

Electronic Structure Modulation of Pd_n(n=2~5) Nanoclusters in the Hydrogenation of Cinnamaldehyde

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Experimental section

Chemicals

(NH₄)₂PdCl₄, sodium borohydride (NaBH₄, 98%, Sinopharm), tetra-n-octylammonium bromide (TOAB, 98%, TCI), ethanol (C₂H₅OH, analytical grade, Sinopharm), methanol (CH₃OH, analytical grade, Sinopharm), toluene (C₇H₈, analytical grade, Sinopharm), dichloromethane (CH₂Cl₂, analytical grade, Sinopharm), Cinnamaldehyde (C₉H₈O, analytical grade, Aladdin), 3-Phenylpropionaldehyde (C₉H₁₀O, analytical grade, Aladdin), Cinnamic alcohol (C₉H₁₀O, analytical grade, Aladdin), 3-phenylpropanol (C₉H₁₂O, analytical grade, Aladdin), Di-1-adamantylphosphine (C₂₀H₃₁P, analytical grade, Aladdin). All the reagents purchased from commercial sources were used as received without further purification. The water used in all experiments was ultrapure.

Synthesis of Pd₅ nanoclusters

A standard preparation method of Pd₅ nanoclusters was provided in detail, which was divided into synthesis and separation processes. In synthesis, (NH₄)₂PdCl₄ (28.4 mg, 0.100 mmol) was dissolved in a mixture of 10 mL dichloromethane (CH₂Cl₂) and 5 mL H₂O, which was conducted in a 50 mL round-bottom flask. After 5 minutes, TOAB (TOAB: Tetra-n-octylammonium bromide) (103.8 mg, 0.190 mmol) was added stirring for 30 minutes and the CH₂Cl₂ phase turns red. Then, the H₂O was removed. Di-1-adamantylphosphine (45.4 mg, 0.15 mmol) was added and the solution turns golden, indicating the successful combination of Pd and ligands. After 60 minutes, the NaBH₄ (30.0 mg, 0.79 mmol) was dissolved into 3 mL ice water and the mixture was poured into the flask. Immediately, the solution turns black, indicating the formation of Pd clusters. The reaction proceeded at room temperature for 12 h. In separation process, the mixture was dried by vacuum rotary evaporator and washed with a large amount of methanol and acetone. The Pd₅ nanoclusters was obtained by extracting with CH₂Cl₂.

Synthesis of Pd₄ nanoclusters

The Pd₄ nanoclusters was obtained by different separation from Pd₅ nanoclusters. After the same reaction proceed as Pd₅ nanoclusters, the mixture was washed by amount of MeOH and CH₂Cl₂ was used to extracted the Pd₄ nanoclusters. Then, the mixture was dried by vacuum rotary evaporator and acetone was added to extracted Pd₄ nanoclusters.

Synthesis of Pd₃ nanoclusters

The Pd₃ nanoclusters was obtained following the same synthesis method of Pd₅ nanoclusters, but with addition of excess NaBH₄ (60.0 mg, 1.58 mmol). In the separation part, the mixture was washed by massive MeOH and the Pd₃ was extracted from the mixture with acetone.

Synthesis of Pd₂ nanoclusters

The Pd₂ nanoclusters was obtained in the present of excess ligands (90.8 mg, 0.30 mmol). In the separation part, the mixture was washed by massive MeOH and the Pd₂ was extracted from the mixture by using acetone.

The synthesis of Pd₅/C, Pd₄/C, Pd₃/C and Pd₂/C nanocluster catalysts

500 mg activated charcoal was dispersed in a mixture of 20 mL CH₂Cl₂ and 20 mL EtOH with a string of 500 rpm. Equivalent nanoclusters were added as 0.5 wt% Pd/C string for 6 h. The nanocluster catalysts were dried in vacuum overnight.

