

Electronic Supplementary Information (ESI)

Well-Defined Palladium-Ceria Interfacial Electronic Effects Trigger CO Oxidation†

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Experimental Procedures

1.1. Catalyst syntheses

For the synthesis of CeO₂ rods,^[1] CeCl₃ · 7H₂O (0.45 g) was dissolved in 5 mL de-ionized water to form a solution, which was added into 25 mL of NaOH solution (C_{NaOH} = 9 mol L⁻¹) under vigorous stirring. The suspension was transferred to a 50 mL Teflon-lined stainless-steel autoclave and held in 140 °C for 48 h. After the autoclave was cooled to room temperature naturally, fresh precipitates were separated by centrifugation, washed with de-ionized water to neutrality, dried, and calcined at 400 °C for 4 h to give the CeO₂ rods.

For the synthesis of Pd cubes, we followed the protocol developed by Xia and co-workers.^[2] In a typical procedure, 40 mL of an aqueous solution containing poly(vinyl pyrrolidone) (PVP, 0.525 g), L-ascorbic acid (0.3 g), KCl (0.925 g) and KBr (0.025g) were placed in a 250 mL conical flask, and pre-heated in air under magnetic stirring at 80 °C for 10 min. Then, 15 mL of an aqueous solution containing Na₂PdCl₄ (0.285 g) was added. After the conical flask had been capped, the reaction was allowed to proceed at 80 °C for 3h. The as-prepared solution (25 mL) was added into a 20 mL of an aqueous solution containing CeO₂ rods (1 g) to get Pd/CeO₂. The pure Pd and Pd/CeO₂ were collected by centrifugation and washed 10 times with water to remove excess PVP.

1.2. HRTEM images

HRTEM images were carried out with a JEOL JEM-2100F field-emission gun transmission electron microscope operating at an accelerating voltage of 200 kV and equipped with an ultra-high resolution pole-piece that provides a point-resolution better than 0.19 nm. Fine powders of the materials were dispersed in ethanol, sonified, and sprayed on a carbon coated copper grid, and then allowed to air-dry for imaging. TEM and HRTEM images of the Pd cubes were also carried out with An FEI TITAN ETEM G2 80–300 kV instrument equipped with an objective Cs aberration corrector.

1.3. X-ray absorption spectra

The Ce L_3 -edge X-ray absorption near edge structure (XANES) spectroscopy were measured at BL14W of the SSRF with an electron beam energy of 3.5 GeV and a ring current of 200-300 mA. Data were collected with a fixed exit mono-chromator using two flat Si(111) crystals. Harmonics were rejected by using a grazing incidence mirror. The XANES spectra were acquired at an energy step of 0.5 eV. The raw data were analyzed using the IFEFFIT 1.2.11 software package.

1.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectra (XPS) were collected using an ESCALAB 250Xi Instrument (ESCALAB 250Xi, ThermoFisher Scientific) with a monochromated Al-K α X-ray gun (1486.6 eV), which was operated at high voltages of 12.5 kV with emission currents of 16 mA. Spectra were acquired at normal emission with a passing energy of 40 eV. XPS were referenced to the C 1s peak at the binding energy (BE) of 284.6 eV. Data analysis and processing were undertaken using the XPSPeak4.1 software with the Shirley type background.

For the Pd 3d XPS, the splitting energy between Pd 3d_{5/2} and Pd 3d_{3/2} spin-orbit doublet peaks was fixed at 5.26 eV. The peak area ratio of Pd 3d_{3/2} to Pd 3d_{5/2} was fixed at 2/3. The full width at half maxima (FWHM) and Lorentzian-Gaussian ratio of all the peaks were set to be equal to the others. For the O 1s XPS, the full width at half maxima (FWHM) and Lorentzian-Gaussian ratio of all the peaks were set to be equal to the others. For the Ce 3d XPS, the peak fitting is rather complex. It could be resolved into several Ce 3d_{5/2,3/2} spin-orbit doublet peaks with splitting of around 18 eV^[3] The peak area ratio of Ce 3d_{3/2} to Ce 3d_{5/2} was fixed at 2/3. The full width at half maxima (FWHM) and Lorentzian-Gaussian ratio of all the peaks were set to be equal to the others.

