

Supporting Information

Sintering resistance of Pd single atoms on steam-modified ceria: deciphering the role of hydroxyl group

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1. Experimental details

1.1 Catalyst preparation

A-CeO₂ nanorods were synthesized through a hydrothermal method.¹ 20 mL of 8.75 M NaOH (98%, Alfa Aesar) aqueous solution was slowly added to 20 mL of 0.15 M Ce(NO₃)₃·6 H₂O (99.5%, Alfa Aesar) aqueous solution, and the mixed solution was stirred at 700 rpm for 30 min. Then, the mixed solution was transferred into a 50 mL Teflon hydrothermal autoclave and heated at 130 °C for 24 h. The precipitate was collected by centrifugation (8000 rpm) after cooling to room temperature (~25 °C), and then washed several times with deionized water until the pH reached 7. The dried sample (A-CeO₂) could be obtained after drying overnight in an oven at 80 °C, and then calcined in a tube furnace at 250 °C for 2.5 h with an airflow of 50 sccm and a ramp rate of 10 °C/min. OH-CeO₂ was obtained by treating A-CeO₂ with steam at 750 °C according to previous literature.² A-CeO₂ was located in a quartz boat inside a quartz tube and heated in a tube furnace at 750 °C for 9 h at a ramp rate of 10 °C/min. The system was filled with argon (Ar) flowing through a water bubbler at a rate of 100 sccm (2 vol.% H₂O). The sample was cooled to 300 °C for 1 h using dry Ar after calcination. D-CeO₂ was prepared under the same conditions as OH-CeO₂ without connecting to the water bubbler. Subsequently, Pd was loaded using a wet chemical method. After mixing 500 mg OH-CeO₂ (or D-CeO₂), 2.88 mg palladium (II) acetylacetonate (34.7% Pd, Alfa Aesar), and 21 mL ethylene glycol in a 50 mL round bottom flask, the solution was preheated in a water bath at 50 °C for 10 min (500 rpm). Then, the bottle was transferred to an oil bath and heated at 145 °C for 1.5 h (250 rpm). The product was washed three times with ethanol and collected by centrifugation (6000 rpm). The precipitate was dried in an oven at 60 °C overnight

and then calcined at 800 °C with a 20% O₂ (mixed with He) at a 20 sccm flow rate for 5 h, and denoted as Pd/OH-CeO₂ (or Pd/D-CeO₂).

1.2 Characterizations

Quasi situ X-ray photoelectron spectroscopy (*Quasi situ* XPS) was conducted using an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Scientific) with an Al K α source (1486.7 eV). There is a reactor in front of the conventional XPS sample chamber to preprocess the sample. After the samples were treated with different gases in the reactor, they were cooled to RT (~25 °C), evacuated, and then transferred to the sample chamber of the conventional XPS using the sample transfer rod for XPS collection. The whole process was carried out without exposing samples to air. CO oxidation conditions: a mixed gas (2% CO, 20% O₂, 78% He) with a 50 sccm feed flow rate was introduced to the reactor. All the XPS spectra were calibrated with the position of Ce 3d u''' (916.7 eV).³

in situ diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) study of CO adsorption was carried out using a ThermoFisher Nicolet Model Nexus 670 infrared spectrometer equipped with a mercury-cadmium-telluride (MCT) detector, a Praying Mantis diffuse reflection accessory, and a high-temperature reaction chamber from Harrick Scientific Products Inc. The *in situ* DRIFTS spectra were recorded at a resolution of 4 cm⁻¹ and 16 scans with a CaF₂ cell window. The samples were pre-treated at 450 °C for 90 min under helium (He) prior to each DRIFTS experiment. The gases of "CO (1 vol.%, mixed with He)-N₂-CO (1 vol.%, mixed with He)-O₂ (0.25 vol.%, mixed with He)" was passed successively at RT (~25 °C) for 15 min, and the data was collected during this process.

