

Electronic Supplementary Information

Sharp Size-Selective Catalysis in Liquid Solution over Pd Nanoparticles Encapsulated in Hollow Silicalite-1 Zeolite Crystals

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Experimental

Synthesis of HS-1 zeolite. Parent silicalite-1 zeolite was synthesized from the clear solution method with some modifications using a starting composition of 1 SiO₂:0.27 TPAOH:46 H₂O.²⁰ 15 g tetrapropylammonium hydroxide (TPAOH) aqueous solution (25 wt%), 48 mL H₂O and 15.4 mL tetraethoxysilane (TEOS) was mixed and stirred at room temperature for 5 h to ensure complete TEOS hydrolysis to form a clear solution. The gel was then crystallized in a 100 mL Teflon-lined steel autoclave at 160 °C for 48 h. The product was recovered and calcined to remove the template in static air at 823 K for 6 h and denoted as S-1. The resulting solid was treated with 0.3 M TPAOH solution in an autoclave at 160 °C for 24 h to obtain a hollow core of the silicalite-1.²¹ The resulting solid was recovered and calcined to remove the template in static air at 823 K for 6 h and denoted as HS-1.

Synthesis of Pd@HS-1. 0.25 g hollow silicalite-1 were added a mixture of ethylene diamine (EDA) (0.78 g, 0.013 mol) and carbon tetrachloride (CTC) (1.73 g, 0.011 mol). The resultant mixture was stirred at 90 °C for 6 hours. Then, the obtained product was washed with deionized water and ethanol for 10 times at least until supernatant became colorless, and dried at ambient temperature, resulting in a brown powder (denoted as PEC@HS-1). Then 930 μL Na₂PdCl₄ aqueous solution (0.0564 M) was added and stirred 24 hours at RT. Excess Pd²⁺ adsorbed at outside surface of the hollow zeolite particles was washed away to ensure exclusive loading of Pd nanoparticles inside the nanoreactor. Then 25 mL of 0.15 M sodium formate solution was added and the mixture was stirred for 5 h. Then the solid was recovered by centrifugation and washed with distilled water for five times. After drying at room temperature, Pd@hollow silicalite-1 composite was obtained and denoted as Pd@HS-1.

Synthesis of Pd/S-1. Pd/silicalite-1 with Pd metal clusters located on the external surface (denoted as Pd/S-1) was prepared for control experiments. 0.25 g silicalite-1 sample without calcination was added into 7.5 mL of dichloromethane, then the mixture was added with 0.25 mL 3-aminopropyltrimethoxysilane (APTMS), and the slurry was stirred for 16 h at room temperature. The APTMS functionalized zeolite powder was then repeatedly washed with dichloromethane for 5 times and dried in a vacuum. The samples obtained were loaded with Pd cluster using conventional method.

Size-selective hydrogenation. The size-selective catalysis was carried out in a Teflon-lined stainless steel reactor. Typically, 20 mg catalysts with Pd loading of 3 wt %, 0.5 mmol 3-methyl-2-butenal or cinnamaldehyde or 3,3-diphenylacrylaldehyde, and 7.5 mL H₂O were loaded into the reactor (total volume: 25 ml). The reactor was sealed and purged with high-purity H₂ for three times under stirring to replace the air. Then the reactor was sealed and H₂ pressure was adjusted to 1 MPa. The autoclave was heated to 100 °C and lasted for certain time. After reaction, the reactor was quenched in cold water. The resulting hydrogenation products were extracted with 5- ml ethyl acetate and analyzed by GC-2010 Plus.

Characterization. Scanning electron microscopy (SEM) images were obtained on a JEOL-6701F scanning electron microscope at 10.0 kV. Transmission electron microscopy (TEM) was carried out on a JEOL 2100F electron microscope operated at 200 kV. The XRD measurements were carried out in Shimadzu XRD-7000 diffractometer equipped with CuK α radiation (wavelengths $\lambda = 0.154$ nm). The hydrogenation products were measured using Shimadzu GC-2010 Plus. Nitrogen adsorption-desorption isotherms was obtained on Quantachrome Autosorb AS-1. Elemental analysis was obtained on Flash EA 1112. Thermogravimetric analysis (TGA) was performed on NETZSCH/STA 409 PC Luxx simultaneous thermal analyzer with a heating rate of 5 °C/min under an air flow rate of 20 mL/min. Leaching of Pd was characterized by ICPE (Shimadzu ICPE-9000). X-ray photoelectron spectroscopy was obtained on VG ESCA Lab 220i-XL equipped with Mg/Al ultra-high vacuum X-ray binode-system. The FTIR spectrum of the interior polymer dots was recorded on a Nicolet iN10-iZ10 infrared spectrophotometer in 4000-400 cm⁻¹ after HF etching.

