Electronic Supplementary Information for

In-situ generation of resin-supported Pd nanoparticles under mild catalytic conditions: a green route to highly efficient, reusable hydrogenation catalysts

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General information

All reactions and manipulations were routinely performed under nitrogen atmosphere by using standard Schlenk techniques, unless otherwise stated. Diethyl ether and dichloromethane were distilled over Na-benzophenone and CaH_2, respectively. DOWEX® 50WX2 - 100 (H^+ form, 2% cross-linked, gel-type, 50-100 mesh [150-300 μm] bead size, 4.8 meq/g exchange capacity), DOWEX® 50WX2 - 400 (H^+ form, 2% cross-linked, gel-type, 200-400 mesh [38-75 μm] bead size, 4.8 meq/g exchange capacity) strong cation-exchange resins and DOWEX® 1X2 - 100 (Cl^- form, 2% cross-linked, gel-type, 50-100 mesh [150-300 μm] bead size, 3.5 meq/g exchange capacity) strong anion-exchange resin were obtained from Aldrich. Palladium nitrate and potassium tetrachloropalladate were obtained from Aldrich. Benzylideneacetone was recrystallized from n-pentane prior of use. All the other chemicals were reagent grade, commercial products and were used as received without further purification. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance DRX-400 spectrometer operating at 400.13 and 100.61 MHz, respectively. Chemical shifts are relative to tetramethylsilane as external reference. ESEM (Environmental Scanning Electron Microscopy) measurements were performed on a FEI Quanta 200 microscope operating at 25 KeV accelerating voltage in the low-vacuum mode (1 torr) and equipped with an EDAX Energy Dispersive X-ray Spectrometer (EDS). X-ray maps were acquired on the same instrument using a 512x400 matrix, 25 KeV accelerating voltage and 350 μm horizontal full width. Samples for EDS maps were prepared by inclusion of the resin beads into Struers EpoFix® epoxy resin, followed by lapping. The same samples were used for TEM (Transmission Electron Microscopy) analyses after cutting with a RMC MT-XL ultramicrotome. TEM measurements were carried out using a CM12 PHILIPS instrument. Statistical nanoparticle size distribution analysis was typically carried out on 300-400 particles. XRD (X-ray Diffraction) spectra were recorded with a PANanalytical XPERT PRO powder diffractometer, employing CuKα radiation (λ=1.54187 Å), a parabolic MPD-mirror and a solid state detector (PIXcel). The samples were subjected to measurement without grinding and prepared on a silicon wafer (zero background) that was rotating (0.5 rotations per second) during spectra acquisition. All XRD spectra were acquired at room temperature in a 2θ range from 4 to 95°, applying a step size of 0.0263° and a counting time of 77.5 seconds. Small-Angle X-ray Scattering (SAXS) experiments were performed on a Hecus X-ray System GMBH Graz S3micro equipped with an ultra brilliant point microfocus source Gemix-Fox 3D (Xenoxs, Grenoble). The impinging radiation was the 1.54 Å CuKα. The scattered X-rays were detected by a two-dimensional position sensitive detector with a sample-to-detector distance of 273 mm. The primary beam was masked by a 2 mm W filter, positioned so that the region of scattering vectors q [$Å^{-1}$] was in the range 0.008<q<0.54. Here q has a modulus of $(4\pi/\lambda)\sin(\Theta/2)$, with λ the X-Ray wavelength and Θ the scattering angle. Samples were contained in a paste cell holder. The sample thickness was varied to have a transmittance around 0.8, measured as the area of the primary beam transmitted through the sample holder and a 1 mm Ni filter, without and with the sample. All measurements were collected at room temperature and with X-Ray source power of 12W. The scattering profile was modelled with the empirical multiple level fit method developed by Beaucage, stopped at the second level plus a background term, to account for primary particles and their clusters. In order to be safely compared, the reduced data were normalized taking into account the acquisition time, the transmission and the source power. Reactions under a controlled pressure of hydrogen were performed using either a non-metallic Büchi Miniclave® (up to 10 bar) or a stainless steel autoclave (20 mL internal volume) constructed at ICCOM-CNR (Firenze, Italy) and equipped with a magnetic stirrer, a Teflon ® inset and a pressure controller for higher pressures. The temperature control was achieved by an oil bath thermostat accurate to ± 0.2 °C. GC analyses were performed on a Shimadzu GC-2010 gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm ID, 0.25 μm FT) Varian VF-WAXms capillary column. GC-Ms analyses were performed on a Shimadzu QP2010S spectrometer equipped with an identical capillary column. The metal content in the resin-supported catalysts was determined by Atomic absorption spectrometry (AAS) using a AANALYST200 spectrometer. Each sample (20-50 mg) was treated in a microwave-heated digestion bomb (Milestone, MLS-200, 20 min.@ 220 °C) with concentrated HNO_3 (1.5 mL), 98% H_2SO_4 (2 mL), and 0.5 mL of H_2O_2 30%. After filtration, the solutions were analyzed. The content of metal leached in the heterogeneous catalysis solutions was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) with a Varian 720ES instrument at a sensitivity of 500 ppb. The solutions were analyzed directly after 1:5 dilution in 0.1 M hydrochloric acid.

