

Electronic Supporting Information for

Tetraglyme-mediated Synthesis of Pd Nanoparticles for Dehydrogenation of Ammonia Borane

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General methods

Materials. All experiments were conducted under a nitrogen atmosphere using Schlenk techniques or in an HE-493 dry box (Vacuum Atmosphere Co., Hawthorne, CA, USA). Pd acetate [Pd₃(OAc)₆] was purchased from Colonial Metals Inc. Pd acetylacetonate [Pd(acac)₂], and Pd chloride (PdCl₂) were purchased from Strem Chemicals Inc. Na₂[PdCl₄] was prepared following the procedure as described in the literature.¹ The solvents were dried over Na (tetraglyme, TG) and CaH₂ (methanol) and distilled under nitrogen. The deuterated solvents were dried through trap-to-trap distillation from CaH₂ (CDCl₃) and deoxygenated using three freeze-pump-thaw cycles.

Synthesis of PdNPs from Pd₃(OAc)₆. PdNPs were synthesized from palladium acetate, Pd₃(OAc)₆ (**1**). **1** (0.2 g, 0.3 mmol) was added to 20 mL of TG and held at 25 °C for 3 h. The color of the solution changed from orange to black. The product was separated by centrifugation. The resulting residue was washed with methanol (50 mL) twice, yielding 6.4 nm PdNPs. Three-hour thermolysis of a TG solution was conducted at temperatures of 50, 80, 110, 140, 170, 220, and 270 °C, yielding PdNPs with sizes of 6.5, 5.9, 5.3, 4.2, 3.9, 4.1, and 7.1 nm, respectively.

Synthesis of PdNPs from Pd(acac)₂. Pd acetylacetonate [Pd(acac)₂] (0.3 g, 1.0 mmol) was added to 30 mL of TG and held at 200 °C for 3 h. The color of the solution changed from orange to black. 50 mL of methanol was added, and the product was separated by centrifugation.

Synthesis of PdNPs from Na₂[PdCl₄]. A solution of Na₂[PdCl₄] (0.011 M) in ethanol (250 mL) was prepared by reacting PdCl₂ (0.50 g, 2.82 mmol) and NaCl (0.33 g, 5.64 mmol) at room temperature. Na₂[PdCl₄] (10 mL, 0.11 mmol) was added to a TG (40 mL) solution and held at 25 °C for 1 h. The color of the solution changed from yellow to black. After that, 50 mL of methanol was added, and the product was separated by centrifugation.

Synthesis of PdNPs from PdCl₂. PdCl₂ (0.2 g, 1.1 mmol) and TG (5 mL) were added to 20 mL of acetonitrile. The resulting solution was heated to 80 °C and held at this temperature for 1 h. The color of the solution changed from orange to black. Methanol (30 mL) was added, and the product was separated by centrifugation.

Analytical Methods. The PdNP samples were analyzed using field-emission transmission electron microscopy (TEM, FEI Tecnai F20), electron diffraction (ED), and energy-dispersive X-ray fluorescence spectroscopy (EDX). Powder X-ray diffraction (XRD) data were collected on a Rigaku D/MAX-2500 (18 kW) diffractometer. For the XRD measurements, the PdNP sample was dried, mixed with 325-mesh Si powder, and placed on a Si wafer sample holder. The XPS study was performed using a Thermo Electron Corporation theta probe (UK) with a photon energy of 1486.6 eV (Al K α). Solution NMR spectra were collected at room temperature using a Mercury-300BB spectrometer (Varian Inc., Palo Alto, CA, USA) unless otherwise stated. The spectral frequency was 96.3 MHz for ¹¹B, and NMR shifts in ppm were reported with reference to external standards of BF₃·Et₂O for the ¹¹B nucleus. IR spectra were recorded on a Nicolet Avatar 330 Fourier transform IR (FT-IR) spectrometer (Thermo Fisher Scientific, Rochester, NY, USA) with a KBr pellet. Quadrupole mass spectroscopy (QMS) data were obtained using a quadrupole mass spectrometer (Stanford Research Systems, Sunnyvale, CA, USA, RGA200) attached to a glass vacuum line system. UV-vis absorption spectra were acquired using a Varian Cary 50 spectrophotometer.

