Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Study on the Selective Hydrogenation of Nitroaromatics to N-aryl hydroxylamines using a Supported Pt nanoparticle Catalyst

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Catalyst preparation: 0.7% c-Pt/C

Colloidal Pt nanoparticles (c-Pt) were prepared from 2.4 L H_2O, 84 g 30% (hexadecyl)(2-hydroxyethyl)dimethylammonium (HHDMA) solution, 0.9 g Pt (as H_2PtCl_6) at 95°C and pH=5.0, stirred in a beaker for 2 hours. This colloidal solution was added to a slurry containing 120 g of activated carbon and 1.2 L H_2O. After an additional 30 minutes, the catalyst was filtered off and washed with an excess of r.t. H_2O until Cl^- free ($AgNO_3$ test). Then, the catalyst was dried in an oven at 120°C for 4 h.

Metal contents were verified by ICP-AES analysis on an IRIS Intrepid II.

Ar physisorption BET-surface area: 1346 m^2/g.

XPS relative abundance data [mol%]: Pt (4f) 1.21, O (1s) 6.96, C (1s) 89.77, N (1s) 1.04, Cl (2p) 0.58, P (2p) 0.44.

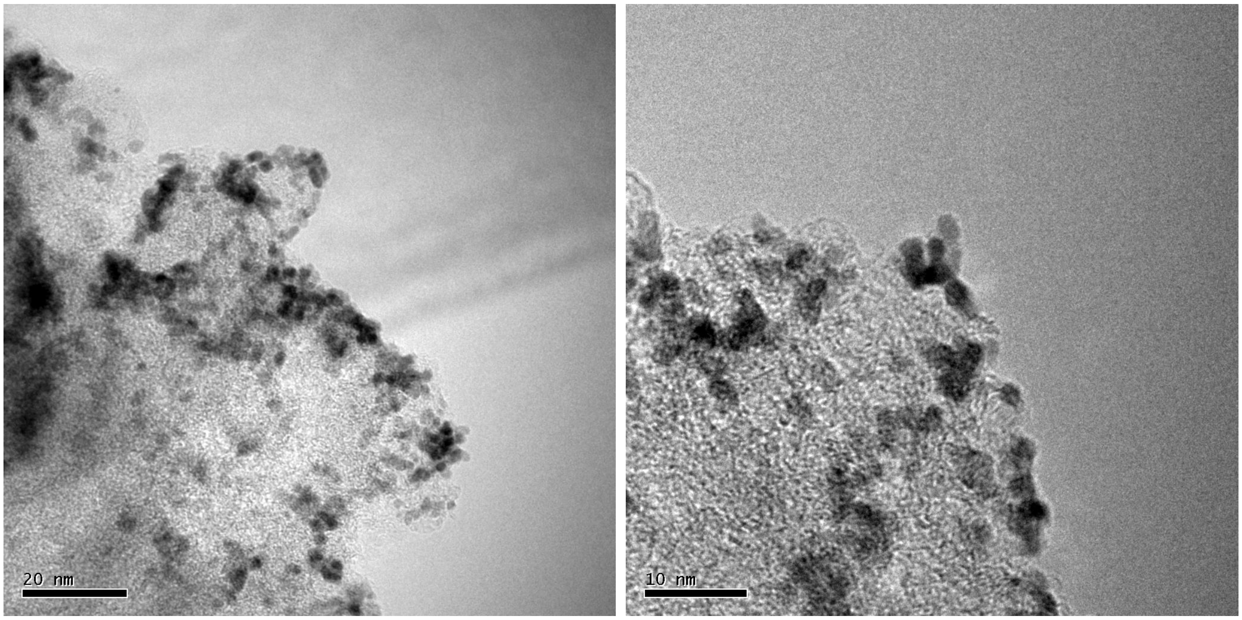


Figure 1. TEM images of 0.7% c-Pt/C with an average Pt particle size of 2.3±0.3 nm.

