Electronic Supporting Information

Selective Hydrogenation of C=C bond in α,β–Unsaturated Aldehydes and Ketones over Ultra-small Pd-Au Clusters

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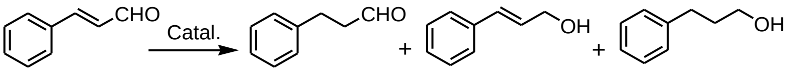
Experimental Section

Materials Synthesis. The Pd-Au clusters were prepared through a stepwise reduction of gold and palladium salts in THF by sodium borohydride at room temperature. 56 mg H_2PdCl_4 was dissolved in 15 mL THF at room temperature, and 31 μL phenylethanethiol was then added under stirring. 0.225 mmol Au-PA (Au–C≡C–Ph) was dropped into the solution and further stirred for 30 min. 5.65 mmol $NaBH_4$ (dissolved in 3 mL water) was rapidly added and the mixture was kept for 6 h. THF was removed via rotary evaporation; the crude product was thoroughly washed with methanol, and the Pd-Au clusters were extracted with CH_2Cl_2. The Pd-Au/CeO_2 catalyst was prepared by an impregnation method. 4 mg Pd-Au clusters was dissolved in 10 mL CH_2Cl_2, and 1.0 g CeO_2 was added. After stirring for 12 h at room temperature, the solid was collected by centrifugation and dried at 373 K under vacuum. ***Characterization.*** Scanning transmission electron microscopy (STEM) was performed on a JEOL ARM 200F operated at 200 kV. TEM was recorded on a Hitachi 7000 microscope.

Inductively coupled plasma–mass spectrometry was recorded on PerkinElmer ICP-MS NexION 300D, which showed that the metal loading on the catalyst was 0.35 wt.%.

Catalytic test. In a typical hydrogenation reaction, substrate (0.1 mL), Pd-Au/CeO_2 (50 mg), and 20 mL solvent were added into an autoclave (50 mL), and the reactor system was pressurized with H_2 to 10 Bar. The reaction was tested at 303 or 323 K for 18 h. After the reaction, the catalyst was separated by centrifugation, and the liquid product was extracted by ethyl acetate and analysed by a gas chromatograph and a mass spectrometer. The conversion of the reactant and selectivity of the products were determined on molar basis.

Table S1. Hydrogenation of cinnamaldehyde on the Pd-Au/CeO_2, Pd/CeO_2 and Au/CeO_2 catalysts.



1 2 3

Catalyst	Conversion (%)	Selectivity (%)		
		1	**2**	**3**
Pd-Au/CeO_2	93	85	3	12
Au/CeO_2	13	65	0	35
Pd/CeO_2	100	80	0	20

Reaction conditions: 0.1 mL cinnamaldehyde, 50 mg Pd-Au/CeO_2 catalysts, 20 mL dioxane, H_2 10 bar, 323 K, 18 h.

Obviously, the alloyed clusters (~1.8 nm) were more selective for the hydrogenation of the C=C bond in the substrate than the monometallic clusters with similar sizes (Pd ~1.9 nm, Au ~2.0 nm).

