

Solvent-free dehydrogenation of decahydroquinoline over palladium nanoparticles supported on oxide carriers

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Catalyst Preparation

In this work we have supported Pd nanoparticles on the commercial oxide carriers γ -Al₂O₃ ($S_{\text{BET}} = 220 \text{ m}^2 \text{ g}^{-1}$, $V_{\text{por}} = 0.46 \text{ cm}^3 \text{ g}^{-1}$, $D_{\text{por}} = 8 \text{ nm}$), SiO₂ (mesoporous KSKG CHIMMED GOST 3956-76; $S_{\text{BET}} = 100 \text{ m}^2 \text{ g}^{-1}$, $V_{\text{por}} = 1.08 \text{ cm}^3 \text{ g}^{-1}$, $D_{\text{por}} = 30 \text{ nm}$), TiO₂ (nonporous P-25 EVONIC: $S_{\text{BET}} = 57 \text{ m}^2 \text{ g}^{-1}$). The catalysts on γ -Al₂O₃ were prepared by an incipient wetness impregnation of the carrier with an aqueous solution of Pd(NH₃)₂Cl₂ followed by keeping in a closed weighing bottle at room temperature for 2 h, drying in an oven at 60 °C for 7 h and reduction in quartz tube under H₂ flow at 400 °C for 3 h. The SiO₂- and TiO₂-supported Pd nanoparticle samples were synthesized *via* the deposition-precipitation of Pd polyhydroxo-complexes (PHC) followed by their reduction to Pd⁰ with H₂ at 23 °C in an aqueous slurry by the procedure that we developed and described in detail previously [S1],[S2]. The important conditions of catalyst preparation are given in Table S1. In addition, thus prepared 1%Pd/TiO₂ samples were reduced in an H₂ flow at 200-400 °C for 3 h to reveal the influence of reduction treatment with H₂ on the catalytic activity. The Pd content in wt.% is indicated in the sample names.

Table S1. The important conditions of the catalyst preparation procedure *via* the deposition-precipitation of Pd polyhydroxo-complexes.^a

Sample	Na ₂ CO ₃ : Pd	pH ₄	pH ₂₃	pH ₆₀	τ_r , h	pH _{ms}	pH _{w1}	pH _{w2}	pH _{w3}
1%Pd/TiO ₂	2.10	3.83	7.0-7.32	7.82	4	8.52	8.80	8.90	8.56
1%Pd/SiO ₂ -1	1.71	6.98	7.4-8.18	8.75	3	9.05	9.75	9.97	10.23
1%Pd/SiO ₂ -2	1.26	-	-	7.96	3	8.99	9.53	9.89	9.93

^a Initial solution: Pd concentration 4.09 mM, molar ratio HCl: PdCl₂ = 1.26. Conditions: total molar ratio HCl: PdCl₂ = 2.55; time of reduction in a slurry (τ_r); pH after stirring a slurry in an ice bath for 1 h (pH₄), at 23 °C for 1 h (pH₂₃) and at 60 °C for 3 h (pH₆₀); pH of a mother solution after a precursor reduction in a slurry (pH_{ms}); pH after steps of washing a separated catalyst (pH_{ws}).

The average size of Pd crystallites supported on SiO₂ was determined by XRD analysis using an ARL X'TRA (Thermo Fisher Scientific, Waltham, MA, USA) diffractometer equipped with a theta–theta goniometer (CuK α radiation, $2\theta = 5^\circ$ – 70° , a scanning rate 1 deg min^{-1} , CCDC data files). The morphology of the samples on the TiO₂ and Al₂O₃ support was studied using a Hitachi HT7700 transmission electron microscope. Images were acquired in the bright-field TEM mode at a 100 kV accelerating voltage. Before measurements, the samples were deposited on the 3 mm carbon coated copper grids from an isopropanol suspension. A target-oriented approach was utilized for the optimization of the analytical measurements [S3]. The total number of analyzed particles for a sample was 300, and 8 TEM images were used to obtain the statistics of the particle size distribution and a mean particle size.