1.5. Synchrotron X-ray diffraction patterns

Synchrotron X-ray diffraction (SXR) patterns were performed at BL14B of the Shanghai Synchrotron Radiation Facility (SSRF) at a wavelength of 0.6883 Å. Rietveld refinement analyses of the diffraction profiles were conducted using Rietica v1.77 program.

1.6. Catalytic oxidation of CO

Catalytic activity measurements for CO oxidation were performed using a continuous-flow fixed-bed reactor. 100 mg of catalyst (250-380 μm) was sandwiched between two quartz wool layers in the microreactor. Before the test, the catalyst was pretreated under the feed gas (1.0 vol% CO and 21.0 vol% O₂ in N₂) at a total flow rate of 100 mL min⁻¹ at 170 °C for an hour, and stored in the feed gas when cooling. Then the reaction temperature began with room temperature at a ramp of 5 °C min⁻¹ to test the catalytic activity for CO oxidation. The composition of the outgoing gas stream was determined by an on-line Agilent 7890B gas chromatograph equipped with TCD and FID detectors. The activity of pure Pd was investigated by using inert Al₂O₃ for dispersing the Pd cubes.

For all the characterations mentioned above, all the samples were pretreated under the feed gas (1.0 vol% CO and 21.0 vol% O₂ in N₂) at a total flow rate of 100 mL min⁻¹ at 170 °C for an hour, and stored in the feed gas when cooling.

Figures and Tables

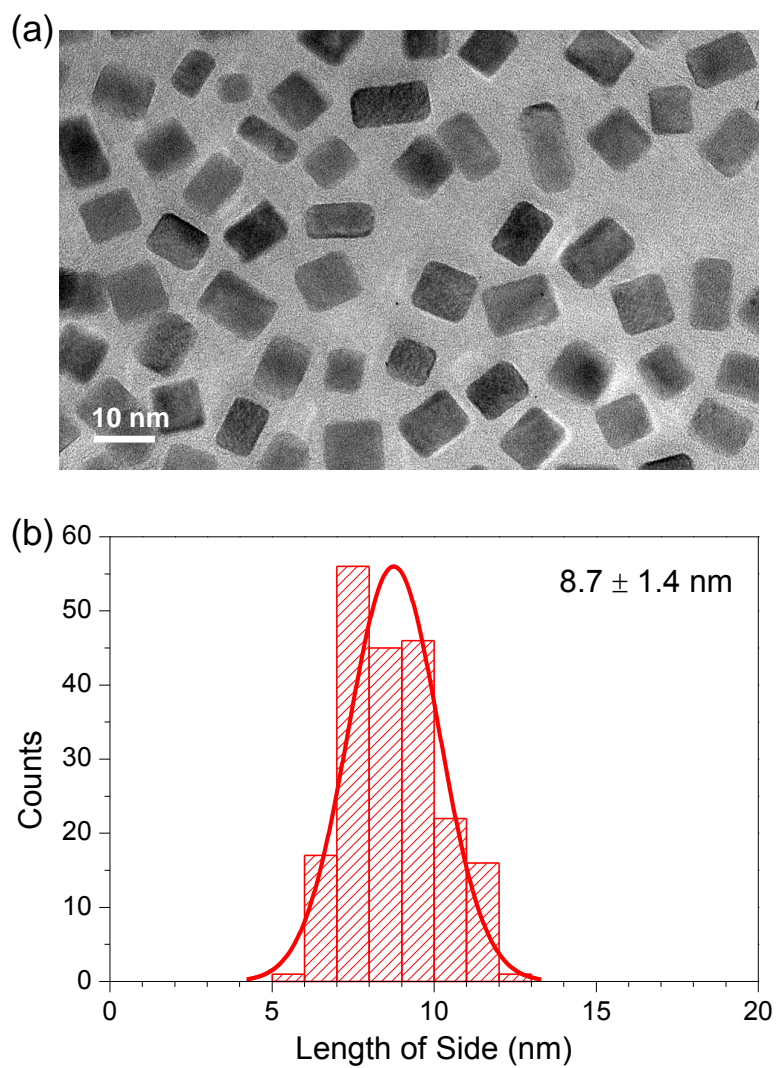


Fig. S1 (a) TEM image of the Pd cubes. (b) Size distributions of the Pd cubes counted from the TEM images.

