



Aqueous biphasic treatment of some nitrocompounds with hydrogen in the presence of a biogenerated Pd-polysaccharide

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A strain of *Klebsiella oxytoca* BAS-10, known to produce a specific exopolysaccharide (EPS), when grown aerobically in static mode in the presence of Pd(NO₃)₂, generated the species Pd-EPS that was used as catalyst precursor in the aqueous biphasic treatment of some nitrocompounds with hydrogen. Nitrobenzene was hydrogenated to aniline with almost quantitative yields and the catalyst, embedded in the aqueous phase, was used with success and with near the same efficiency in three recycling experiments. In the case of 1-iodo-4-nitrobenzene only nitrobenzene was obtained while the unsaturated nitro compound β-methyl-β-nitrostyrene afforded both the corresponding oxime and the saturated nitro derivative.

Introduction

The realization of greener and sustainable processes may be achieved using environmentally benign solvents and efficient catalysts; in particular, the use of water as sole solvent, or co-solvent for biphasic reactions, and easily recyclable hydrophilic catalysts seem a highly desirable way to this target [1–3]. As matter of fact metallic species, stabilized by suitable ligands and confined in the aqueous phase, are known to work at the interface as catalysts for carbon–carbon bond formation and for hydrogenation and oxidation reactions [1–4]; at the end of the process, after separation of the aqueous phase from reagents and products present in a suitable immiscible organic phase, the catalyst may be easily re-used more times if no leaching or degradation phenomena occur. In the past years natural compounds, such as aminoacids, peptides, proteins, sugars or more complex bacteria membranes were used as ligands for metallic species active as catalysts in water, but these catalysts sometimes may have drawbacks that reduce the advantage of their use [5–12]. Very recently we envisaged a new way of producing some metal–polysaccharides catalysts, that are not water soluble but require water to be active

and remain confined in water phase, using bacteria to produce them during their growing in the presence of suitable metal salts. In particular, a strain of *Klebsiella oxytoca* BAS-10, isolated from acid mine drainage of pyrite mines, was found to be able to produce a peculiar exopolysaccharide (EPS), during citrate fermentation, that is able to carry out or bind different metallic salts or metals as such [13,14]. So the BAS-10 strain, grown aerobically in static mode in the presence of sodium citrate as sole carbon and energy source and of Pd(NO₃)₂ added to the culture, may produce palladium species bound to the exopolysaccharide EPS; after centrifugation to eliminate bacterial cells, the colloidal material is dried out under *vacuum* to obtain Pd-EPS as a solid material to be already used in some Pd-catalyzed processes [15,16]. In this paper we decided to study further applications of this catalyst on substrates containing nitro groups to reduce.

Materials and methods

NaHCO₃, Na₂CO₃, NH₄Cl, MgSO₄·7H₂O, NaH₂PO₄, KCl, Na-citrate, Pd(NO₃)₂ dihydrate, nitrobenzene, 1-iodo-4-nitrobenzene, β-methyl-β-nitrostyrene and THF were Aldrich products. Pd-EPS was prepared as described in the literature [16]. TEM, XPS and atomic absorption analyses were carried out as described in a previous

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work [16]. GC analyses were carried out on an Agilent 6850A gas chromatograph (HP1 column 30 m × 0.32 mm × 0.25 μm) and GC–MS analyses were performed by using an Agilent MS Network 5937 (HP-5MS column 30 m × 0.25 mm × 0.25 μm).

