

Supporting Information

Localized Surface Plasmon Resonance Assisted Photo-Thermal Catalysis of CO and Toluene Oxidation over Pd-CeO₂ Catalyst under Visible Light Irradiation

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1. Synthesis

All agents (AR grade) for the synthesis of the catalysts were from Aladdin Industrial Corporation, China.

Ce(NO₃)₃ solution (3 mL, 0.1 M) was added dropwise into the NH₃ and hexadecyl trimethyl ammonium bromide (CTAB) mixed solution (M_{NH3}: 0.004 M, M_{CTAB}: 0.025 M) under stirring. The obtained CeO₂·xH₂O colloid was washed twice by deionized water and then redispersed into 8 mL water.

The (PdO, CeO₂)·xH₂O colloid was prepared by adding H₂PdCl₄ solution (0.94 mL, 0.01 M) into the washed CeO₂·xH₂O colloidal solution. After that, 0.2 mL ice-cold NaBH₄ solution (0.06 M) was added to the above solution.

After that, Pd-CeO₂/Al₂O₃ catalysts were prepared by adding the inactive α-Al₂O₃ powder into the Pd-CeO₂ colloid and subsequently stirring for 5 min. The CeO₂/Al₂O₃ catalysts were obtained by adding the support into the CeO₂ colloidal solution

directly.

The obtained mixtures were all freeze-dried for 24 h and then calcined at 773 K for 6 h in the furnace to remove the remaining CTAB. The obtained yellowish PdO-CeO₂/Al₂O₃ catalysts were reduced by H₂ at 423 K for 90 min to get the gray Pd-CeO₂/Al₂O₃ powder (Pd: 1 wt %, CeO₂: 3 wt %). The CeO₂/Al₂O₃ catalyst (CeO₂: 3 wt %) was also calcined and H₂-reduced under the same condition.

The obtained yellowish PdO-CeO₂/Al₂O₃ catalyst powder and the gray Pd-CeO₂/Al₂O₃ powder were denoted as PCA-R and PCA, respectively. Similarly, the CeO₂/Al₂O₃ and H₂-reduced CeO₂/Al₂O₃ catalysts were denoted as CA and CA-R, respectively.

2. Catalyst characterization

The catalysts were investigated on a high-resolution transmission electron microscopy (HR-TEM, FEI TECNAIG2 F30) at 300 KV, the electron energy loss spectroscopy (EELS). During the EEL spectra acquisition, the incident electron beam was perpendicular to the ceria nanoparticles. The EELS data were post-processed in Digital micrograph. The X-ray photoelectron spectroscopy (XPS) was conducted with a Physical Electronics PHI5802 instrument using X-rays magnesium anode (monochromatic K_α X-rays at 1253.6 eV) as a source. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) experiments of the PCA-R catalysts were performed on a Shimadzu Corporation-ICP-7500.

Crystalline structure of the catalysts was characterized in the range of 20-80° (2θ)

through a D/MAX-RB X-ray diffraction diffractometer (XRD, Rigaku, Japan) using Cu K α radiation at a scan rate (2θ) of 5° min^{-1} , operated at 40 kV and 100 mA. The Raman spectroscopy was performed on a LabRAM HR 800 (HORIBA Jobin Yvon, France) spectrometer at room temperature (RT) and atmospheric pressure. The excitation wavelength of the laser is 532 nm.

UV-visible diffuse reflectance spectra (DRS) were obtained on a Cary 5000 UV-Visible near-infrared spectrophotometer (varian, USA) at room temperature, in which BaSO $_4$ was used as an internal reflectance standard. And the diffuse reflectance spectroscopy was transformed to the absorption spectra according to the Kubelka-Munk equation.