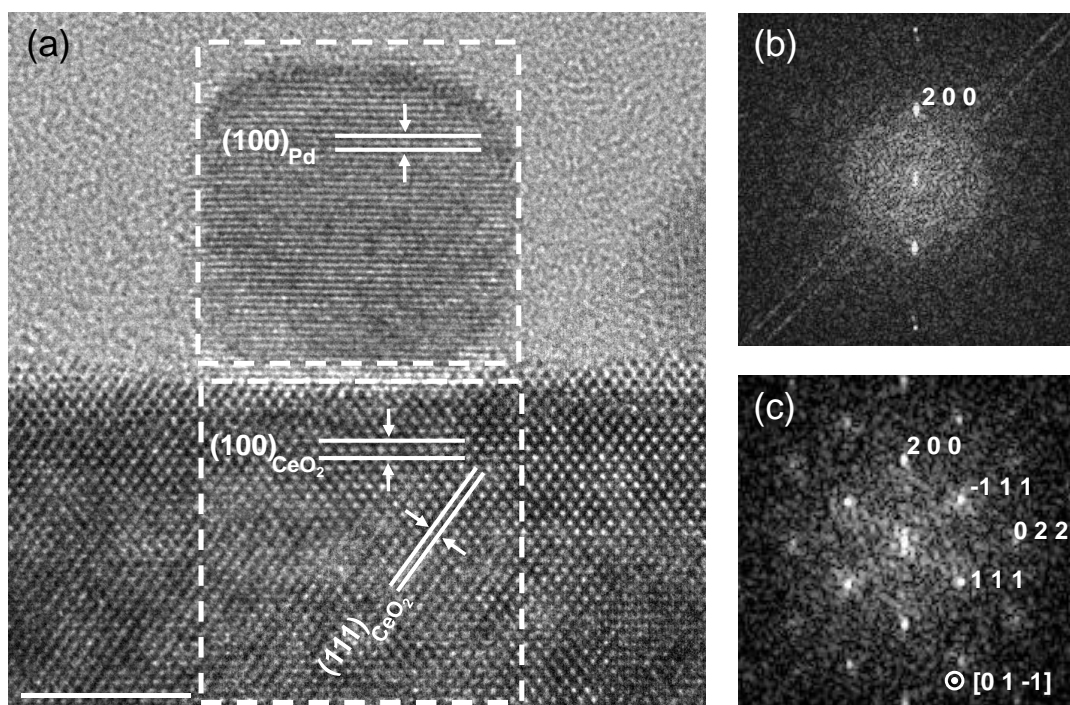


Fig. S2 (a) Side-viewed HRTEM image of Pd/CeO₂ and the corresponding Fast Fourier transform pattern for the Pd cube (b) and the CeO₂ rod (c).

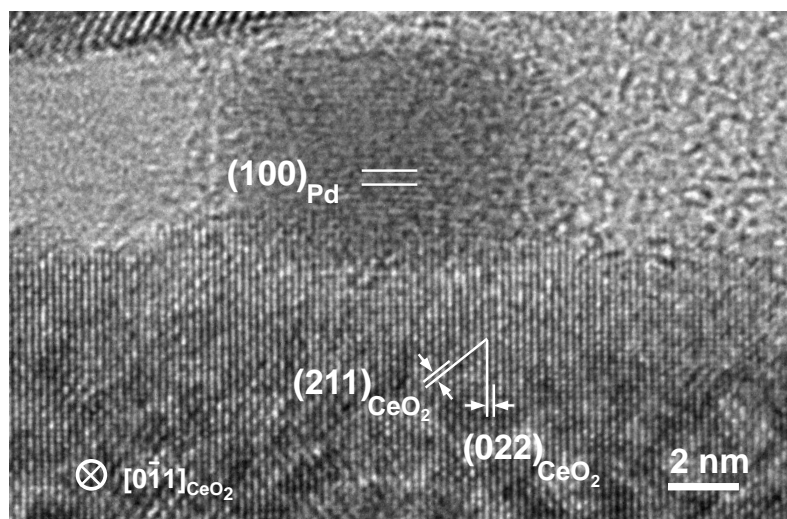


Fig. S3 Side-viewed HRTEM image of Pd/CeO₂.