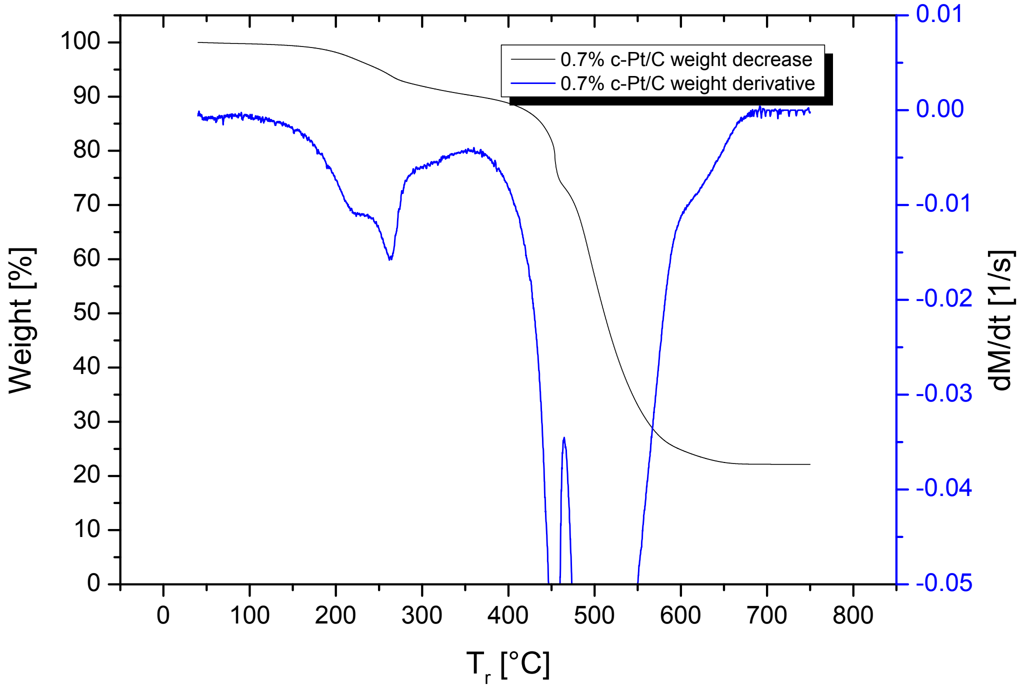


Figure 2. TGA scan of the 0.7% c-Pt/C catalyst with weight loss versus temperature and weight loss derivative versus temperature plots.

Thermogravimetric analysis was performed on a Mettler Toledo DSC 1 machine under a gas flow of 20 mL/min O_2 and 40 mL/min He. About 30 mg of compound was loaded into a ceramic crucible. The temperature was kept constant at 40°C for 30 minutes before the linear temperature increase of 10°C/min from 40°C to 750°C. 9.9 wt.% of hydrocarbons (the HHDMA surfactant) is burned off till T_r = 361°C in 32 minutes, after that the activated carbon support starts to be oxidized.

Catalyst preparation: 0.6% c-Pd/C

Colloidal Pd nanoparticles (c-Pd) were prepared from 200mL H_2O, 7 g 30% (hexadecyl)(2-hydroxyethyl)dimethylammonium (HHDMA) solution, 0.1 g Pd (as $Na_2PdCl_4.3H_2O$) at 85°C and pH=3.0. This colloidal solution was added to a slurry containing 17 g of activated carbon. After an additional 30 minutes, the catalyst was filtered off and washed with an excess of r.t. H_2O until Cl^- free ($AgNO_3$ test). Then, the catalyst was dried in an oven at 120°C for 4 h.

Metal contents were verified by ICP-AES analysis on an IRIS Intrepid II.

XPS relative abundance data [mol%]: Pd (3d) 0.53, O (1s) 5.71, C (1s) 92.8, N (1s) 0.63, Cl (2p) 0.33.

