

Supporting Information

Temperature and reaction environment influence the nature of platinum species supported on ceria

Xiansheng Li^{a,b}, Xing Wang^{a,b}, Ilia I. Sadykov^{a,c}, Dennis Palagin^b, Olga V. Safonova^c, Junhua Li^d, Arik Beck^a, Frank Krumeich^a, Jeroen A. van Bokhoven^{a,b*} and Luca Artiglia^{b,e*}

^aInstitute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland

^bLaboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institute, 5232 Villigen, Switzerland

^cLaboratory for Operando Spectroscopy, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

^dSchool of Environment, Tsinghua University, Beijing, 100084, China

^eLaboratory of Environmental Chemistry, Paul Scherrer Institute, 5232 Villigen, Switzerland

corresponding authors email:

(L.A.) luca.artiglia@psi.ch;

(J.A.vB) jeroen.vanbokhoven@chem.ethz.ch

METHODS

Catalyst preparation

1 wt % Pt/CeO₂ catalyst was prepared by incipient wetness impregnation. Ce(NO₃)₃·6H₂O (99%; Sigma-Aldrich) was heated in air at 350 °C for 2 h to obtain bare ceria support. An appropriate amount of chloroplatinic acid (Alfa Aesar, 99.9%) was dissolved and the solution was added drop-wise to the ceria while grinding. The powder was then dried at 80°C for 12 h. Afterwards, the sample was directly calcined and thermally aged at 800°C for 12 h in flowing air. Such sample is designated as Pt/CeO₂. Pt/CeO₂ (0.3 g) was loaded in a quartz tube flow reactor and steam treated by 10% H₂O in Argon (70 mL/min) at 750 °C for 9 h. The sample was then cooled down to 300 °C and the water vapor was discontinued. Subsequently, the sample was purged in the same carrier gas for 1 h before cooling down to room temperature. The resulting sample is designated as Pt/CeO_{2_s}. Ceria was also thermally aged under the same conditions as described above, and designated as CeO_{2_s}. The calcination and steam treatment heating ramp was 5°C/min. N₂ adsorption and desorption measurements were conducted at 77 K using a Micromeritics 3 Flex automatic surface area and pore size analyzer. BET surface area of Pt/CeO₂, Pt/CeO_{2_s} and CeO₂ are 17.4, 14.9 and 106.2 m²/g.

Electron microscopy

Transmission electron microscopy (TEM) was performed using a Jeol JEM 2010 at 300 kV at the Electron Microscopy Facility (EMF) of the Paul Scherrer Institute. Scanning TEM (STEM) at 200 kV using high-angle annular dark field (HAADF) imaging was performed with a Hitachi HD 2700 electron microscope equipped with a Cs-corrector at the Scientific Center for Optical and Electron Microscopy (ScopeM) of ETH Zurich. Electron microscopy was acquired ex situ, in vacuum (10⁻⁶ mbar pressure range). Fresh Pt/CeO₂ and Pt/CeO_{2_s} samples were synthesized and transferred to the TEM facility while exposed to air.

CO oxidation performance

CO oxidation reaction was conducted in an atmospheric pressure fixed-bed quartz micro-reactor. 30 mg of catalyst, sieved to 40 to 60 mesh, were diluted with inert SiO₂ powder (0.3 g) to prevent temperature gradients. The concentrations of CO and CO₂ at the outlet were continually monitored with an FTIR spectrometer (MultiGas TM 2030 FTIR Continuous Gas Analyzer). The catalyst was pretreated with 100 sccm (standard cubic centimeter per minute)

of 10% O₂/Ar at 300°C for 1h before cooling down to room temperature. For CO oxidation reaction, the reaction temperature was ramped up from 30 °C to 500 °C with a heating rate of 2 °C /min. The flow mixture was 1.15% CO, 5% O₂ and N₂ balance, total flow rate was 100 sccm, velocity was 200 000 h⁻¹.

FIGURES AND TABLES

Table S1. Peak Fitting Parameters (Position and FWHM) of Pt4f Photoemission Spectra.