AB Dehydrogenation Procedure

Apparatus and procedure for PdNPs catalyzed dehydrogenation.

The reactor consisted of a three-neck round-bottom flask with a water-cooled reflux condenser, a septum port for syringe sampling, and a powder addition funnel for Pd catalyst addition. A three-way connector was modified to allow the system to be purged with argon gas and to allow hydrogen gas produced during the dehydrogenation reaction to pass through a mass flow meter (MFM). The experimental procedure involved filling the reactor with AB (0.12 g, 4 mmol) containing 0.03 mL of TG. The reactor was heated in a silicon oil bath to 85 °C and subsequently flushed with argon for at least 5 min to minimize the moisture level inside the vessel. After the thermal equilibration of the reactor and the low-temperature trap, 2 mol% of PdNPs was added to the AB/TG mixture. The reaction time began when the catalyst was introduced into the mixture and ended when H₂ evolution ceased. The progress of the reaction was monitored by examining the amount of hydrogen generated using a volumetric technique that allowed real-time tracking of the reaction. In the apparatus, a -90 °C low-temperature bath (liquid N₂ with CH₂Cl₂) trapped the volatiles to ensure that the gas volume measured as it passed through the MFM system was only hydrogen.

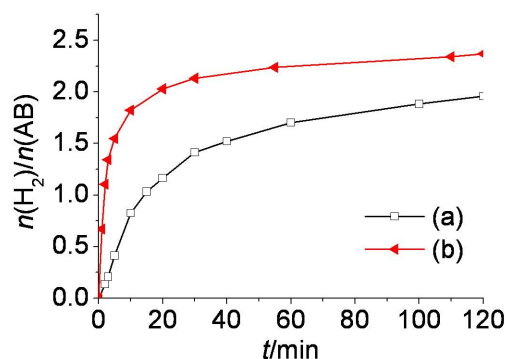


Fig. S1 Kinetic profiles of AB dehydrogenation at 85 °C by the PdNPs catalyst prepared at (a) 25 °C (Fig. 2A(2)) and (b) 140 °C (Fig. 2A(6)).