Bacterial strain cultivation

Cells of *K. oxytoca* BAS-10, kept in cryovials at –80°C in 25% glycerol, were retrieved in Nutrient broth (Difco). For preparation of the aerobic biogenerated catalyst **Pd-EPS** was used the following medium (NAC medium) which contains per liter: 2.5 g NaHCO₃, 1.5 g NH₄Cl, 1.5 g MgSO₄·7H₂O, 0.6 g NaH₂PO₄, 0.1 g KCl, and 50 mM (14.7 g L⁻¹) Na-citrate [16]. The medium was buffered at pH 7.6 with NaOH. A pre-inoculum (50 ml) of BAS-10 strain was previously prepared and then 1 L NAC was finally inoculated (1:100, v/v) in 500 ml NAC medium in 1 L glassware flask. When the cell density (≈1.0 Abs_{600nm}) was reached, the BAS-10 culture was amended with 25 mg of Pd as Pd(NO₃)₂. The culture was incubated for further three days at 30°C until the metal-enriched polysaccharide was extracted from the cell culture.

Metal polysaccharide extraction

The aerobic culture of *K. oxytoca* was harvested by centrifuging each 500 ml at 4000 × g for 25 min. The metal binding polysaccharide (**Pd-EPS**) was separated from the cells by centrifugation. The fraction containing **Pd-EPS** was resuspended in a phosphate buffer (PBS pH 7.4) and was treated with 95% cooled ethanol (4°C) to reach a 70% alcohol final concentration to precipitate the metal enriched polysaccharide. The cold precipitate was dried out under vacuum to obtain a solid material, which was pulverized by a mortar, and then stored at 4°C until the use.

Catalytic experiments

All the reactions were carried out following a procedure similar to that below described for the **Pd-EPS** catalyzed reduction of nitrobenzene (**I**). Experimental details are reported in Tables 1–3.

In a Schlenk tube, 8.5 mg (corresponding to 0.00098 mmol of Pd) of **Pd-EPS** were stirred under nitrogen in 2 ml of distilled water for about 10 min. A solution of 120 mg (0.98 mmol) of freshly distilled nitrobenzene (**I**) in 2 ml of THF was then added to the aqueous phase. The Schlenk tube was then transferred into a

TABLE 1

H₂-treatment of nitrobenzene (**I**) catalyzed by **Pd-EPS**

Entry	Conversion (%)	II yield (%)
1	99.0	99.0
2 ^a	99.5	99.5
3 ^a	99.6	99.6
4 ^a	99.1	99.1

Reaction conditions: substrate = 0.98 mmol; substrate/Pd = 1000/1 (molar ratio); T = 80°C; t = 24 hours; p(H₂) = 5 MPa; H₂O = 2 ml; THF = 2 ml.

^a Reaction carried out by using the catalytic phase recovered from the previous experiment.

150 ml stainless steel autoclave under nitrogen, pressurized with 5 MPa of H₂ and stirred for 24 hours at 80°C (Table 1). The reactor was then cooled to room temperature and the residual gases released. Diethyl ether was added and the organic phase was separated, dried on Na₂SO₄ and analyzed by GC and GC–MS. To recycle the catalyst for further experiments, the aqueous phase was extracted 3–5 times with 3 ml portions of diethyl ether until both the substrate and the reduction products were no more present in the organic extract (analyses carried out by GC and GC–MS), and then used as catalytic phase in a recycling experiment.

Results and discussion

Recently we described the preparation of **Pd-EPS** [16]. This species, containing 1.7% of palladium (wt%), presented particles with diameters ranging from about 30 nm for the smallest ones up to 550 nm in the case of particles aggregation; moreover, XPS measurements showed that palladium was initially present as Pd(II) ions and during hydrogenation a part of it was transformed in Pd(0) [16]. **Pd-EPS** was successfully employed as catalyst precursor in the aqueous biphasic hydrodechlorination of aromatic chlorocompounds and in the hydrogenation of carbon–carbon double bonds [15,16]. On the basis of these results, we decided to explore the activity and selectivity of this species also in the reduction of some model nitro compounds, being the corresponding amino-compounds widespread used in the chemical industry for the production of pigments, azo dyes, rubbers, amino-resins, herbicides and other fine chemicals [17,18]. Traditional production

