

Supplementary Information

Regulating the Pt1-CeO2 interaction via alkali modification for boosting the catalytic performance of single-atom catalyst

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Material and methods

Catalyst synthesis

Support ceria was prepared by thermal decomposition of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Macklin) at 300 °C for 3h. $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ (D-chem) and KNO_3 (Macklin) were solved in deionized water as a precursor solution, then 1 wt.% Pt and potassium ions were deposited on CeO_2 by incipient wetness impregnation, where the Pt/K atomic ratio was 1:3. After the samples were subsequently dried at 80 °C overnight, those powders were calcined in a muffle furnace for 10 h at 800 °C, where the temperature was heating up at 2 °C per minute. The obtained samples were denoted as Pt/ CeO_2 and K-Pt/ CeO_2 . As a reference, pure CeO_2 also be calcined at 800 °C with the same process as above, which was denoted as CeO_2 -800.

Characterizations

The X-ray diffraction (XRD) patterns were recorded on a Philips X'pert Pro diffractometer using Ni-filtered Cu $\text{K}\alpha_1$ radiation ($\lambda = 0.15418$ nm). The scanning degree is from 10° to 80° with a scanning rate of 10°/min. The X-ray tube was operated at 40 kV and 30 mA.

The special surface area and pore volume measurements were analyzed by N_2 adsorption-desorption under -196 °C via Micromeritics ASAP-2020. All samples pre-degassed at 300 °C for 3h before each measure.

Atomic-resolution high angle annular dark-field scanning transmission electron microscopic (HAADF-STEM) images were collected on a FEI Titan Cubed G2 60-300 aberration-corrected S/TEM instrument at 200 kV accelerating voltage. The probe convergence angle was 25 mrad. The images of energy dispersive spectroscopy (EDS) elemental mapping in the STEM mode were obtained from the Titan electron microscope using SuperX system.

X-ray absorption spectroscopy (XAS) for Pt L_3 -edge was measured in fluorescence mode at 7-BM QAS beamline of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory. The beamline could provide X-ray energies ranging from 4.7 to 31 keV. The

monochromator has a Si(111) channel-cut crystal and runs in continuous scan mode. 50 scans were collected and merged for each sample. The XAS data including X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) was analyzed using Demeter software package.

The Raman spectra were collected on LabRAM Aramis (Horiba, Japan) Laser Raman spectroscopy using Ar⁺ laser beam with 532 nm wavelength.

The redox performance of samples was analyzed by H₂-temperature programmed reduction. H₂-TPR was carried out in a quartz U-tube reactor detected by a TCD with 7% H₂/Ar as reductant. Before the test, each sample was pretreated in a pure N₂ stream at 200 °C for 1 h to sweep off impurities.

O₂-TPD profiles were collected in a quartz U-tube reactor and detected by TCD with He as the carrier gas, the samples were pretreated with He at 200 °C for 1.5 h, followed by oxygen adsorption to saturation at 40 °C and He purging until the baseline was stable.

XPS of prepared catalysts were collected on a PHI 5000 VersaProbe system. The accelerating power of monochromatic K α radiation is 15 kW. The binding energy of all samples was calibrated with C1s at 284.6 eV.

The *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) were collected on a Thermo Nicolet iS50 FTIR spectrometer detected by an MCT detector. About 30 mg catalysts were loaded in a sample cell and pretreat in flowing 20% O₂/He (50 mL/min) at 400 °C for 1 h before each test. After cool down to 50 °C, background spectra were collected from 500 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹ for 64 scans. In CO adsorption, samples were exposed at a flowing gas (1% CO + 1% O₂/ He balanced, 50 mL/min) under 50 °C for 90 min. CO desorption was purged in pretreat gas at 50 °C for 30 min. The aging process was set at 400 °C with purge with the same atmosphere as CO adsorption.

Catalytic activity measurements

CO oxidation: Approximately 10 mg sample (40-60 mesh) was used in each CO oxidation test attenuated by 190 mg SiC. Before the reaction, the samples were pretreated for 1 h under pure air stream at 200 °C with a flowing rate at 30 ml·min⁻¹. Then atmosphere was switched to feed gas that made up of 1% CO, 1% O₂ and He balanced, corresponding to a weight hourly space velocity of 150,000 mL·g_{cat}⁻¹·h⁻¹. The oxidation reacted in a fixed-bed reactor, and the composition of outlet gas was analyzed by an online gas chromatograph furnished with a flame ionization detector (FID).