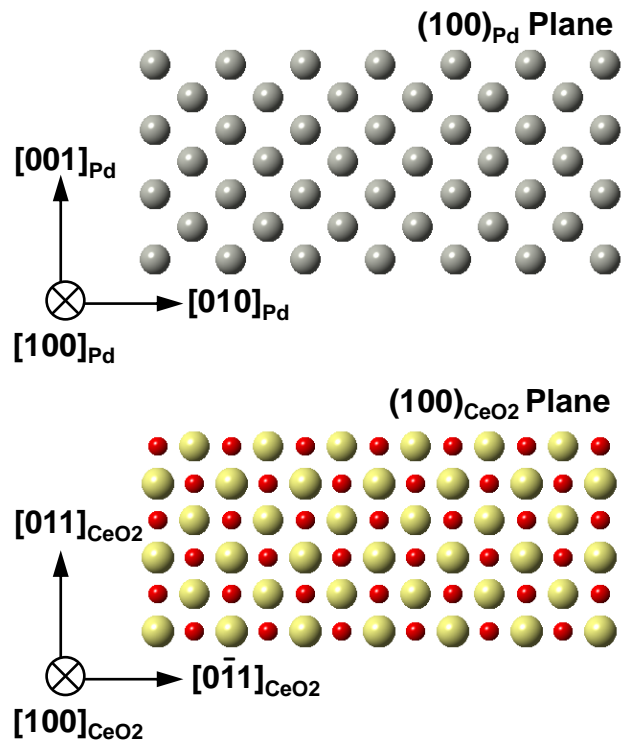


Fig. S4 Atom arrangements of the $(100)_{\text{Pd}}$ plane and the $(100)_{\text{CeO}_2}$ plane showing a primitive lattice misfit for the interfacial atom arrangements.