Diffuse reflectance infrared Fourier transform spectroscopic (DRIFTS) of CO adsorption was measured with a Fourier transform infrared spectroscopy (Thermo Scientific Nicolet IS50, USA). To determine the initial states of Pd species, the spectra of CO adsorption at 298 K were recorded after the sample was exposed to CO (1 vol %) in a nitrogen flow (100 mL min^{-1}) for 30 min and then purged with a nitrogen flow (100 mL min^{-1}) for 30min to remove the weak adsorbed CO. To obtain the spectra of CO adsorption under reaction conditions, the carbonate species should firstly be removed by thermal treating under N $_2$ (100 mL min^{-1}) purging at 573 K for 30 min. After that the catalyst was exposed to CO (1 vol %) in N $_2$ flow (100 mL min^{-1}) for 30 min to adsorption and then purged by N $_2$ flow (100 mL min^{-1}) for 15 min to remove the weak adsorbed carbon monoxide. The spectra of CO adsorption under reaction conditions were recorded as the sample was exposed to CO (0.1 vol %) + O $_2$

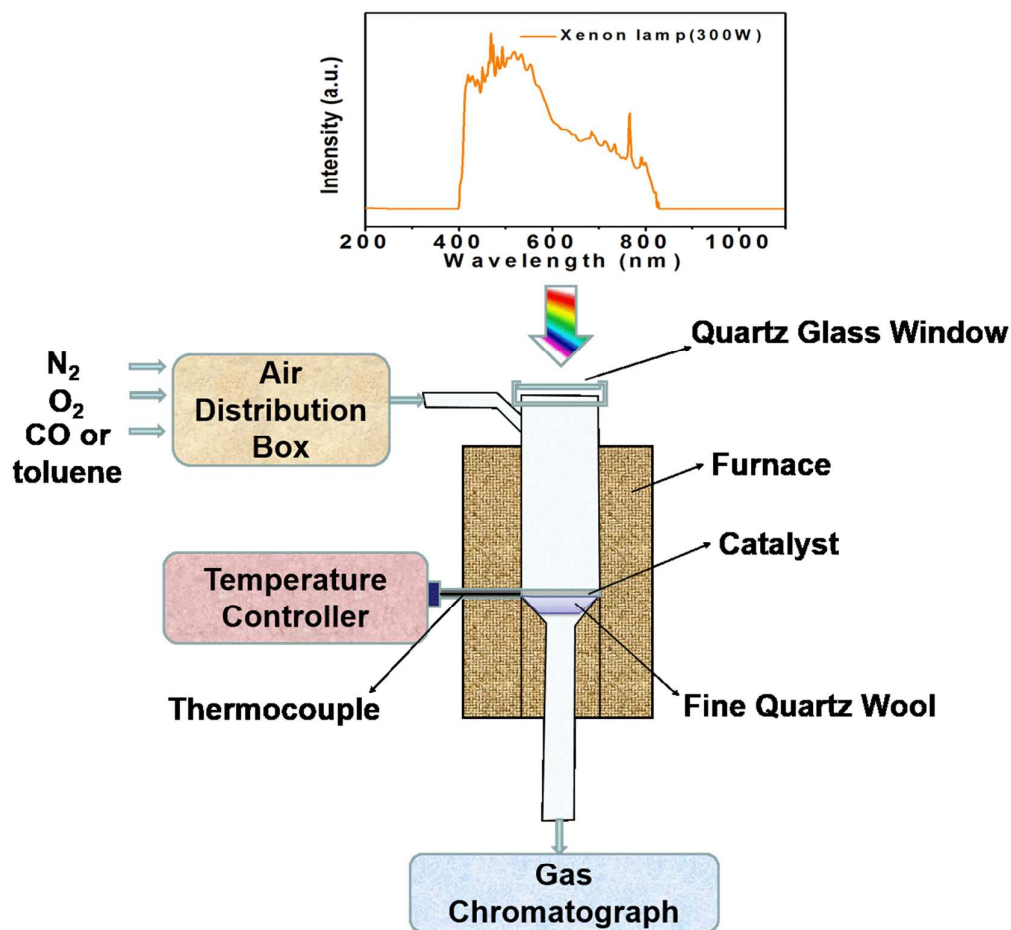
(21 vol %) + N₂ (79 vol %) flow for 30 min at each temperature.

3. Catalytic performance tests

The experimental apparatus in Scheme 1 was used to measure the activities of different catalysts for CO and toluene oxidation reaction. The fixed-bed flow reactor with inner diameter of 15 mm has a quartz window to allow visible-light irradiation. The Xeon lamp (100-300 W, CEAULIGHT, Beijing) with a 400-800 nm cutoff filter was used as visible-light source, of which the emission spectra were recorded by an S-4100 UV-Visible spectrophotometer (SCINCO, Korea) and shown in the inset of Scheme 1. The light intensity onto the sample ranged from 40 to 145 mW cm⁻², measured by a CEL-NP2000 optical power and energy meter (CEAULIGHT, Beijing).