X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses were conducted on the TPS 44A beamline of the National Synchrotron Radiation Research Center (NSRRC). The TPS 44A beamline used a Si (111) single crystal to obtain a monochromatic X-ray beam with an operating voltage of 3.0 GeV. The Pd *K*-edge (24150-25000 eV) spectra were collected in the fluorescence mode using a 7-element silicon drift detector. The reference spectra (PdO and Pd foil) were collected in the transmission mode. The energy of each scan was calibrated using Pd foil. The Fourier transformation of the EXAFS oscillation (*k* space) was performed to obtain a radial distribution function (*R* space). Data transformation and fitting analysis were performed using Athena and Artemis software.

Hydrogen temperature-programmed reduction (H₂-TPR) was conducted using a Micromeritics AutoChem II 2920 chemisorption analyzer equipped with a thermal conductive detector (TCD). Around 100 mg catalysts were pretreated in helium (He) at 450 °C for 90 min and tested under a 10% H₂/Ar gas mixture in the temperature range of 50–900 °C and at a ramp rate of 10 °C/min.

High-resolution transmission electron microscopy (HRTEM) images were obtained using JEOL JEM-2100 Plus with an accelerating voltage of 200 kV. Energy dispersive X-ray spectroscopy (EDS) data were obtained using a JEOL SDD system (100 mm² × 2).

Catalytic reactions: The stability test for CO oxidation was evaluated in a fixed-bed reactor. An appropriate amount of catalyst was diluted with sand and then filled into a U-shaped quartz tube. Before the reaction, the catalysts were pretreated at 450 °C for 1 h in a helium (He) atmosphere to remove the adsorbed water and impurities. All the samples were kept under the reaction atmosphere at RT for at least 15 min to reach a steady state prior to the heating program. The reactor outlet was connected to an online mass spectrometer (MKS-Cirrus 2) for *in situ* analysis,

from which the partial pressure of CO₂ could be tested directly. The catalytic performance was calculated using the pressure of CO₂.⁴ The CO conversion was calculated from the pressure of CO₂ using the following formula:

$$X_{CO}^T = \frac{P_{CO_2}^T - P_{CO_2}^{bypass}}{P_{CO_2}^{full} - P_{CO_2}^{bypass}} \times 100\%$$

where X_{CO}^T represents the conversion of CO at temperature T. $P_{CO_2}^T$, $P_{CO_2}^{full}$, $P_{CO_2}^{bypass}$ are the pressure of CO₂ at temperature T, full conversion of CO, and the mixed gas bypasses through the catalysts, respectively.

1.3 Theoretical calculation

Calculations of spin-polarized DFT were performed using the CP2K software package in the high-performance computing (HPC) platform of ShanghaiTech University. The ion-electron interactions were represented by the Gaussian and plane wave (GPW) method, and the electron exchange-correlation by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.⁵ The DFT+U method (U = 5 eV) was used to describe the Ce 4f states, in which U is a Hubbard-like term describing the on-site coulombic interactions. This approach improves the description of localized states in ceria, where standard LDA and GGA functionals fail.⁶ A cut-off energy of 400 eV for the planewave, a force threshold of 0.05 eV Å⁻¹ for geometric optimization, and an SCF convergence criteria of 10⁻⁵ eV were used. The ceria unit cell was cleaved into the (111) plane and fully optimized. Gamma-centered k-point grids (5 × 5 × 1) were used in the calculation, and a 15 Å vacuum slab was added to the CeO₂ (111) surface to minimize the interaction between the slabs. The slab model used for the calculation contained three layers of O-Ce-O atoms. The atoms of the bottom O-Ce-O layer were fixed, and the

remaining two O-Ce-O layers were relaxed with optimized atom position. After the surface optimization of CeO₂ (111) was completed, one O atom on the surface was replaced with an OH group to form the CeO₂-OH (111) surface structure, and the optimization calculation was continued. In the electronic self-consistent-field calculation and the calculation of the density of states (DOS), the k-point grids were twice as large as those when optimized.

The calculated energy was the Gibbs free energy at 0 K, including the kinetic energy of the ions and the energy of the Nosé thermostat. The doping energy of Pd atom was calculated according to the equation below:

$$E_{\text{Pd-dope}} = E_{\text{total}} - E_{\text{slab}} - E_{\text{Pd}}$$

where the $E_{\text{Pd-dope}}$ is the doping energy, E_{total} is the total energy of the system with Pd-doping, E_{slab} is the energy of the optimized CeO₂ (111) or OH-CeO₂ (111) slab, and E_{Pd} is the energy of the isolated Pd atom.

