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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
29 August 2013 (29.08.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/124391 A1

(51) International Patent Classification:
B01J 37/02 (2006.01) *B01J 35/00* (2006.01)
B01J 23/60 (2006.01) *C07C 29/17* (2006.01)

(21) International Application Number:
PCT/EP2013/053511

(22) International Filing Date:
22 February 2013 (22.02.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
12156805.9 24 February 2012 (24.02.2012) EP

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(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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, 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, 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, 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, ML, MR, NE, SN, TD, TG).

Published:

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

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2013/124391 A1

(54) Title: METAL POWDERDOUS CATALYST COMPRISING A COCRMO-ALLOY

(57) **Abstract**: The present invention is related to a new metal powder catalytic system (catalyst) comprising a cobalt/chrome-alloy as a carrier, its production and its use in hydrogenation processes.

METAL POWDERDOUS CATALYST COMPRISING A COCRMO-ALLOY

The present invention is related to a new metal powder catalytic system (catalyst) comprising a cobalt/chrome-alloy as a carrier, 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.

A 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 do 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).

The main components of the powderous metal alloy are cobalt (Co), chromium (Cr) and molybdenum (Mo).

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.

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

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 as such is a very stable system. It is i.e. stable in regard to acids as well as to water.
- The catalyst is easy to produce.
- The catalyst is easy to handle.
- The hydrogenation can be carried out without any solvents.
- The catalyst is free from lead.
- The catalyst shows high selectivity 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.

Therefore it is surprising that such materials have excellent properties, when they are used as catalysts in hydrogenations.

Preferably, the present invention relates to a powderous catalytic system (II), wherein the metal alloy 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, and

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

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 also relates to a powderous catalytic system (III), which is a powderous catalytic system (I) and/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 a powderous catalytic system (I), (II) and/or (III), wherein the alloy comprises carbon.

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

Therefore the present invention also relates to a powderous catalytic system (V), wherein powderous catalytic system (I), (II), (III) and/or (IV) the metal oxide layer is non-acidic (preferably basic or amphoteric).

Preferred is a powderous catalytic system (V'), which is powderous catalytic system (V), wherein the non-acidic metal oxide layer comprises Zn, Cr, Mn, Cu and/or Al (more preferably the oxide layer comprise ZnO and optionally at least one further metal oxide wherein the metal is chosen from the group consisting of Cr, Mn, Mg, Cu and Al).

Preferred is also a powderous catalytic system (V''), which is powderous catalytic system (V') wherein the non-acidic metal oxide layer is essentially free from Pb.

The metal alloy is preferably coated with a thin layer of ZnO (0.5 - 3.5 μm thickness) 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 (I), (II), (III), (IV), (V), (V') and/or (V"), wherein the metal alloy is coated with a thin layer of ZnO and optionally at least one further metal (Cr, Mn, Mg, Cu and/or Al) oxide.

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

Usually the catalyst of the present invention comprises between 0.1 wt-% and 50 wt-%, based on the total weight of the catalyst, of ZnO, preferably between 0.1 wt-% and 30 wt-%, more preferably between 1.5 wt-% and 10 wt-% and most preferably between 2 wt-% and 8 wt-%.

Therefore the present invention also relates to a powderous catalytic system (VII), which is powderous catalytic system (I), (II), (III), (IV), (V), (V'), (V") and/or (VI), wherein the catalyst comprises between 0.1 wt-% and 50 wt-%, based on the total weight of the catalytic system, of ZnO (preferably between 0.1 wt-% and 30 wt-%, more preferably between 1.5 wt-% and 10 wt-% and most preferably between 2 wt-% and 8 wt-%).

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

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

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

When a mixture of ZnO and Al_2O_3 is used then it is preferred that the ratio of

ZnO : 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 powderous catalytic system (VIII), wherein the ratio of ZnO : Al_2O_3 is from 2:1 to 1:2 (preferably 1:1).

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.

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 and most preferably of between 7 to 10 nm. (The size is measured by light scattering methods).