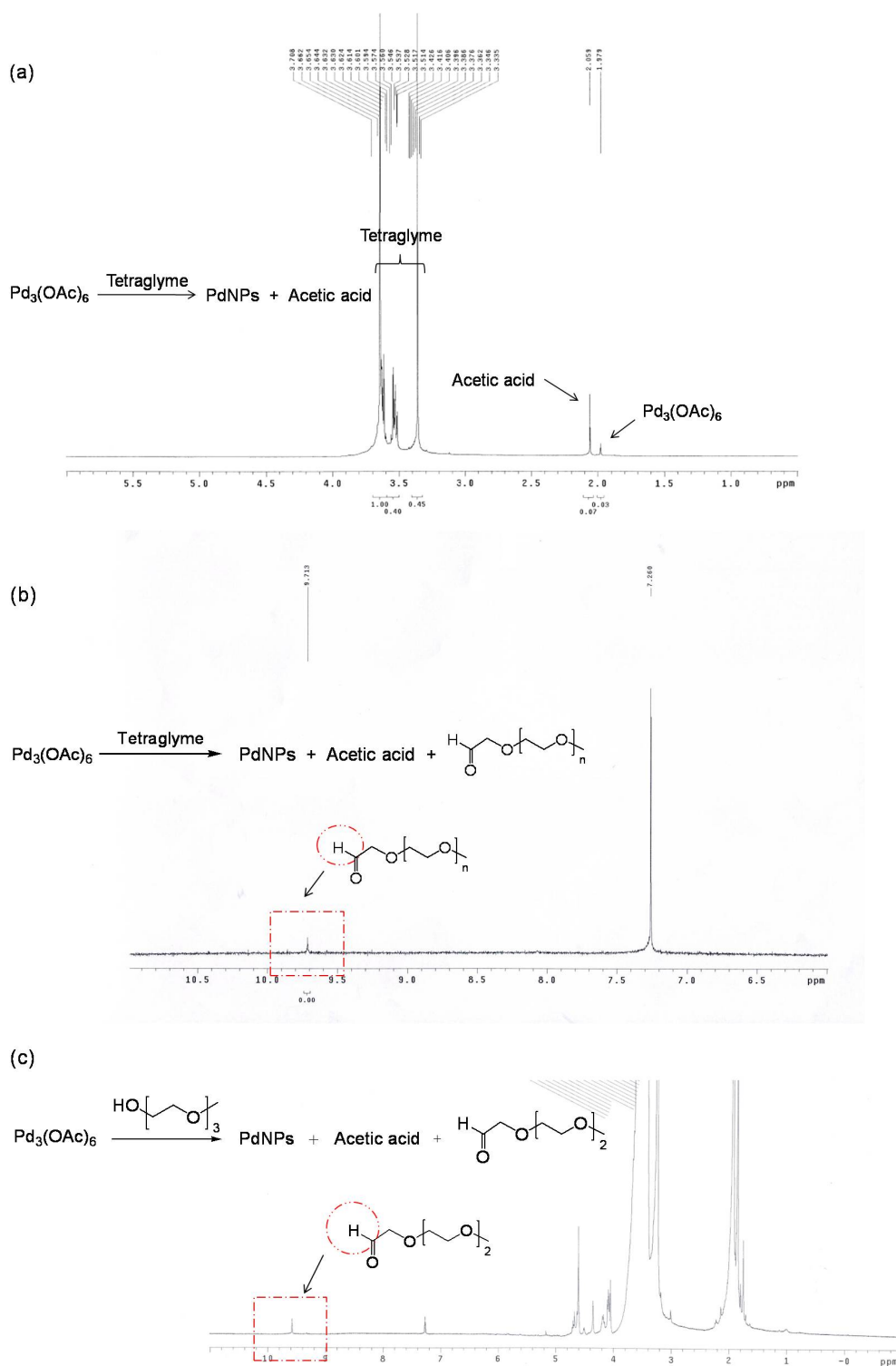


Fig. S2. (a) A peak assignable to acetic acid at δ 2.06 of ^1H NMR after standing NMR solution of $\text{Pd}_3(\text{OAc})_6$ in tetraglyme. (b) An aldehyde peak detected at δ 9.73 in the expanded ^1H NMR spectrum of (a). (c) Two distinctive peaks for acetic acid and aldehyde found in triethylene glycol monomethyl ether (TME) solution of $\text{Pd}_3(\text{OAc})_6$.

We first checked the tetraglyme used for the activation of $\text{Pd}_3(\text{OAc})_6$ and found that residual

amounts of polyethyleneglycol monomethyl ether (PME) were present in tetraglyme. Most of our synthetic work has used 99% purity tetraglyme from Aldrich (product no. 172405). We identified small amounts of PMEs by means of GC and GC-Mass and correlate their role for the activation to PdNPs. As reviewer advised, PME could be responsible for the reduction of $\text{Pd}_3(\text{OAc})_6$. To check this possibility, ^1H NMR analysis was carried out on the synthesis solution of tetraglyme after the colloid formation.