Synthesis of initial substrate

The initial decahydroquinoline (DHQ) **1** was synthesized *via* the quinoline catalytic hydrogenation by known procedures [S4] at a hydrogen pressure of 3 MPa and 85 °C in the following way. Quinoline (16 g, 120 mmol), isopropyl alcohol (30 mL), 5%Rh/C catalyst (1.5 g) were placed in an autoclave at room temperature. The autoclave was triply purged with hydrogen, and then stirring was turned on. The reaction was performed for 14 hours. After completing the reaction, the catalyst was separated by filtration, and the obtained solution was vacuum evaporated. The product (*cis*-DHQ 79% *trans*-DHQ 21%) was analyzed by GC and ¹H NMR and ¹³C NMR.

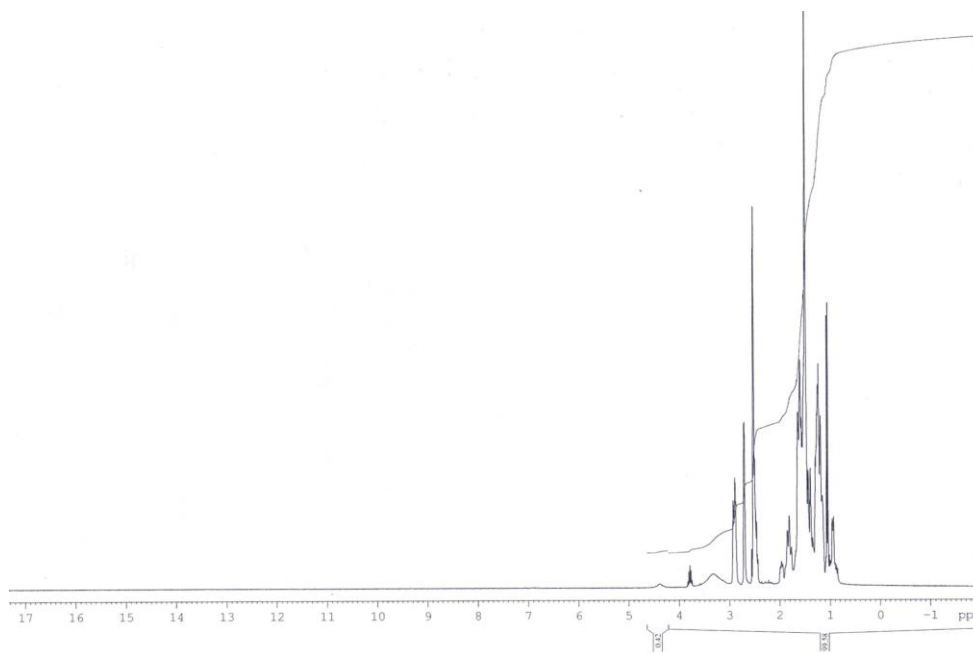


Figure S1. ¹H NMR of initial decahydroquinoline DHQ **1**, (300 MHz, DMSO-d₆).

cis/trans-Isomer mixture, δ_{H} : 1.4-1.6 (m, 2H), 2.4-2.6 (m, 2H), 2.8-3 (m, 2H), 3.0-4.5 (s, NH).