CO conversion is calculated by

$$\text{CO conversion} = \left(1 - \frac{[CO]_{out}}{[CO]_{in}} \right) \times 100\%$$

C₃H₈ oxidation: 60 mg catalyst (40-60 mesh) was first mixed into 300 mg by 240 mg SiC, then diluted catalysts were tested in a fixed-bed reactor. For each reaction, the atmosphere consisted of 4000 ppm C₃H₈, 4% O₂ and Ar balanced, and the weight hourly space velocity (WHSV) was set at 100,000 mL·g_{cat}⁻¹·h⁻¹. The outlet gas was analyzed by an online mass spectrometer. The mass to charge (m/z) ratio used for the detection of CO₂ was 44.

Table S1 Texture property and reaction ability of samples

	S_{BET} (m ² /g) ^[a]	Pore Volume (m ³ /g) ^[b]	T ₁₀ (°C) ^[c]	T ₅₀ (°C) ^[d]
CeO ₂	65.0	0.22	298	393
CeO ₂ -800	6.5	0.04	363	470
Pt/CeO ₂	32.4	0.12	282	385
K-Pt/CeO ₂	11.0	0.11	151	228

[a][b] S_{BET} and pore volume are determined by N₂ adsorption-desorption; [c] T₁₀ represents the temperature where 10% CO in the reaction atmosphere converted to CO₂. [d] T₅₀ represents the temperature spot that 50% CO was oxidized to CO₂.

Table S2 EXAFS Pt L₃-edge fitting results of Pt/CeO₂ and K-Pt/CeO₂. (Shell: chemical bond; CN: coordination number; R: bond length; ΔE_0 : inner potential correction; σ^2 : Debye-Waller factor)

	Shell	CN	R (Å)	ΔE_0 (eV)	σ^2 (10^{-3} Å ²)
Pt	Pt-Pt	12.0 ± 0.8	2.76 ± 0.01	7.6 ± 0.5	4.13 ± 0.56
PtO ₂	Pt-O	6.0 ± 1.0	2.02 ± 0.02	11.1 ± 2.2	0.14 ± 2.15
	Pt-O-Pt	6.0 ± 1.0	3.12 ± 0.06	14.1 ± 6.1	3.57 ± 3.34
Pt/CeO ₂	Pt-O	6.5 ± 1.3	1.99 ± 0.02	7.4 ± 2.4	2.78 ± 2.78
	Pt-O-Ce	4.0 ± 3.6	3.10 ± 0.06	-0.4 ± 7.5	4.35 ± 7.65
K-Pt/CeO ₂	Pt-O	6.3 ± 0.5	2.00 ± 0.02	7.8 ± 1.9	2.78 ± 2.78
	Pt-O-Ce	2.9 ± 1.1	3.07 ± 0.06	-2.8 ± 8.2	4.35 ± 7.65

Table S3 ICP-OES results of different samples.

Samples	Pt/wt. %	K/wt. %	Theoretical K/Pt ratio	Measured K/Pt ratio
K-Pt/CeO ₂ - 0.2	0.20	0.05	3.00	1.23
K-Pt/CeO ₂ - 0.5	0.46	0.07	3.00	0.79
K-Pt/CeO ₂ - 0.8	1.03	0.15	3.00	0.72
K-Pt/CeO ₂ - 1.0	0.99	0.15	3.00	0.75
K-Pt/CeO ₂ - 1.5	1.40	0.22	3.00	0.78
K-Pt/CeO ₂	0.95	0.15	3.00	0.77
K/CeO ₂	0	0	-	-

Table S4 Chemical state distribution and surface atomic concentration of Pt/CeO₂ and K-Pt/CeO₂

	Pt ²⁺ /Pt (%)	Pt ^{2+δ} /Pt (%)	Ce ³⁺ (%)	O content (%)		Surface atomic concentration (%)			
				O _{α}	O _{β}	K	Pt	Ce	O
				Pt/CeO ₂	93.3	6.7	21.6	72.3	27.7
K-Pt/CeO ₂	85.4	14.6	20.0	72.2	27.8	2.0	1.6	22.1	74.3

The data listed above were determined by XPS.

