

Electronic Supplementary Information

Atomic Layer Deposition–Created Sacrificial Template for the Construction of MIL–53 Shell to Increase Selectivity in Hydrogenation Reactions

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Experimental Procedures

Materials: All the reactants are of analytical grade and were used without further purification. Cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), PdCl_2 , NaBH_4 and NaOH were purchased from Sinopharm Chemical Reagent Co. Ltd. trimethylaluminum and diethylzinc were purchased from Macklin. The atomic layer deposition (ALD) process was carried out in a hot-wall, closed chamber-type ALD reactor. Furfural, cinnamaldehyde, cuminaldehyde, octanol and glycol were analytical grade and were supplied from Shanghai Macklin Biochemical Co. Ltd. Deionized water was employed in this work.

Sample Preparation

Preparation of the CeO_2 spheres: 1 g of $\text{Ce}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ was dissolved in 1 ml of deionized water. After that, 30 ml of ethylene glycol and 1 ml of acetic acid was added under magnetic

stirring. The mixture was stirred for 45 min before being transferred into a 50 mL Teflon-lined autoclave. Then the autoclave was maintained at 180 °C for 200 min. After cooling to room temperature naturally, the product was washed by water and ethanol several times, and dried in a vacuum at 80 °C for 12 h.

Preparation of CeO₂/Pd: 150 mg of as-prepared CeO₂ was added to 100 ml of deionized water and sonicated. Then 0.5 ml of PdCl₂(1 g/100 ml) solution was added and stirred for 1 h. After that, the pH of the slurry was adjusted to neutral with NaOH and aged for 30 min. 2 ml of NaBH₄(10 mg) aqueous solution was added dropwise under stirring. After 10 min, the product was washed by water several times, and dried in a vacuum at 80 °C for 12 h.

Preparation of CeO₂/Pd@Al₂O₃: The deposition of Al₂O₃ onto CeO₂/Pd surface was achieved by means of atomic layer deposition (ALD). Prior to the ALD process step, the CeO₂/Pd was dispersed in ethanol by ultrasonic agitation and then added dropwise onto a quartz wafer. After being air-dried, the Al₂O₃ layer was deposited at 125 °C using trimethylaluminum (TMA) and deionized H₂O as the aluminum and oxygen source, respectively. The obtained sample was denoted as CeO₂/Pd@Al₂O₃-n, where n represents the number of ALD cycles.

Preparation of CeO₂/Pd@MIL-53: In a typical synthetic procedure, 10 mg of CeO₂/Pd@Al₂O₃ and 10 mg of terephthalic acid were added to a glass bottle containing a mixed solvent of DMF/H₂O (8 mL, 1:1 v/v). The reaction was carried out at 60 °C for 24 h with medium stirring. Then the product was washed with DMF and ethanol three times, and dried in a vacuum at 60 °C for 12 h.

Preparation of CeO₂/Pd@ZnO: The ZnO layer was deposited at 125°C using Diethylzinc and deionized H₂O as the zinc and oxygen source, respectively.

Preparation of CeO₂/Pd@Zn-MOF: In a typical experiment, 2-methylimidazole (3.66M) and CeO₂/Pd@ZnO (0.015g) were in sequence added to a Teflon-lined stainless-steel autoclave (25 mL) containing 10 mL of methanol. After sonication for 1 min, the white powder was

aged for 20 min at room temperature. Finally, the product was collected by centrifugation and washed by fresh DMF and ethanol for several times, and dried in a vacuum at 60°C for 12 h.

Sample Characterizations

The as-prepared samples were characterized by X-ray powder diffraction (XRD) on a Japan Rigaku D/Max- γ A rotating anode X-ray diffractometer equipped with Cu K α radiation ($\lambda=1.54178$ Å). The morphology and structure of samples were studied by transmission electron microscopy (TEM) (JEM 2100) and high resolution TEM (JEOL 2100F), and scanning electron microscopy (SEM-SU8010) equipped with an energy dispersive X-ray spectrometer (EDS). Fourier transform infrared (FT-IR) spectroscopic analysis was carried out using pressed KBr disks in the region of 4000-400 cm⁻¹. The nitrogen adsorption-desorption measurements were performed on a Micromeritics Tristar II 3020 instrument at 77 K. All the samples were degassed at 200°C under vacuum for over 6 h. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. The Pd content in catalyst was determined by inductively coupled plasma mass spectrometer (ICP-MS, Thermo Scientific XSeries-2). X-ray photoelectron spectra (XPS) were taken using a ThermoFisher ESCALABXi+ equipped with a polychromatic Al source. To achieve Pd information, the etching is carried out with monatomic mode by Ar sputtering under the conditions of a background vacuum of 2.0×10^{-8} mbar. The ion energy is controlled at 4000 eV and the etching time is 60 seconds.