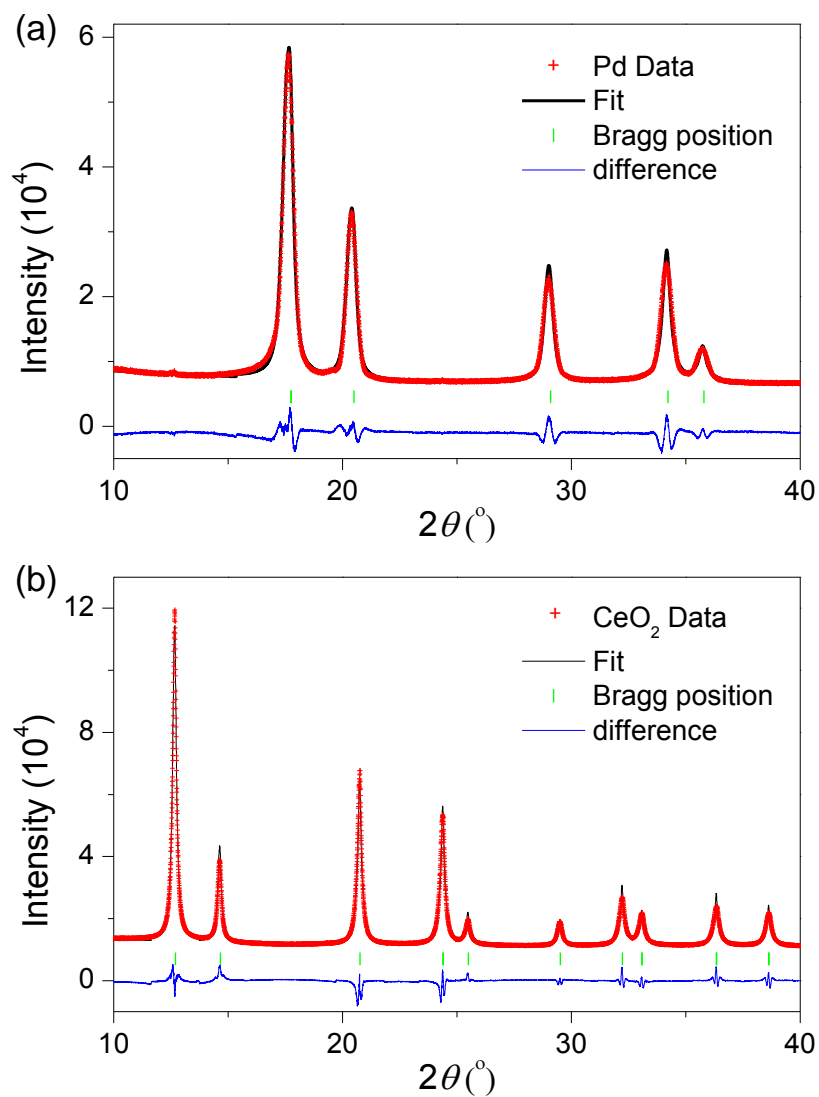


Fig. S5 XRD patterns of Pd (a) and CeO₂ (b) including the Rietveld refinements.

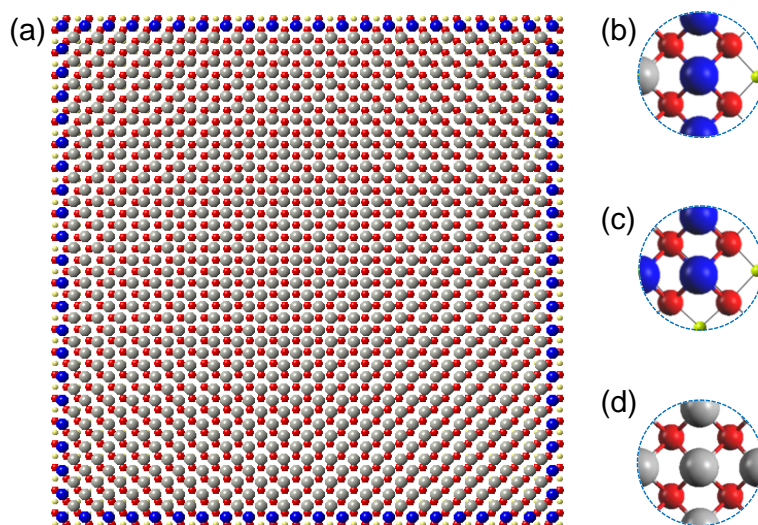


Fig. S6 Scheme illustrating the interfacial atom arrangement (a), and the PdO₄ motifs at the edge (b), the corner (c) and in the interior (d) of the interfacial square. According to the size distribution of the Pd cubes in Figure S, the Pd atoms at the edges is calculated to be ~95% with respect to all Pd atoms at the periphery of the Pd cubes directly contacted with CeO₂, i.e., 95% of CASs of Pd/CeO₂ are uniform.