The corresponding ^1H NMR spectra are presented in Fig. S2 of the supporting information. As shown in Fig. S2(a), during the reduction process free acetic acid is produced from the TG solution and this acetic acid is believed to be the product of the acetate ligands stripped off from the precursor $\text{Pd}_3(\text{OAc})_6$. We speculate that alcohol group of the PME be the origin of acetic acid found in NMR spectrum. Both aldehyde and acetic acid were identified in the ^1H NMR as shown in Fig. S2(b). In particular, detection of aldehyde peak at $\delta 9.73$ implies that alcohol group of PME is oxidized. Based on the peak analysis of the stated ^1H NMR spectra, small amounts of PMEs (hydroxyethers) contained in tetraglyme are believed to activate the reduction process of Pd^{2+} to Pd^0 . To further consolidate PdNPs formation by the hydroxyethers of PME, the synthesis of the PdNPs was carried out in a related triethyleneglycol monomethyl ether (TME, hydroxyether) solution. Indeed, $\text{Pd}_3(\text{OAc})_6$ produced a dark colloidal solution at room temperature without need for surfactants or organic compounds and aldehyde and acetic acid were detected as shown in Fig. S2(c). This supports reviewer's opinion on the activation of $\text{Pd}_3(\text{OAc})_6$ to $\text{Pd}(0)$ colloid by hydroxyethers contained in TG solution.

Other possible reduction process was also considered; involvement of the acetate ligand (OAc^-) in $\text{Pd}_3(\text{OAc})_6$. Yee et al. showed the generation of Pd nanoparticles by thermal decomposition of palladium acetate or palladium chloride and sodium acetate, whereby the acetate radical formed in the reaction was suggested to assist the reduction from Pd^{2+} to Pd^0 . But we have not observed any direct evidence which can go along with this mechanism.

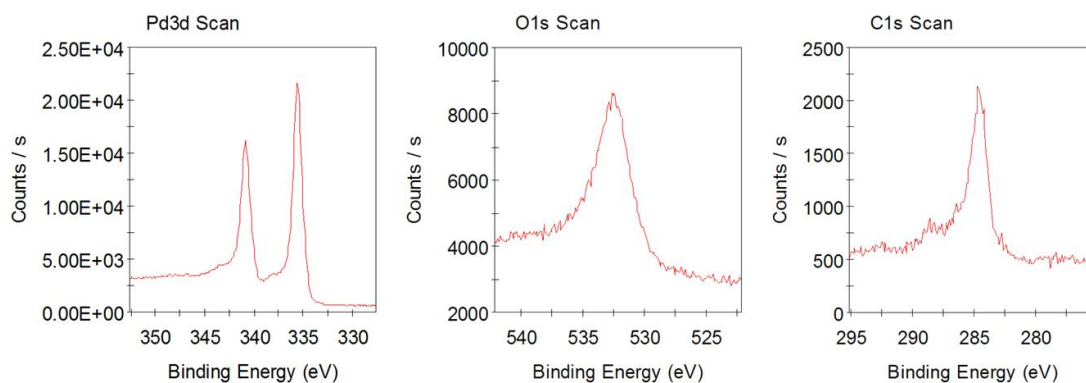


Fig. S3A Palladium 3d, oxygen 1s, and carbon 1s X-ray photoelectron spectra for as-prepared post treated PdNPs (2).

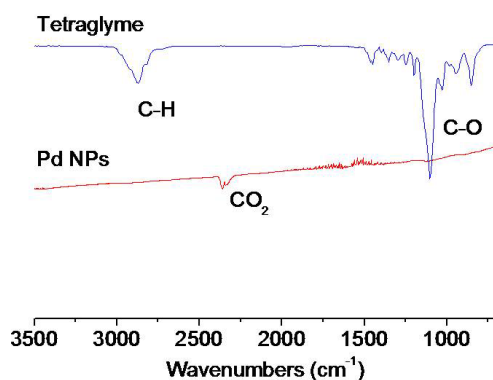


Fig. S3B. Fourier transform IR (FT-IR) spectrum of PdNPs (2).