Catalyst Tests

The experiments for hydrogenation of aldehydes (furfural, cinnamyl aldehyde and cuminaldehyde) was conducted in an autoclave reactor made of 316 stainless-steel with a volume of 10 mL. Typically, the aldehydes (0.04 g), solvent (4.0 g) and the catalyst (20 mg) were loaded into the reactor at room temperature. The reactor was then purged with N₂ (99.99%) for 3 times, and then pressurized with hydrogen. The reactor was heated to the

required temperature in less than 10 min and held for a certain time that will be detailed in the text. After finishing the experiments, the reactor was quenched and the liquid products were extracted by centrifugation for the further analysis with a GC-MS-2020 plus (Shimadzu) equipped with a Wax pillar column (length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 μm). The temperature of the column was initially maintained at 50°C for 3 min and then was then heated to 250°C with a ramping rate of 10°C/min and maintained at 250°C for 3 min. The products were qualitatively analysed with a standard library (NIST MS Search 2014) and quantified by an external standard method. The conversion of aldehydes and the yield of products were calculated by the following equations:

$$\text{Conversion of aldehydes (\%)} = \frac{\text{Mole of aldehydes consumed}}{\text{Mole of aldehydes loaded}} \times 100\% \quad (1)$$

$$\text{Yield of the product (\%)} = \frac{\text{Mole of the product produced}}{\text{Mole of aldehydes loaded}} \times 100\% \quad (2)$$

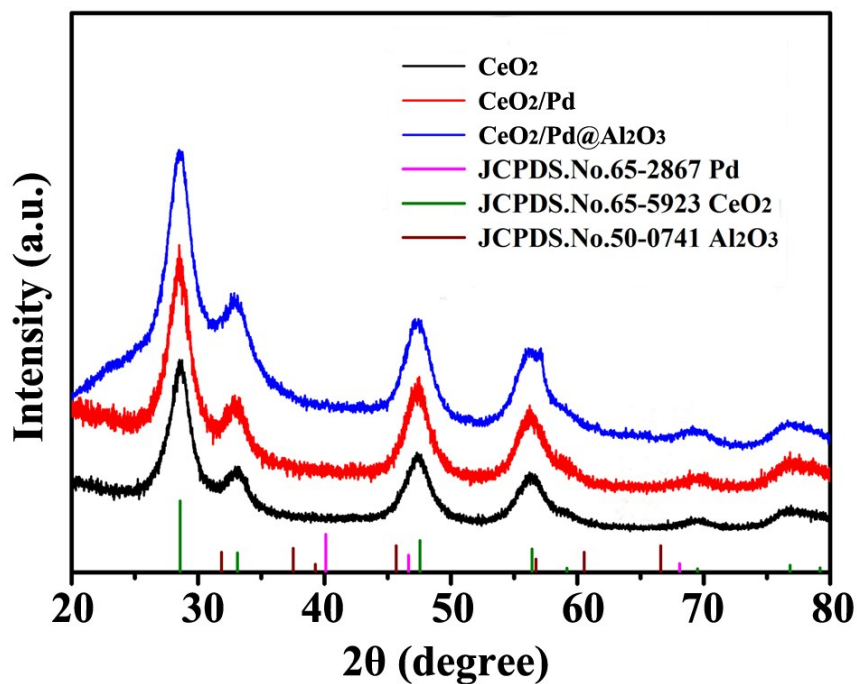


Figure S1. XRD patterns of CeO_2 , CeO_2/Pd and $\text{CeO}_2/\text{Pd}@Al_2O_3$ samples.