Catalysis test

The catalyst test was conducted in the autoclave. Approximately 50.0 mg catalyst and 20 μL substrates were placed into a 25 mL autoclave with 10 mL toluene. The system was purged with H₂ flow to remove air, and then pressurized by 1.0 MPa H₂. After reaction, the product mixture was analyzed by gas chromatography. The product was further confirmed by gas chromatography-mass spectrometry. Conversion and selectivity are determined by external standard method and the calculations are shown as follows:

$$\text{Conversion of CAL(\%)} = \frac{\text{moles of converted CAL}}{\text{initial moles of CAL}} * 100\%$$

$$\text{Selectivity of HCAL(\%)} = \frac{\text{moles of HCAL}}{\text{moles of converted CAL}} * 100\%$$

Characterization

UV-vis absorption spectroscopy (Uv-vis)

UV-vis spectrum was performed on a Metash UV-8000s spectrophotometer (dissolved in dichloromethane) at room temperature.

Electrospray ionization mass spectrum (ESI-MS)

The ESI-MS of the Pd_n nanocluster was tested by Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (SolariX XR-15T), and the nanocluster was dissolved

in dichloromethane. A drop of solvents was added in a mixture of toluene and methanol (v: v= 1:1).

High Angle Annular Dark Field - Scanning Transmission Electron Microscopy (HAADF-STEM)

The HAADF-STEM was performed on a Titan Themis ETEM G3 transmission electron microscope under low temperature by the liquid nitrogen. The samples were prepared by dropping an ethanol dispersion of samples onto carbon-coated copper grids and immediately evaporating the solvent.

X-ray photoelectron spectroscopy (XPS)

XPS data were recorded on a Thermofisher Escalab 250 Xi⁺ spectrometer using a standard Al K α mono-chromated flood source (150 W, pass energy = 200 eV, spot size = 500 μ m). All binding energies were referenced to C1s peak at 284.8 eV.

Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)

The concentration of palladium was determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) on a PerkinElmer ICP-OES 7300DV.

Attenuated Total Reflection IR (ATR-IR)

The ATR data were collected at Bruker's Platinum ATR.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was conducted on a TG-Q50 (TA) thermal analyzer heated from room temperature to 120 °C at a rate of 10 °C min⁻¹ in N₂ and kept for 10 minutes to remove water. Then it was heated from 120 °C to 700 °C at a rate of 10 °C min⁻¹ in N₂.

Gas chromatograph- mass spectrometer (GC-MS)

The hydrogenation products are analyzed by the Agilent GC-MS and GC (7890B) equipped with DB-35MS capillary column.

Density functional theory (DFT) calculations

The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form and a cutoff energy of 600 eV for planewave basis set were adopted. A 2 \times 2 \times 2

Monkhorst-Pack grid was used for sampling the Brillouin zones at structure optimization. The ion-electron interactions were described by the projector augmented wave (PAW) method. The convergence criteria of structure optimization were chosen as the maximum force on each atom less than 0.01 eV/Å with an energy change less than 1×10^{-5} eV.

Table S1. The ICP-OES analysis of catalysts.

Entry	Catalysts	Pd (wt%)
1	Pd ₂ /C	0.51
2	Pd ₃ /C	0.53
3	Pd ₄ /C	0.51
4	Pd ₅ /C	0.57

Table S2. The XPS element analysis of catalysts.

Catalysts	Fraction of Components	
	Pd ²⁺	Pd ^{δ+}
Pd ₂ /C	83.3%	16.7%
Pd ₃ /C	46.3%	53.7%
Pd ₄ /C	59.2%	40.8%
Pd ₅ /C	33.8%	66.2%