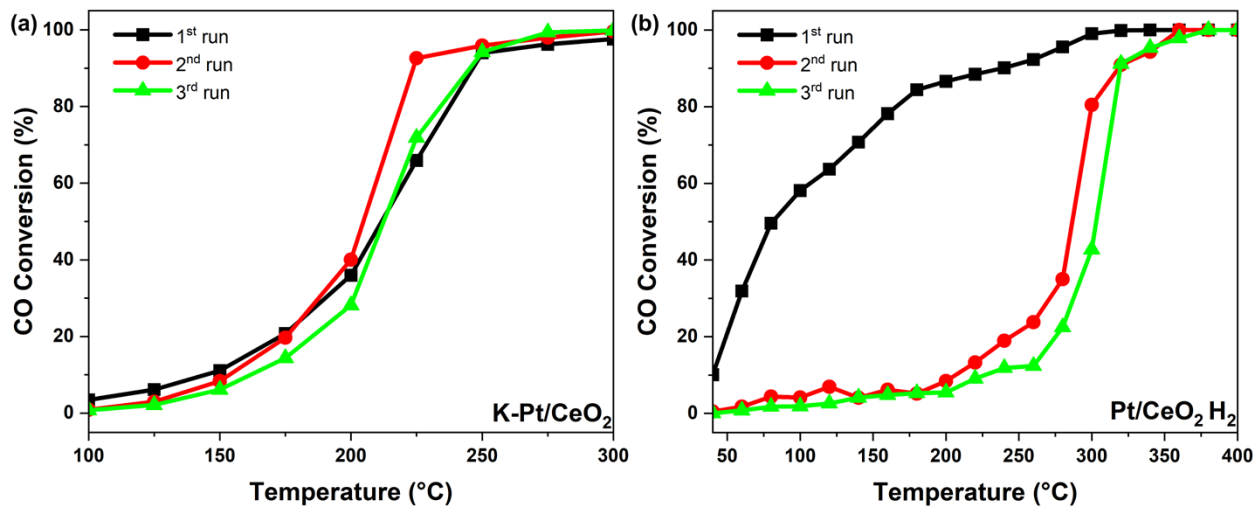


Fig. S1 Cycling stability experiments of (a) K-Pt/CeO₂ and (b) Pt/CeO₂ H₂ (activated by 7% H₂/He at 400 °C for 1h), from ambient temperature to 550 °C and hold for 1 h.

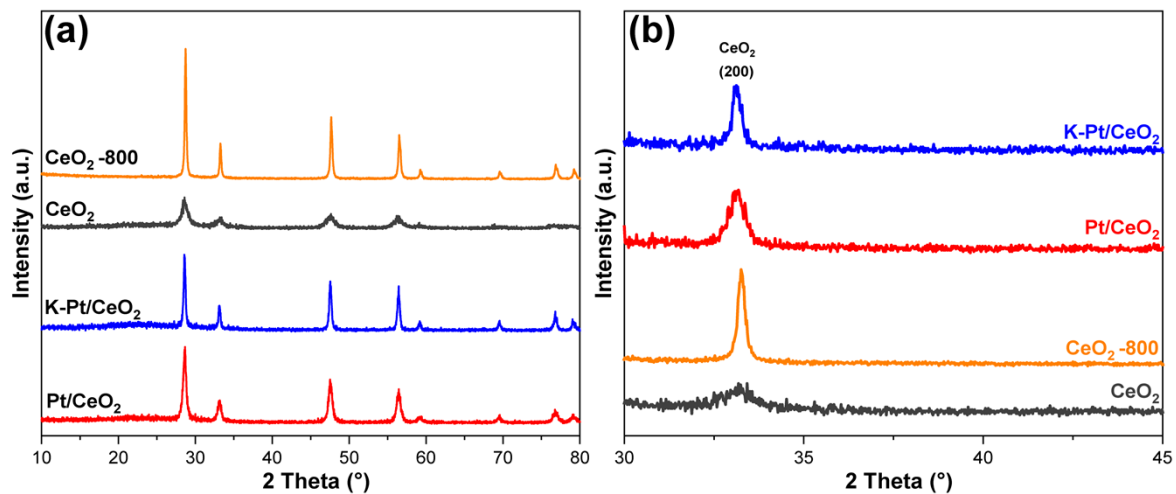


Fig. S2 XRD patterns with diffraction (a) degree from 10° to 80° and (b) enlarged from 30° to 45° of CeO_2 , CeO_2 -800, Pt/CeO_2 , and $\text{K-Pt}/\text{CeO}_2$