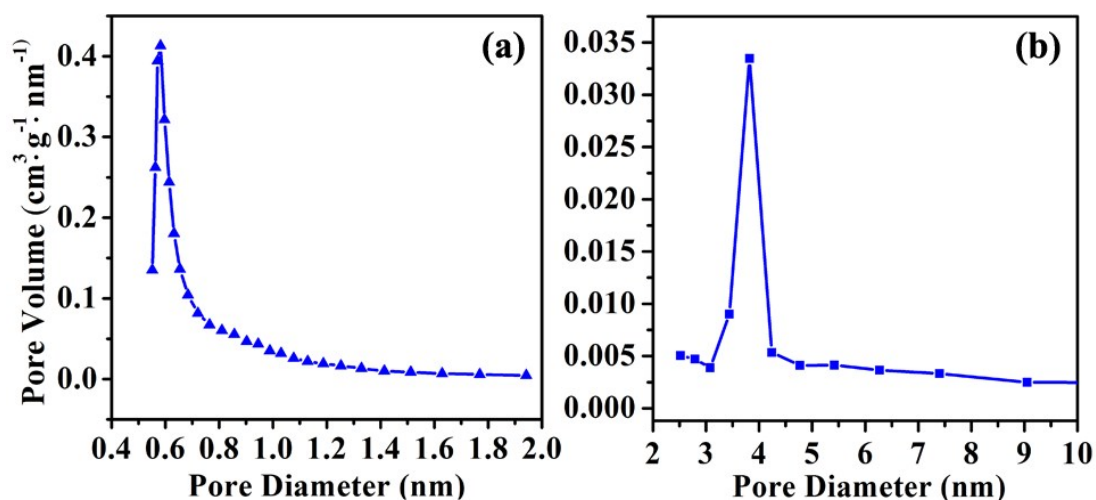


Figure S2. The BJH pore size distribution of the $\text{CeO}_2/\text{Pd}@MIL-53(\text{Al})$ sample.

The corresponding pore size distribution curve, determined from the desorption branches using the BJH method, is shown in Figure S2. They clearly confirm that the $\text{CeO}_2/\text{Pd}@MIL-53(\text{Al})$ sample shows bimodal size distributions of pores, which are composed of the micropores and mesopores.

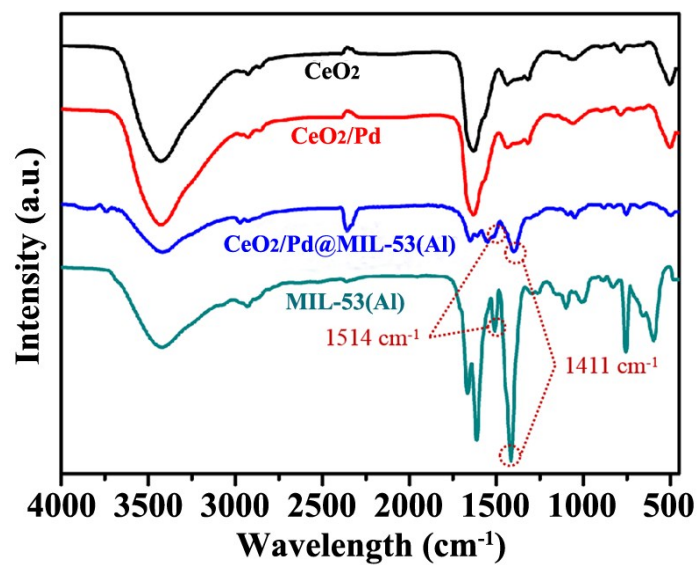


Figure S3. The FT-IR spectra of CeO₂, CeO₂/Pd, CeO₂/Pd@Al₂O₃ and CeO₂/Pd@MIL-53(Al).

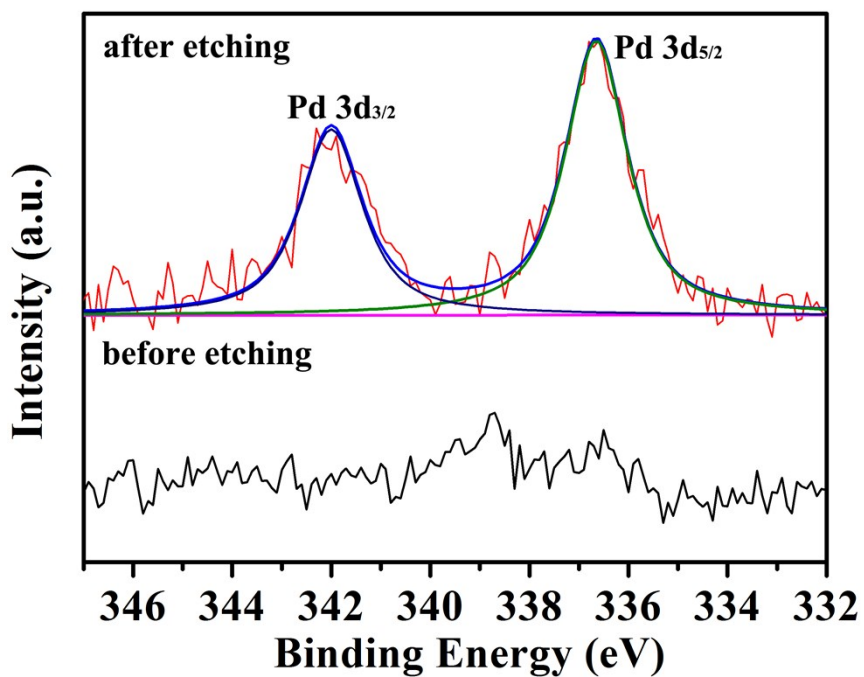


Figure S4. XPS spectra of Pd before and after etching for CeO₂/Pd@MIL-53(Al).