Therefore the present invention also relates to a powderous catalytic system (IX), which is powderous catalytic system (I), (II), (III), (IV), (V), (V'), (V"), (VI), (VII), (VIII) and/or (VIII'), 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 and most preferably of between 7 to 10 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-%.

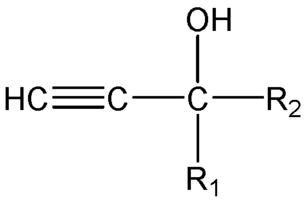
Therefore the present invention also relates to a powderous catalytic system (X), which is powderous catalytic system (I), (II), (III), (IV), (V), (V'), (V"), (VI), (VII), (VIII), (VIII') and/or (IX), wherein the catalyst comprises between 0.001 wt-% and 5 wt-%, based on the total weight of the catalyst, 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 thermo activation in 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), (II), (III), (IV), (V), (V'), (V"), (VI), (VII), (VIII), (VIII'), (IX) and/or (X) 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)



$$HC{\equiv}C-\overset{\displaystyle OH}{\underset{\displaystyle R_1}{C}}-R_2 \qquad (I)$$

,

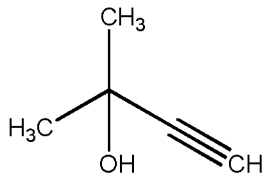
wherein

R_1 is linear or branched C_5-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, with hydrogen in the presence of a catalyst (I), (II), (III), (IV) (V), (V'), (V"), (VI), (VII), (VIII), (VIII'), (IX) and/or (X).

Hydrogen is usually used in the form H_2 gas.

Preferred compounds of formula (I) are the following:



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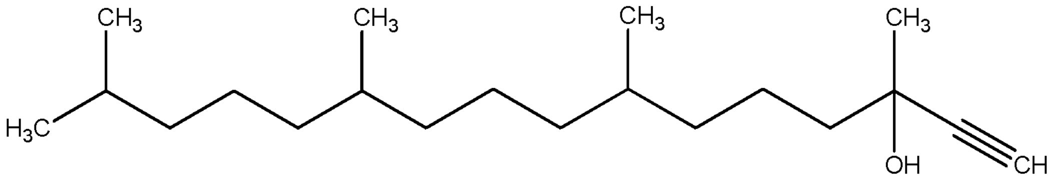

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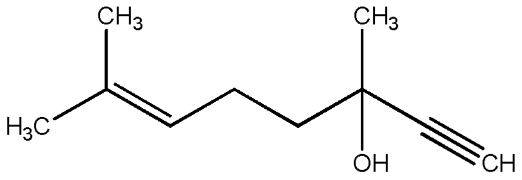

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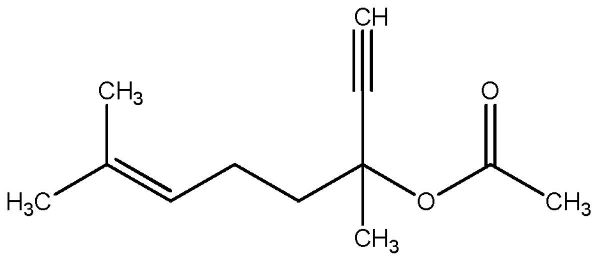

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The following examples serve to illustrate the invention. All percentages are related to weight and the temperatures are given in degree Celsius, if not otherwise stated.

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Examples

Example 1: *Synthesis of the catalyst (Cobalt/Chromium/Molybdenum alloy coated by Al_2O_3/ZnO and Pd deposition)*

Step 1: *Thermal pre-treatment*

The metal alloy powder (EOS CobaltChrome MP1 ® commercially available from EOS GmbH, Germany) was subjected to a thermal pre-treatment at 450°C for 3 h.