Preparation of the resins

The following operations were performed in air atmosphere. The commercial resins were washed prior of use to remove incidental impurities. 20 g of cation exchange resin were washed with refluxing deionised water for 2 h and with refluxing methanol for 1 h using a Soxhlet apparatus. After cooling down to room temperature, the resin was washed sequentially with dichloromethane (3 x 100 ml), methanol (3 x 100 ml) and diethyl ether (3 x 100 ml). 20 g of anion exchange resin were placed in a glass filter and washed sequentially with hot methanol (50 ºC) (3 x 100 ml), dichloromethane (3 x 100 ml), methanol (3 x 100 ml) and diethyl ether (3 x 100 ml). The resins were then dried in a stream of nitrogen and stored under nitrogen.

Lithiation of strong cation-exchange resins: 5 g of the protonated form of the commercial resin purified as above were added to a 1M solution of lithium hydroxide (150 ml) in air atmosphere. The mixture was stirred at 150 rpm at room temperature for 24 h using an orbital stirrer. The resins obtained were placed in a glass filter and washed repeatedly with deionised water (n x 100 ml) until neutral pH of the washings. Then, they were washed with methanol (3 x 100 ml) and diethyl ether (3 x 100 ml) and dried in a stream of nitrogen. The products obtained as white beads were stored under nitrogen.

Preparation of the resin-supported Pd species

Resin-Palladium(II) species: In a typical procedure, 1 g of dry cation-exchange resin was added to a solution of palladium nitrate dihydrate (38.7 mg, 0.145 mmol, ratio Pd/sulfonic groups = 1/33) in deionised water (55 ml). The mixture was stirred at room temperature for 24 h using an orbital stirrer. The resin obtained was transferred into a glass filter via a Teflon tube under nitrogen and washed sequentially with deionised water (3 x 75 ml), methanol (3 x 75 ml) and diethyl ether (3 x 75 ml), before being dried in a stream of nitrogen overnight. The palladiated resin obtained as orange-brownish beads was stored under nitrogen in the dark. AAS analysis showed the resin to contain 1% (w/w) of Pd. A similar procedure was adopted for the preparation of the resins with a 5% Pd loading, except that 1 g of dry resin was added to a solution of palladium nitrate dihydrate (159.8 mg, 0.600 mmol, ratio Pd/sulfonic groups = 1/8) in deionised water (100 ml). In the case of the anion-exchange resin, 1 g of dry chlorinated resin was added to a solution of potassium tetrachloropalladate(II) (34.6 mg, 0.106 mmol, ratio Pd/ammonium groups = 1/33) in deionised water (50 ml). The resin was then treated as previously described, to afford the palladiated orange resin with 1% (w/w) Pd loading, which was stored under nitrogen in the dark.