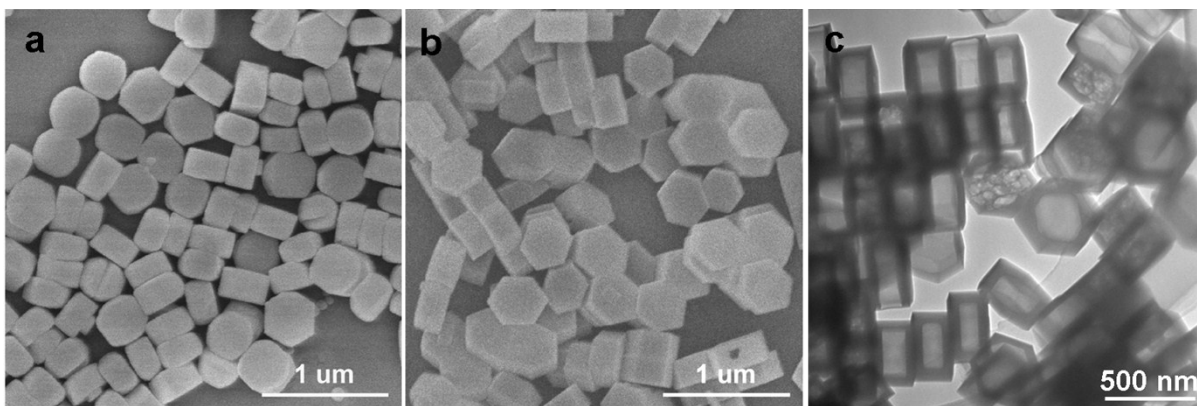


Fig. S1 SEM image of (a) S-1, (b) HS-1, and (c) TEM image of HS-1

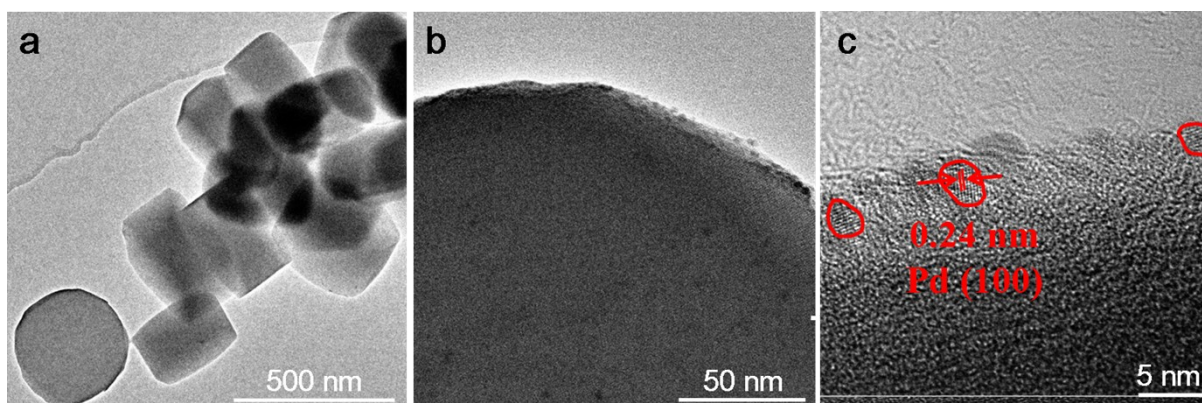


Fig. S2 TEM images of Pd/S-1 in low (a, b) and high (c) magnification

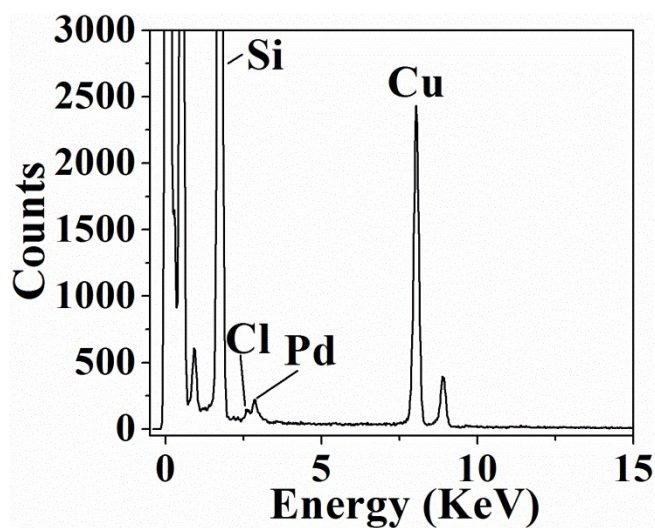


Fig. S3 EDX spectrum of Pd@HS-1

Table S1 Elemental analysis of Pd@HS-1

Element	Composition (wt %)
C	4.16
H	0.90
N	1.03

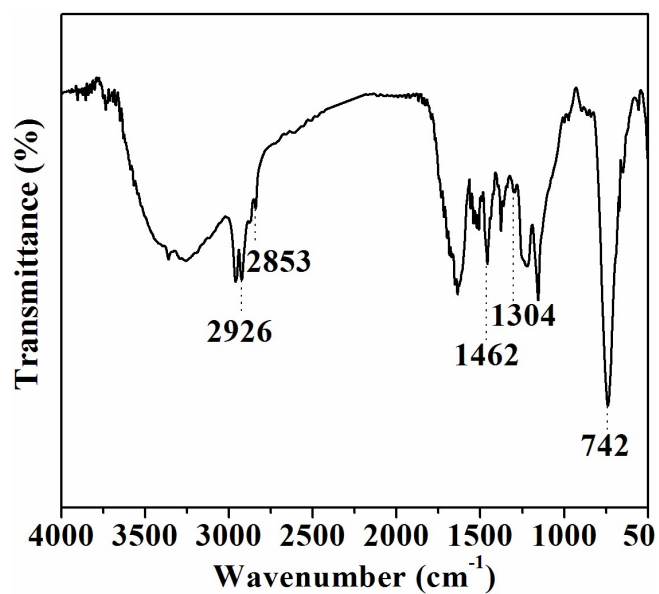


Fig. S4 FTIR spectrum of interior polymers

