

ELECTRONIC SUPPLEMENTARY INFORMATION

Polyol synthesis of palladium hydride: Bulk powders vs. nanocrystals

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Materials

Bulk palladium powder (0.25-0.55 μm , 99.95%), sodium borohydride (NaBH_4 , 98%), and tetraethylene glycol (TEG, 99%) were purchased from Alfa Aesar. Palladium salt, Na_2PdCl_4 , was purchased from Acros Organic. Ethylene glycol (EG, 99%) was purchased from JT Baker. Poly(vinyl pyrrolidone) (PVP, MW = 55,000) was purchased from Sigma Aldrich. All chemicals obtained from commercial sources were used as received without additional purification.

Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Bruker Advance D8 X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) data were recorded using a JEOL JEM 1200EX-II operating at 80 kV. Samples for TEM analysis were prepared by dispersing nanocrystals in ethanol and depositing a drop of dispersion onto a carbon coated nickel grid, followed by evaporating the solvent. Gas chromatography (GC) measurements were performed on a Varian Aerograph Model 90-P with a thermal conductivity detector (TCD) and room temperature molecular sieve column with helium as a carrying gas.

Synthesis of palladium hydride

20 mg of bulk palladium powder was dispersed in 20 mL of TEG via sonication, followed by heating to 90 – 210 $^\circ\text{C}$ while bubbling with Ar. A fresh solution of 3 mL of TEG and 45 mg of NaBH_4 was added dropwise to the hot TEG solution containing Pd powder while stirring for 2 min. The resulting solution was then slowly cooled down to room temperature. The particles were collected through centrifugation, washed with ethanol, and then dried at room temperature.

Pd nanocrystals were synthesized by simultaneously injecting a 3.3 mL EG solution of Na_2PdCl_4 (135 mg) and a 3.3 mL EG solution of PVP (80 mg) into 7 mL of EG at a rate of 45 mL per hour under an air purge at 110 $^\circ\text{C}$, followed by stirring for 3 h at 110 $^\circ\text{C}$. Pd^{2+} ions were reduced by hot EG in the presence of PVP. The resulting Pd nanocrystals were isolated with acetone through centrifugation, washed with ethanol, and then dried under vacuum at room temperature.

25 mg of nanocrystalline Pd was re-dispersed in 10 mL of TEG with 20 mg of PVP via sonication. This Pd dispersion was added into 20 mL of heated TEG along with additional 10

mg of PVP at 90 – 190 °C under purging Ar gas, followed by dropwise addition of a solution of 45 mg of NaBH₄ in 3 mL of TEG with stirring for 2 min. The resulting nanocrystalline palladium hydride was isolated, washed with ethanol through centrifugation, and dried at room temperature.

Under typical conditions studied (e.g. 190 °C), PdH_x was not observed as a product upon heating Pd nanocrystals in TEG with H₂ bubbling through it. Similarly, under conditions where BH₄⁻ rapidly hydrolyzes to produce H₂ (e.g. pH-neutral H₂O), PdH_x was not observed when heated in an autoclave with Pd nanocrystals. This is in agreement with the results of ref. 10, which hypothesized a metal-assisted borohydride hydrolysis reaction. These studies, like ours, argue against a direct reaction between the metal and H₂ under these conditions.

Any differences in behavior, e.g. hydrogen release, between PdH_x made using traditional methods (heating in H₂) and PdH_x made in polyol solvents with borohydride could be attributed to small amounts of interstitial or surface carbon (solvent decomposition) or boron (borohydride). Gas chromatography (representative data shown below) confirms the presence of hydrogen, based on pure H₂ as the standard for determining retention times. A small N₂ impurity is also present from sample handling.