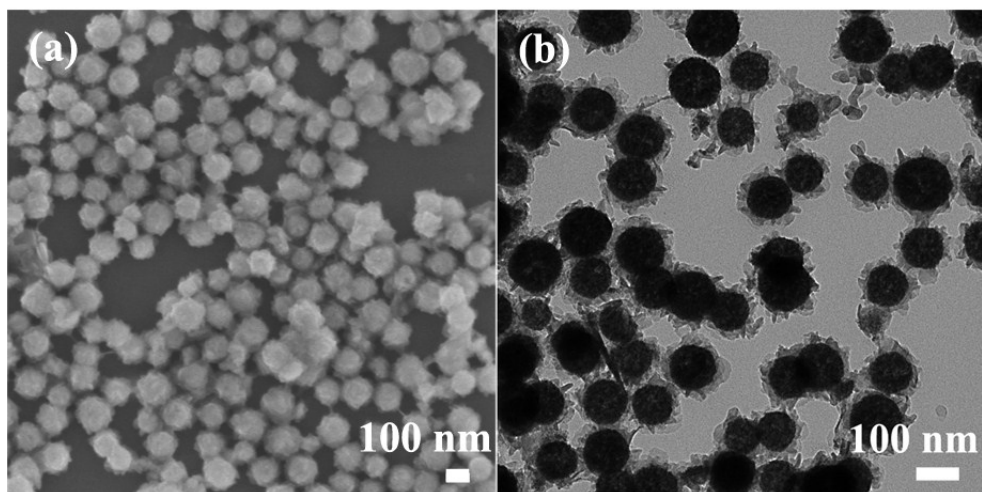


Figure S5. SEM (a) and TEM images (b) of $\text{CeO}_2/\text{Pd}@MIL-53(\text{Al})$.

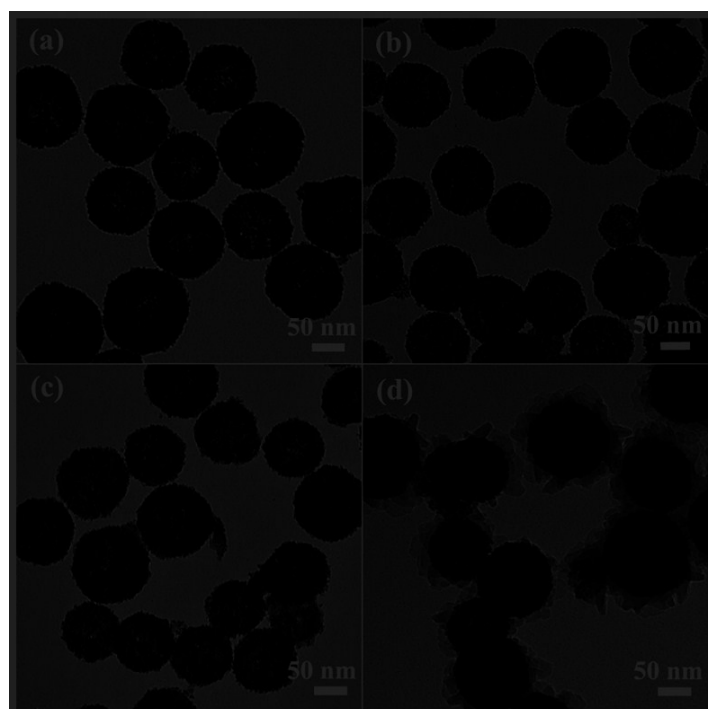


Figure S6. TEM images of CeO_2 (a), CeO_2/Pd (b) and $\text{CeO}_2/\text{Pd}@Al_2O_3$ (c), $\text{CeO}_2/\text{Pd}@MIL-53(\text{Al})$ samples.

