## **Supporting Information**

# Controlling metal-support interaction with steammodified ceria to boost Pd activity towards lowtemperature CO oxidation

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#### 1. Experimental details

#### 1.1 Catalyst preparation

A-CeO<sub>2</sub> nanorods were synthesized using a hydrothermal method.<sup>1</sup> 20 mL of 8.75 M NaOH (98%, Alfa Aesar) aqueous solution was slowly added to 20 mL of 0.15 M Ce(NO<sub>3</sub>)<sub>3</sub>  $\cdot$  6 H<sub>2</sub>O (99.5%, Alfa Aesar) aqueous solution and stirred at 700 rpm for 30 min. The mixed solution was transferred to a 50 mL Teflon hydrothermal autoclave reactor and heated at 130 °C for 24 h. After cooling to room temperature (~25 °C), the precipitate was collected by centrifugation (8000 rpm) and washed several times with deionized water until the pH reached 7. Then, the precipitate was dried overnight in an oven at 80 °C. The dried sample (A-CeO<sub>2</sub>) was grounded well 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. A-CeO<sub>2</sub>-ST was obtained by treating A-CeO<sub>2</sub> with steam at 750 °C. The conditions for the steam treatment were obtained from literature.<sup>2</sup> The detailed operation is shown in Figure S1. A-CeO<sub>2</sub> 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.%  $H_2O$ ). After calcination, the sample was cooled to 300 °C for 1 h using dry Ar. A-CeO<sub>2</sub>-750 was prepared under the same conditions as A-CeO<sub>2</sub>-ST without connecting to the water bubbler. Subsequently, Pd was loaded using a wet chemical method. Exactly 500 mg A-CeO<sub>2</sub>-ST (or A-CeO<sub>2</sub>, A-CeO<sub>2</sub>-750), 2.88 mg palladium (II) acetylacetonate (34.7% Pd, Alfa Aesar), and 21 mL ethylene glycol were mixed in a 50 mL round bottom flask and 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%  $O_2$  (mixed with He) at a 20 sccm flow rate for 5 h. The final sample was denoted as Pd\_A-ST (or Pd\_A, Pd\_A-750).

#### **1.2 Characterizations**

Powder X-ray diffraction (PXRD) patterns were collected in the 2 $\vartheta$  range of 10–90° using a Bruker D8 Advanced X-ray diffractometer (Cu K $\alpha$  radiation,  $\lambda$  = 1.5418 Å) operated at 40 kV and 40 mA. The scanning rate is 0.0025 °/s. Rietveld refinement was analyzed with a computer program (TOPAS). The metal content was determined using an iCAP 7400 inductively coupled plasma-optical emission spectroscopy (ICP-OES). Raman data were obtained using a Raman spectrometer (SR-500I-D2-1F1). The laser wavelength was 532 nm and a silicon wafer was used to calibrate the position. High-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained using JEOL JEM-2100 Plus with an accelerating voltage of 200 kV and JEOL JEM-ARM300F with double spherical aberration (Cs) correctors at 300 kV, respectively. Energy dispersive X-ray spectroscopy (EDS) data were obtained using a JEOL SDD system (100 mm<sup>2</sup> × 2). The powder samples were dispersed in ethanol and dropped onto a copper grid for TEM testing. The morphological study was conducted using a JEOL JSM-7800F field-emission scanning electron microscopy (SEM) with an accelerating voltage of 10 kV.

Conventional X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Scientific) with an Al K $\alpha$  source (1486.7 eV). The powder sample was placed on a double-sided tape, pressed into a tablet, and then placed on a multi-position sample stage for testing with the flood-gun source. All the XPS spectra were calibrated with the position of Ce 3d u<sup>III</sup> (916.7 eV).<sup>3,4</sup> When analyzing changes in oxygen