TABLE 2

H₂-treatment of 1-iodo-4-nitrobenzene (**III**) catalyzed by **Pd-EPS**

Entry	Base	Conversion (%)	I yield (%)	II yield (%)	III yield (%)
1 ^a	–	100	100	nd	nd
2	–	68.5	68.5	nd	nd
3	Buffer pH 10	87.5	87.5	nd	nd
4 ^b	Buffer pH 10	34.5	34.5	nd	nd
5	Na ₂ CO ₃	100	100	nd	nd
6 ^b	–	56.0	56.0	nd	nd
7	Na ₂ CO ₃	100	100	nd	nd
8 ^b	Na ₂ CO ₃	100	100	nd	nd
9 ^b	Na ₂ CO ₃	100	100	nd	nd

Reaction conditions: substrate = 0.98 mmol; substrate/Pd = 1000/1 (molar ratio); H₂O = 2 ml; THF = 2 ml; p(H₂) = 3 MPa; T = 80°C; t = 24 hours. Buffer pH 10 = 2 ml; Na₂CO₃/substrate = 1/1 equiv.

^a p(H₂) = 5 MPa. ^b Reaction carried out by using the catalytic phase recovered from the previous experiment. nd = not detected in the reaction mixture.

TABLE 3

H₂-treatment of β -methyl- β -nitrostyrene (V) catalyzed by Pd-EPS

Entry	Conv. (%)	VI yield (%)	VII yield (%)	VIII yield (%)	IX yield (%)
1 ^a	100	7.5	41.0	51.5	nd
2	92.0	4.0	23.0	65.0	nd
3 ^b	100	3.5	21.5	75.0	nd
4 ^b	99.0	2.5	20.5	76.0	nd

Reaction conditions: substrate = 0.98 mmol; substrate/Pd = 1000/1 (molar ratio); H₂O = 2 ml; THF = 2 ml; T = 60°C; p(H₂) = 3 MPa; t = 24 hours.

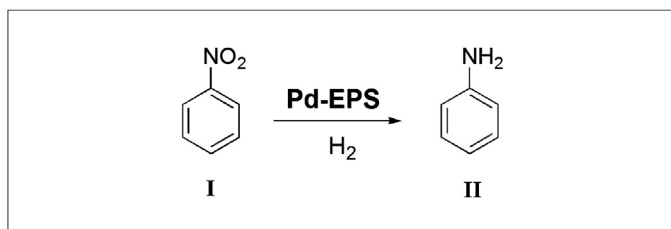
^a T = 80°C; p(H₂) = 5 MPa. ^b Reaction carried out by using the catalytic phase recovered from the previous experiment. nd = not detected in the reaction mixture.

routes, via reduction using Fe or sulphides, are not sustainable due to the formation of waste sludge [19]. Catalytic hydrogenation over supported transition metals represents a cleaner alternative but the formation of toxic azo- and azoxy-derivatives is still a drawback [20,21], therefore more active and selective catalytic systems are always under investigation for lowering some possible risks. Palladium is an active transition metal which has been used in different forms to reduce nitro derivatives; as a matter of fact palladium complexes are able to reduce nitrobenzene to aniline in homogeneous phase as well as in aqueous biphasic system or when supported on polymers [22–25], therefore we carried out a preliminary study on nitrobenzene (I), chosen as model substrate (Scheme 1).

The reaction, carried out in the system water/THF at 80°C and 5 MPa of H₂ for 24 hours, by using a substrate to palladium molar ratio 1000/1, furnished exclusively aniline (II) with 99% yield. After extraction of the organic products with diethyl ether, Pd-EPS was easily recovered by separation of the aqueous phase from the organic one and used in three recycling experiments without loss of activity (Table 1). Noteworthy, no detectable dissolution of palladium during hydrogenation was registered.