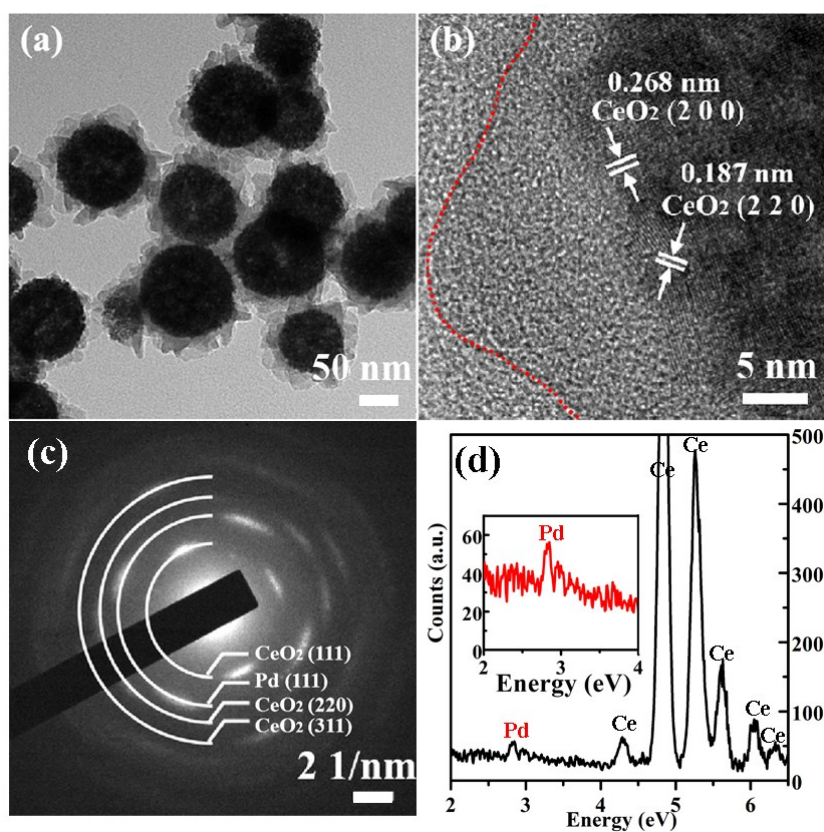


Figure S7. TEM (a), HRTEM (b) images (c) SAED pattern and EDX (d) of $\text{CeO}_2/\text{Pd}@MIL-53(\text{Al})$.

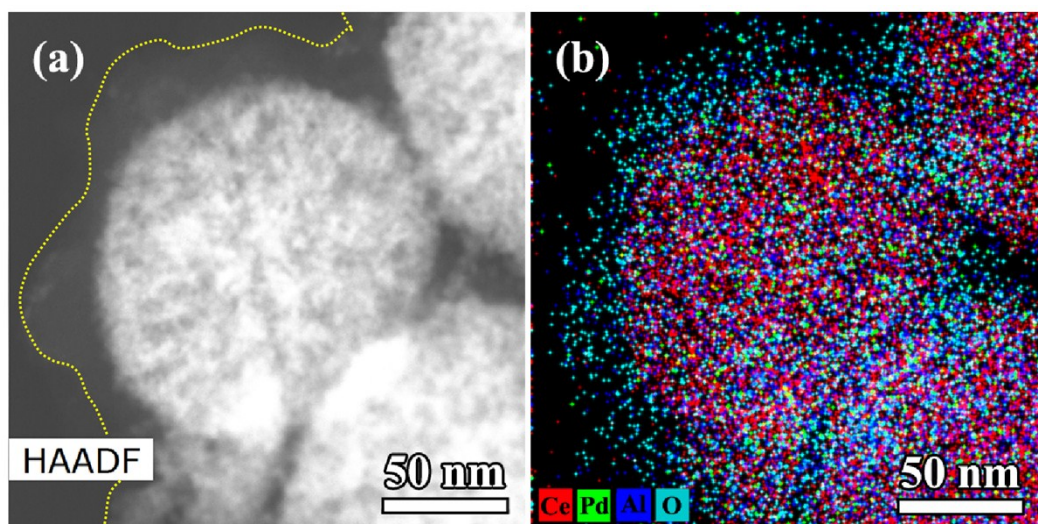


Figure S8. STEM (a) and elemental mapping (b) of $\text{CeO}_2/\text{Pd}@MIL-53(\text{Al})$. The dashed line in (a) is the outline of MIL-53(Al).