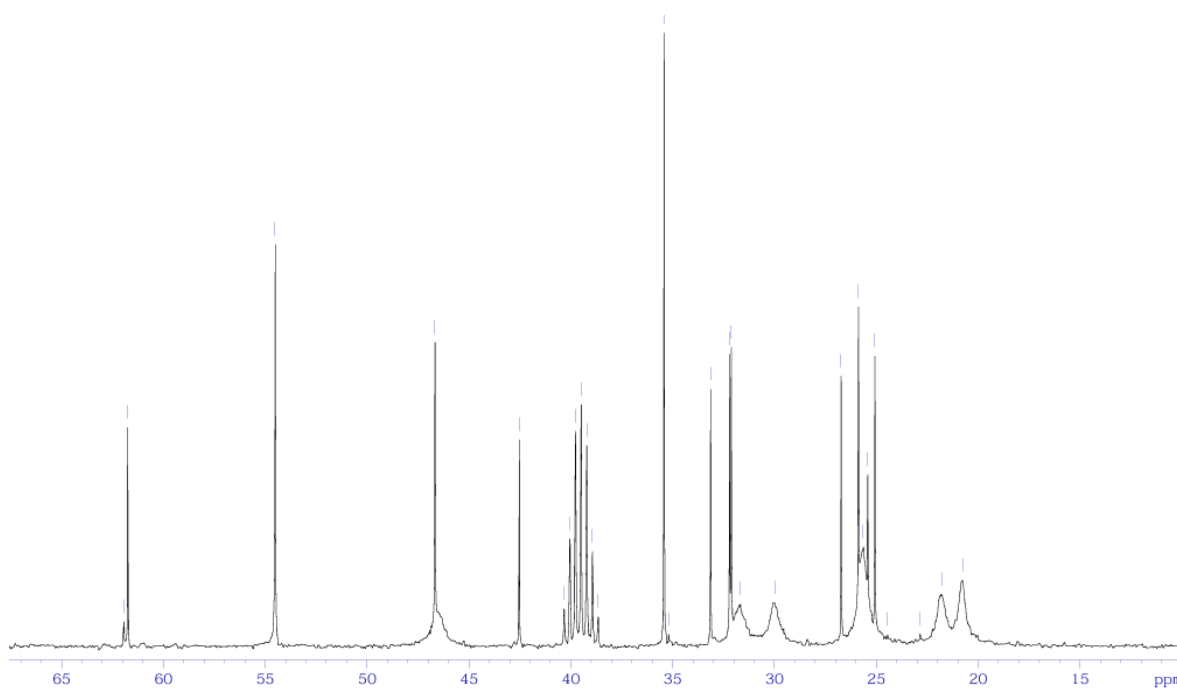


Figure S2. ^{13}C NMR of initial decahydroquinoline DHQ **1** (75 MHz, DMSO-d_6 , 25 $^\circ\text{C}$). *trans*-Isomer, δ_{C} : 62.0 ($\text{C}^{8\text{a}}$), 46.7 (C^2), 42.5 ($\text{C}^{4\text{a}}$), 33.1 (C^8), 32.2 (C^5), 32.1 (C^4), 26.7 (C^3), 25.9 (C^6), 25.1 (C^7); see ref. [S5]. *cis*-Isomer, δ_{C} : 54.1 ($\text{C}^{8\text{a}}$), 46.3 (br.s, C^2), 35.4 ($\text{C}^{4\text{a}}$), 31.6 (br.s), 30.0 (br.s), 25.6 (br.s), 21.8 (br.s), 20.8 (br.s); see ref. [S6].

Catalytic activity characterization

For comparison of the catalytic behavior in DHQ dehydrogenation, the different catalysts were tested under the same conditions: 75 mg of a catalyst ($7.05 \cdot 10^{-3}$ mmol of Pd for the catalyst with a Pd loading of 1 wt%) and 1000 mg (7.19 mmol) of DHQ were loaded into the reactor (a 25 mL pear-shaped flask) with a bar for stirring at room temperature; then the flask was connected to the gas volume analysis line (consisted from an air condenser and a burette graduated in 1 cm^3 for measuring the gas volume) using a pass-through adaptor and Teflon sleeve. The system was purged with an argon flow, and the reactor was introduced into a stirring oil bath preliminarily heated to the required temperature (200–220 $^\circ\text{C}$). This set up provided the formation of condensate fast flowing downslope only on the flask and adaptor walls (no visible condensate in a condenser), as well as exhibited the highest reproducible results. An increase in a gas volume in a burette due to H_2 release was monitored for 300 min. After switching off the stirring, the reactor was removed from the system, cooled to room temperature; and a 100 μL probe of the obtained reaction mixture was withheld, diluted in methanol (1.0 mL) and analyzed by GC internal standard method using 2-ethylhexanol (100 μL) as a standard. The CrystaLux 4000M GC instrument (FID, a $30 \text{ m} \times 0.25 \text{ mm}$ capillary column Optima-1 filled with the OV-1 phase, nitrogen as a carrier gas) was used to perform a probe analysis. The column temperature was 150 $^\circ\text{C}$, the temperatures of the evaporator and detector were 250 $^\circ\text{C}$. The retention time was 2.18 min for the standard, 2.76 min for *trans*-DHQ, 2.87 min for *cis*-DHQ, 3.17 min for 5,6,7,8-tetrahydroquinoline (THQ **3**), 3.32 min for Q and 4.09 min for 1,2,3,4-tetrahydro-quinoline

