Supplementary Material for Chemical Communications

Supporting Information for

A Metal Nanoparticle-Based Heterosuparmolecular Approach for Aqueous Biphasic Hydrogenation Reactions

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Materials: 3,3,5-trimethyl-2-cyclohexenone, 1-cyclohexene-1-carboxaldehyde, *trans*-cinnamaldehyde, and α-methyl-*trans*-cinnamaldehyde used in hydrogenations were of analytical grade (Aldrich), while the solvents were minimum purity of 99.9% (Fisher). The commercial Pd-black catalyst was from Engelhard (code E3113). Sodium tetrachloropalladate(II), sodium borohydride, and adamantane were purchased form Acros. β-cyclodextrin was donated from Cerestar. The perthiolated β-cyclodextrin was synthesized according to a previous report (reference 2c). This compound was fully characterized before using. All aqueous solutions were prepared by deionized water (18.1 MΩ·cm), which is passed through a four-cartridge Barnstead Nanopure II system.

Synthesis, purification and characterization of Pd nanoparticles modified with perthiolated β-cyclodextrin: A general procedure for the synthesis and characterization of Pd nanoparticles modified with perthiolated β-CD was published by one of the authors before (reference 2c). The average particle size was estimated by counting over 100 individual particles from a typical TEM image. The surface coverage of β-CD (estimated by elemental analysis) on each particle was 50%. Figure SI1 and SI2 show TEM image and ^{1}H NMR spectrum of β-CD/Pd nanoparticles.

TEM measurements: The TEM measurements were carried out on a JEOL4000FX instrument. A few drops of β-CD/Pd nanoparticle aqueous solution were transferred onto a carbon coated copper grid. The water was naturally evaporated at room temperature. The TEM images were obtained at 200 KeV acceleration voltages respectively.

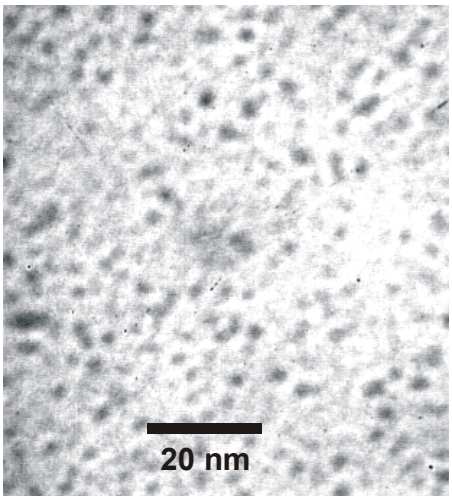
^{1}H NMR: ^{1}H NMR spectra (400 MHz) were recorded with a Varian UI400 NMR spectrometer. ^{1}H NMR spectra (Figure SI2) of free β-CD and surface-anchored β-cyclodextrin was obtained from a D_2O solution containing either free β-CD or perthiolated β-cyclodextrin modified Pd nanoparticles which are very similar with the results from perthiolated β-cyclodextrin modified gold nanoparticles reported previously (reference 2c).

Hydrogenation reactions: The hydrogenations were performed in a Berghof HR-100 autoclave at room temperature (25 °C). The catalytic system including the catalyst, solvent and substrate (10 mg of catalyst, 5 ml of solvent and 1 mmol of substrate) was

placed into an inert Teflon liner. The liner was put into the autoclave, and the system was flushed with hydrogen several times and filled to 20 bar hydrogen pressure and stirred (1000 rpm) for the required reaction time (usually 2 h). Occasional alterations from this general procedure will be noted in the text. We also found that the pretreatment did not have any effect on the hydrogenation activity of the catalyst. Thus the experiments were carried out without prehydrogenation step. Turnover frequencies (TOF) were calculated based on the amount of substrate transformed by each Pd atom in 1 hour period. The TOF values are given in h^{-1} units.

Analysis of hydrogenation product: The product identification was monitored by GC-MS (Shimadzu QP 5050 System), while the product yields were determined by gas chromatography (HP 5890 GC-FID, 30 m long Betadex (Supelco) capillary column). The results were reproducible within 1%.

Figure SI1. A typical TEM image of β-CD modified Pd nanoparticles.



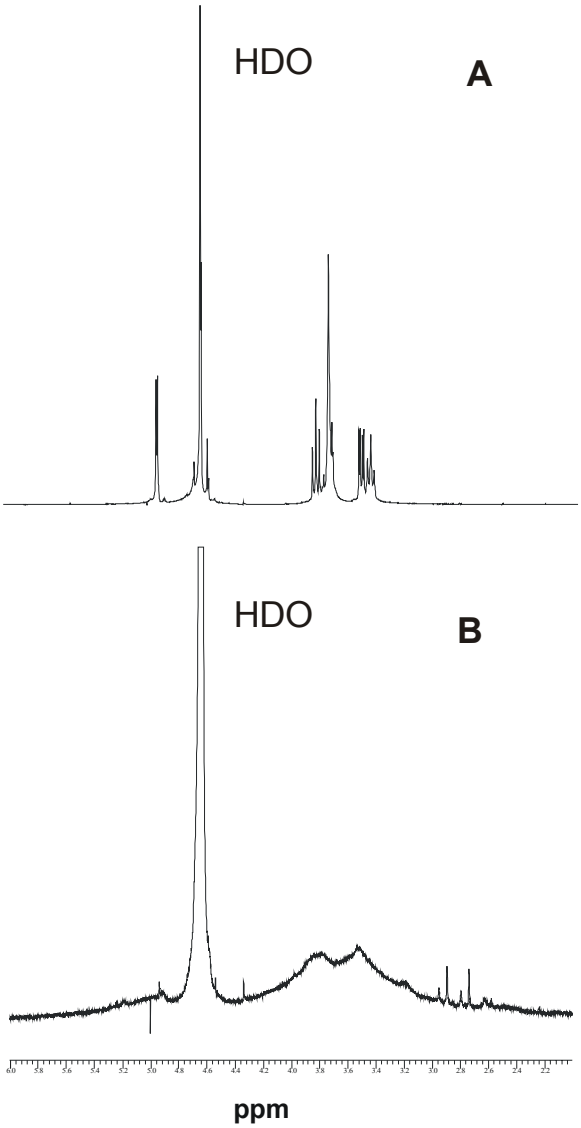


Figure SI2. ^{1}H NMR of (A) β-CD and (B) β-CD on Pd nanoparticles in D_2O