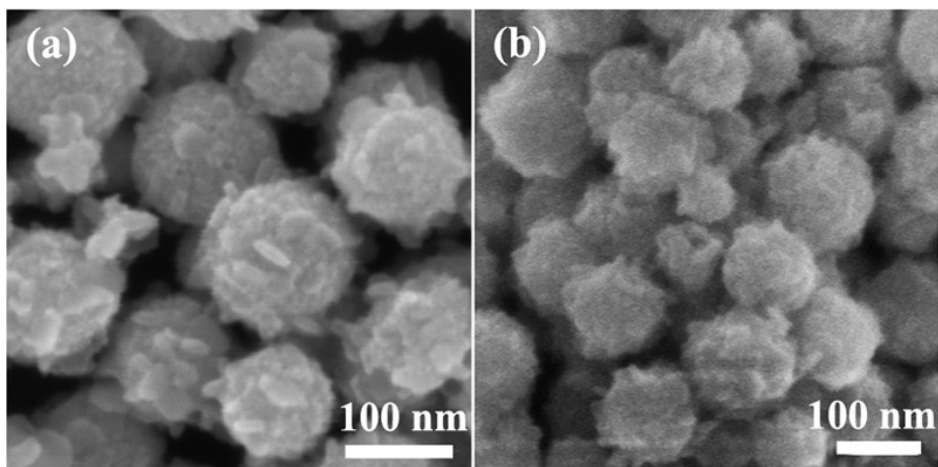


Figure S9. SEM images of (a) $\text{CeO}_2/\text{Pd}@MIL-53(\text{Al})-200$, (b) $\text{CeO}_2/\text{Pd}@MIL-53(\text{Al})-50$.

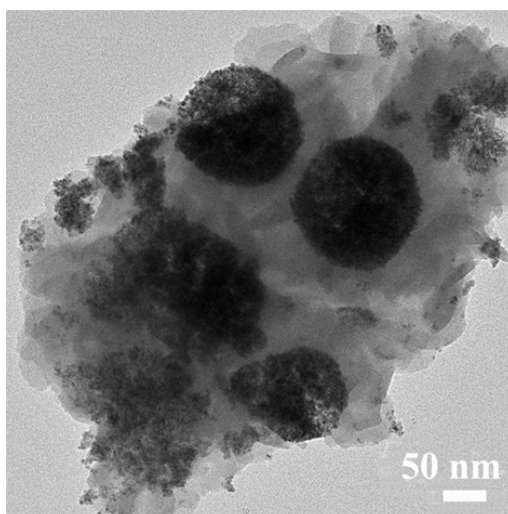


Figure S10. TEM image of $\text{CeO}_2/\text{Pd}@MIL-53(\text{Al})$, which is achieved by impregnation method, followed by reaction with terephthalic acid.

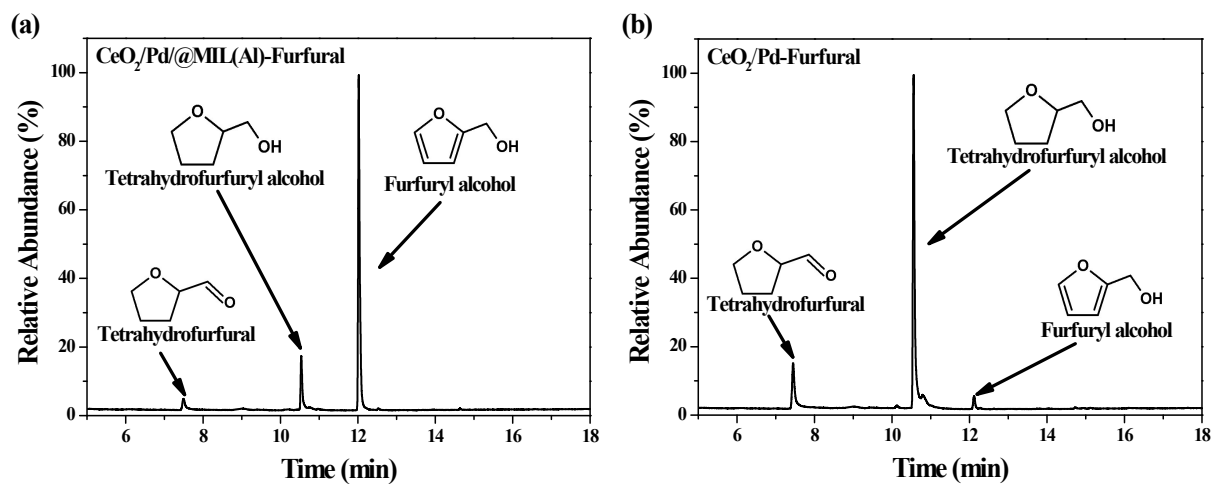


Figure S11. GC spectra of products distribution from the hydrogenation of furfural over (a) $\text{CeO}_2/\text{Pd}@MIL-53(\text{Al})$ and (b) CeO_2/Pd . Reaction conditions: furfural: 0.04 g, H_2O : 4 g, catalyst: 20 mg, $T = 80^\circ\text{C}$, reaction time: 120 min, H_2 : 6 MPa.