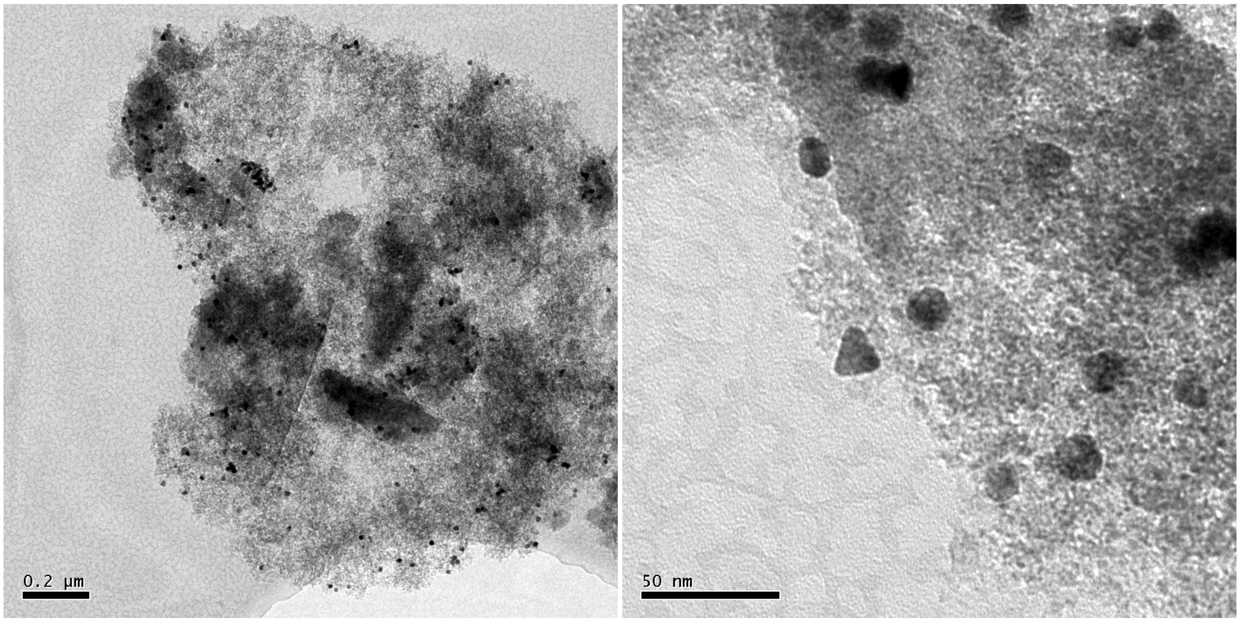


Figure 3. TEM images of 0.6% c-Pd/C with an average Pd particle size of 15.2±1.6 nm.

TEM images of 5% Pt/C catalyst:

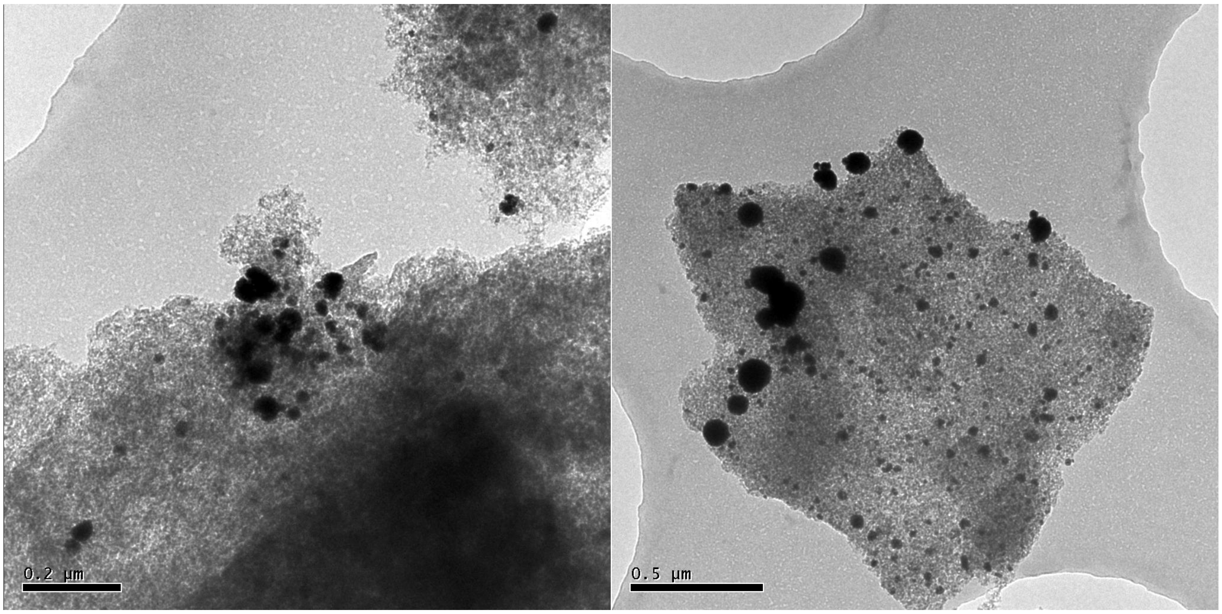


Figure 4. TEM images of 5% Pt/C as obtained from STREM chemicals showing a very broad distribution of Pt crystallites.

Transmission Electron Microscopy

TEM imaging was performed on a FEI F20 electron microscope (200 kV, field emission gun) equipped with an 8kx8k CMOS camera. Samples were prepared by adding a few drops of solid material dispersed in ethanol on the carbon coated copper grid. Images were analyzed with ImageJ software.

X-ray Photoelectron Spectroscopy

The XPS measurements were carried out with a Thermo Scientific K-Alpha, equipped with a monochromatic small-spot X-ray source and a 180° double focusing hemispherical analyzer with a 128-channel detector. Spectra were obtained using an aluminium anode (Al Kα = 1486.6 eV) operating at 72W and a spot size of 400µm. Survey scans were measured at a constant pass energy of 200 eV and region scans at 50 eV. The background pressure was 2×10^{-9} mbar and during measurement 3×10^{-7} mbar Argon because of the charge compensation dual beam source.

Pt Leaching Experiment

62 mg 0.7% c-Pt/C, 2.75 g (22.3 mmol) nitrobenzene ($S/Pt=10 \times 10^3$), 2.23 mmol TMEDA and 80 mL absolute ethanol were added to a 100 mL stainless steel autoclave equipped with a heating jacket, a hydrogen supply system, a sampling unit, and a mechanical stirrer. This mixture was heated to 30°C after which the reactor was flushed with hydrogen and pressurized with H_2 to 23 bar. The reaction was initiated by switching on the mechanical stirrer at 1500 rpm. The pressure was kept constant with a mass-flow controller (which also logs the total gas consumption) and the temperature was kept at 30°C during the reaction. The reaction was stopped 5 minutes after initiation and the reaction solution was filtered using a syringe with 0.45µm syringe filter. After filtration, the filtrate is fed back to the reactor and the previous steps were repeated before initiation in absence of any catalyst.