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species, a semi-quantitative calculation analysis was performed using the following formula:

$$\frac{N_{Ox}}{N_{Ce}} = \frac{I_{Ox}/\sigma_{Ox}}{I_{Ce}/\sigma_{Ce}}$$
(1)

where *N* is the number of atoms, *I* represent the peak area of the spectrum,  $\sigma$  is the cross section of O 1s or Ce 3d at 1486.7 eV (Al-K $\alpha$ ) incident photon energy, and  $O_x$  represents the different oxygen specious (x: lattice oxygen; defect-related oxygen; hydroxyl group, etc.). *In situ* XPS experiments were performed using a SPECS Surface Nano Analysis system. A monochromatized Al-K $\alpha$  source (1486.7 eV) and an infrared laser heater were used. A-CeO<sub>2</sub>-ST and A-CeO<sub>2</sub> were first pre-treated in an argon atmosphere at 200 °C for 1 h to remove surface-adsorbed impurities. Spectra were then collected at 525, 575, 625, and 675K under ultrahigh vacuum conditions. All the spectra were obtained when the samples reached a steady state.

Hydrogen temperature-programmed reduction ( $H_2$ -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%  $H_2$ /Ar gas mixture in the temperature range of 50–900 °C and at a ramp rate of 10 °C/min.

The adsorption heat and adsorption capacity of CO on palladium were collected using an integrated system of calorimeter (SenSys EVO) – chemisorption analyzer (PCT Pro) – mass spectrometer (TILON) instruments. The sample (~100 mg) was pretreated under a helium (He) atmosphere at 200 °C for 1 h and then cooled to 25 °C before the test. The flow of CO pulse (5 vol.% CO, mixed with He) was controlled by the chemisorption analyzer, and the flow was introduced once every 10 min. The instrument uses a quantitative loop to determine the throughput of each pulse, which is 1.174 µmol CO per pulse injection.

Fourier Transform Infrared spectroscopy (FTIR) was collected on the Thermo Fisher iS10 system. The samples were dried in a vacuum oven at 180 °C for 24 hours before testing, then taken out and quickly added to paraffin oil to isolate the air. Then, under the irradiation of the infrared lamp, the sample mixed with paraffin oil was ground well into a paste, and coated in the middle of BaF<sub>2</sub> infrared window for testing.

*Catalytic reactions:* The catalytic performance 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 10 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 CO<sub>2</sub> could be tested directly. The catalytic performance was calculated using the pressure of CO<sub>2</sub>. The CO conversion was calculated from the pressure of CO<sub>2</sub> using the following formula:

$$X_{CO}^{T} = \frac{P_{CO_2}^{T} - P_{CO_2}^{bypass}}{P_{CO_2}^{full} - P_{CO_2}^{bypass}} \times 100\%$$
(2)

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 CO<sub>2</sub> at temperature T, full conversion of CO, and the mixed gas bypasses through the catalysts, respectively.

#### 2. Results



**Figure S1.** Schematic illustration of steam modification process on ceria support. Step 1, synthesis of A-CeO<sub>2</sub>; Step2, steam treatment on A-CeO<sub>2</sub>; Step3, loading metal process on steam treated A-CeO<sub>2</sub>.



**Figure S2.** Catalytic CO oxidation performance of (a) Pd loaded on ceria with and without ST process including Pd\_A, Pd\_A-450, Pd\_A-ST-450; and (b) Pd loaded on ceria with different ST temperatures including Pd\_A-ST-450, Pd\_A-ST-600 and Pd\_A-ST-750. Pd\_A-450 obtained from the A-CeO<sub>2</sub> treated at 450 °C without steam. Pd\_A-ST-X, (X = 450, 600, 750), represents the Pd loaded on different ceria supports obtained from A-CeO<sub>2</sub> treated with steam at 450, 600, and 750 °C, respectively. A mixed gas (2% CO, 20% O<sub>2</sub>, 78% He) at a GHSV of 15000 mL·h<sup>-1</sup>·g<sub>cat</sub><sup>-1</sup> was used for the reaction condition.