Step 2 *Deposition of ZnO + Al_2O_3 (coating of the metal alloy carrier)*

To a 100 ml-flask 20.0 g (53.3 mMol) of $Al(NO_3)_3$ $9H_2O$ and 70 ml of water were added. The mixture was stirred until the $Al(NO_3)_3 \cdot 9H_2O$ was completely dissolved. The solution was heated up to 95° C. Then 4.34 g (53.3 mMol) of ZnO powder was slowly added to the reaction solution. Heating and stirring were maintained until the ZnO was completely dissolved. The solution was then cooled down to room temperature and filtrated through a membrane filter.

The deposition of ZnO/Al_2O_3 was performed by adding the oxidized metal alloy powder (10.0 g) from step 1 to the precursor solution and stirring the mixture at room temperature for 15 min.

The powder was then filtered off via a membrane filter and dried in air at 40° C and 125 mbar for 2h followed by a calcination step at 450° C for 1h. The stirring-drying-calcination cycle was repeated 3 times. Finally, the powder support was calcined in air at 550° C for 1h.

9.38 g of coated metal alloy powder was obtained.

Step 3: *Preparation and deposition of the Pd-nanoparticles*

318 mg (1.31 mmol) of sodium molybdate dihydrate and 212 mg (1.20 mmol) of palladium(II) chloride anhydrous were added to 60 ml of deionized water under heating (ca. 95°C). The mixture was stirred. The heating and stirring were continued until complete evaporation of the water (solid residue was formed). Afterwards, 60 ml of deionized water were added to the residue under stirring. The evaporation-dissolving cycle was repeated two times in order to completely dissolve $PdCl_2$. Finally, 100 ml of hot water were added to the solid residue. The deep brown solution was cooled down to room temperature and filtrated through a paper filter. The filter was washed with water until the final volume of the precursor solution was 120 mL.

Afterwards the Pd° suspension was formed by bubbling hydrogen through the precursor solution for 1 h in a glass cylinder at room temperature.

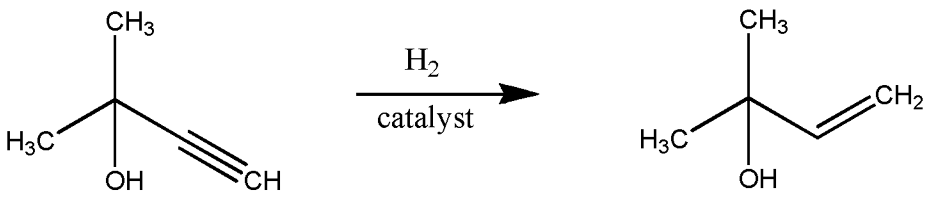
The so obtained Pd° suspension and 9.38 g of the coated metal alloy powder (from step 2) were added to a 200 ml-flask. The mixture was stirred at room temperature for 15 min. The powder was filtered off via a filter paper and dried in air at 40° C and 125 mbar for 2 h. This process was repeated twice.

Step 4: *Thermo activation of the catalyst in H_2*

The powder catalyst obtained from step 3 was subjected to a temperature treatment at 300° C for 4 h under H_2-Ar flow. Then, it was cooled down to room temperature under the same H_2-Ar flow.

8.85 g of the powderous catalyst according to the present invention was obtained.

Example 2a: *Selective hydrogenation of MBY to MBE*



To 285 g (3.38 Mol) of MBY 1.5 g of the catalyst of Example 1 was added under stirring. The reaction was carried out at 65°C and 4 bar pressure for about 7 hours.

At the end of the reaction the selectivity of the reaction was 96.42 % and the conversion was 99.43%.

It can be seen that the new powderous catalyst has excellent properties as a catalyst for selective hydrogenations.