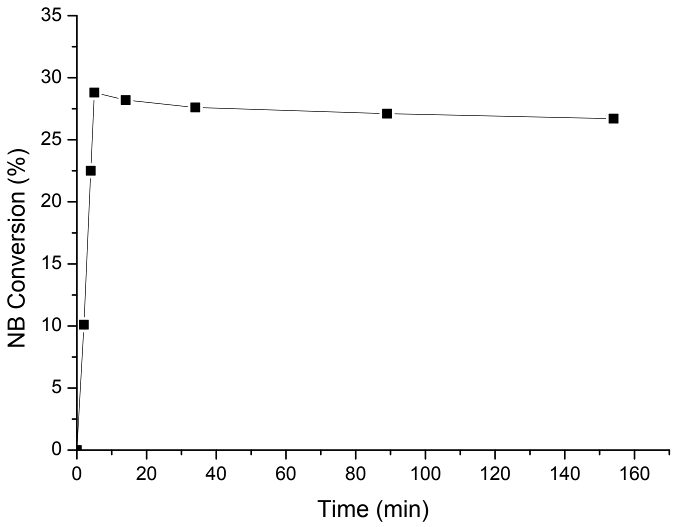


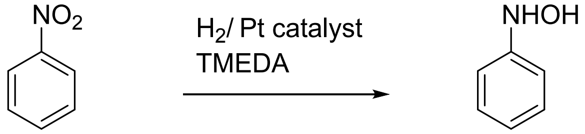
Figure 5. Pt-catalyzed hydrogenation of nitrobenzene under 23 bar H_2 and 30°C . Reaction is stopped after 5 minutes after which the catalyst is filtered off and the filtrate is fed back to the reactor and reactivity is reinitiated.

Table 1. Effect of H_2 pressure on *N*-PHA selectivity and NB hydrogenation activity. Conditions: 22.3 mmol nitrobenzene (S/C=10 x 10^3), 80 mL EtOH at 30°C with S/TM= 10,000.

	H_2 Pressure	Time (min)	NB conversion (%)	*N*-PHA Selectivity (%)	R_0 (M s^{-1} g_M^{-1})
0.6 c-Pd/C	4 bar	105	74.2	44.2	0.074
0.7% c-Pt/C	4 bar	15.9	72.0	79.1	0.47
0.7% c-Pt/C	23 bar	8.4	66.2	91.1	0.82
5% Pt/C	4 bar	195	45.5	35.6	0.022
5% Pt/C	23 bar	180	62.9	76.5	0.036

Catalytic hydrogenation of nitroarenes in a 100 mL autoclave (Table 4)

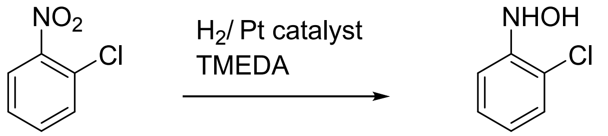
62 mg 0.7% c-Pt/C, 60 mL THF/EtOH (1/1) and 33.4 µL TMEDA were added to a 100 mL stainless steel autoclave equipped with a heating jacket, a hydrogen supply system, a sampling unit, and a mechanical stirrer. Nitroarene substrate (22.3 mmol, S/Pt=10 x 10^3) was dissolved in 20 mL THF/EtOH (1/1) and added to a stainless steel dropping funnel. The catalyst solution was flushed three times with 10 bar H_2 and pressurized to 50 bar at room temperature and stirred for 10 minutes at 1500 rpm. The pressure was kept constant with a mass-flow controller, which also logs the total gas consumption. For the reaction to initiate the dropping funnel's valve was opened and substrate solution was hereby added to the active catalyst. When the uptake of hydrogen decreased dramatically to where it almost completely stopped, the reaction had completed and the reactor was stopped and the H_2 pressure was released. 10 mol% 1,3,5-trimethoxybenzene was added as internal standard. A ^{1}H NMR spectrum of the reaction mixture was obtained within 1 hour by placing three drops of the reaction mixture into an NMR tube with 0.6 mL of methanol-d^4. For the determination of isolated yields no i.s. was added, but a few additional steps were required. Firstly, the reaction mixture was filtered through a syringe filter (0.45 µM) to remove catalyst particles. Solvent and aniline were then evaporated by rotary evaporation at r.t. and 10 mbar. *N*-Phenylhydroxylamine was obtained via precipitation and crystallization from apolar n-hexane/ethyl acetate as an off-white crystalline solid. *N*-Arylhydroxylamine products were stored in a freezer at -30°C.



N-Phenylhydroxylamine (Table 4, entry 1)

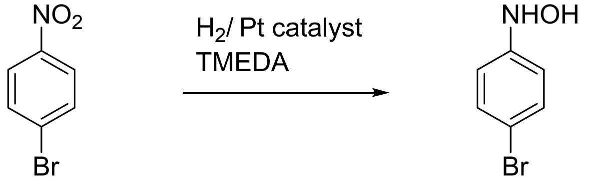
^{1}H NMR (500 MHz, CD_3OD) δ [ppm]; 7.22 (t, 2H, J^3=8.6 Hz), 6.98 (d, 2H, J^3=8.6 Hz), 6.87 (t, 1H, J^3=7.3 Hz).