100 mg catalyst was put into the reactor. The gas mixture containing 80% N₂, 20% O₂, 1000 ppm CO or 500 ppm toluene with a total flow rate of 100 mL min⁻¹ was used as the reactant gas. CO and CO₂ concentrations were analyzed by a Fourier transform infrared spectroscopy (Thermo Scientific Nicolet iS10, USA) equipped with a 2-meter gas cell. The spectral resolution was 4 cm⁻¹. The concentrations of toluene were analyzed by a GC-7920 gas chromatograph (CEAULIGHT, Beijing) equipped with a flame ionization detector.

Scheme S1. Schematic Diagram of the Experimental Setup.



4. The kinetic analysis

The kinetic analysis was performed in the same fixed-bed reactor of the performance test as mentioned in the Supporting Information. The feed gases were measured with mass flow controllers. Before any kinetic measurement, the catalyst was always treated for 1.5 h in H₂ (5 vol %) in N₂ flow (30 mL min⁻¹). The only difference of the two the Arrhenius plots is the lighting condition (light on or light off) in Figure 6c. The visible light intensity onto the sample is 145 mW cm⁻². The reaction rates used for the Arrhenius plots were obtained by controlling the reaction temperature and the gas flow. The reaction temperature was controlled from 20 °C to

240 °C.

In order to remove the influence of internal diffusion and external diffusion, during kinetic measurements, the gas hour space velocity of the reactants was kept at 60000 h⁻¹ and the reactor was operated in a differential mode with the conversion not exceeding 20%. And such important information about the kinetic analysis condition was also stated in detail in the kinetic analysis section in the Supporting Information.

5. SEM image of the inactive α -Al₂O₃

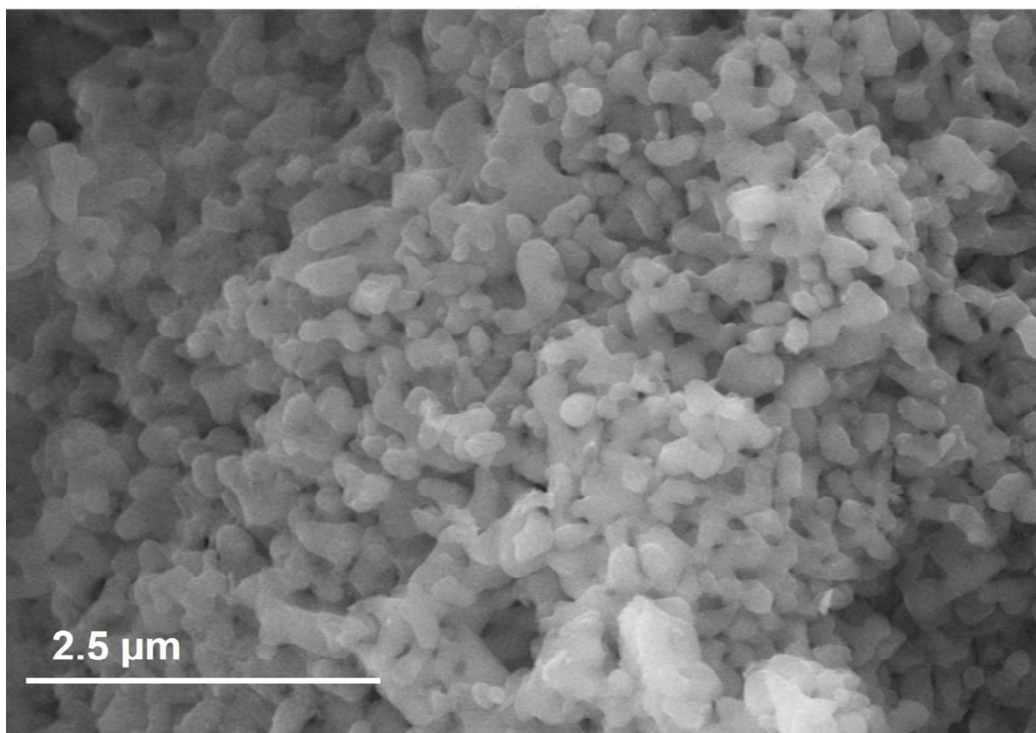


Figure S1. SEM image of the inactive α -Al₂O₃

According to Figure S1, the particle size of the α -Al₂O₃ support is about 200 nm.