**Figure S3.** TEM images of (a) ceria nanorod A-CeO<sub>2</sub>, and (b) polyhedral ceria Lack-CeO<sub>2</sub>. (c) Normalized Raman spectra of A-CeO<sub>2</sub> and Lack-CeO<sub>2</sub>. Lack-CeO<sub>2</sub> refers to a lack of defect ceria corresponding to polyhedral ceria.<sup>5</sup>

The peak at 250 cm<sup>-1</sup> in the Raman spectrum is attributed to the Ce-O longitudinal stretching of atoms in the outermost layers of ceria, and its intensity is related to the surface/bulk ratio of the ceria crystal.<sup>6</sup>



**Figure S4.** Normalized Raman spectra of Rich-CeO<sub>2</sub>. Rich-CeO<sub>2</sub> refers to commercial ceria nanorods with rich defects.

The peak at 1050  $\rm cm^{\text{-}1}$  in the Raman spectrum is attributed to the stretching vibrations of nitrate.  $^7$ 



**Figure S5.** SEM images and EDS spectra of (a-b) Pd\_A-ST before (a) and after (b) catalysis; (c-d) Pd\_Lack-ST before (c) and after (d) catalysis.



**Figure S6.** Cyclic performance for catalytic CO oxidation of (a) Pd\_Lack-ST, and (b) Pd\_A-ST. A mixed gas (2% CO, 20% O<sub>2</sub>, 78% He) at a GHSV of 15000 mL·h<sup>-1</sup>· $g_{cat}^{-1}$  was used for the reaction condition.



Figure S7. XPS spectra of Pd 3d core line of Pd\_A-ST before and after catalysis.



**Figure S8.** Schematic diagram of the synthesis processes of Pd\_A-ST, Pd\_A, (Pd\_A)-ST, and (Pd\_wd)-ST.

The ceria prepared by the hydrothermal method in the first step is denoted as A-CeO<sub>2</sub>. Then, A-CeO<sub>2</sub> was treated with steam at 750 °C to obtain A-CeO<sub>2</sub>-ST, and then loaded with 0.2 wt% palladium by wet chemical method, and calcined to be fully dispersed in an oxygen atmosphere (20% O<sub>2</sub> mixed with He) at 800 °C.<sup>8, 9</sup> Pd\_A was obtained by directly loading and dispersion process of Pd on A-CeO<sub>2</sub>. The obtained fully dispersed sample of Pd\_A was then treated with steam to obtain the sample 3, denoted as (Pd\_A)-ST. Another posted steam-treated sample is (Pd\_wd)-ST, which is obtained by direct steam treatment after metal loading process on A-CeO<sub>2</sub> without metal dispersion step.



**Figure S9.** Comparison of catalytic CO oxidation performance of Pd\_A-ST, Pd\_A, (Pd\_A)-ST, and (Pd\_wd)-ST. The GHSV was 100000 mL $\cdot$ h<sup>-1</sup>·g<sub>cat</sub><sup>-1</sup> for the reaction condition.

Catalyst	TemperatureMass specific activity $\times 10^{2 a}$ (°C)(mol <sub>co</sub> ·h <sup>-1</sup> ·g <sub>Metal</sub> <sup>-1</sup> )		Def
Catalyst			Kel.
Pd_A-ST	27	972 <sup>b)</sup>	this study
Pd_A-ST	27	317 <sup>c)</sup>	this study
$Pt_1/CeO_2-Al_2O_3$	27	296	10
(Pt 300)	27	230	
$1Pd/CeO_2-Al_2O_3$	27	128	11
Pt <sub>1</sub> /FeO <sub>x</sub>	27	44	12
Pt/FeO <sub>x</sub>	27	18	12
Pt/CeO <sub>2</sub>	27	9	13
Pd/CeO <sub>2</sub>	27	21	14
Pd/CeO <sub>2</sub>	27	23	15
Pd/CeO <sub>2</sub>	27	17	16

**Table S1.** Comparison of the mass specific activity of samples at room-temperature (27 °C) inthe literature and this study.