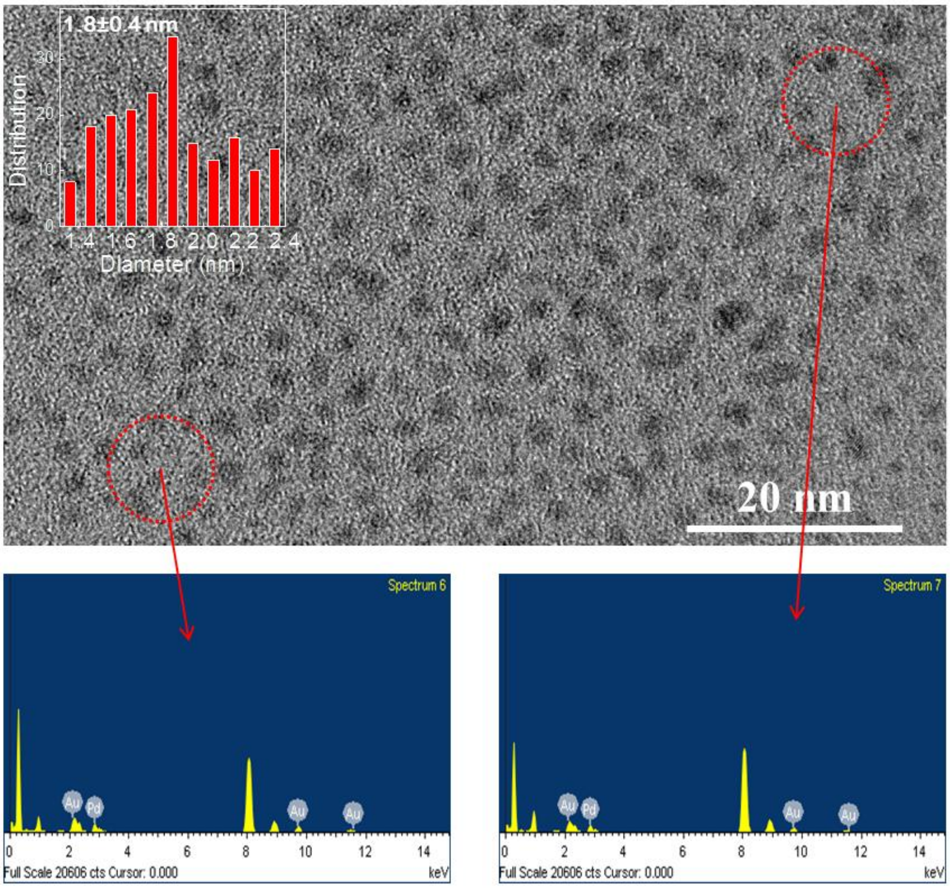


Figure S1. TEM image and EDX profiles of the as-prepared Pd-Au clusters. Inset is the size distribution.

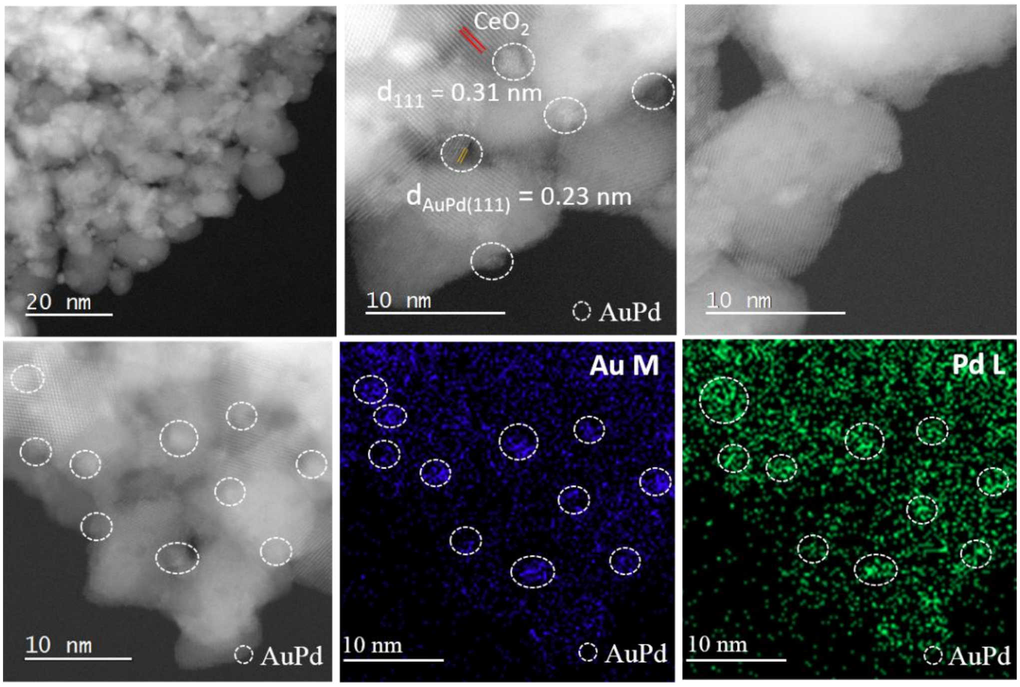


Figure S2. STEM images and EDS mapping of the Pd-Au/CeO_2 catalyst. Element mapping indicated that gold and palladium atoms are unfirmly distributed in the clusters, showing an alloy packing pattern.

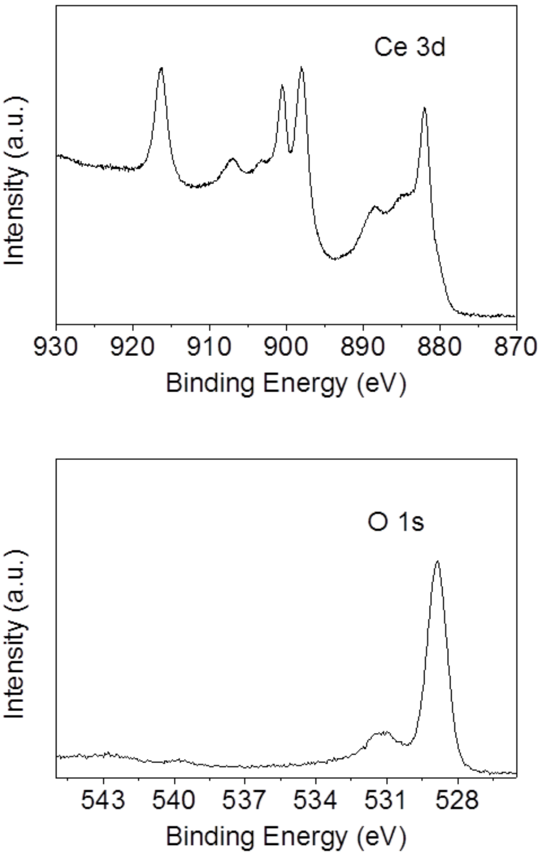


Figure S3. XPS spectra of Ce 3d and O 1s in the Pd-Au/CeO_2 catalyst.