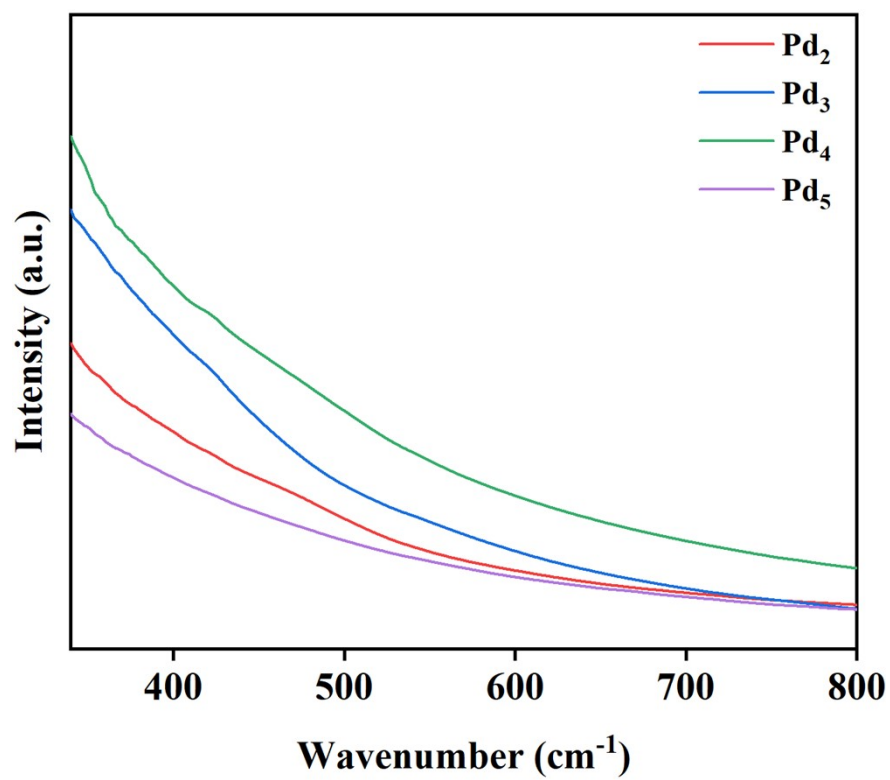


Figure S1. Uv-vis spectra of different Pd_n nanoclusters.

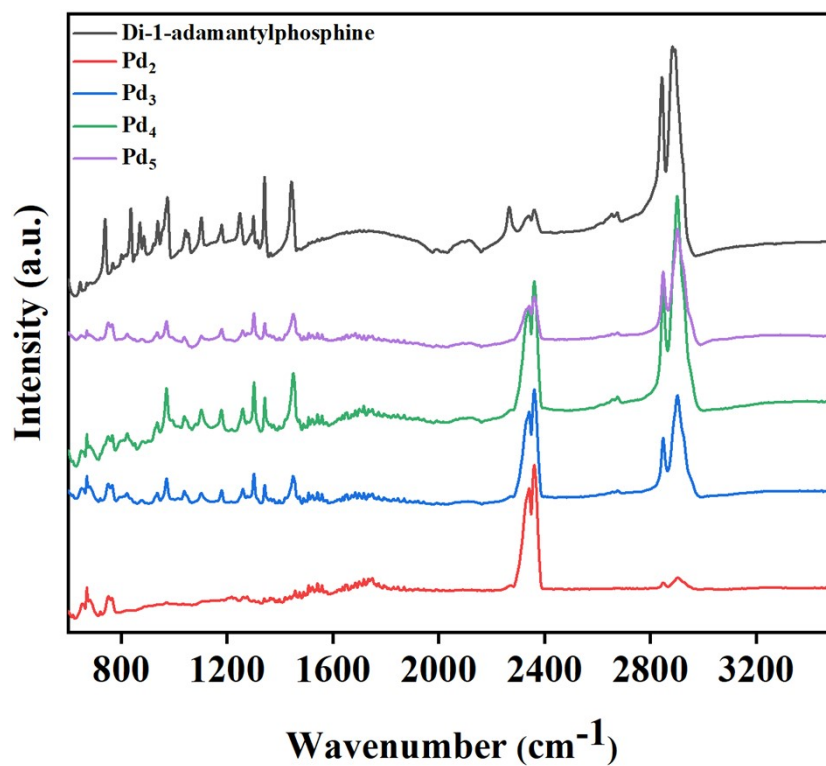


Figure S2. ATR-IR spectra of different Pd_n nanoclusters and Di-1-adamantylphosphine.