2. Results

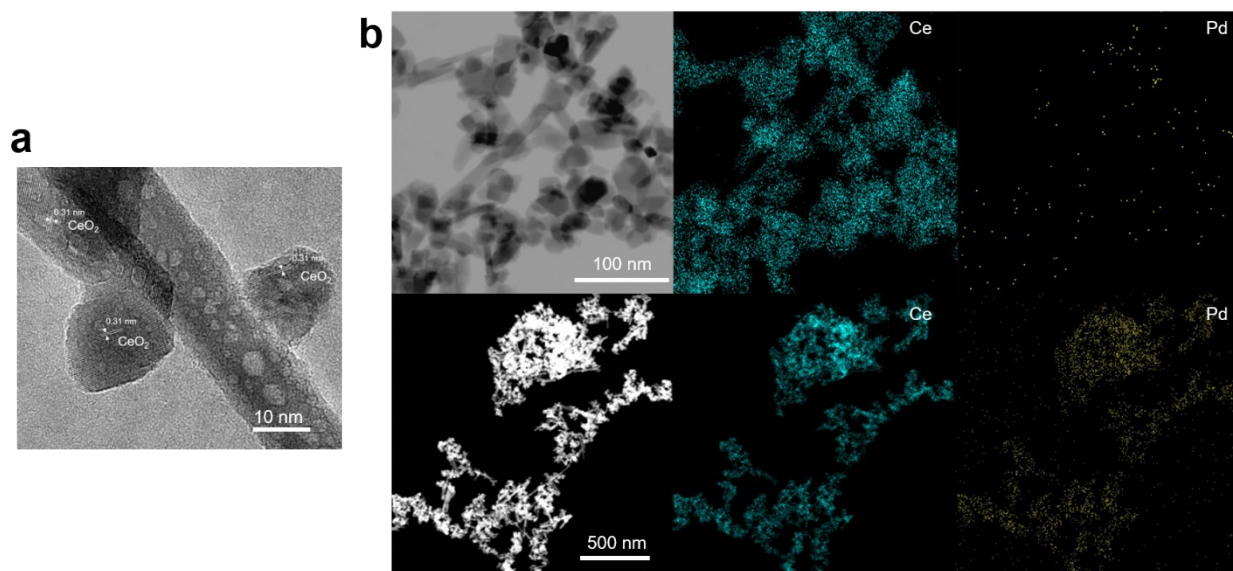


Figure S1. (a) HRTEM and (b) EDS images of Pd/OH-CeO₂.

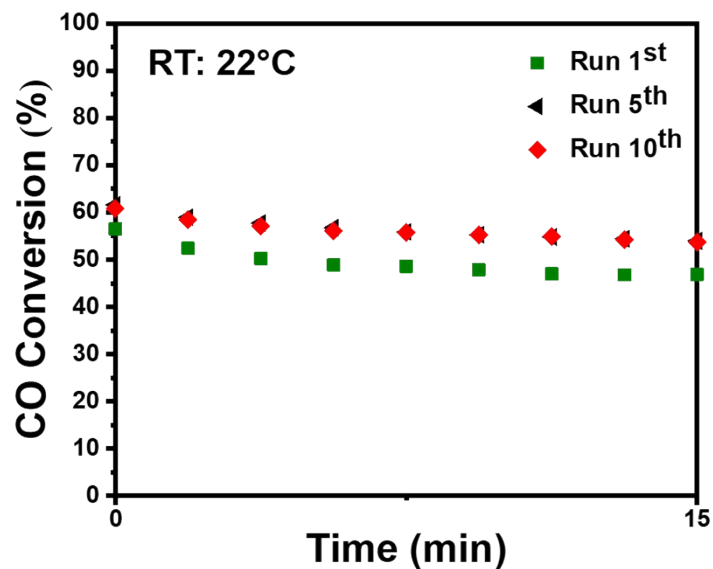


Figure S2. Catalytic performance of Pd/OH-CeO₂ towards CO oxidation at room temperature (22 °C) in the 1st, 5th, and 10th cycles test. 200 mg sample (0.4mg Pd, ICP) mixed with sand was used for catalysis. Reaction conditions: a mixed gas (2% CO, 20% O₂, 78% He) with a 50 sccm feed flow rate was introduced to the reactor.