Resin-Palladium(0) species: Method a) Reduction with $NaBH_4$: solid $NaBH_4$ (55.0 mg, 1.45 mmol) was slowly added to 0.5 g of 1% (w/w) palladium(II)-resin in 30 ml of deionised water at 0 °C. The resin became immediately black. The suspension was then stirred at 160 rpm at room temperature for 3h, using an orbital stirrer. The resin obtained was transferred into a glass filter via a Teflon tube under nitrogen and washed with deionised water (5 x 75 ml), methanol (3 x 75 ml) and diethyl ether (3 x 75 ml), and was dried in a stream of nitrogen overnight. The product, obtained as black beads, was stored under nitrogen in the dark. Method b) Reduction with a flow of H_2: 0.5 g of 1% (w/w) palladium(II)-resin were suspended in 30 ml of methanol under nitrogen. Hydrogen gas was bubbled at 1 bar at room temperature for 2 h under orbital stirring at 160 rpm.

The resin became slowly black (ca. 20 min.). After that time, the resin was transferred into a glass filter under nitrogen via a Teflon tube, it was washed with methanol (3 x 75 ml), diethyl ether (3 x 75 ml) and then dried in a stream of nitrogen overnight. The product, obtained as black beads, was stored under nitrogen in the dark. Method c) Reduction with a static atmosphere of H_2: 0.5 g of 1% (w/w) palladium(II)-resin were placed into a non-metallic autoclave under nitrogen. 30 ml of methanol were then added via a Teflon tube under nitrogen. Nitrogen was replaced by hydrogen with three cycles 2 bar / normal pressure and the autoclave charged with 2 bar H_2. The mixture was kept at room temperature for 1 h with orbital stirring at 160 rpm. The resin became slowly black. After that time, the autoclave was depressurized and the resin obtained was washed by decantation with degassed methanol (3 x 75 ml) and diethyl ether (3 x 75 ml), before it was dried in a stream of nitrogen for 2 h. The autoclave was then opened and the resin transferred into a glass filter where it was dried under a stream of nitrogen overnight.

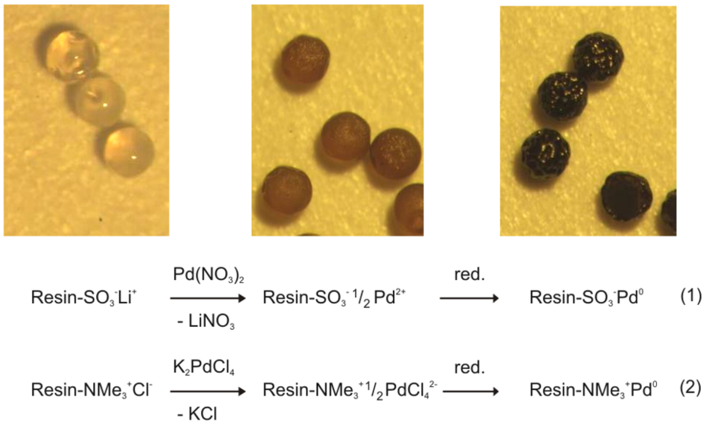
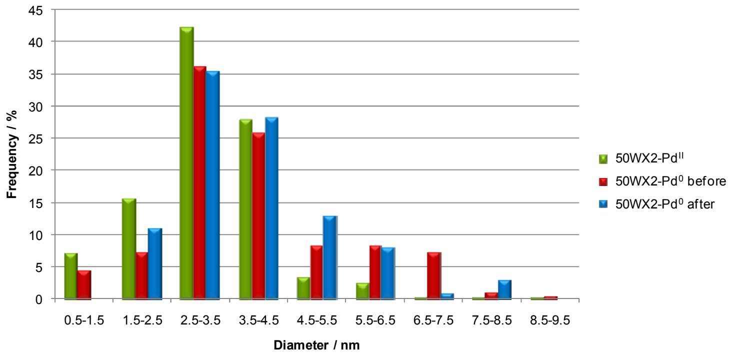


Fig. S1 Scheme of the synthetic procedure for the preparation of pre-reduced, cation-exchange (1) and anion-exchange (2) resin-supported Pd^0 catalysts. Top: optical microscope images of the anionic resins in each step (200 magnifications).