(THQ 2). The analyte to standard peak area ratio and calibration curves were used to determine the molar fractions of substrates and products.

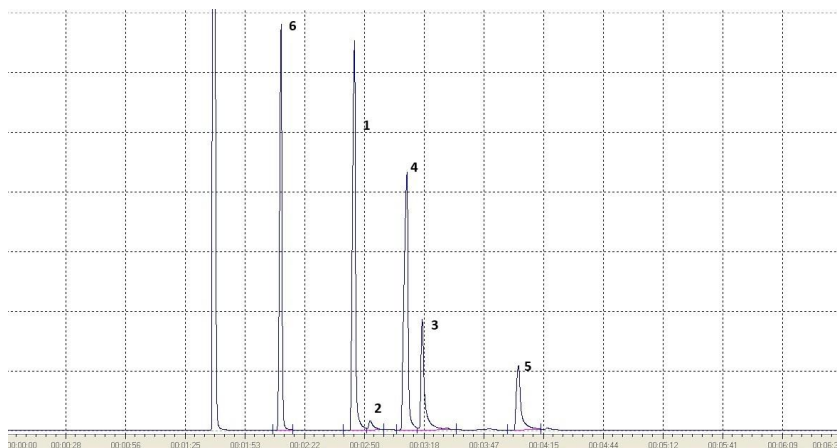


Figure S3. A chromatogram of the DHQ dehydrogenation products

- 1 – Decahydroquinoline *trans*-isomer *trans*-1
- 2 – Decahydroquinoline *cis*-isomer *cis*-1
- 3 – Quinoline 4
- 4 – 5,6,7,8-Tetrahydroquinoline 3
- 5 – 1,2,3,4-Tetrahydroquinoline 2
- 6 – Standard 2-ethylhexanol

The DHQ conversion values were calculated based on GC analysis.

The formed H_2 amount values and H_2 efficiency (yield) were calculated using both the H_2 released volume data and the results of GC analysis. The experimentally obtained H_2 release volumes were recalculated to the H_2 amount by the equation

$$n(H_2)_{\text{exp}} = 273V(H_2)_{\text{exp}} * P_{\text{lab}} / (22.4 * 760 T_{\text{lab}}) , \text{ mmol}$$

where $V(H_2)_{\text{exp}}$ is the measured total H_2 release, P_{lab} and T_{lab} are the pressure and temperature in the laboratory. The amount of possible hydrogen release was calculated based on the results of GC analysis as follows:

$$n(H_2)_{\text{cal}} = 7.19(3N_{\text{py-THQ}} + 3N_{\text{bz-THQ}} + 5N_{\text{Q}})/100, \text{ mmol}$$

where N_{Q} , $N_{\text{py-THQ}}$ and $N_{\text{bz-THQ}}$ are the molar fractions of quinoline and intermediates revealed by GC. The H_2 cite time yield was determined by the equation

$$STY_{H_2} = (n(H_2)_{\text{exp}} + n(H_2)_{\text{cal}}) / (2 * n(\text{Pd}) * t), \text{ h}^{-1}$$

where $n(\text{Pd})$ is the Pd amount in a sample tested, t is the reaction time. The H_2 yield as to a complete dehydrogenation to Q was calculated as follows