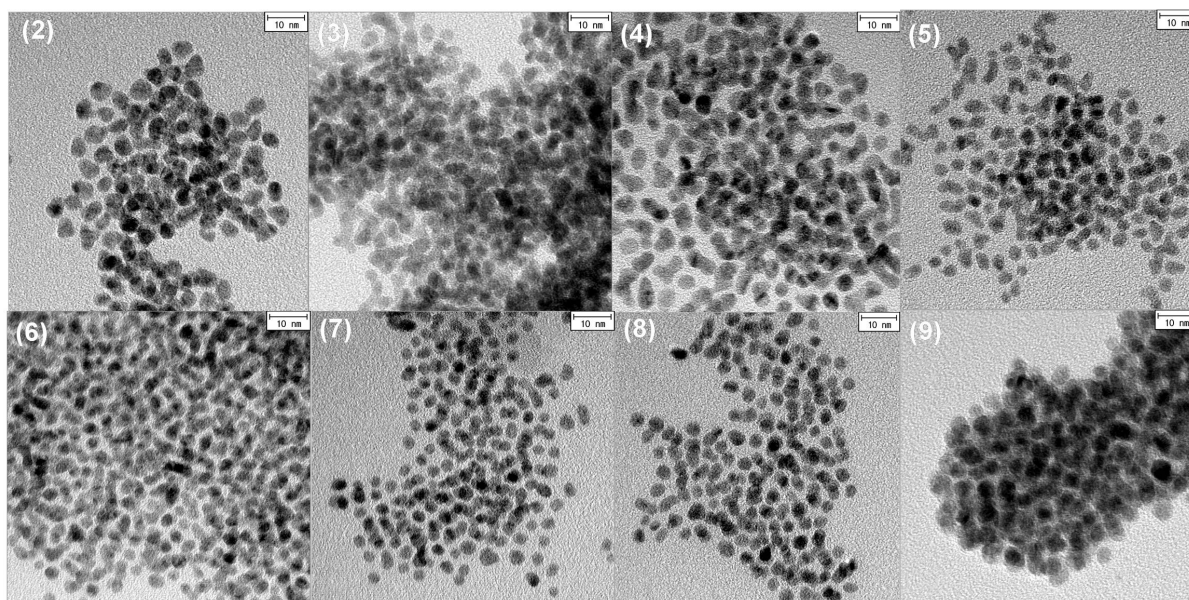
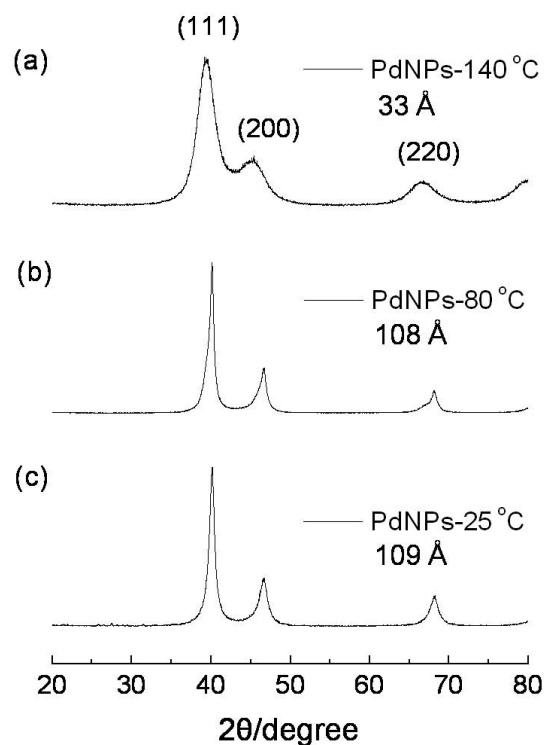


Fig. S4 High-resolution transmission electron microscopy (HRTEM) images of PdNPs obtained by 3 h thermolysis in tetraglyme at temperatures of (2) 25 °C, (3) 50 °C, (4) 80 °C, (5) 110 °C, (6) 140 °C, (7) 170 °C, (8) 220 °C, and (9) 270 °C. Scale bar = 10 nm.



synthetic condition	FWHM ^[a]	Mean diam/Å	2θ of (111)/deg	<i>d</i> ^[b] /Å
PdNPs-140 °C	2.558	33	39.322	2.2894
PdNPs-80 °C	0.821	108	40.084	2.2477
PdNPs-25 °C	0.814	109	40.096	2.2470

[a] full width at half-maximum, [b] (111) interplanar spacing.