Example 2b: *Repeated selective hydrogenation of MBY to MBE*

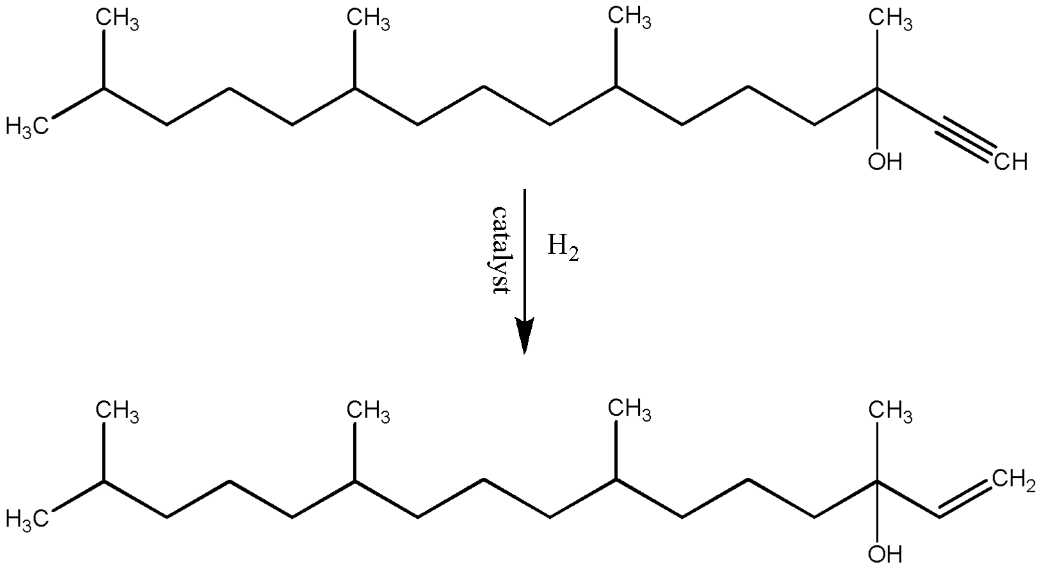
The same reaction conditions as in Example 2a have been used. At the end of the reaction (after about 7 - 9 hours), the reaction mixture was cooled down under inter atmosphere and the reaction solution was exchanged with new MBY (again 285 g) and the hydrogenation was started again.

11 cycles have been run. The following table shows the results of the cycles.

Cycles	Selectivity [%]	Conversion [%]	Yield [%]
1	95.79	99.97	95.8
2	95.28	99.96	95.2
3	95.13	99.89	95.0
4	95.01	99.96	95.0
5	94.82	99.95	94.8
6	94.64	100.0	94.6
7	94.62	99.97	94.6
8	94.47	99.92	94.4
9	94.33	100.0	94.3
10	93.54	99.91	93.5
11	93.43	99.78	93.2

It can be seen that the new powderous catalyst keeps the excellent catalytic properties even after 11 cycles (without treating the catalyst).

Example 3a – 3d: Selective hydrogenation of Dehydroisophytol (DIP)



DIP

IP

To 285 g (0.97 Mol) of DIP 1.5 g of the catalyst of Example 1 was added under stirring. The reaction was carried out at 85°C and 4 bar pressure for about 4.5 hours.

At the end of the reaction the selectivity of the reaction was 81.76 % and the conversion was 87.15%.

This example was repeated 3 times, wherein the following conversion and selectivity values resulted:

Example	**Conversion [%]**	**Selectivity [%]**
3b	85.41	86.68
3c	92.19	85.24
3d	99.45	83.84

It can be seen that the new powderous catalyst has excellent properties as a catalyst for selective hydrogenations.

<u>Example 3e – 3i:</u> Selective hydrogenation of Dehydroisophytol (DIP) with a basic modifier.

To 285 g (0.97 Mol) of DIP 1.5 g of the catalyst of Example 1 and a basic modifier (Tegochrome 22 = 2,2-Ethylenedithiodiethanol) was added under stirring. The reaction was carried out at 85°C and 4 bar pressure for about 7 hours.

At the end of the reaction the selectivity of the reaction was 82.02 % and the conversion was 87.51%.

This example was repeated 4 times, wherein the following conversion and selectivity values resulted:

Example	**Conversion [%]**	**Selectivity [%]**
3f	86.56	87.03
3g	90.88	86.29
3h	94.59	85.48
3i	99.45	83.84

<u>Example 3k:</u> *Repeated selective of dehydroisophytol (DIP) with a basic modifier.*

The same reaction conditions as in Examples 3e – 3i have been used.