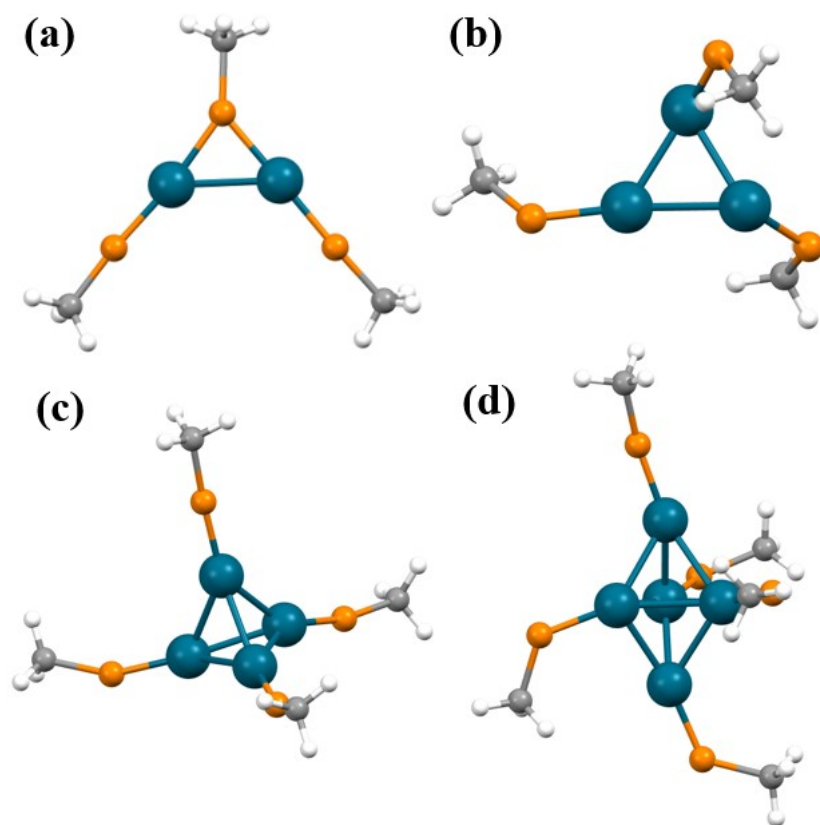


Figure S3. The optimized structures of (a) Pd₂, (b) Pd₃, (c) Pd₄ and (d) Pd₅ nanoclusters based on DFT calculations.

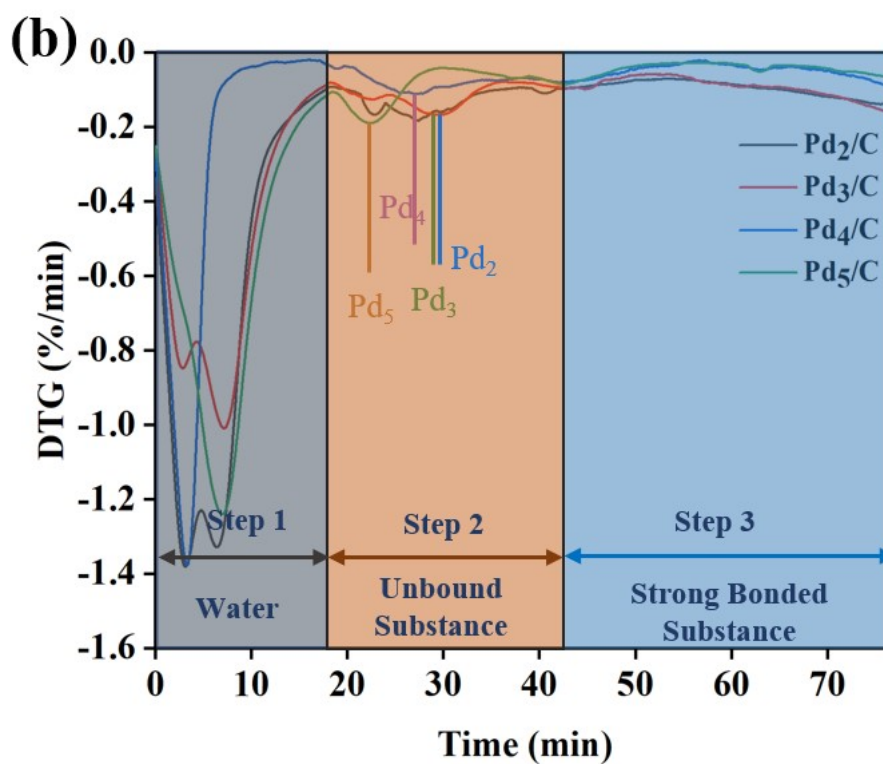
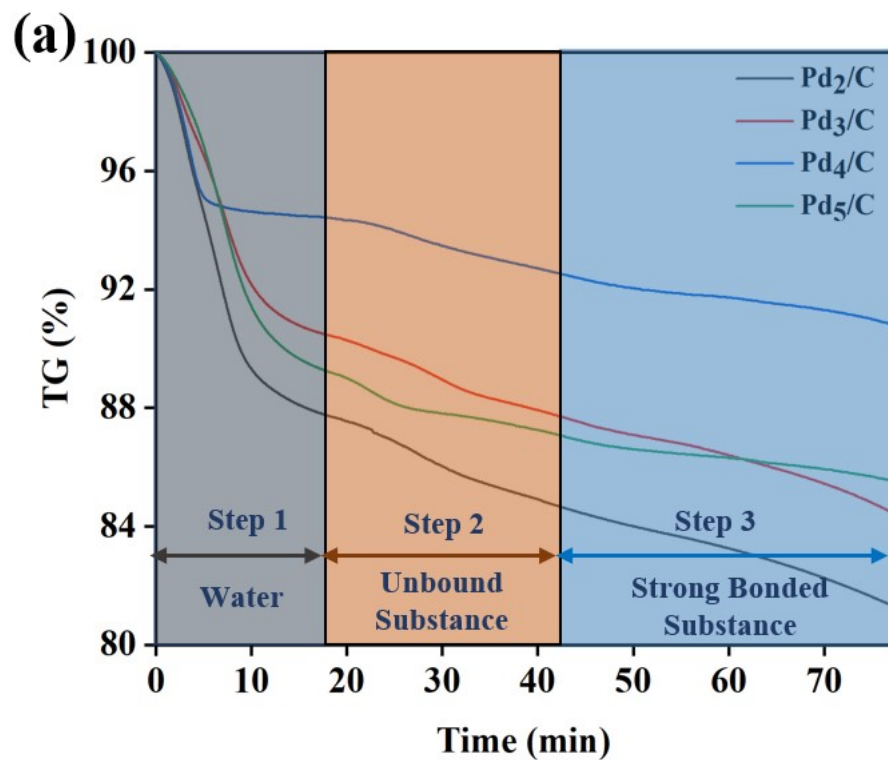