Fig. S5 XRD spectra of PdNPs prepared at (a) 140 °C, (b) 80 °C, and (c) 25 °C. The evolution of the crystal size (in Å) was also calculated using the Scherrer formula.² In this case, the peak width was determined from the full width at half-maximum (FWHM) considering only the $\lambda_{\alpha 1} = 1.54060$ Å contribution. Particle sizes obtained from the width of the (111) reflections are depicted.

Table S1 Catalytic activity over ten cycles of dehydrogenation of AB

Cycle test	1th	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
Mat. wt. %	10.7	10.2	10.5	10.6	10.1	9.8	9.6	10.3	9.5	9.7
H ₂ flow rate ^[a]	0.084	0.081	0.079	0.082	0.080	0.076	0.073	0.079	0.073	0.080

[a] g/s per kg AB

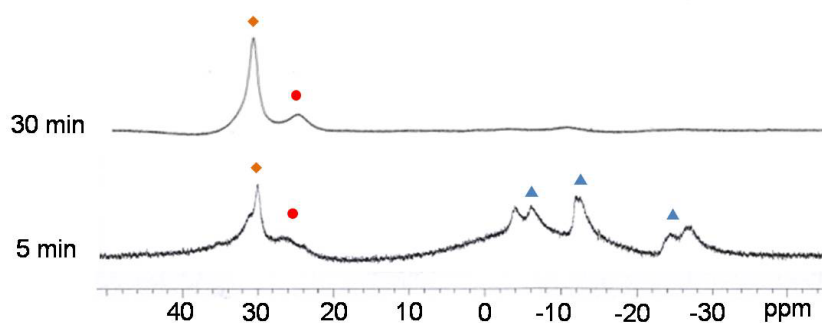


Fig. S6 Evolution of the ^{11}B NMR spectra of AB dehydrogenation (96.3 MHz, TG, 2 mol% PdNPs). \blacklozenge borazine; \bullet PB (polyborazylene); \blacktriangle B-(cyclodiborazanyl)aminoborohydride (BCDB) 3 . Spectra were recorded after 5 min and 30 min reaction times at 85 °C.

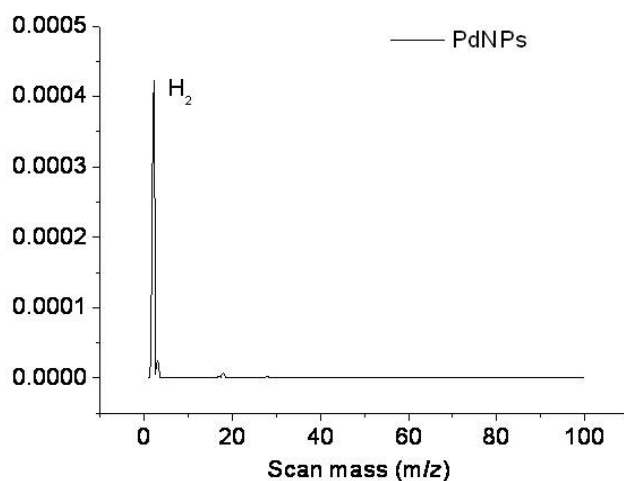


Fig. S7 Mass spectrum of the volatile compounds from AB dehydrogenation with PdNPs. Highest-intensity mass number was $m/z = 2.0$, indicating that H_2 was detected.

Reference

- 1 M.Ganesan, R. G. Freemantle and S. O. Obare, *Chem. Mater.* 2007, **19**, 3464.
- 2 B. D. Cullity, *Elements of X-ray Diffraction*, 2nd ed., Addison-Wesley, Reading, MA, 1978.
- 3 W. J. Shaw, J. C. Linehan, N. K. Szymczak, D. J. Heldebrant, C. Yonker, D. M. Camaioni, R. T. Baker and T. Autrey, *Angew. Chem. Int. Ed.* 2008, **47**, 7493.