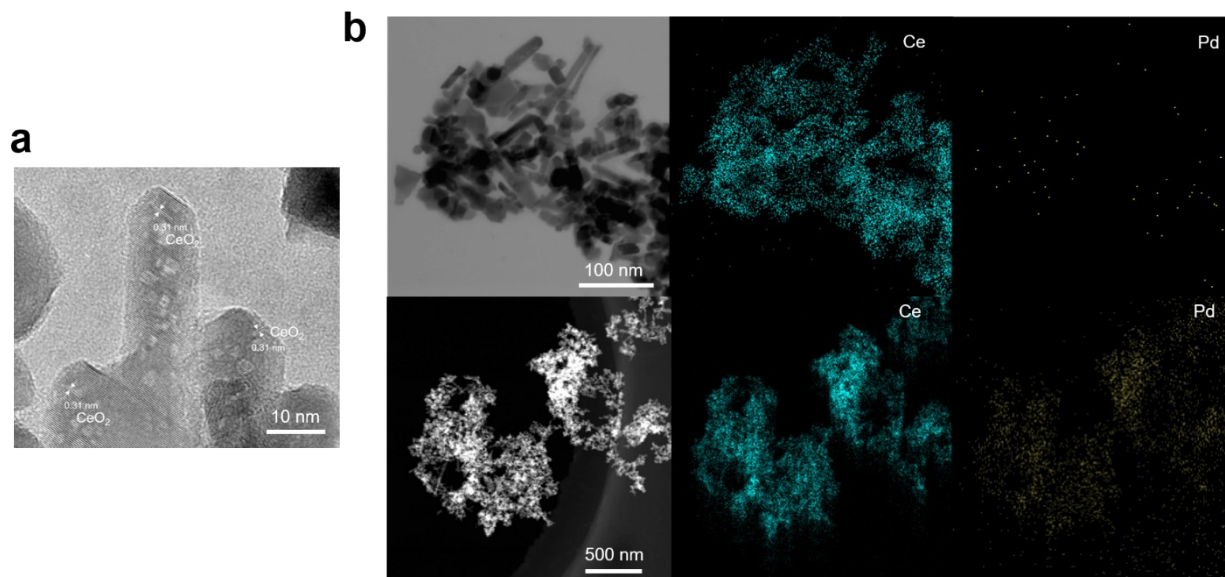


Figure S3. (a) HRTEM and (b) EDS images of Pd/D-CeO₂.

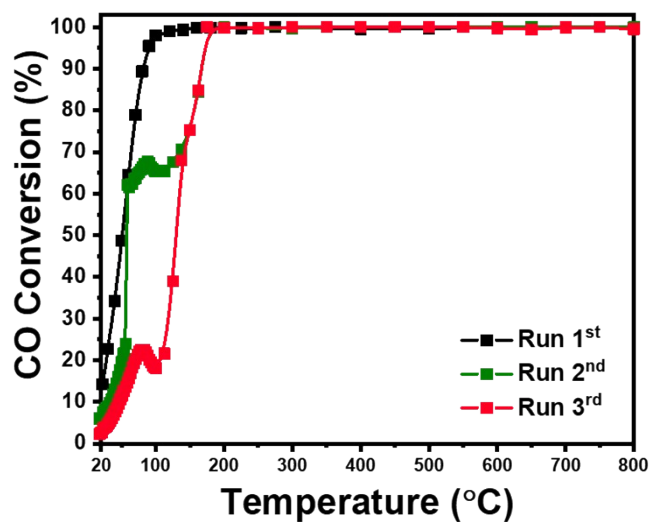


Figure S4. Catalytic performance of Pd/D-CeO₂ towards CO oxidation from RT to 800 °C. 200 mg sample (0.48 mg Pd, ICP) mixed with sand was used for catalysis. Reaction conditions: a mixed gas (2% CO, 20% O₂, 78% He) with a 50 sccm feed flow rate was introduced to the reactor.