Pt species	Position/eV	FWHM/eV	Asymmetry parameters	
			TS	TL
Pt⁰	71.0±0.05	1.13	0.3	110
Pt²⁺	72.7±0.1	1.13	0	1

Table S2. EXAFS fitting parameters of Pt foil, Pt/CeO₂ and Pt/CeO₂_s.

Sample	Shell	CN	R(Å)	σ^2 (Å ²)	ΔE_0 (eV)	S_0^2
Pt/CeO₂	Pt-O	4.1±0.7	2.00±0.02	0.0004±0.002	4.8±2.2	0.88
Pt/CeO₂_s	Pt-O	2.0±1.3	1.92±0.03	0.01±0.01	4.3±1.7	0.88
	Pt-Pt	10.1±2.8	2.68±0.02	0.012±0.004	4.3±1.7	0.88
Pt foil	Pt-Pt	12	2.76±0.005	0.0051±0.0005	6.0±0.7	0.88

CN, coordination number; R, distance between absorber and backscatter atoms; σ^2 , Debye–Waller factor of the reference compound; ΔE_0 , inner potential correction to account for the difference in the inner potential between the sample and the reference compound. The amplitude-reduction factor S_0^2 was established for the Pt foil reference and was fixed for EXAFS fitting.

Table S3. Bader charge differences for platinum in bulk platinum oxides and atomically dispersed platinum species on ceria (223) surface.

	Platinum species	Space group	Bader charge(e)
Bulk references	PtO ₂ bulk	pnnm	1.51
	PtO bulk	P4 ₂ /mmc	0.88
	Pt bulk	Fm $\bar{3}$ m	0.00
Molecule/cluster references	PtO ₂	-	1.15
	(PtO ₂) ₄ on ceria (111)	-	1.26
Pt AD structures	Platinum in [Pt-4O]	-	1.07
	Platinum in [Pt-4O]-Ov	-	0.74

Table S4. LCF results of XANES spectra acquired under different conditions.

Experiment	Sample	Acquisition condition	Pt ⁰ /%	error	Pt ²⁺ /%	error	Pt ⁴⁺ /%	error
Steady state	Pt/CeO ₂	RT in air	0.0	9.1	29.5	11.7	70.5	7.3
	Pt/CeO _{2_s}	RT in air	63.8	2.4	16.4	3.1	19.7	1.9
In situ steaming	Pt/CeO ₂	RT in air	0.0	10.4	15.0	13.3	85.0	8.3
		96°C	0.0	5.8	20.7	7.4	79.3	4.5
		201°C	0.8	5.5	26.7	7.0	72.5	4.3
		301°C	11.2	6.5	22.8	8.3	66.1	5.1
		406°C	3.7	5.9	39.7	7.4	56.7	4.6
		506°C	0.0	6.2	48.3	7.8	51.7	4.8
		611°C	7.4	6.0	41.4	7.6	51.1	4.7
		691°C	9.2	4.1	51.0	5.3	39.7	3.2
		800°C	24.9	3.8	35.0	4.8	40.1	2.9
In situ reaction	Pt/CeO ₂	300°C O ₂	0.0	7.1	49.9	8.9	50.1	5.5
		220°C CO+O ₂	0.0	6.6	59.3	8.4	40.7	5.1
		300°C CO+O ₂	0.0	5.2	67.3	6.5	32.7	4.0
		400°C CO+O ₂	0.0	4.6	68.2	5.9	31.8	3.6
	Pt/CeO _{2_s}	300°C O ₂	46.2	3.5	21.1	4.4	32.7	2.7
		100°C CO+O ₂	32.8	2.8	64.2	3.5	3.0	2.2
		150°C CO+O ₂	38.5	1.8	45.0	2.2	16.6	1.4
		200°C CO+O ₂	29.4	2.6	61.5	3.3	9.1	2.0

Table S5. Comparison of results using different methods for platinum speciation quantification.