Catalyst	Dimension (nm)
50WX2-Pd^{II}	3.19 ± 1.32
50WX2-Pd^0 before	3.70 ± 1.51
50WX2-Pd^0 after	3.90 ± 1.24

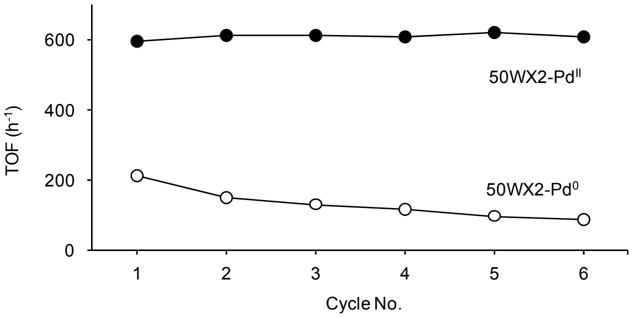
Fig. S2 Size distribution of resin-embedded Pd nanoparticles, before and after use in catalysis (Li^+, 50-100, 1% Pd, from H_2 reduction).

Hydrogenation reactions and catalysts recycle

Low pressure: In a typical experiment, the supported catalyst precursor, either resin-Palladium(0) or resin-Palladium(II) (50 mg, ca. 1% Pd w/w, ca. 0.005 mmol of palladium), was added under nitrogen into a flask containing a degassed solution of the substrate (1.04 mmol) in methanol (6 ml). Hydrogen gas was bubbled with stirring at 0.8 bar H_2 and 15 mL/min at room temperature, using an orbital stirrer at 160 rpm. This was taken as the start time of the reaction. If the resin-Palladium(II) was used, this became immediately black. After the desired time, the methanol solution was completely removed under a stream of hydrogen using a gas-tight syringe. A sample of this solution (0.5 μl) was used for GC (product yield), GC-MS (product identification) and ICP-OES analysis (Pd leaching), while the remaining aliquot was used for the Maitlis test (catalyst leaching test, see below). A fresh solution of the substrate (1.04 mmol) in methanol (6 ml) was then transferred under hydrogen via a gas-tight syringe into the flask containing the recovered supported catalyst. The mixture was stirred at 160 rpm and room temperature under hydrogen flow and, after the desired time, the mixture was treated as described above. The same recycling procedure was used in the subsequent hydrogenation cycles. After use in catalysis, the solid catalyst was washed with methanol (3 x 10 ml) and diethyl ether (3 x 10 ml), dried in a stream of nitrogen overnight and stored under nitrogen for later characterization. Catalyst leaching test: an additional portion of the substrate (1.04 mmol) was added under hydrogen to the clear solution recovered after the first and subsequent cycles, Hydrogen was then bubbled through the solution at room temperature for 1h and the mixture analyzed by GC for conversion measurement.