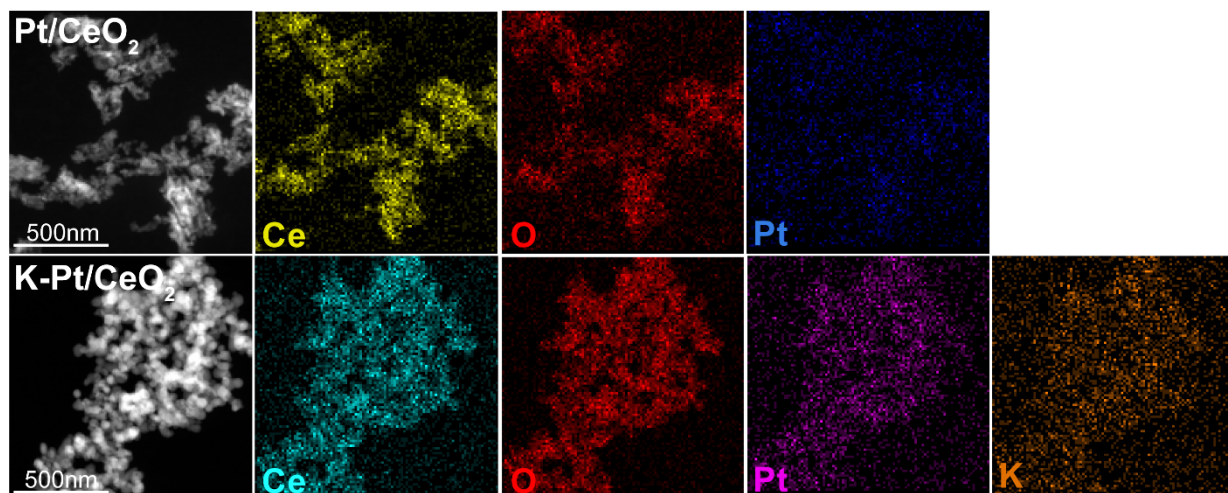


Fig. S3 The element-sensitive mapping images of Ce, O, Pt, K of both samples.

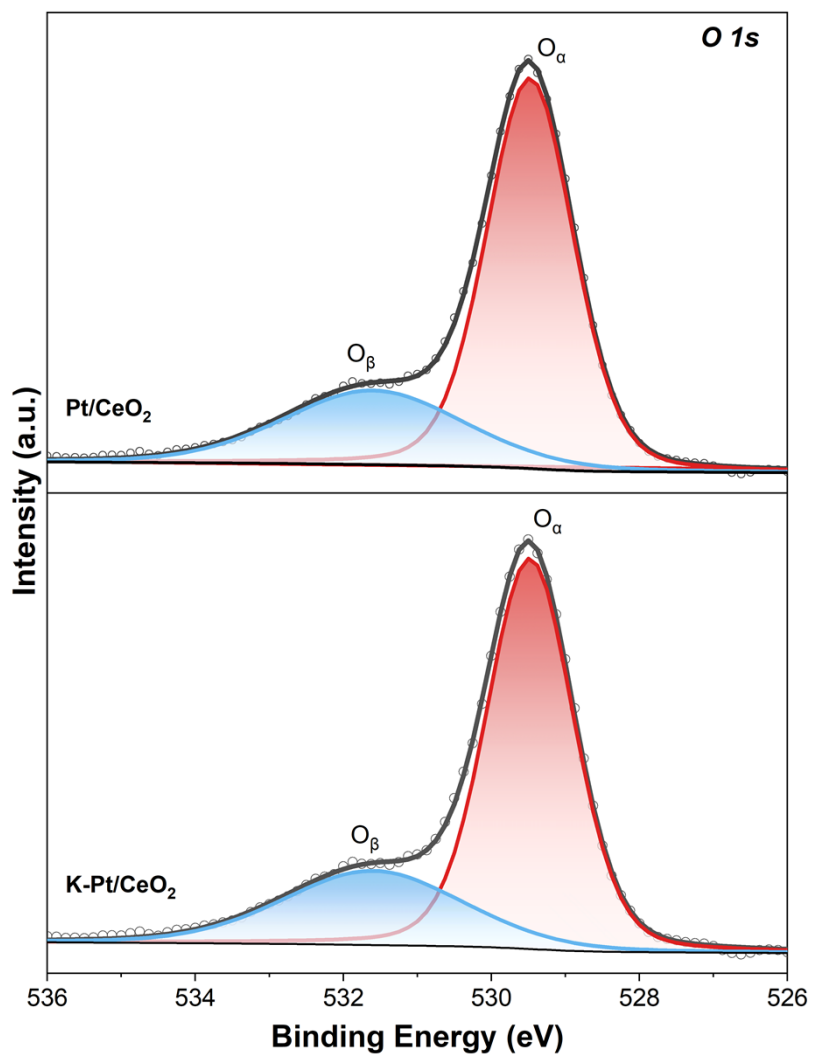


Fig. S4 O 1s XPS spectra of the catalyst: Pt/CeO₂ and K-Pt/CeO₂.

