

Supporting information

Ionic liquid-supported Pt nanoparticles as catalysts for enantioselective hydrogenation

*Matthias Josef Beier, Jean-Michel Andanson, Tamas Mallat, Frank Krumeich and Alfons Baiker**

Department of Chemistry and Applied Biosciences, ETH Zurich, Hönggerberg, HCI, CH-8093

Zurich, Switzerland.

Experimental

Chemicals and materials. PtCl_4 (Fluka, purum), $\text{H}_2\text{Pt}(\text{OH})_6$ (Johnson Matthey, assay 62.77%), cinchonidine (CD, Sigma), NaOH (Merck), MeOH (Fluka, purissimum), methyl benzoylformate (Acros, 99%), acetic acid (Fluka, purissimum), formic acid (Merck, 98%-100%), 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF₆]) (Acros, 98%+), 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF₄]) (Acros, 98%+), 1-Butyl-3-methylimidazolium tris(perfluoroethyl)trifluorophosphate ([BMIm][FEP]) (Merck, high purity), 1-butyl-4-methylpyridinium tetrafluoroborate ([BMPy][BF₄]) (Merck, for synthesis) were used as received. 5%Pt/Al₂O₃ (Engelhard 4759) was pretreated by heating to 400 °C in flowing N₂, switching to H₂ for 30 min, cooling to room temperature and switching to N₂ again. The catalyst was stored in flowing N₂ overnight and used immediately afterwards.

Glassware deactivation. Glassware was pretreated by immersing it in aqua regia for 15 min. After washing with water and drying, the glassware was treated with a solution of 10 % (v/v) trimethylsilyl chloride (Alfa Aesar, 98%+) in toluene for 30 min. The glassware was washed thoroughly with toluene, methanol and acetone and dried in vacuum for further use. Using deactivated glass both during the synthesis and the catalytic reaction led to a much better reproducibility (Table S1): without glass deactivation the reproducibility was poor even when NPs from the same batch were used in two consecutive runs (entries 1a and b), while similar performance was obtained with deactivation of the glassware even for NPs from different batches (entries 2a and b).

Table S1. Importance of using deactivated glassware for the reproducibility and catalytic performance of Pt-NPs in the hydrogenation of MBF. Reaction conditions: 25 °C, 30 bar H₂.

Entry	Catalyst	Time (h)	Glass deactivation	Conv. (%)	ee ^a (%)	TOF (h ⁻¹) ^b
1a	Pt _{CD} @[BMIm][FEP] ^{c,d}	1	NO	53	68	270
1b	Pt _{CD} @[BMIm][FEP] ^{c,d}	1	NO	43	58	220
2a	Pt _{CD} @[BMIm][FEP] ^{e,f}	0.5	YES	80	78	3200
2b	Pt _{CD} @[BMIm][FEP] ^{e,f}	0.5	YES	75	77	3000

^a (*R*)-selective. ^b TOFs were calculated based on the overall Pt amount. ^c Pt/CD/MBF 1/2/500.

^d NPs from the same batch. ^e Pt/CD/MBF 1/5/2000. ^f NPs from different batches.

IL supported NPs. For the synthesis of chloride-free NPs, 100 mg H₂Pt(OH)₆ and 25.6 mg NaOH were dissolved in 50.0 mL water and filtered through glass wool. Note that using water-insoluble H₂Pt(OH)₆ directly resulted in less active catalysts with the same *ee*. 11.3 mL of this stock solution (77 μmol Pt) and 8.7 mL water were added to a Schlenk tube equipped with a reflux condenser and a magnetic stir bar. 0.5 mL IL were added. When the mixture was refluxing again, 5.0 mL 0.1 molar formic acid was added under vigorous stirring (1000 rpm). The mixture was refluxed for 10 min after which no unreacted precursor could be found in the solution. Volatiles were removed in flowing N₂ at 40 °C overnight, followed by drying under high vacuum over several hours. The IL supported NPs were stored under N₂ atmosphere and are denoted as Pt@IL. NPs with CD as co-stabilizer were prepared by dissolving 22.5 mg CD in the formic acid prior to its addition to the aqueous precursor solution. Unsupported NPs were prepared

without the addition of an IL and redispersed in MeOH for easier handling. MeOH was removed prior to a catalytic run.

Hydrogenation of MBF. Hydrogenation reactions were carried out in a 25 mL stainless steel Parr (Germany) autoclave equipped with a 16 mL glass liner, a PTFE cover, and a magnetic stirrer at $25\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$. Around 15 mg (corresponding to ca. 1.5 - 2 μmol Pt) of the IL-supported NPs were filled into the glass liner. CD was added to achieve an overall CD to Pt molar ratio of 5 as well as MBF to reach a substrate-to-catalyst molar ratio of 2000. A stir bar was added. The mixture was stirred under N_2 atmosphere at 750 rpm. After 30 min of preconditioning, N_2 was replaced by H_2 and the reaction started at a constant pressure of 30 bar. After the reaction, a sample for GC analysis was taken and immersed in toluene. The sample was diluted in heptane to precipitate any IL. The solution was filtered and analyzed with a Thermo Finnigan Trace gas chromatograph equipped with an FID and an Agilent CP-Chirasil-Dex CB column (25 m x 0.25 mm x 0.25 μm). Reactions were usually carried out in duplicates and average values are presented here. The reported *ee*-values are reproducible within $\pm 1\%$ and TOFs (based on the total amount of Pt) within $\pm 5\%$. For reuse experiments, the product mixture was extracted several times with cyclohexane/toluene (4:1) followed by drying in N_2 and vacuum. Removal of the product prior to the next catalytic run was checked with GC analysis.

Control experiments with Pt/Al₂O₃. Pt/Al₂O₃ was freshly activated as described above. 10 mg of the catalyst were placed into the glass inlet followed by 1 mg CD, 3 mL solvent (toluene or [BMIm][BF₄]) and 1.5 mmol MBF. The reaction was performed under 10 bar H_2 atmosphere at room temperature and analyzed as described above.

Transmission electron microscopy (TEM). The supported ILs were diluted in acetophenone and deposited on a holey carbon film supported on a copper grid. Measurements were performed on a Tecnai F30 microscope (FEI, field emission gun operated at 300 kV). The particle size distribution was automatically calculated using the ImageJ 1.40 g software package (National Institutes of Health, USA) after enhancing the contrast manually. The mean particle size was obtained from Gaussian fitting where the full width at half maximum (FWHM) is provided as a measure of the broadness of the particle size distribution.