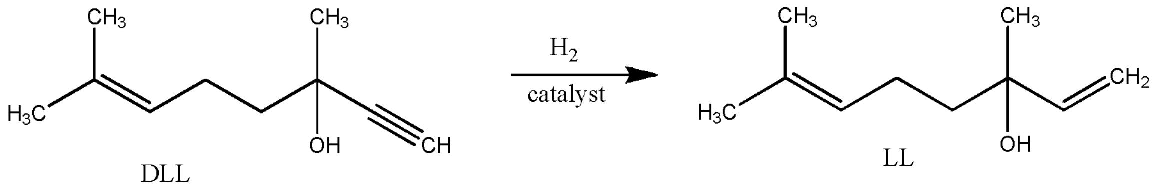
At the end of the reaction (after about 2,5 - 3 hours), the reaction mixture was cooled down under inter atmosphere and the reaction solution was exchanged with new DIP (again 285 g) and the hydrogenation was started again.

5 cycles have been run. The following table shows the results of the cycles.

Cycles	**Selectivity [%]**	**Conversion [%]**	**Yield [%]**
1	82.46	99.82	82.30
2	81.65	99.65	81.40
3	81.57	99.15	80.90
4	81.20	99.39	80.70
5	82.36	98.38	81.00

It can be seen that the new powderous catalyst keeps the excellent catalytic properties even after 5 cycles (without treating the catalyst).

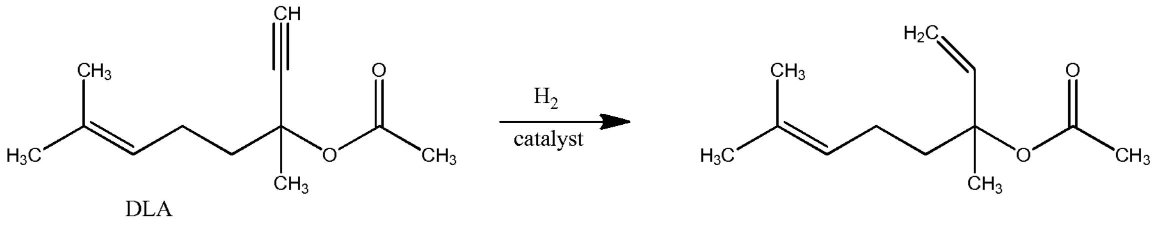
Example 4: Selective hydrogenation of Dehydrolinalool (DLL).



To 285 g (1.87 Mol) of DLL 1.5 g of the catalyst of Example 1 was added under stirring. The reaction was carried out at 55°C and 4 bar pressure for about 6 hours.

At the end of the reaction the selectivity of the reaction was 92.08 % and the conversion was 99.38%.

Example 5: Selective hydrogenation of dehydrolinalyl acetate (DLA)



To 285g (1.45 Mol) of DLA 1.5 g of the catalyst of Example 1 was added under stirring. The reaction was carried out at 40°C and 4 bar pressure for about 7 hours.

At the end of the reaction the selectivity of the reaction was 88.22% and the conversion was 94.98%.

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CLAIMS

1. A powderous catalytic system comprising

   a metal alloy carrier comprising

   (i) 55 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.

2. Catalyst according to claim 1, wherein the metal alloy comprises further metals.

3. Catalyst according to any of the preceeding claims, wherein the metal alloy comprises carbon.

4. Catalyst according to any of the preceeding claims, wherein the metal alloy comprises 55 wt-% – 70 wt-%, based on the total weight of the metal alloy, of Co.

5. Catalyst according to any of the preceeding claims, wherein the metal alloy comprises 20 wt-% – 35 wt-%, based on the total weight of the metal alloy, of Cr.

6. Catalyst according to any of the preceeding claims, wherein the metal alloy comprises 4 wt-% – 10 wt-%, based on the total weight of the metal alloy, of Mo.