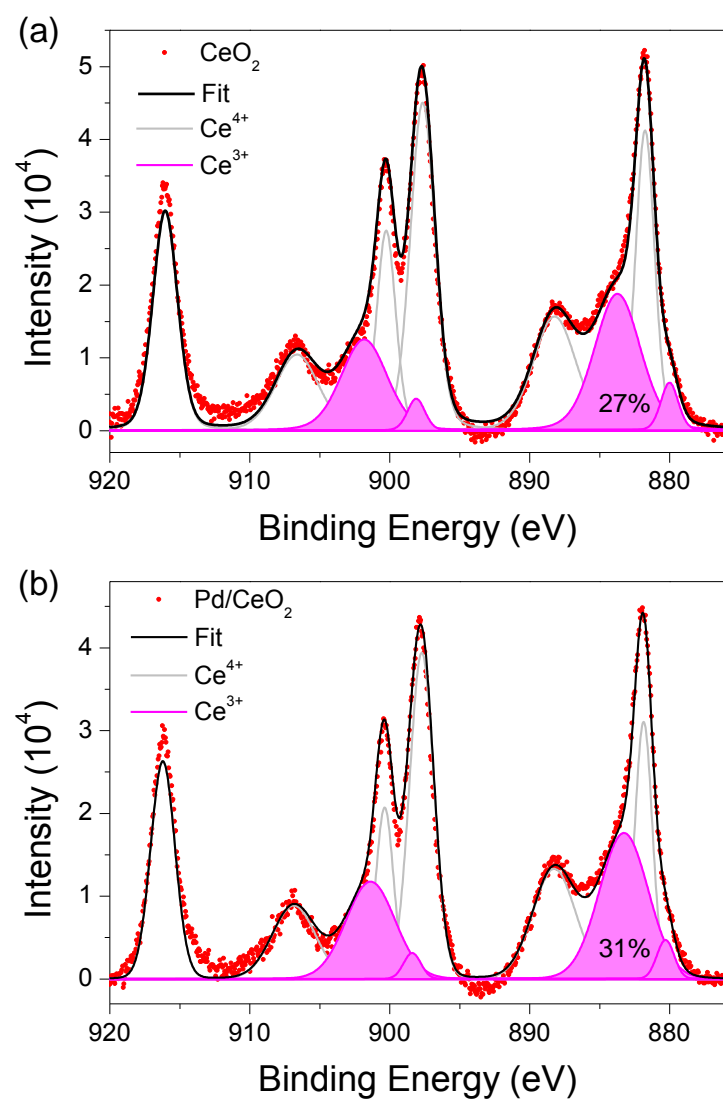


Fig. S7 Ce 3d XPS of Pd/CeO₂ and CeO₂.

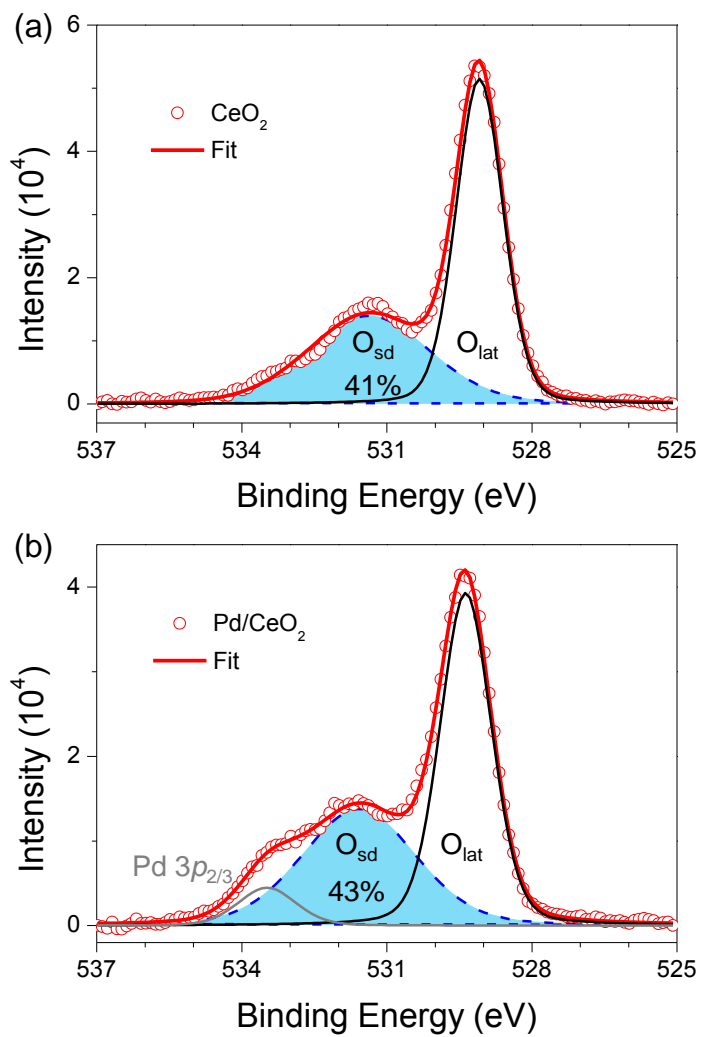


Fig. S8 O 1s XPS of Pd/CeO_2 and CeO_2 . After the Pd loading, defect oxygen ions increase ~2%.