Figure S4. Thermogravimetric analysis of catalysts. (a) TG curve. (b) DTG curve.

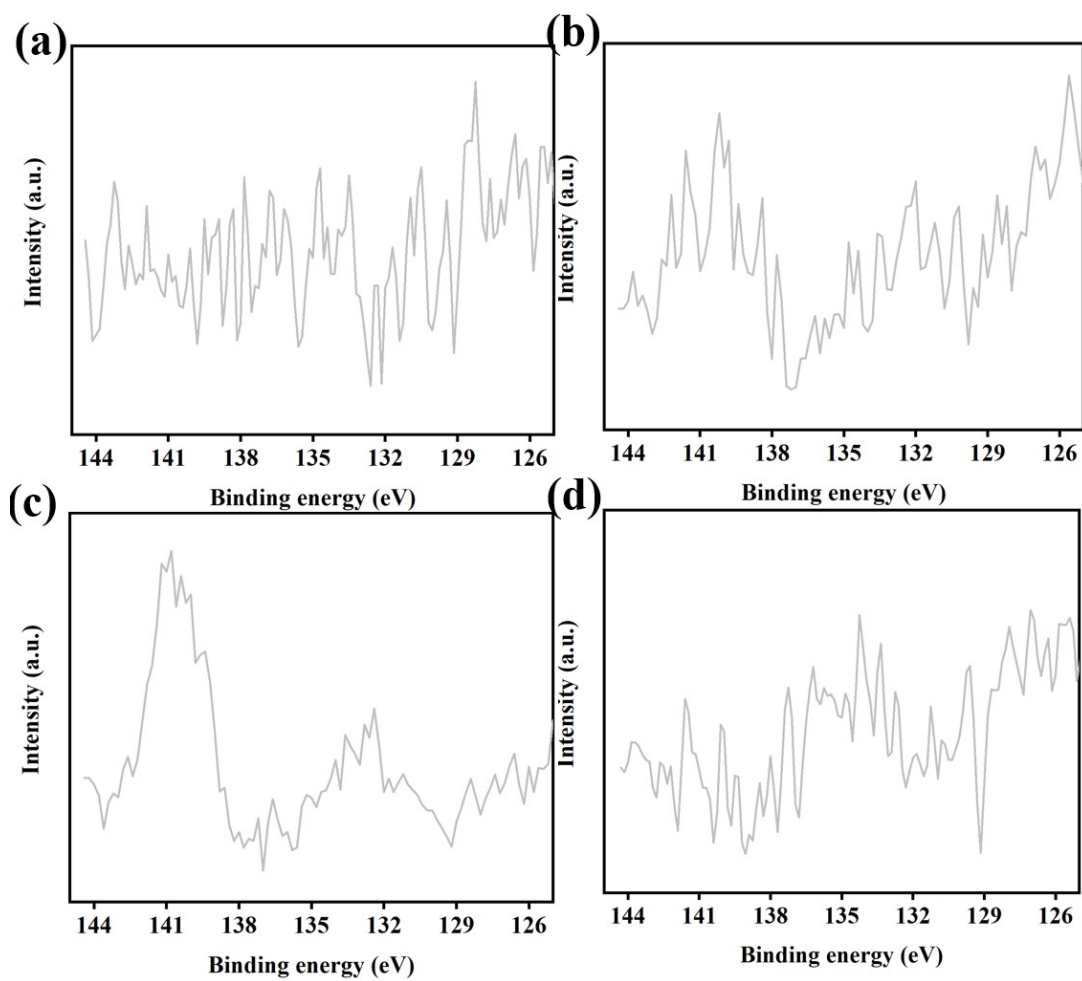


Figure S5. High resolution XPS analysis of Pd 2p. (a) Pd₂/C; (b) Pd₃/C; (c) Pd₄/C; (d) Pd₅/C.

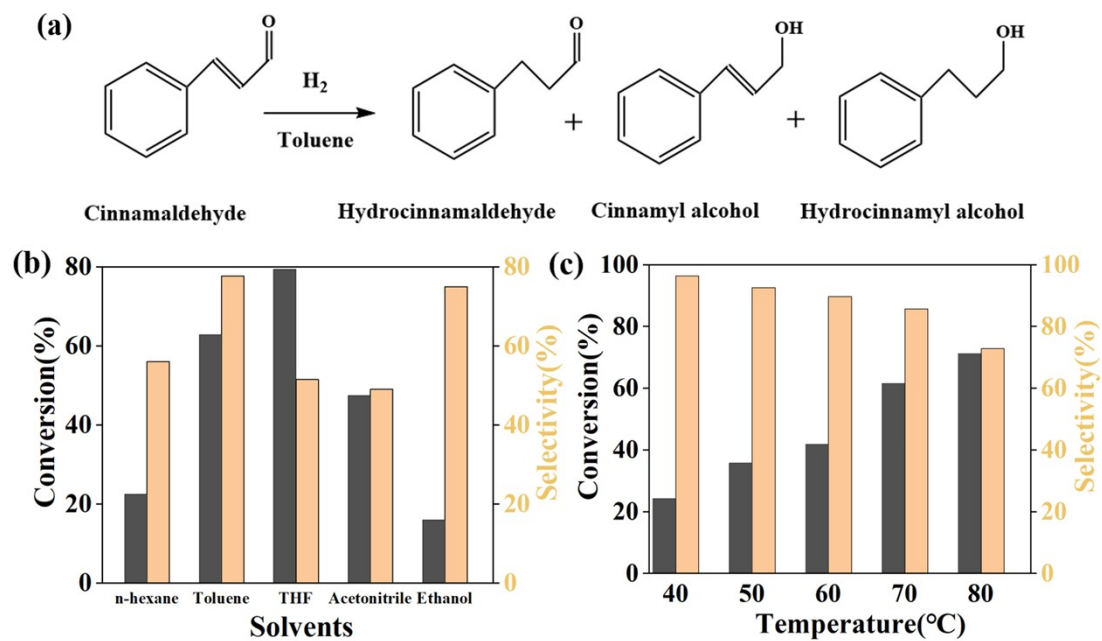


Figure S6. (a) Reaction products of the hydrogenation of cinnamaldehyde. (b) Catalytic tests of Pd₅/C in different solvents. Conditions: 20 mg catalysts, 100 μL substrates, 60 °C, 60 min, 1 MPa H₂, 1000 rpm. (c) Catalytic tests of Pd₅/C under different temperature. Conditions: 20 mg catalysts, 100 μL substrates, 10 mL toluene, 4 h, 1 MPa H₂, 1000 rpm.