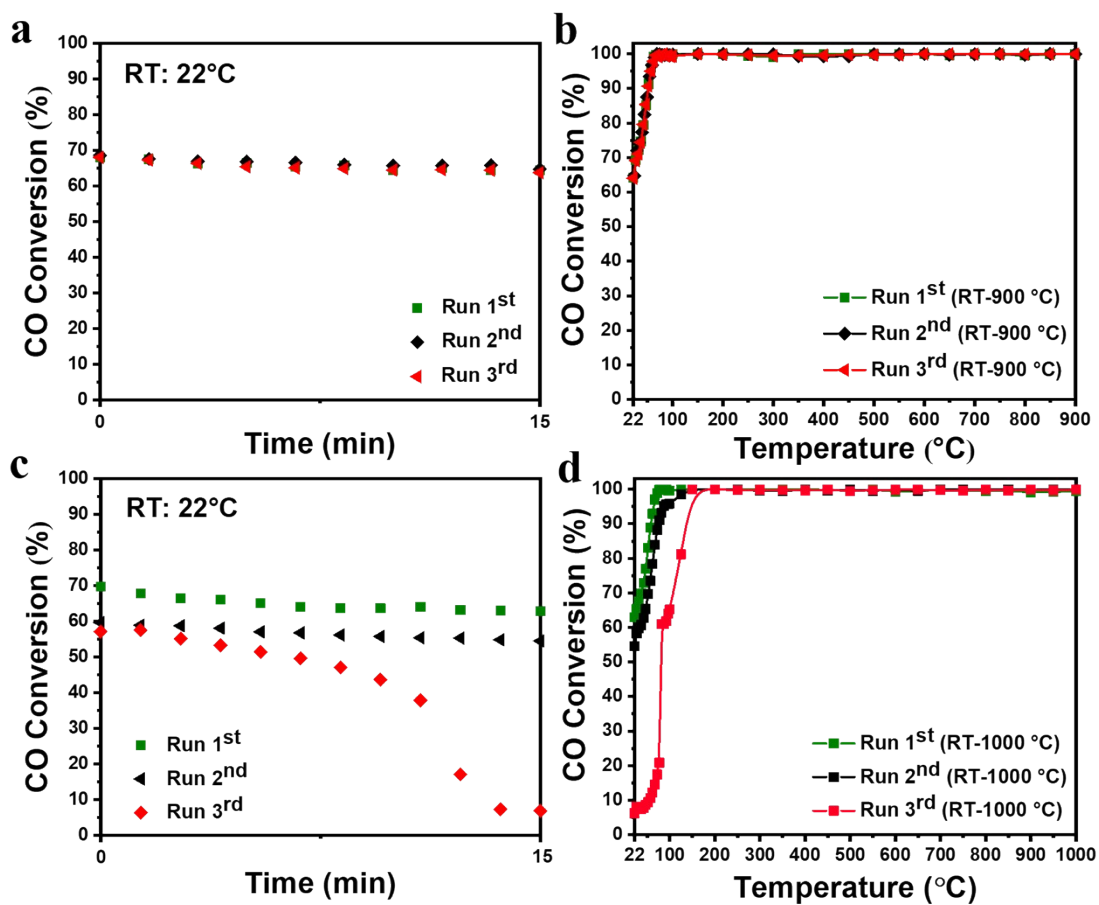


Figure S5. Catalytic performance tests of Pd/OH-CeO₂ towards CO oxidation, (a–b) RT to 900 °C; (c–d) RT to 1000 °C. 200 mg sample (0.5 mg Pd, ICP) was mixed with sand for catalysis. Reaction conditions: a mixed gas (2% CO, 20% O₂, 78% He) with a 50 sccm feed flow rate was introduced to the reactor.

Table S1. Comparison of the reaction temperature range and catalytic cycle numbers of different Pd-/Pt- catalysts towards CO oxidation.