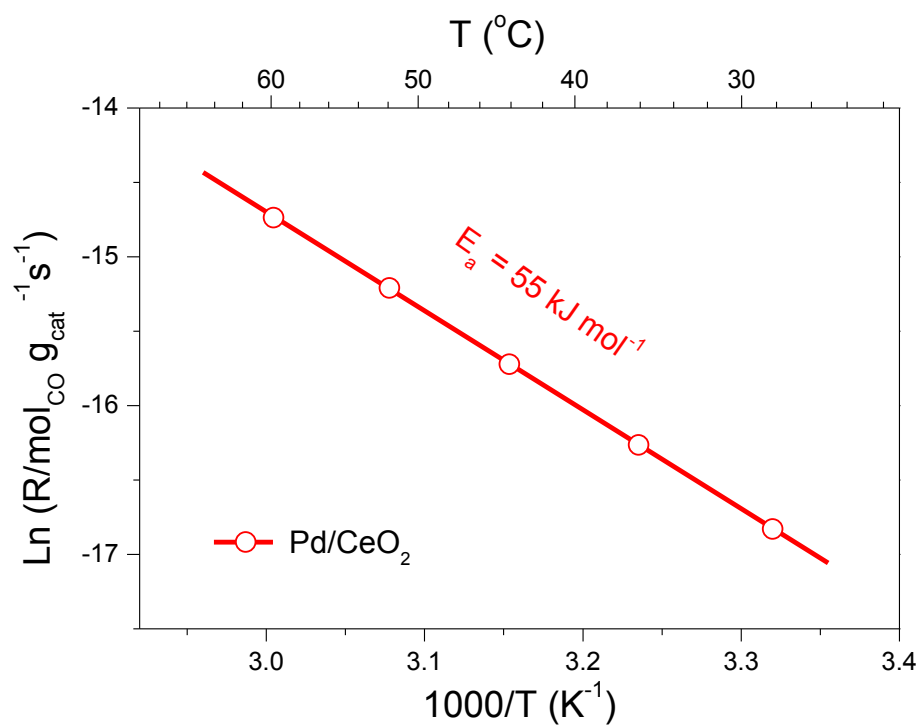


Fig. S9 Arrhenius plot for the reaction rates in the CO oxidation and the corresponding E_a over Pd/CeO_2 .

Table S1. Crystallographic data and details of Pd and CeO₂ in the SXRD data collections and the Rietveld refinements.

Sample	Pd	CeO ₂
Chemical formula	Pd	CeO ₂
Crystal system	cubic	cubic
Space group	<i>FM-3m</i>	<i>FM-3m</i>
Z ^[a]	4	4
<i>a</i> / Å	3.897(6)	5.417(5)
<i>V</i> / Å ³	59.2(1)	159.0(0)
<i>R_p</i> ^[b] / %	5.24	8.35
<i>R_{wp}</i> ^[c] / %	6.88	10.35
<i>R_{exp}</i> ^[d] / %	1.34	1.45
χ^2 ^[e]	1.29	5.43
Wavelength / Å	0.6888	0.6888
<i>2θ</i> range / °	3-40	3-40
<i>2θ</i> step width / °	0.004	0.004

^[a] Z, the number of the formula of Pd or CeO₂ units per unit cell;

^[b] *R_p*, the unweighted profile factor;

^[c] *R_{wp}*, the weighted profile factor;

^[d] *R_{exp}*, the expected *R* parameter;

^[e] χ^2 , the goodness of fitting, defined as the square of the ratio of *R_{wp}*/*R_{exp}*.

Table S2. Structure constants of the Pd and CeO₂ determined by the Rietveld refinement of the corresponding SXRD data.

Sample	Atom	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy
Pd	Pd	0	0	0	1.0
CeO ₂	Ce	0	0	0	1.0
	O	0.2500(0)	0	0	1.0

References

- [1] Q. Wu, F. Zhang, P. Xiao, H. Tao, X. Wang, Z. Hu and Y. Lü, *J. Phys. Chem. C*, 2008, *112*, 17076.
- [2] M. Jin, H. Liu, H. Zhang, Z. Xie, J. Liu and Y. Xia, *Nano Res.*, 2011, *4*, 83.
- [3] C. Anandan and P. Bera, *Appl. Surf. Sci.* **2013**, 283, 297.