^{13}C NMR (151 MHz, CD_3OD) δ [ppm]; 151.3, 128.2, 120.6, 113.7.



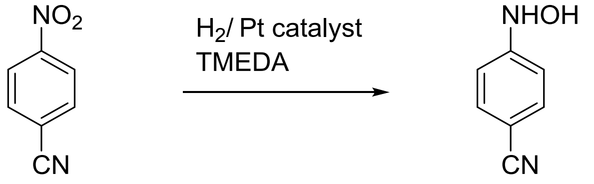
2-Chloro-N-phenylhydroxylamine (Table 4, entry 2)

^{1}H NMR (500 MHz, CD_3OD) δ [ppm]; 7.29 (d, 1H, J^3=8.4 Hz), 7.23 (m, 2H), 6.84 (t, 1H, J^3=7.4 Hz).
^{13}C NMR (151 MHz, CD_3OD) δ [ppm]; 147.3, 128.4, 127.2, 120.6, 118.1, 114.8.



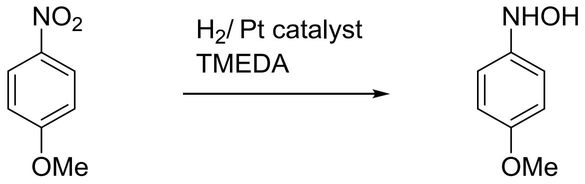
4-Bromo-N-phenylhydroxylamine(Table 4, entry 3)

^{1}H NMR (500 MHz, CD_3OD) δ [ppm]; 7.32 (d, 2H, J^3=8.9 Hz), 6.88 (d, 2H, J^3=8.9 Hz).
^{13}C NMR (151 MHz, CD_3OD) δ [ppm]; 150.9, 131.0, 115.1, 111.8.



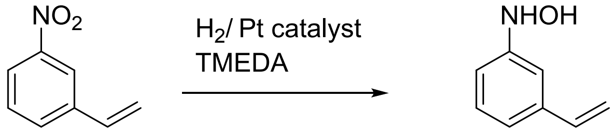
4-Cyano-N-phenylhydroxylamine (Table 4, entry 4)

^{1}H NMR (500 MHz, CD_3OD) δ [ppm]; 7.52 (d, 2H, J^3=8.9 Hz), 6.98 (d, 2H, J^3=8.9 Hz).
^{13}C NMR (151 MHz, CD_3OD) δ [ppm]; 155.8, 132.8, 119.6, 112.2, 100.6.



4-Methoxy-N-phenylhydroxylamine (Table 4, entry 5)

^{1}H NMR (500 MHz, CD_3OD) δ [ppm]; 6.98 (d, 2H, J^3=9.1 Hz), 6.84 (d, 2H, J^3=9.1 Hz), 3.76 (s, 3H).
^{13}C NMR (151 MHz, CD_3OD) δ [ppm]; 155.0, 144.6, 116.2, 113.7, 54.6.



3-vinyl-N-phenylhydroxylamine (Table 4, entry 6)

^{1}H NMR (500 MHz, CD_3OD) δ [ppm]; 7.16 (t, 1H, J^3=7.9Hz), 7.05 (s, 1H), 6.92 (d, 1H, J^3=7.6 Hz), 6.86 (d, 1H, J^3=8.1Hz), 6.68 (dd, 1H, J^3=17.6Hz, J^3=10.9Hz), 5.72 (d, 1H, J^3=17.6Hz), 5.18 (d, 1H, J^3=10.9Hz).
^{13}C NMR (151 MHz, CD_3OD) δ [ppm]; 151.7, 138.0, 137.2, 128.4, 118.7, 113.3, 112.2, 111.1.