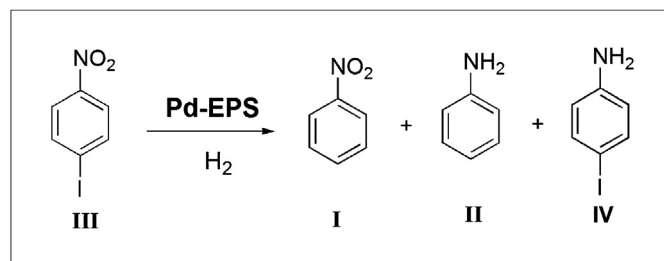
The good capability to catalyze the hydrogenation of the nitro group of nitrobenzene spurred us to test the selectivity of our catalytic system in the reduction of a substrate containing both a nitro- and a halo-group. Pd-EPS had been successfully used by us in the hydrodehalogenation of aromatic halocompounds [15] but the chance to selectively reduce the nitro group without hydrogenolysis of the carbon–halo bond represented an exciting challenge: for this purpose we chose 1-iodo-4-nitrobenzene (III) as model substrate (Scheme 2) with the aim to selectively obtain 4-iodo-aniline (IV).

Surprisingly, a first reaction carried out in H₂O/THF at 80°C and 5 MPa for 24 hours, gave a complete conversion to nitrobenzene (I) but no product deriving from the hydrogenation of the nitro group was formed; by lowering the H₂ pressure to 3 MPa the only result was a lower conversion (Table 2).



SCHEME 1

H₂-treatment of nitrobenzene (I) catalyzed by Pd-EPS.

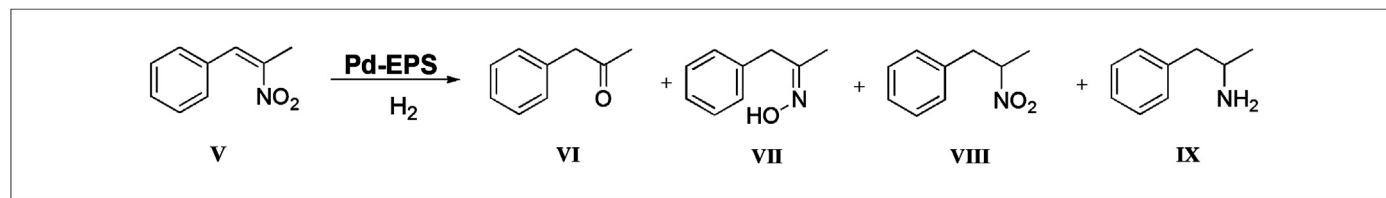


SCHEME 2

H₂-treatment of 1-iodo-4-nitrobenzene (III) catalyzed by Pd-EPS.

We tried to explain the inactivity of Pd-EPS towards the reduction of –NO₂, at these reaction conditions, by hypothesizing that HI, formed in the reaction, could cause the deactivation of the catalytic system; therefore, to prevent the effect of HI we carried out some experiments always at 80°C and 3 MPa of H₂ for 24 hours but in an alkaline medium (Table 2). By using an aqueous phosphate buffer (pH = 10) conversion was increased but, also in this case, only nitrobenzene (I) was formed: when the catalytic phase was used in a recycling experiment, the conversion strongly decreased (entry 4, Table 2). The reaction was then carried out in the presence of Na₂CO₃: the conversion was quantitative but only adding fresh Na₂CO₃ in every recycling experiment the catalytic activity was maintained; in any case the only product was nitrobenzene (I), the nitro group remaining unchanged. This result was rather disappointing for our target, that is, 4-iodo-aniline (IV), and difficult to rationalize. Palladium is known to be an excellent catalyst for the dehalogenation of aromatic halides and for the reduction of the aromatic nitro group, and the goal to hydrogenate the nitro group with no hydrogenolysis of the carbon–halo bond is indeed a difficult task. However, also the selective removal of the halide is quite uncommon and perhaps, at the best of our knowledge, never described before. It is known that the selectivity of this reaction may be affected by the presence of additives, such as for example triphenylphosphite, or by a pre-treatment of the palladium catalyst with a sulfoxide and then with hydrazine [26]; moreover, the catalytic activity can be influenced also by metal dispersion, support interactions or by the presence of a second metal [27]. On the basis of these facts it will be necessary to find a suitable modifier for the Pd-EPS catalyst if the synthetic target is to reduce the nitro group avoiding the breaking of the carbon–halo bond.

