Palladium Nanoparticles Entrapped in Aluminum Hydroxide: Dual Catalyst for Alkene Hydrogenation and Aerobic Alcohol Oxidation

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Supporting Information

Synthesis of the Catalyst 1: Pd(PPh₃)₄ (260 mg, 0.225 mmol), tetra(ethylene glycol) (418 mg, 2.20 mmol), (*sec*-BuO)₃Al (9.50 g, 38.5 mmol), and 1-butanol (3 mL, 32.7 mmol) were added 50 mL round bottom flask equipped with condenser. After being stirred at 120 °C for 10 h to give black suspension, water (2 mL) was added dropwise. The reaction mixture was further stirred at 120 °C for 30 min. The black solid was filtered, washed with acetone, and dried at room temperature in the air to give **1** as dark olive-green powder (2.75 g; 0.86 wt % of Pd).

Hydrogenation of Cholesterol: To a solution of cholesterol (387 mg, 1.00 mmol) in EtOAc (5 mL), **1** (247 mg, 2 mol% Pd) was added, and the reaction mixture was stirred at room temperature for 6 h under a H₂ balloon. The catalyst was filtered and washed with EtOAc (3 mL), and then dried in the air for reuse. Solvent was removed from the filtrate under reduced pressure to give analytically pure cholestanol (386 mg, >99%).

Aerobic Oxidation of 1-phenylethanol: To a solution of 1-phenylethanol (122 mg, 1.00 mmol) in toluene (2 mL), **1** (25 mg, 0.20 mol% Pd) was added, and the reaction mixture was heated at 80 °C for 6 h under air. The catalyst was filtered and washed with acetone. Solvent was removed from the filtrate under reduced pressure to give analytically pure acetophenone (120 mg, 99%).

One-pot Transformation of Cholesterol to Cholestan-3-one: To a solution of cholesterol (387 mg, 1.00 mmol) in toluene (5 mL), **1** (247 mg, 2 mol% Pd) was added, and

the reaction mixture was stirred at room temperature for 6 h under a H₂ balloon. After replacing the balloon with a condenser, the reaction mixture was heated at 110 °C for 24 h to give analytically pure cholestan-3-one in (384 mg, 99%).

Characterization of 1: The catalyst **1** was characterized by transmission electron microscopy (TEM). A distinct fibrous morphology is shown in the low magnification TEM image (Figure 1), and palladium nanoparticles of about 2-3 nm in the high-resolution TEM images (Figure 2). The specific surface area of **1** was determined to be 611.5 m²/g by the N₂ BET method at 77 K. Chemisorption of CO at room temperature gave a metal area of 216.53 m²/g catalyst assuming that a CO molecule titrates a single Pd surface atom. This corresponds to a 48% metal dispersion or a crystallite size of 2.34 nm, which is consistent with the sizes of nanoparticles seen in the TEM image.

Figure 1. A low magnification TEM image of **1**.

Figure 2. High resolution TEM images of 1.