Supplementary Information for

CO_2 as a regulator for controllable preparation of highly dispersed chitosan-supported Pd catalysts in ionic liquid

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1. Materials

Palladium acetate ($Pd(OAc)_2$) was purchased from J&K Chemical. Chitosan with a stated deacetylation degree of 80.0-95.0% was purchased from Sinopharm Chem. Reagent Co. Ltd, and dried at 150 ^{o}C under vacuum before dissolution. The average molecular weight of the native chitosan is 2.59 105 Da, which can be obtained by measuring the intrinsic viscosity of chitosan/CH_3COOH/CH_3COONa solution using an Ubbelodhe viscometer. The ionic liquid [Bmim]OAc used in the experiment were purchased from Lanzhou Greenchem ILs, LICP, CAS, China (Lanzhou, China) with purity over 99.9%. [Bmim]OAc was dried at 50 ^{o}C under vacuum for 96 h before used; water content of the ionic liquid is less than 1000 ppm after the drying process.

2. Preparation of Pd catalyst supported on chitosan

In a typical procedure, $NaBH_4$ (0.1 g) was dissolved in ionic liquid [Bmim]OAc (1 g) in a flash of 10 mL at 100 ^{o}C. Then, the finely ground mixture of $Pd(OAc)_2$ (0.02 g) and chitosan (0.6 g) was added into the solution under the continuous stirring until a clear solution was formed. Finally, the solution was cooled to room temperature. In order to obtain the chitosan-supported Pd catalysts, different anti-solvents including ethanol, water and CO_2, were added into the as-prepared mixture to recover Pd particles and chitosan from [Bmim]OAc. After washed with ethanol and dried at 50 ^{o}C for 12 h under vacuum, the catalyst Pd/chitosan was obtained.

In the processes using CO_2 as the anti-solvent, the apparatus was similar to that reported by our previous work.[S1,S2] The apparatus consisted of a high-pressure cell, a pressure pump, a pressure gauge (±0.025 MPa) and a temperature controller (±0.1 ^{o}C). In a typical experiment, the ionic liquid solution contained Pd/chitosan were loaded into the high-pressure cell. The CO_2 was flowed into the cell until the desired pressure was reached. The system was kept several hours, then CO_2 was released by depressurization to obtain the catalyst Pd/chitosan.

3. Characterization of the catalyst

The transmission electron microscopy (TEM) images were obtained on TEM JeoL-2100F with an accelerating voltage of 200 kV. The sample was dispersed in ethanol with the aid of sonication and dropped on an amorphous carbon film supported on copper grid for TEM analysis. Powder XRD patterns were recorded on Rigaku D/max-2500 X-ray diffractometer using Cu-Kα radiation (λ=0.15406 nm) at a scanning rate of 8 degree per minute. The tube voltage was 40 kV and the current was 200 mA. The X-ray photoelectron spectroscopy (XPS) data were obtained with a Thermo ESCALab250 xi electron spectrometer from Thermo Scientific using 300 W Al-Kα radiation. The base pressure was about 1.68×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. FT-IR spectra were obtained using a Bruker Tensor 27 spectrometer, and the samples were prepared by the KBr pellet method. The contents of Pd in the samples were determined by ICP-AES (VISTAMPX). Thermogravimetric analysis was performed on a thermogravimetric analysis system (Netzsch STA 409 PC/PG, Germany) in N_2 atmosphere at a heating rate of 20 ^{o}C/min.

4. Hydrogenation reactions

For the hydrogenation reaction, styrene (2 g) and Pd/chitosan (20 mg) were placed in a 20 mL stainless steel reactor. The reactor was sealed and evacuated with H_2 (three times). After H_2 was added into the reactor with a desire pressure, the reaction was conducted at desire temperatures under stirring with a rate of 500 rpm. In the reaction process, the pressure of H_2 was kept to be constant during the reaction, which was monitored by a pressure transducer (Foxboro/ICT model 930). After a certain time, the product was separated with the catalyst by centrifugation (14000 rpm) and the product was analyzed by a gas chromatograph (Agilent 7890) equipped with a flame ionization detector (FID) and a PEG-20M capillary column (0.25 mm in diameter, 30 m in length).

5. Catalyst reuse

In the experiments to test the reusability of the Chit-Pd-14.2MPa, the catalyst was recovered by centrifugation, washed using ethyl ether. After drying under vacuum at 80 ^{o}C for 12 h, the catalyst was reused for the next run.