No.	Catalyst ^[a]	Temperature range of cyclic test		Cycles	Reference
		T ₅₀ ^[b]	T _{upper} ^[d]		
1	Pd/OH-CeO ₂ (SAC) (this study)	22 °C (RT) ^[c]	800 °C	10	This study
2	Pt/CeO ₂ (Particle)	88 °C	137 °C	5	7
3	Pd ₁ /CeO ₂ _AT (SAC)	139 °C	180 °C	2	8
4	CeO ₂ -AA-Pt (SAC)	61 °C	80 °C	6	9
5	Pt/CeO ₂ _S (SAC)	132 °C	300 °C	8	2
6	Pt ₁ /CeO ₂ (SAC)	148 °C	170 °C	4	10
7	Pd/CeO ₂ -Rod (SAC)	125 °C	300 °C	2	11
8	1PdFSP (SAC)	108 °C	300 °C	2	3
9	Pd/CeO ₂ (Particle)	35 °C	60 °C	2	12
10	Pd-O-Ce solid solution	84 °C	105 °C	6	13
11	Pd _n (I-Cys) _m /CeO ₂ (Particle)	88 °C	110 °C	5	14
12	0.2Pt/m-Al ₂ O ₃ -H ₂ (SAC)	264 °C	400 °C	60	15

^[a]: Except for the samples studied in this paper, other samples were selected from the reported studies with more than two cycles of stable cyclic activity.

^[b]: T₅₀ represents the temperature of 50% CO conversion.

^[c]: Due to the CO conversion is over 50% at RT, T₅₀ was recorded as room temperature.

^[d]: T_{upper} represents the upper limit temperature reached in the cycle test.

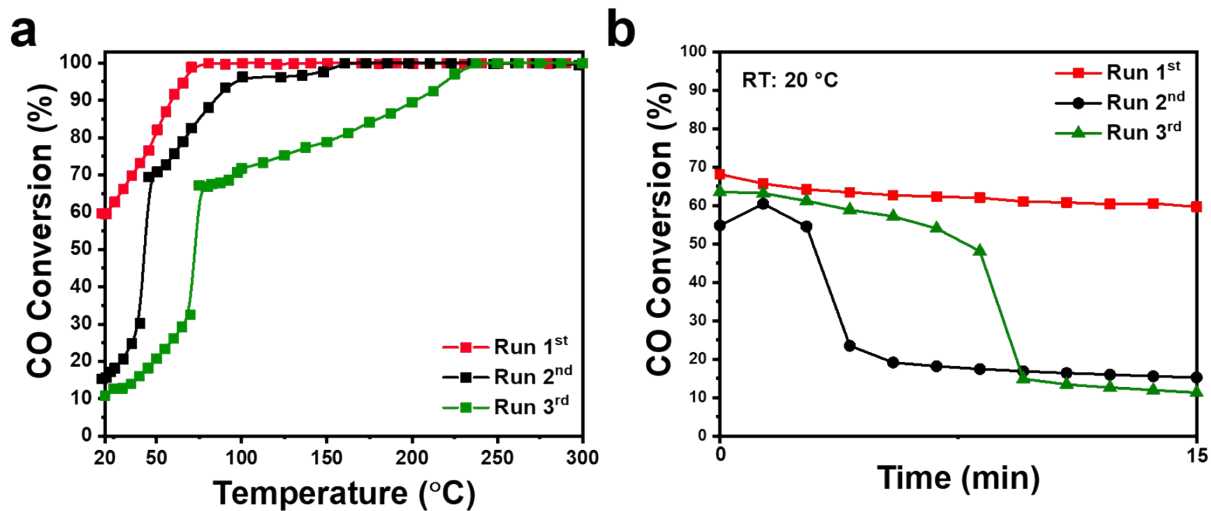


Figure S6. Catalytic performance of Pd_f-ST towards CO oxidation (a) from RT to 800 °C; (b) at RT for 15 mins. 200 mg sample was mixed with sand for catalysis. Reaction conditions: a mixed gas (2% CO, 20% O₂, 78% He) with a 50 sccm feed flow rate was introduced to the reactor.

Table S2. Best fitting results for Pd k-edge EXAFS data of Pd/OH-CeO₂ and Pd/D-CeO₂.