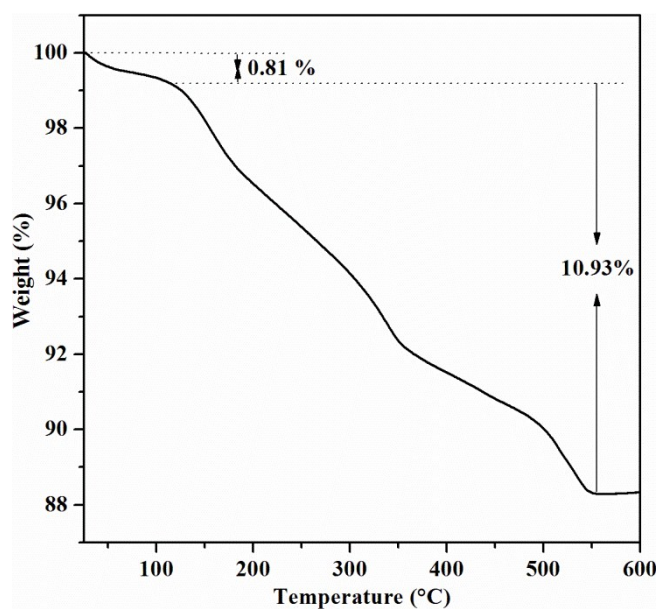


Fig. S5 TGA curve of Pd@HS-1

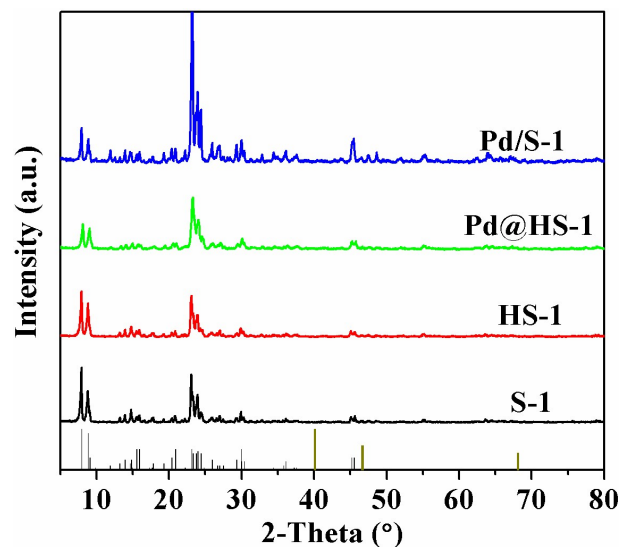


Fig. S6 XRD patterns of S-1, HS-1, Pd@HS-1 and Pd/S-1

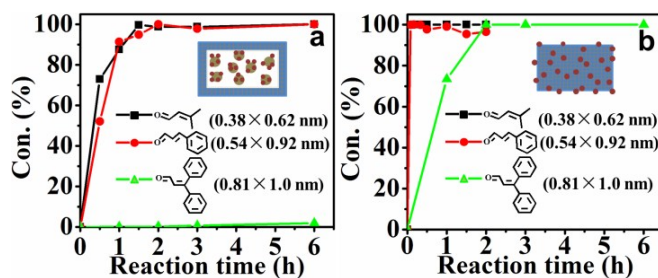


Fig. S7 Curves of conversion vs time of hydrogenation of olefin aldehydes over (a) Pd@HS-1 and (b) Pd/S-1.

Scheme S1 Hydrogenation reactions of (a) 3-methyl-2-butenal, (b) cinnamaldehyde and (c) 3, 3-diphenylacrylaldehyde