<sup>a)</sup> mass specific activity was calculated at 27 °C; <sup>b)</sup> the catalysis condition of Pd\_A-ST was at a GHSV of 300000 mL·h<sup>-1</sup>·g<sub>cat</sub><sup>-1</sup>. The Pd loading amount was determined by ICP-OES. <sup>c)</sup> the catalysis condition of Pd\_A-ST was at a GHSV of 15000 mL·h<sup>-1</sup>·g<sub>cat</sub><sup>-1</sup>.



Figure S10. (a-b) TEM and (c) SEM images of A-CeO<sub>2</sub>.



Figure S11. Normalized Raman spectra of A-CeO<sub>2</sub> and A-CeO<sub>2</sub>-ST.



Figure S12. FTIR spectra of A-CeO<sub>2</sub>, A-CeO<sub>2</sub>-ST and A-CeO<sub>2</sub>-750.



Figure S13. XPS analysis of O 1s of A-CeO<sub>2</sub>-ST and A-CeO<sub>2</sub>.

**Table S2.** The ratio of oxygen species relative to cerium in XPS analysis of O 1s and Ce 3d in A-CeO2-ST and A-CeO2.

	O <sub>lat.</sub> /Ce	O <sub>def.</sub> /Ce	O <sub>hyd.</sub> /Ce
A-CeO <sub>2</sub> -ST	2.05	0.09	0.15
A-CeO <sub>2</sub>	1.97	0.49	0.22



**Figure S14.**  $O_{all}/Ce$  ratio in the A-CeO<sub>2</sub> with the increase of temperature (from 525 to 675 K).

All spectra were obtained at a steady state.



**Figure S15.** (a) XRD, (b) Normalized Raman, (c) Nitrogen adsorption-desorption curves, and (d) FTIR of A-CeO<sub>2</sub>-750.



**Figure S16.** Comparison of catalytic CO oxidation performance of (a) Pd\_A-750, Pd\_A-ST and (b) A-CeO<sub>2</sub>-750, A-CeO<sub>2</sub>-ST. The GHSV was 15000 mL·h<sup>-1</sup>·g<sub>cat</sub><sup>-1</sup> for the reaction condition.



**Figure S17.** PXRD patterns of Pd\_A, Pd\_A-750, and Pd\_A-ST. Histograms are standard diffraction patterns for  $CeO_2$  (green), PdO (orange), and Pd (blue).



Figure S18. HAADF-STEM images and EDS spectra of (a-d) Pd\_A-ST, (e-h) Pd\_A-750, and (i-l)

Pd\_A.



**Figure S19.** (a) HRTEM, and (b) atomically resolved HAADF-STEM images of Pd\_A-ST. (c) The intensity analysis of atom A in (b) in different atomic directions (row  $X_1$  and column  $Y_1$ ) with the controlled intensities by column  $Y_2$ . (d-i) Atomically resolved HAADF-STEM images of (d-f) Pd A-750 and (g-i) Pd A. Palladium single atoms or clusters are circled with yellow circles.

Since the atomic number of Pd ( $Z_{Pd}$ ) is smaller than Ce ( $Z_{Ce}$ ), it is difficult to distinguish the darker Pd single atoms by an electron microscope under the dark field mode. Thus, the most likely doping site of atomic palladium can only be inferred from the analysis of the atomic intensity around the thin edge region.



**Figure S20.** XPS spectra of (a) Ce 3d and (b) Pd 3d core line of Pd\_A-ST, Pd\_A-750 and Pd\_A. All XPS spectra were calibrated with the position of Ce 3d u''' (916.7 eV). Gray ball: original experiment data. Gray solid line: peak fitting. Red solid line: total fitting results.



**Figure S21.** (a-b) From top to bottom: CO pulses detection of CO adsorption heat-CO chemisorption residual-online MS analysis of (a) Pd\_A-ST and (b) Pd\_A-750, respectively. (c) Detection of the heat released from CO adsorption on the samples of  $(A-CeO_2)$ -800,  $(A-CeO_2$ -750)-800, and  $(A-CeO_2$ -ST)-800 when the CO pulse passed through the samples. (X)-800 (X: different ceria supports) represents that different ceria supports have been calcined in an oxygen atmosphere (20% O<sub>2</sub> mixed with He) at 800 °C, in order to be compatible with the composite catalyst preparation process.