To further evaluate both activity and selectivity of Pd-EPS we turned our attention to β -methyl- β -nitrostyrene (V), a molecule that presents both a C=C double bond and a nitro group (Scheme 3).



SCHEME 3

H_2 -treatment of β -methyl- β -nitrostyrene (V) catalyzed by Pd-EPS.

It is known that the reduction of a nitro group conjugated to a carbon-carbon double bond depends on the modality of addition of H_2 that in turn depends on the reagent used. In particular, the 1,4- H_2 addition leads to the reduction of the $\text{C}=\text{C}$ so furnishing only the saturated nitro compound [28]. In this context, β -nitrostyrenes can be reduced to β -nitroethylbenzenes with 60–90% yield in the presence of homogeneous rhodium catalysts [29], while β -aminoethylbenzenes can be obtained in about 80% yield by carrying out the hydrogenation in the presence of 10% Pd/C in acidic medium (HCl) at 85°C and 3.5 MPa of H_2 [30]. When the modality of H_2 -addition is 1,2, then the reaction products can be oximes, hydroxylamines, amines and carbonyl compounds deriving from the hydrolysis of the corresponding oximes [31]. Oximes can be formed also by hydrogenation of β -nitrostyrenes catalyzed by Pd in pyridine [32]. Pd/C is very active for the hydrogenation of *trans*- β -nitrostyrene at 90°C and 10 bar of H_2 but scarcely selective, affording both the corresponding oxime and the saturated nitro compound, besides the contemporary formation of N,N-bis(2-phenylethyl)amine and the complete hydrogenation of the substrate to the saturated amino compound [33]. The selective and almost exclusive reduction of the nitro group to the amine is achieved in good yields on a Pd/ CaCO_3 catalyst poisoned with Pb (Lindlar catalyst) thanks to the addition of a carboxylic acid [27]. A first hydrogenation experiment was carried out on β -methyl- β -nitrostyrene (V) at 80°C and 5 MPa of H_2 for 24 hours, by using a water/THF mixture as solvent (entry 1, Table 3). At these conditions conversion was quantitative and the reaction products were the oxime VII and the saturated nitroderivative VIII, formed in similar amounts, besides a small amount of the ketone VI, this latter due to the hydrolysis of the oxime VII [29]. To improve the selectivity of the reaction, β -methyl- β -nitrostyrene (V) was hydrogenated at 60°C and 3 MPa for 24 hours: conversion was 92% and the selectivity towards the hydrogenation of the $\text{C}=\text{C}$ double bond was enhanced, with the formation of 65% of the saturated nitrocompound VIII.

Noteworthy, the aqueous catalytic phase was used in two consecutive recycling experiments without loss of activity (Table 3).

Conclusions

This study shows that Pd-EPS is an interesting pre-catalyst potentially useful for H_2 -treatment of compounds containing a nitro group functionality with fine activity, peculiar selectivity and good recyclability. In some compounds nitro group is the reactive group, in other cases other functional groups are more reactive or exclusively reduced. The use of both an easily recyclable biogenerated catalytic system and water as co-solvent can represent a sustainable methodology to obtain some valuable derivatives. As observed in previous works [15,16], though Pd-EPS is not soluble in water but only suspended in it, the presence of water is fundamental for a good performance of the catalyst. As a matter of fact, when the hydrogenations, above described, were carried out by using only THF as reaction medium, conversions were practically negligible. This confirms our hypothesis that that water plays a fundamental role in the activity of this species, probably because it induces a swelling of the polymeric structure so allowing to the metal particles to be more available for interaction with the reagents; in particular, starting from a twisted exopolysaccharide with the metal nanoparticles embedded in it, water can unroll this structure so rendering palladium particles less hindered and more available to act as catalyst. Some peculiar selectivities, here observed, show however that the polysaccharide backbone may play also a relevant valuable role. Noteworthy, in all the performed experiments no relevant leaching phenomenon was observed.