Sample□	Path	R (Å) ^[a]	CN ^[b]	σ^2 (Å ²) (Debye-Waller factor)	R-factor (%)
Pd/OH-CeO ₂	Pd-O (OH-Pd _{doped})	1.99±0.01	3.6±0.4	0.001±0.001	0.7
	Pd-Ce (OH-Pd _{doped})	3.21±0.02	2.6±0.8	0.003±0.002	
Pd/D-CeO ₂	Pd-O	1.99±0.02	3.7±0.3	0.002 ^[c]	2.6
	Pd-Pd (oxide)	3.15±0.04	2.2±1.2	0.002 ^[c]	
Pd foil	Pd-Pd	2.74±0.01	12	0.005±0.001	0.3
	Pd-O	2.02±0.02	4	0.001±0.001	
PdO	Pd-Pd	3.05±0.03	4	0.001±0.001	0.9
	Pd-Pd	3.46±0.03	8	0.001±0.001	

[a]: Atomic distance.

[b]: Coordination number.

[c]: Fixed parameter.

Table S3. The energy difference (ΔE) between each step during the process of cerium replaced with Pd on CeO₂ (111) surface with or without OH group.

State	ΔE (kJ·mol ⁻¹)	
	Pd-Str. 2_w/o	Pd-Str. 1 OH
I→II	2071.5	1617.3
II→III	-581.5	-426.3
III→IV	71.4	-1.9

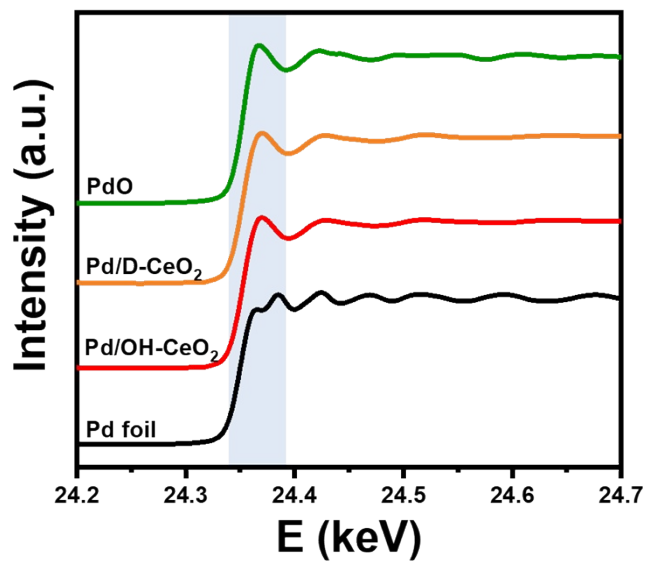


Figure S7. XANES spectra of Pd K-edge for Pd/OH-CeO₂ and Pd/D-CeO₂. The spectra of PdO and Pd foil were collected from standard samples.

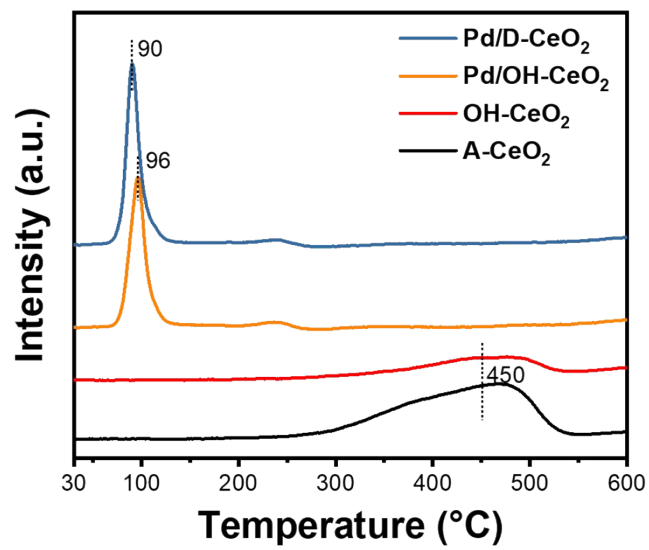


Figure S8. H₂-TPR profiles of A-CeO₂, OH-CeO₂, Pd/OH-CeO₂, and Pd/D-CeO₂.