6. Elements contents detected by SEM-EDS

Scanning electronic microscope (SEM) and the energy dispersive spectrum analysis

(EDS) of PCA-R catalyst was conducted. It can be seen that the content of Pd is 0.72 wt % in Figure S2.

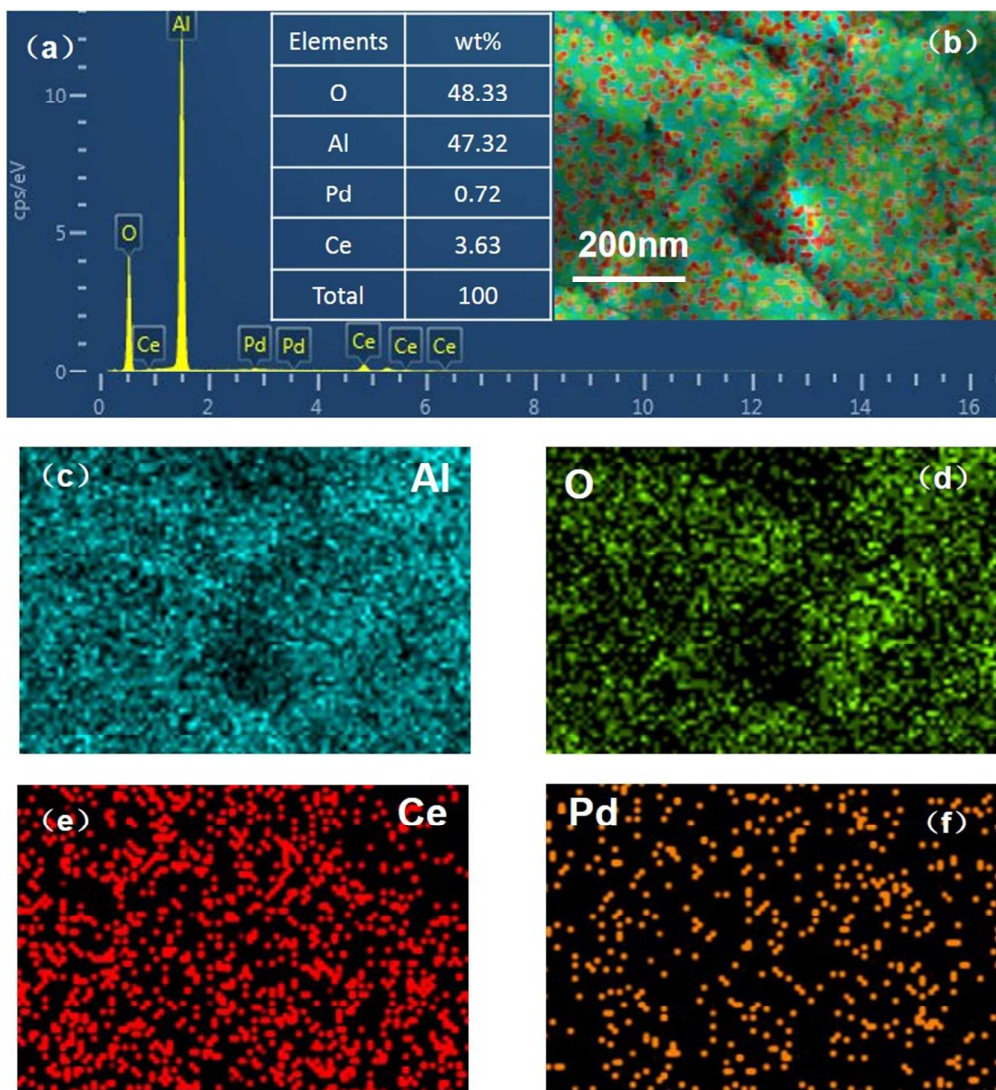


Figure S2. Elements content (a), elements distribution (b), and corresponding EDS mapping for Al (c), O (d), Ce (e), and Pd (f).