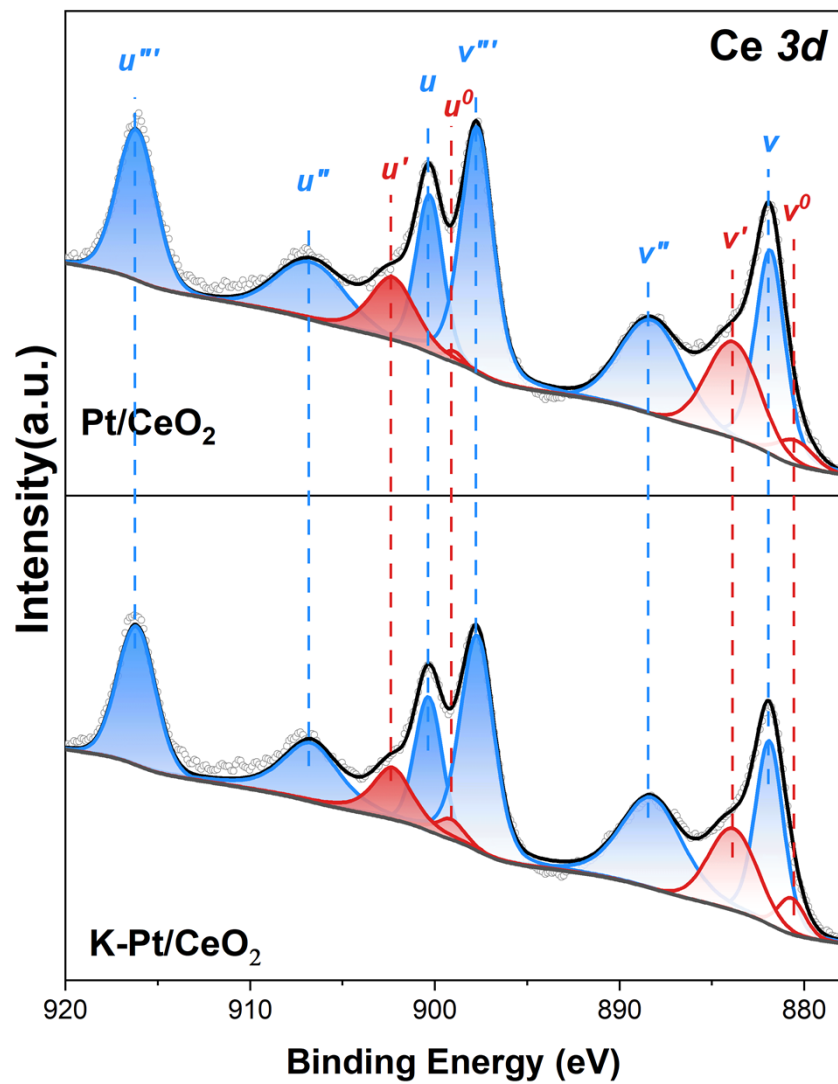


Fig. S5 Ce 3d XPS spectra of the catalyst: Pt/CeO₂ and K-Pt/CeO₂.

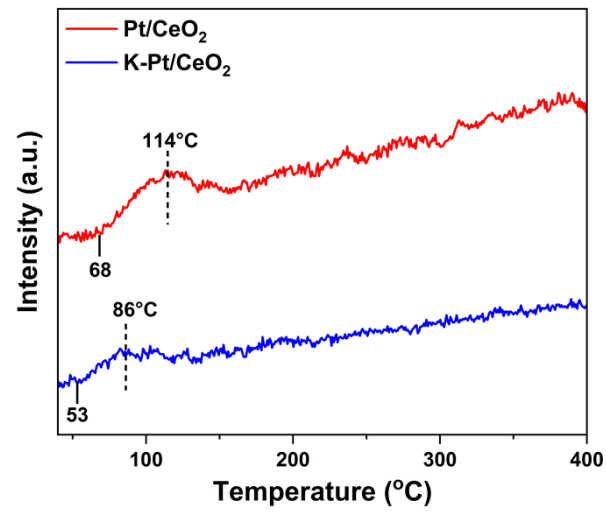


Fig. S6 O₂-TPD profiles for Pt/CeO₂ and K-Pt/CeO₂.