6. Fig S1

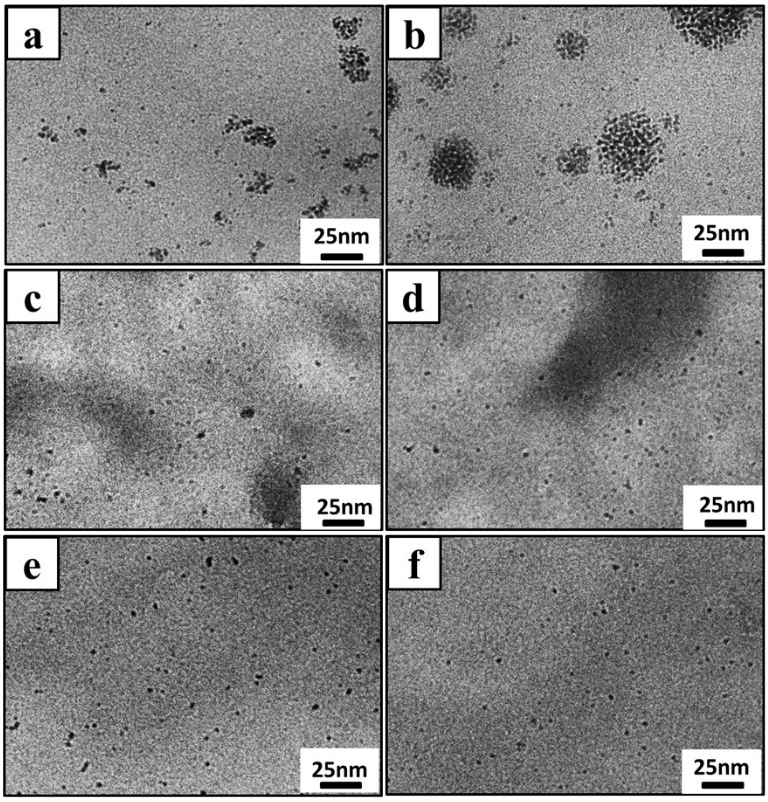

Fig. S1. TEM images of the materials prepared with different anti-solvents. (a) Water; (b) ethonol; (c) 7.2 MPa CO_2; (d) 9.2 MPa CO_2; (e) 12.2 MPa CO_2; (f) 14.2 MPa CO_2.

7. Fig S2

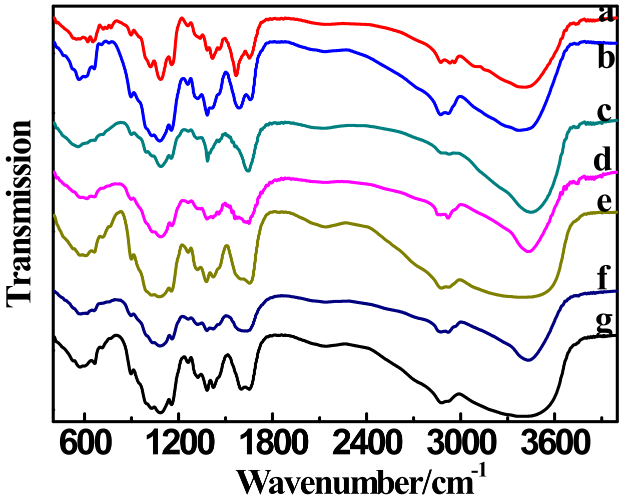

Fig. S2. FT-IR spectra for chitosan and Pd/chitosan obtained by using different anti-solvents. (a) Water; (b) Ethanol; (c) 7.2 MPa CO_2; (d) 9.2 MPa CO_2; (e) 12.2 MPa CO_2; (f) 14.2 MPa CO_2; (g) raw chitosan.

8. Table S1

Table S1. Pd content of various Pd/chitosan obtained by using different anti-solvents.

Catalyst	Pd Content (wt%)
Chit-Pd-7.2MPa	0.78
Chit-Pd-9.2MPa	0.80
Chit-Pd-12.2MPa	0.82
Chit-Pd-14.2MPa	0.88
Chit-Pd-H_2O	1.34
Chit-Pd-Ethanol	1.43

9. Fig. S3

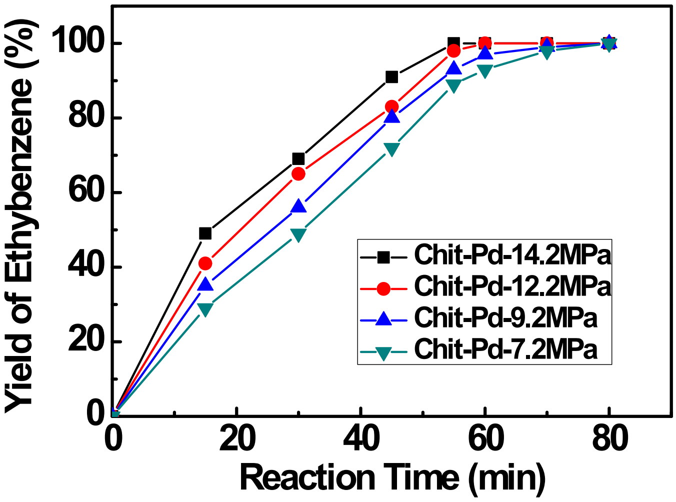

Fig. S3. Time-conversion plots for the hydrogenation of styrene catalyzed by the Pd/chitosan using CO_2 as the anti-solvents. Reaction conditions: temperature: 50 °C; styrene 2 g; catalyst 20 mg; H_2 pressure 2 MPa.

10. Fig. S4

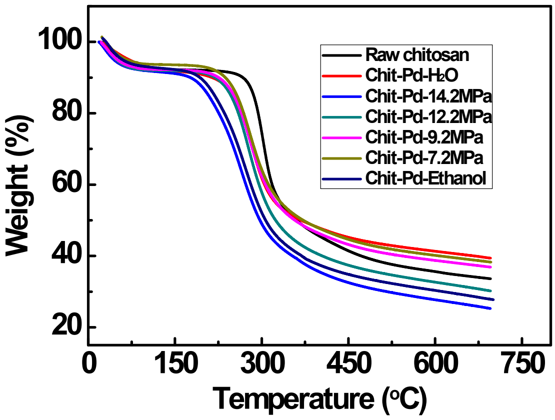

Fig. S4. Thermogram of raw chitosan and the as-prepared Pd/chitosan catalysts.

11. Reference

S1. X. F. Sun, Z. M. Xue and T. C. Mu, *Green Chem.*, 2014, **16**, 2102.

S2. X. F. Sun, Y. L. Chi and T. C. Mu, *Green Chem.*, 2014, **16**, 2736.