Medium-High pressure: In a typical experiment, the supported catalyst precursor, either resin-Palladium(0) or resin-Palladium(II) (50 mg, ca. 1% Pd w/w, ca. 0.005 mmol of palladium), was placed under nitrogen into a metal-free autoclave. A degassed solution of substrate (1.04 mmol) in methanol (6 ml) was transferred under nitrogen via a Teflon tube into the autoclave. Nitrogen was replaced by hydrogen with three cycles pressurization/depressurization. The autoclave was finally charged with the desired pressure of hydrogen and then stirred at room temperature at 160 rpm, using an orbital stirrer. After the desired time, the reactor was depressurized and the solution was removed under a stream of hydrogen using a gas-tight syringe. A sample of this solution (0.5 μl) was used for GC (product yield), GC-MS (product identification) and ICP-OES analysis (Pd leaching), while the remaining aliquot was placed into an autoclave under hydrogen, following the same pressure charge procedure as above, to perform the catalyst leaching test. The same recycling procedure described above was used in the subsequent hydrogenation cycles. After use in catalysis, the solid catalyst was washed with methanol (3 x 10 ml) and diethyl ether (3 x 10 ml), dried in a stream of nitrogen overnight and stored under nitrogen for later characterization.

Table S1 Recycle of palladium catalysts in the hydrogenation of **2**.[a]



Catalyst	Cycle no.	Conversion (%) [c]	TOF (h^{-1}) [d]
50WX2-Pd^{II}	1	89,8	596
	2	92,0	611
	3	92,1	611
	4	91,9	610
	5	93,5	621
	6	91,7	609
50WX2-Pd^{0} [b]	1	32,4	215
	2	22,5	149
	3	19,8	131
	4	17,4	116
	5	14,7	97
	6	13,1	87

[a] Reaction conditions: methanol, r.t., substrate : Pd = 220 : 1 molar ratio, H_2 pressure 0.8 bar, substrate concentration 0.17 M, duration of each cycle 20 min. Resin: Li^+, 50-100, 1% Pd. [b] Prepared by 2 bar H_2 reduction.[c] Selectivity to **2a** > 99.5 %.[d] No Pd detected in solution by ICP-OES.

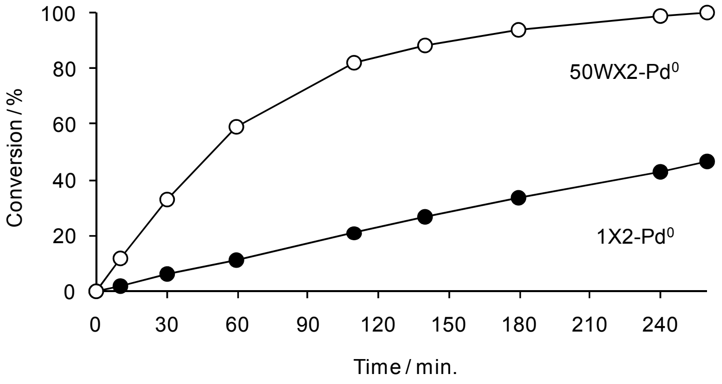
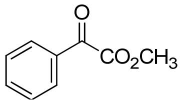
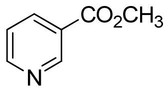


Fig. S3 Hydrogenation of **2** by cation and anion-exchange resins-supported Pd^0 catalysts. Reaction conditions: methanol, H_2 pressure 0.8 bar, r.t., substrate : Pd = 220 : 1 molar ratio, substrate concentration 0.17 M. Catalysts obtained by $NaBH_4$ reduction (50-100 mesh, 1% Pd). (•) trimethylbenzyl chloride exchanger, (O) Lithium sulfonate exchanger.

Table S2 Hydrogenation reactions of **2** and **6** by resin-supported catalysts with different Pd content [a]

Pd loading (% w/w)	Conversion (%)	
	 [b]	 [c]
1	33.4	26.9
5	33.6	34.1

[a] Resin gel, sulfonic, Li$^+$, 50-100. Reaction conditions: methanol, substrate : Pd = 230 : 1 molar ratio, substrate concentration 0.17 M. [b] Catalyst 50WX2-Pd^{II}, r.t., H_2 pressure 0.8 bar, 5 min. [c] Catalyst 50WX2-Pd^0 obtained by 2 bar H_2 reduction, 40 °C, H_2 pressure 4 bar, 24 h.