29-11-2017
		JP 2015521096 A	27-07-2015
		KR 20150005623 A	14-01-2015
		US 2015105580 A1	16-04-2015
		WO 2013156501 A1	24-10-2013
US 2006217579 A1	28-09-2006	AR 044606 A1	21-09-2005
		AU 2004245280 A1	16-12-2004
		BR PI0411026 A	25-07-2006
		CA 2526062 A1	16-12-2004
		CL 2004001399 A1	06-05-2005
		CN 1798716 A	05-07-2006
		EA 200501754 A1	28-04-2006
		EP 1628941 A1	01-03-2006
		JP 2006526499 A	24-11-2006
		KR 20060007056 A	23-01-2006
		MX PA05013092 A	09-03-2006
		TW 200512188 A	01-04-2005
		US 2006217579 A1	28-09-2006
		WO 2004108638 A1	16-12-2004
		ZA 200509711 B	27-12-2006