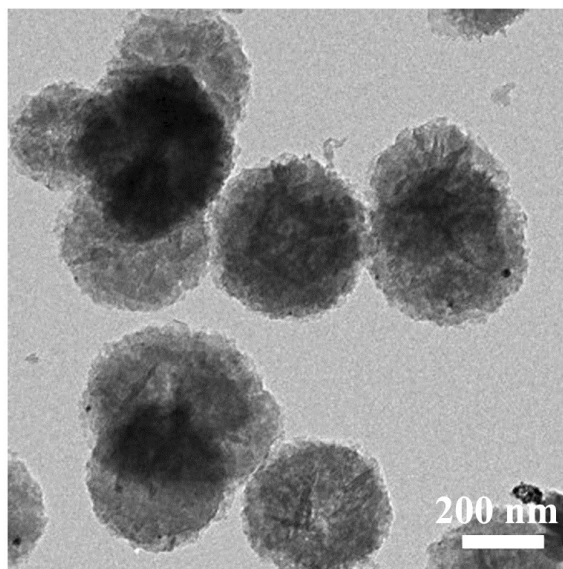


Figure S12. TEM image of $\text{Pd}@MIL-53(\text{Al})$.

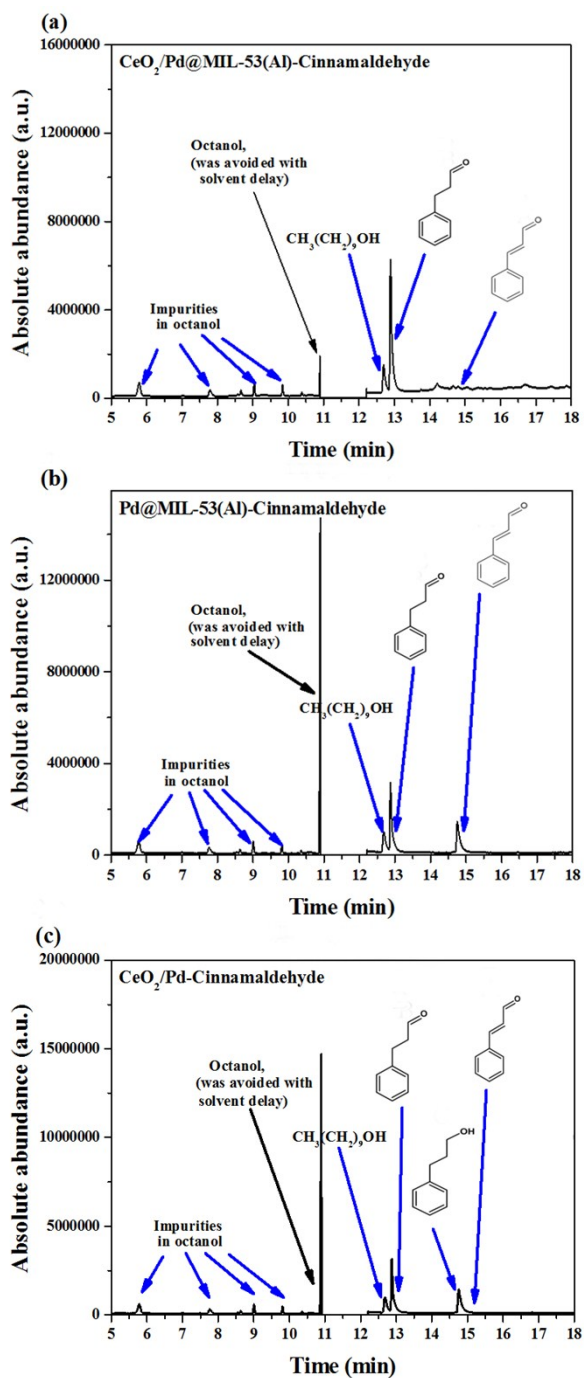


Figure S13. GC spectra of products distribution from the hydrogenation of cinnamaldehyde over (a) CeO₂/Pd@MIL-53(Al), (b) Pd@MIL-53(Al) and (c) CeO₂/Pd. Reaction conditions: cinnamaldehyde: 0.04 g, octanol: 4 g, catalyst: 20 mg, T = 25°C, reaction time: 240 min, H₂: 6 MPa.