Acknowledgements

We are grateful to Dr Laura Sporni for GC-MS analysis (Università Ca' Foscari Venezia), to Mr Michele Gallo (Università Ca' Foscari Venezia) for experimental assistance and to Mrs Barbara Vicentini (Università Ca' Foscari Venezia) for atomic absorption measurements.

References

- Cornils B, Herrmann WA, Horvath IT, Leitner W, Mecking S, Olivier-Bourbigou H, et al., editors. Multiphase homogeneous catalysis. Weinheim: Wiley-VCH; 2005.
- Jøø F, editor. Aqueous organometallic catalysis. Dordrecht: Kluwer Acad. Publ.; 2001.
- Cornils B, Herrmann WA, editors. Aqueous-phase organometallic catalysis. 2nd ed., Weinheim: Wiley-VCH; 2004.
- Lamblin M, Nassar-Hardy L, Hierso J-C, Fouquet E, Felpin F-X. Recyclable heterogeneous palladium catalysts in pure water: sustainable developments in Suzuki, Heck, Sonogashira and Tsuji-Trost reactions. *Adv Synth Catal* 2010;352:33–79.
- Zhang N, Li F, Fu QJ, Tsang SC. Naturally occurring ferritin as a novel catalyst for selective hydroxylation of phenol. *React Kinet Catal Lett* 2000;71:393–404.
- Guibal E. Heterogeneous catalysis on chitosan-based materials: a review. *Prog Polym Sci* 2005;30:71–109.
- Steinreiber J, Ward TR. Artificial metalloenzymes as selective catalysts in aqueous media. *Coord Chem Rev* 2008;252:751–66.
- Marchetti M, Minello F, Paganelli S, Piccolo O. Aqueous biphasic hydrogenations catalyzed by rhodium and iridium complexes modified with human serum albumin. *Appl Catal A Gen* 2010;373:76–80.
- Mao H, Liao X, Shi B. Amphiphilic tannin-stabilized Rh nanoparticles: a highly active and reusable catalyst in biphasic aqueous-organic system. *Catal Commun* 2011;16:210–4.
- Creamer NJ, Mikheenko IP, Yong P, Deplanche K, Sanyahumbi D, Wood J, et al. Novel supported Pd hydrogenation bionanocatalyst for hybrid homogeneous/heterogeneous catalysis. *Catal Today* 2007;128:80–7.
- Wood J, Bodenies L, Bennett J, Deplanche K, Macaskie LE. Hydrogenation of 2-butyne-1,4-diol using novel biopalladium catalysts. *Ind Eng Chem Res* 2010;49:980–8.