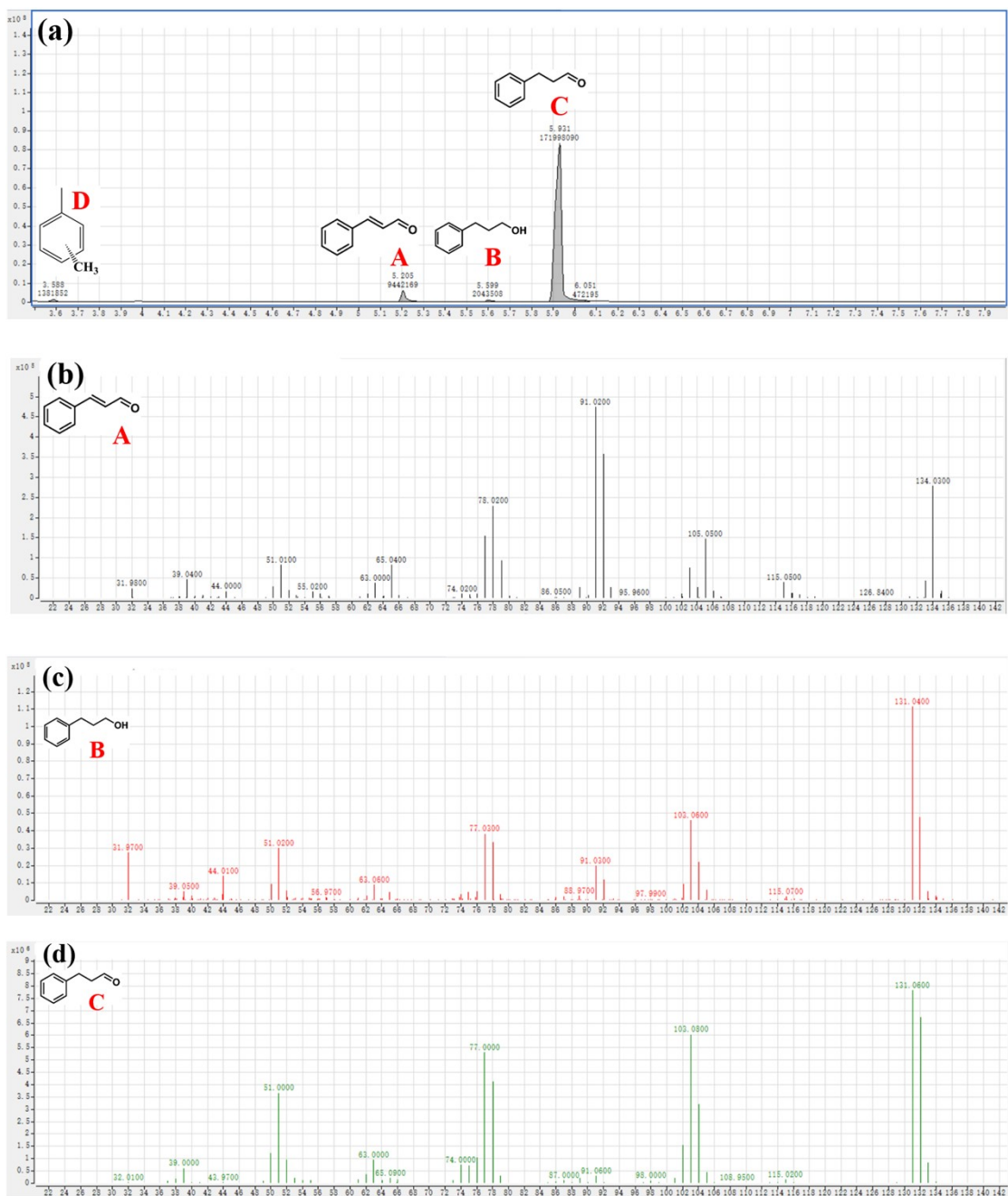


Figure S7. (a) Gas chromatography of the solution after catalytic reaction and the mass spectra of corresponding products (b) cinnamaldehyde, (c) hydrocinnamyl alcohol and (d) hydrocinnamaldehyde. The D (xylene) was from methylbenzene.