7. Catalyst according to any of the preceeding claims, wherein the metal oxide layer is basic or amphoteric.

8. Catalyst according to any of the preceeding claims, wherein the metal oxide layer comprises Zn, Cr, Mn, Cu and/or Al.

9. Catalyst according to any of the preceeding claims, wherein the oxide layer comprises ZnO and optionally at least one further metal oxide chosen from the group consisting of Cr, Mn, Mg, Cu and Al.

10. Catalyst according to any of the preceeding claims, wherein the oxide layer comprises ZnO and Al_2O_3.

11. Catalyst according to any of the preceeding claims comprising between 0.1 wt-% and 50 wt-%, based on the total weight of the catalyst, of the non acidic metal oxide layer.

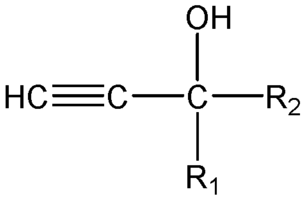
12. Catalyst according to any of the preceeding claims, wherein the metal oxide is mixture of ZnO and Al_2O_3 in a ratio of 2:1 to 1:2 (preferably 1:1).

13. Catalyst according to any of the preceeding claims, wherein the Pd-nanoparticles have an average particle size of between 0.5 and 20 nm.

14. Catalyst according to any of the preceeding claims, wherein the catalyst comprises between 0.001 wt-% and 5 wt-%, based on the total weight of the catalyst, of the Pd- nanoparticles.

15. Use of a catalyst according to claims 1 – 14 in selective catalytic hydrogenation of organic starting material.

16. Use according to claim 15, wherein the organic starting material is a compound of formula (I)



$$HC\equiv C-\underset{\displaystyle R_1}{\overset{\displaystyle OH}{C}}-R_2 \qquad (I)$$

,

wherein

R_1 is linear or branched C_5-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.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/053511

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J37/02 B01J23/60 B01J35/00 C07C29/17
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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SEMAGINA ET AL: "Structured catalyst of Pd/ZnO on sintered metal fibers for 2-methyl-3-butyn-2-ol selective hydrogenation", JOURNAL OF CATALYSIS, ACADEMIC PRESS, DULUTH, MN, US, vol. 251, no. 1, 7 September 2007 (2007-09-07), pages 213-222, XP022235097, ISSN: 0021-9517, DOI: 10.1016/J.JCAT.2007.06.028 abstract page 214, right-hand column, line 16 - page 215, left-hand column, line 41 ----- -/--	1-16

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

☒ See patent family annex.

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Date of the actual completion of the international search 4 June 2013	Date of mailing of the international search report 20/06/2013
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 Fischbach, Malaika

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/053511

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/092280 A1 (DSM IP ASSETS BV [NL]; BONRATH WERNER [CH]; MUELLER THOMAS [CH]; KIWI-) 4 August 2011 (2011-08-04) abstract page 6, line 4 - page 9, line 9 -----	1-16
X	WO 2008/101603 A2 (DSM IP ASSETS BV [NL]; BONRATH WERNER [DE]; GRASEMANN MARTIN [CH]; REN) 28 August 2008 (2008-08-28) abstract page 4, line 1 - page 10, line 19 -----	1-16
X	WO 2012/001166 A1 (DSM IP ASSETS BV [NL]; BONRATH WERNER [CH]; KIWI-MINSKER LIOUBOV [CH];) 5 January 2012 (2012-01-05) abstract page 3, line 6 - page 6, line 29 page 8, line 23 - page 10, line 12 claims 1-3,6,8-14 -----	1-16

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/053511

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011092280 A1	04-08-2011	CN 102741206 A	17-10-2012
		EP 2528882 A1	05-12-2012
		KR 20120130328 A	30-11-2012
		US 2012302801 A1	29-11-2012
		WO 2011092280 A1	04-08-2011
WO 2008101603 A2	28-08-2008	CN 101616733 A	30-12-2009
		EP 2125199 A2	02-12-2009
		WO 2008101603 A2	28-08-2008
WO 2012001166 A1	05-01-2012	CN 102958607 A	06-03-2013
		EP 2588233 A1	08-05-2013
		WO 2012001166 A1	05-01-2012