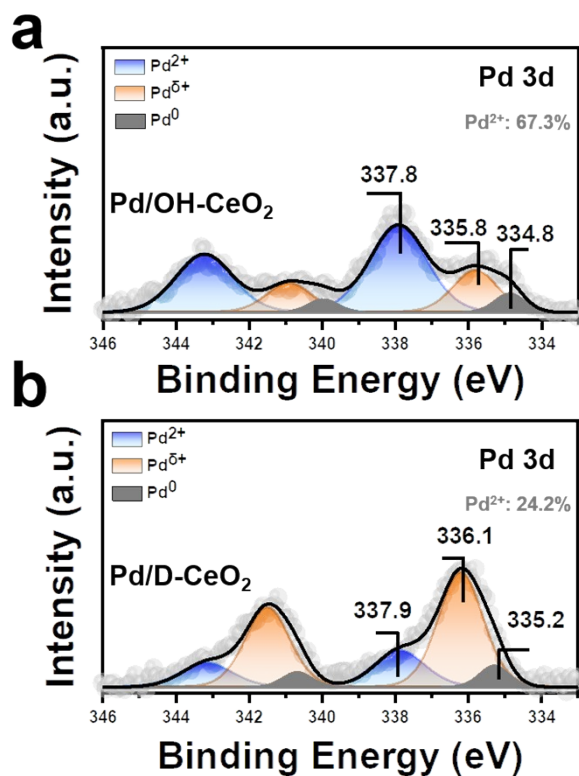


Figure S9. *Quasi situ* XPS spectra of Pd 3d of (a) Pd/OH-CeO₂ and (b) Pd/D-CeO₂. The samples were reacted under the catalytic conditions (2% CO + 20% O₂ + 78% He, 50 sccm) at 100 °C for 20 min in the attached reactor, cooled to RT, evacuated, and then transferred to the sample chamber of the conventional XPS through the sample transfer rod for XPS collection. The whole process is carried out without exposure to air.

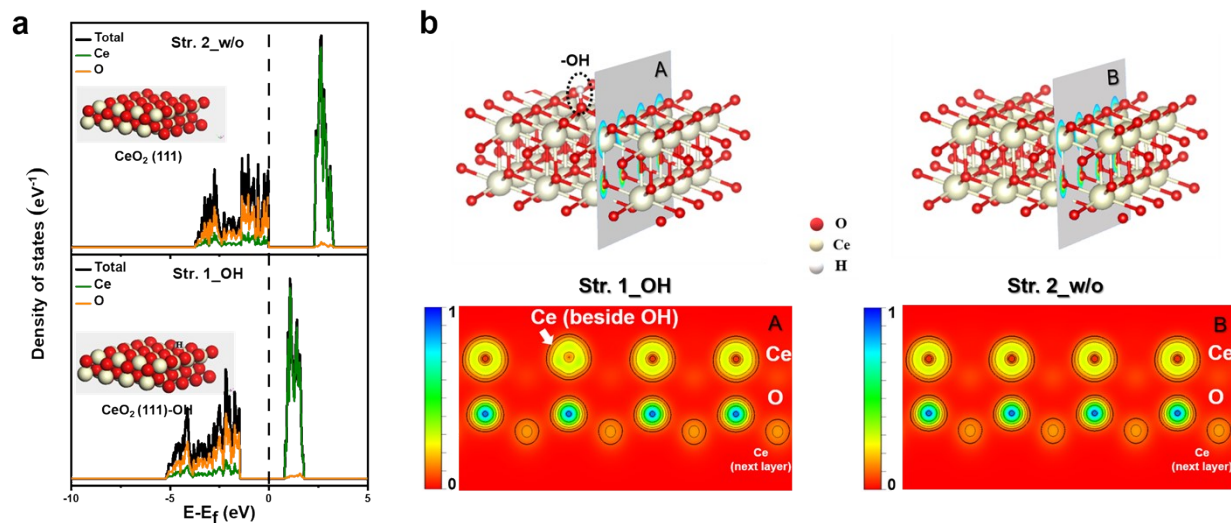


Figure S10. (a) Calculated densities of states (DOS) for ceria supercell model: Str. 1_OH model (with OH group) and Str. 2_w/o model (without OH group). Both structures are idealized models, which are only used to explore the influence of OH groups, without considering the influence of oxygen defects and other issues. The exposed surfaces of both structures are CeO_2 (111). (b) Projected charge density contour plots of Str. 1_OH model (with OH group) and Str. 2_w/o model (without OH group). The color gradient from red (0) to dark blue (100%) represents the increased percentage of relative charge concentration.

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