- [12] Hennebel T, Verhagen P, Simoen H, De Gusseme B, Vlaemick SE, Boon N, et al. Remediation of trichloroethylene by bio-precipitated and encapsulated palladium nanoparticles in a fixed bed reactor. *Chemosphere* 2009;76:1221–5.
- [13] Baldi F, Minacci A, Pepi M, Scozzafava A. Gel sequestration of heavy metals by *Klebsiella oxytoca* isolated from iron mat. *FEMS Microbiol Ecol* 2011;36:169–74.
- [14] Leone S, De Castro C, Parrilli M, Baldi F, Lanzetta R. Structure of the iron-binding exopolysaccharide produced anaerobically by the gram-negative bacterium *Klebsiella oxytoca* BAS-10. *Eur J Org Chem* 2007;31:5183–9.
- [15] Baldi F, Marchetto D, Paganelli S, Piccolo O. Bio-generated metal binding polysaccharides as catalysts for synthetic applications and organic pollutant transformations. *New Biotechnol* 2011;29:74–8.
- [16] Paganelli S, Piccolo O, Baldi F, Tassini R, Gallo M, La Sorella G. Aqueous biphasic hydrogenations catalyzed by new biogenerated Pd-polysaccharide species. *Appl Catal A Gen* 2013;451:144–52.
- [17] Vogt PF, Gerulis JJ. *Ullmann's encyclopedia of industrial chemistry*. Weinheim: Wiley-VCH; 2005.
- [18] Roughley SD, Jordan AM. The medicinal chemist's toolbox: an analysis of reactions used in the pursuit of drug candidates. *J Med Chem* 2011;54:3451–79.
- [19] Blaser HU, Siegrist U, Steiner H, Studer M. Fine chemicals through heterogeneous catalysis. Weinheim: Wiley-VCH; 2001.
- [20] Zhao F, Zhang R, Chatterjee M, Ikushima Y, Araib M. Hydrogenation of nitrobenzene with supported transition metal catalysts in supercritical carbon dioxide. *Adv Synth Catal* 2004;346:661–8.
- [21] Li C-H, Yu Z-X, Yao K-F, Jib S-F, Liang J. Nitrobenzene hydrogenation with carbon nanotube-supported platinum catalyst under mild conditions. *J Mol Catal A Chem* 2005;226:101–5.
- [22] Gao Y, Wang F, Liao S, Yu D. Selective hydrogenation of nitrobenzene to *p*-aminophenol by the polymer-supported palladium-based mono- and bimetallic catalyst. *React Kinet Catal Lett* 1998;64:351–7.
- [23] Jiang H. A remarkable synergic effect of water-soluble bimetallic catalyst in the hydrogenation of aromatic nitrocompounds. *J Mol Catal A Chem* 1999;142:147–52.
- [24] Shah MSAS, Guin D, Panorama SV. Pd @ PEG-PU polymer networks: a convenient catalyst for hydrogenation and Suzuki coupling reactions. *Mater Chem Phys* 2010;124:664–9.
- [25] Dell'Anna MM, Gagliardi M, Mastroilli P, Suranna GP, Nobile CF. Hydrogenation reactions catalysed by a supported palladium complex. *J Mol Catal A Chem* 2000;15:515–20.
- [26] Figueras F, Coqb B. Hydrogenation and hydrogenolysis of nitro-, nitroso-, azo-, azoxy- and other nitrogen-containing compounds on palladium. *J Mol Catal A Chem* 2001;173:223–30.
- [27] Cárdenas-Lizana F, Gómez-Queroa S, Amorimb C, Keane MA. Gas phase hydrogenation of *p*-chloronitrobenzene over Pd-Ni/Al₂O₃. *Appl Catal A Gen* 2014;473:41–50.
- [28] Hudlicky M. *Reductions in organic chemistry*. New York: John Wiley; 1984.
- [29] Harmon RE, Parsons JL, Cooke DW, Gupta SK, Schoolenberg J. 8-Azasteroids. VI. 21-Hydroxylation. *J Org Chem* 1969;34:3694–6.
- [30] Brossi A, van Burik J, Teitel S. Synthesen in der isochinolinreihe syntheses von 7-hydroxy-6-methoxy-2-methyl-1-(4-hydroxy-3,5-dimethoxy-phenäthyl)-1,2,3,4-tetrahydro-isochinolin, einem wichtigen zwischenprodukt zur synthese von homoapomorphin-alkaloiden. *Helv Chim Acta* 1968;51:1965–79.
- [31] Gilsdorf RT, Nord FF. Reverse addition of lithium aluminum hydride to nitroolefins. *J Am Chem Soc* 1952;74:1837–43.
- [32] Lindemann A. Synthesen von 1-(3,4-dimethoxy-benzyl)-5,6-dimethoxy-isoquinoline. *Helv Chim Acta* 1949;32:69–76.
- [33] Corma A, Serna P, Garcia H. Gold catalysts open a new general chemoselective route to synthesize oximes by hydrogenation of α,β -unsaturated nitrocompounds with H₂. *J Am Chem Soc* 2007;129:6358–9.