$$Y_{H_2} = 100n(H_2) / (7.19 * 5) = 2.78n(H_2)$$

Table S2. Effect of the catalyst composition on the DHQ conversion (X) and the reaction rate of DHQ transformation (R), molar content of reaction products (N) and molar ratio of DHQ isomers in the end reaction mixture ($N_{\text{cis}}/N_{\text{trans}}$), H_2 volume calculated based on GC analysis ($V_{\text{H}_2\text{cal}}$) and on the H_2 release measured experimentally ($V_{\text{H}_2\text{exp}}$) as well as corresponding H_2 yield from theoretically possible (Y_{H_2}) over $\text{Pd}/\text{Al}_2\text{O}_3$ and Pd/SiO_2 catalysts.^a

Catalyst	DHQ/Pd mol/mol	X_{DHQ} %	$N_{\text{THQ}2}$ %	$N_{\text{THQ}3}$ %	N_{quinilin} _e %	DHQ $N_{\text{cis}}/N_{\text{trans}}$	$V_{\text{H}_2\text{cal}}$ mL	$V_{\text{H}_2\text{exp}}$ mL	R_{DHQ}^b h^{-1}	$\text{STY}_{\text{H}_2}^b$ h^{-1}	Y_{H_2} %
0.7%Pd/ Al_2O_3	1460	5.1	4.5	1.0	0.6	0.79	31	31	13.2	57	3.9
1%Pd/ SiO_2 - 1 ^c	1000	6.2	4.5	1.1	0.6	2.76	32	21	10.8	68	4.0
1%Pd/ SiO_2 - 2 ^d	1000	9.5	5.7	3.4	0.4	1.08	49	30	24.0	78	6.1

^a Reaction conditions: initial DHQ $N_{\text{cis}}/N_{\text{trans}}=3.00$; DHQ/catalyst=15 g/g; no solvent; 200 °C; 5 h.

^b Reaction rate R is the number of DHQ molecules transformed per one Pd atom per minute. It was calculated at a DHQ conversion below 10%. The STY is the total amount of H_2 (mol) produced per Pd amount unit (mol) per hour. It was calculated at the DHQ conversion in 5 h.

^c Reaction time 360 min, average size of Pd crystallites is 6.4 nm.

^d Reaction time 240 min, average size of Pd crystallites is 8.7 nm.

Table S3. Effect of the reduction temperature of a catalyst (T) on the conversion (X) and the reaction rate of expenditure for DHQ (R), molar fractions of products and DHQ isomers in the final reaction mixture (N), H_2 site time yield (STY) and H_2 efficiency yield (Y) over 1%Pd/ TiO_2 catalysts^a

$T/^\circ\text{C}$	X_{DHQ} %	$N_{\text{py-4HQ}}$ %	$N_{\text{bz-4HQ}}$ %	N_{Q} %	DHQ $N_{\text{cis}}/N_{\text{trans}}$	R_{DHQ}^b h^{-1}	$\text{STY}_{\text{H}_2}^b$ h^{-1}	Y_{H_2} cal/exp %
23	33.6	6.4	24.9	2.2	0.26	68.4	207	21/20
23	34.4	7.4	25.7	1.3	0.44	70.2	216	21/19
200	26.1	5.0	18.8	2.3	0.94	53.4	169	17/19
200	28.8	5.6	21.6	1.6	0.45	58.8	183	15/18
260	28.1	6.3	21.8	0	0.42	57.6	172	17/22
400	27.8	6.1	20.0	1.7	0.49	57.0	177	17/16

^a Reaction conditions: initial DHQ $N_{\text{cis}}/N_{\text{trans}}=3.76$; DHQ/Pd=1020 mol/mol; DHQ/catalyst=15 g/g; no solvent; 205 °C; 5 h.

^b Reaction rate R is the number of DHQ molecules transformed per one Pd atom per minute. The STY is the total amount of H_2 (mol) produced per Pd amount unit (mol) per hour. It was calculated at the DHQ conversion in 5 h.