Total adsorption heat (J)	Total amount of CO	Normalized adsorption
	adsorbed	heat of Pd-CO
	(µmol)	(kJ/mol)
-0.19	2.21	-84.7
-0.27	2.75	-100.1
-0.20	1.83	-107.1
	Total adsorption heat (J) -0.19 -0.27 -0.20	Total amount of CO Total adsorption heat (J) -0.19 2.21 -0.27 2.75 -0.20 1.83

**Table S3.** The results of the adsorption heat and adsorption quantity of CO on Pd\_A, Pd\_A-ST and Pd\_A-750.

### Reference

- 1. X. Liu, K. Zhou, L. Wang, B. Wang and Y. Li, J. Am. Chem. Soc., 2009, **131**, 3140–3141.
- 2. L. Nie, D. Mei, H. Xiong, B. Peng, Z. Ren, X. I. P. Hernandez, A. Delariva, M. Wang, M. H. Engelhard, L. Kovarik, A.K. Datye and Y. Wang, *Science*, 2017, **358**, 1419–1423.
- 3. V. Muravev, G. Spezzati, Y.-Q. Su, A. Parastaev, F.-K. Chiang, A. Longo, C. Escudero, N. Kosinov and E. J. Hensen, *Nat. Catal.*, 2021, **4**, 469–478.
- 4. A. Boronin, E. Slavinskaya, I. Danilova, R. Gulyaev, Y. I. Amosov, P. Kuznetsov, I. Polukhina, S. Koscheev, V. Zaikovskii and A. Noskov, *Catal. Today*, 2009, **144**, 201–211.
- 5. A. Trovarelli and J. Llorca, ACS Catal., 2017, **7**, 4716–4735.
- 6. C. Schilling, A. Hofmann, C. Hess and M. V. Ganduglia-Pirovano, J. Phys. Chem. C, 2017, **121**, 20834–20849.
- 7. A. Filtschew, K. Hofmann and C. Hess, J. Phys. Chem. C, 2016, **120**, 6694–6703.
- 8. X. I. Pereira-Hernández, A. DeLaRiva, V. Muravev, D. Kunwar, H. Xiong, B. Sudduth, M. Engelhard, L. Kovarik, E. J. Hensen and Y. Wang, *Nat. Commun.*, 2019, **10**, 1–10.
- 9. R. Lang, W. Xi, J.-C. Liu, Y.-T. Cui, T. Li, A. F. Lee, F. Chen, Y. Chen, L. Li and L. Li, *Nat. Commun.*, 2019, **10**, 234.
- 10. H. Jeong, D. Shin, B. S. Kim, J. Bae, S. Shin, C. Choe, J. W. Han and H. Lee, *Angew. Chem. Int. Ed.*, 2020, **132**, 20872–20877.
- 11. H. Jeong, O. Kwon, B.-S. Kim, J. Bae, S. Shin, H.-E. Kim, J. Kim and H. Lee, *Nat. Catal.*, 2020, **3**, 368–375.
- 12. B. Qiao, A. Wang, X. Yang, L. F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li and T. Zhang, *Nat. Chem.*, 2011, **3**, 634–641.
- 13. S. Gatla, D. Aubert, G. Agostini, O. Mathon, S. Pascarelli, T. Lunkenbein, M. G. Willinger and H. Kaper, *ACS Catal.*, 2016, **6**, 6151–6155.
- 14. Y. Xia, J. Ye, D.-g. Cheng, F. Chen and X. Zhan, *Catal. Sci. Technol.*, 2018, **8**, 5137–5147.
- 15. Z. Hu, X. Liu, D. Meng, Y. Guo, Y. Guo and G. Lu, *ACS Catal.*, 2016, **6**, 2265–2279.
- 16. H. Jeong, J. Bae, J. W. Han and H. Lee, *ACS Catal.*, 2017, **7**, 7097–7105.