Pt@ZIF-8 Composite for the Regioselective Hydrogenation of Terminal Unsaturations in 1,3-dienes and Alkynes

Casey J. Stephenson,^a Joseph T. Hupp,^{a,*} Omar K. Farha^{a,b,*}

^a Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA.
^b Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia
Email: j-hupp@northwestern.edu; o-farha@northwestern.edu

Materials. Hydrogen hexachloroplatinate (38-40%-Pt, 99.9% purity based on Pt) and zinc nitrate hexahydrate (99.9%) was purchased from Strem Chemicals; *trans*-1,3-hexadiene (95%) was purchased from TCI America; Pt ICP standard, platinum on carbon (10%), poly(vinylpyrrolidone) powder, (MW 29,000), 2-methylimidazole (99%), *trans*-3-hexene (99%), 1-hexene (99.9%), *cis*-cyclooctene (99%), 3-hexyne (99%), 1-hexyne (97%), cyclohexene (>99%), undecane (>99%), mesitylene (98%), ethyl acetate (anhydrous, 99.9%), diethyl ether (ACS reagent, >99%), nitric acid (traceSELECT for trace analysis), hydrochloric acid (ACS regent grade, 37%), and methanol (HPLC grade, 99.99%) were purchased from Sigma Aldrich; hydrogen for catalytic experiments (UHP, 99.999%) was purchased from Airgas; TEM grids (400 mesh, Cu/C) were purchased from Ted Pella. Poly(vinylpyrrolidone) coated Pt nanoparticles were prepared as previously reported.^{1,2}

Physical and Analytical Measurements. GC-TOF data were recorded on a Waters Micromass GCT Premiere with an Agilent 7890 GC inlet and a DB5 30 meter column in EI mode. Samples were diluted in 1 mL diethyl ether. Transmission electron microscopy (TEM) was performed on a Hitachi H-8100 Microscope and a Hitachi HD-2300 Dual EDS Cryo STEM at 200 kV. Samples for TEM analysis were prepared by dropped a methanolic solution of the compound onto Cu/C TEM grids. Scanning electron microscopy (SEM) was performed on a FEI Quanta ESEM. Prior

to analysis, samples were coated with 8 nm of osmium. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed on a Varian Vista MPX ICP spectrometer. Samples were digested in *aqua regia* and diluted in Milli-Q water. Powder X-ray diffraction (PXRD) were performed on a Rigaku Smartlab Thin-film Diffraction WorkStation with 9 kW copper rotation anode x-ray source coupled with a multilayer optic. Spectra were recorded from $2^{\circ} < \theta < 40^{\circ}$.

Synthesis of Pt@ZIF-8. Pt@ZIF-8 composites were prepared by modifying literature procedure.¹ Methanolic solutions of zinc nitrate hexahydrate (50 mL, 0.1 M) and 2-methylimidazole (50 mL, 0.1 M) were mixed in a 250 mL Erlenmeyer flask, followed by the immediate addition of PVP coated Pt nanoparticles. As with the previously reported ZIF composite, removal of excess PVP from the Pt nanoparticles is crucial for the formation of well encapsulated material. The solution slowly became opaque and a grey precipitate slowly formed. After standing for approximately 24 h, the precipitate was isolated by centrifugation and washed several times with methanol. The precipitate was washed several times. The solid was dried on a Schlenk line, overnight.

Catalytic trials. Pt@ZIF-8 or Pt/C were activated for hydrogenation reactions by first heating at 150 °C under vacuum. Samples were then reduced under a H_2 atmosphere for 2 h at the same temperature. The composite was reduced under a H_2 atmosphere for 2 h at the same temperature. Reactions were carried out using Pt@ZIF-8 or Pt/C (0.1 mmol based on Pt) and substrate (2 mmol) in EtOAc using undecane or mesitlyene as an internal standard in 4 mL total volume under 1 bar H_2 for 24 h at room temp. Samples were analyzed by taking an aliquot, diluting it in 1 mL diethyl ether before being analyzed by GC-TOF.



Figure S1: TEM of PVP coated Pt nanoparticles. Image was recorded on a Hitachi H-8100 Microscope at 200 kV.



Figure S2: TEM of Pt@ZIF-8 showing Pt nanoparticles encapsulated within the ZIF crystallite. Image was recorded on a Hitachi HD-2300 Dual EDS Cryo STEM at 200 kV.



Figure S3: GC-TOF chromatogram of the hydrogenation of 1-hexene using Pt@ZIF-8 as a catalyst in EtOAc using mesitylene as an internal standard.



Figure S4: GC-TOF chromatogram of the hydrogenation of cyclohexene using Pt@ZIF-8 as a catalyst in EtOAc using undecane as an internal standard. Note that we perform size selective hydrogenations with substrates besides *cis*-cyclooctene.



Figure S5: GC-TOF chromatogram of the hydrogenation of 3-hexene in EtOAc using Pt@ZIF-8 as a catalyst and undecane as an internal standard.



Figure S6: GC-TOF chromatogram of the hydrogenation of 1,3-hexadiene in EtOAc using Pt@ZIF-8 as a catalyst and mesitylene as an internal standard.



Figure S7: (top) GC-TOF chromatogram of the hydrogenation of 1-hexyne in EtOAc using Pt/C as a catalyst and mesitylene as an internal standard; (bottom) GC-TOF chromatogram of the hydrogenation of 1-hexyne in EtOAc using Pt@ZIF-8 as a catalyst and mesitylene as an internal standard.



Figure S8: (top) GC-TOF chromatogram of the hydrogenation of 1-hexyne in EtOAc using Pt@ZIF-8 as a catalyst and undecane as an internal standard; (bottom) GC-TOF chromatogram of the hydrogenation of 1-hexyne in EtOAc using Pt@ZIF-8 as a catalyst and undecane as an internal standard.



Figure S9: (top) GC-TOF chromatogram of the hydrogenation of 3-hexyne in EtOAc using Pt@ZIF-8 as a catalyst and undecane as an internal standard – note that 3-hexyne overlaps with EtOAc; (bottom)) GC-TOF chromatogram of the hydrogenation of 1-hexyne in EtOAc using Pt/C as a catalyst and undecane as an internal standard – note that 3-hexyne overlaps with EtOAc.

References.

- G. Lu, S. Li, Z. Guo, O. K. Farha, B. G. Hauser, X. Qi, Y. Wang, X. Wang, S. Han, X. Liu, J. S. DuChene, H. Zhang, Q. Zhang, X. Chen, J. Ma, S. C. J. Loo, W. D. Wei, Y. Yang, J. T. Hupp and F. Huo, *Nat Chem*, 2012, 4, 310.
- 2. Teranishi, T., Hosoe, M., Tanaka, T. and Miyake, J. Phys. Chem. B, 1999, 103, 3818.