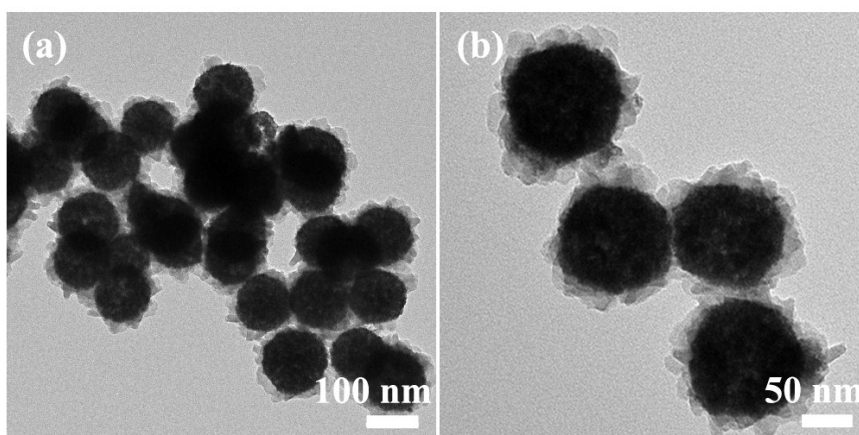


Figure S14. TEM images of $\text{CeO}_2/\text{Pd}@MIL-53(\text{Al})$ after 10 cycles hydrogenation reaction.

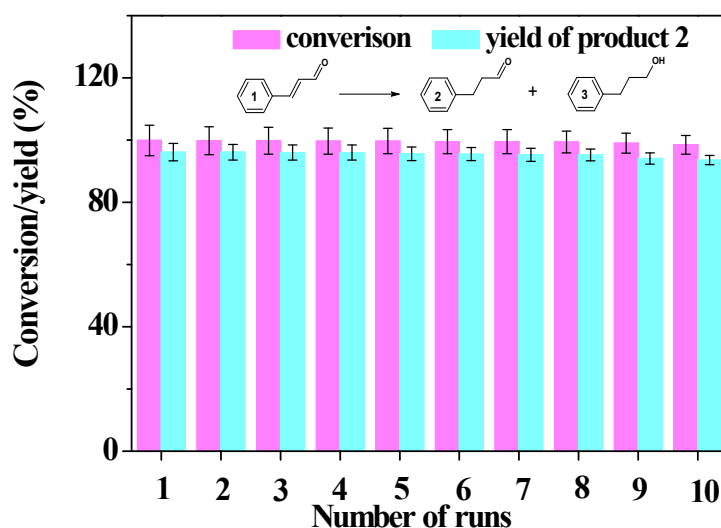


Figure S15. Recycling tests for $\text{CeO}_2/\text{Pd}@MIL-53(\text{Al})$ used in the hydrogenation of cinnamaldehyde in octanol.

Ten runs of the recycling experiments with $\text{CeO}_2/\text{Pd}@MIL-53(\text{Al})$ as the catalyst were performed in an autoclave reactor made of 316 stainless-steel with a volume of 10 mL. 0.04 g of cinnamaldehyde, 4.00 g of octanol and 20 mg of $\text{CeO}_2/\text{Pd}@MIL-53(\text{Al})$ were loaded into the reactor at room temperature (25°C). The reactor was purged with nitrogen (99.99%) for 3 times, and then pressurized with 6 MPa of hydrogen. The hydrogenation of cinnamaldehyde conducted at 25°C for 240 min. After finishing the experiments, the liquid and solid catalysts

was separated by centrifugation. The liquid was tested by GC-MS after dilution in acetone. The solid catalyst was washed with ethanol for 3 times, dried at 80°C for 4 h and re-used in the next turn.

Table S1. Hydrogenation of cinnamaldehyde in octanol^[a]

The reaction scheme shows the hydrogenation of cinnamaldehyde (labeled 1) to produce cinnamyl aldehyde (labeled 2) and cinnamyl alcohol (labeled 3). The structures are represented by benzene rings with a propenal or propyl alcohol side chain.

Entry	Catalyst	T (°C)	t (min)	Conversion/yield (%)		
				1	2	3
1	CeO ₂ /Pd@MIL-53(Al)	60	120	99.9	93.8	3.5
2	CeO ₂ /Pd@MIL-53(Al)	60	240	99.9	93.7	4.0
3	Pd@MOF(Al)	60	120	77.8	67.5	8.8
4	Pd@MOF(Al)	60	240	83.7	72.3	10.0
5	CeO ₂ /Pd	60	120	99.9	23.1	11.1
6	CeO ₂ /Pd	60	240	99.9	15.7	14.2

^[a]Reaction conditions: cinnamaldehyde: 0.04 g, octanol: 4.00 g, catalyst: 20 mg, H₂: 6 MPa.