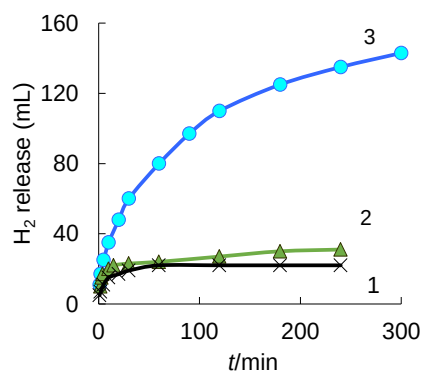


Figure S4. Time dependence of H₂ release over 1%Pd/SiO₂ (1), 0.7%Pd/Al₂O₃ (2) and 1%Pd/TiO₂ (3) samples. Reaction conditions: DHQ (79% *cis*-, 21% *trans*-); DHQ/Pd = 1000 mol/mol; DHQ/catalyst = 15 g/g; no solvent; 200 °C; 5 h.

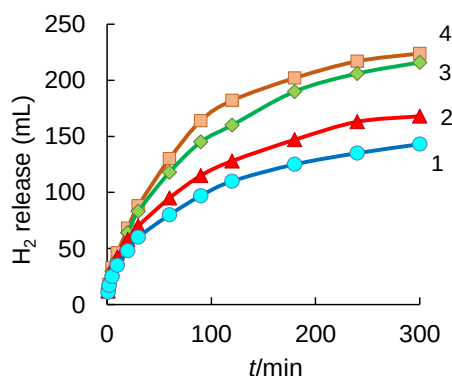


Figure S5. Hydrogen release over the 1%Pd/TiO₂ catalyst at the reaction temperature 200 °C (1), 205 °C (2), 210 °C (3) and 215 °C (4). Reaction conditions: DHQ composition (79% *cis*-, 21% *trans*-); DHQ/Pd=1000 mol/mol; DHQ/catalyst=15 g/g; no solvent; 5 h.

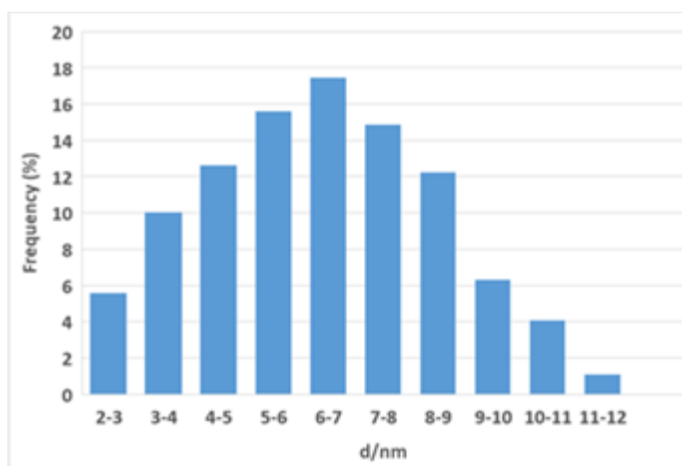
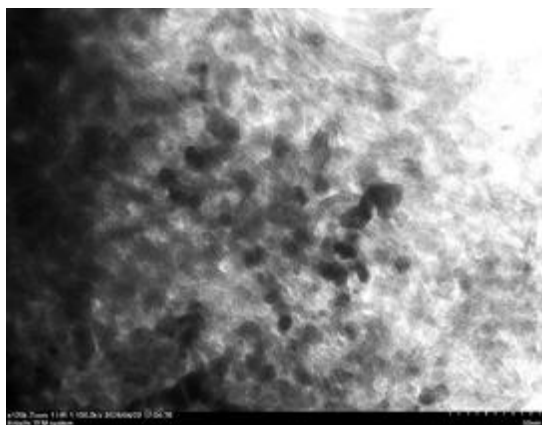


Figure S6. TEM image and particle size distribution for the prepared catalyst 0.7%Pd/ Al₂O₃

References

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