Sample	Pt ⁰ /%	error	Pt ²⁺ /%	error	Pt ⁴⁺ /%	error
Pt/CeO ₂ (-20 to +40 eV)	0.0	11.0	22.8	16.1	77.2	19.5
Pt/CeO _{2_s} (-20 to +40 eV)	63.2	2.4	17.2	3.6	19.5	4.7
Pt/CeO ₂ (-10 to +90 eV)	0.0	9.1	29.5	11.7	70.5	7.3
Pt/CeO _{2_s} (-10 to +90 eV)	63.8	2.4	16.4	3.1	19.7	1.9

Table S6. Proportion of platinum species on Pt/CeO₂ and Pt/CeO_{2_s} in the reaction gas of CO + O₂ at different temperatures during in situ XPS measurement.

	Reaction temperature/°C	Pt⁰ proportion/%	Pt²⁺ proportion/%
Pt/CeO₂	220	0	100
	300	0	100
	400	0	100
Pt/CeO_{2_s}	100	94	6
	150	93	7
	200	90	10

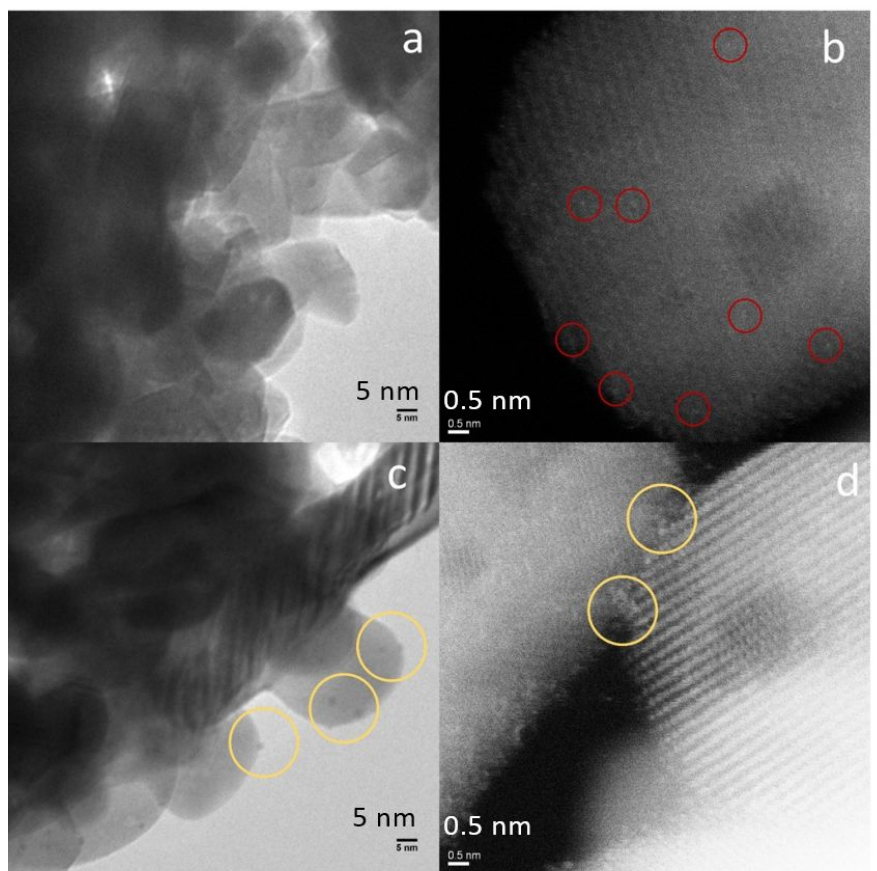


Figure S1. Transmission electron microscope (TEM) morphologies of the Pt/CeO₂(a)(b) and Pt/CeO₂_s(c)(d). (a)(c) were acquired by a high resolution transmission electron microscopy. (b)(d) were implemented by high-angle annular dark field mode scanning transmission electron microscopy (HAADF-STEM). Platinum nanoparticles have been marked in the yellow circles in (c)(d) and atomically dispersed platinum atoms are in red circles in (b).

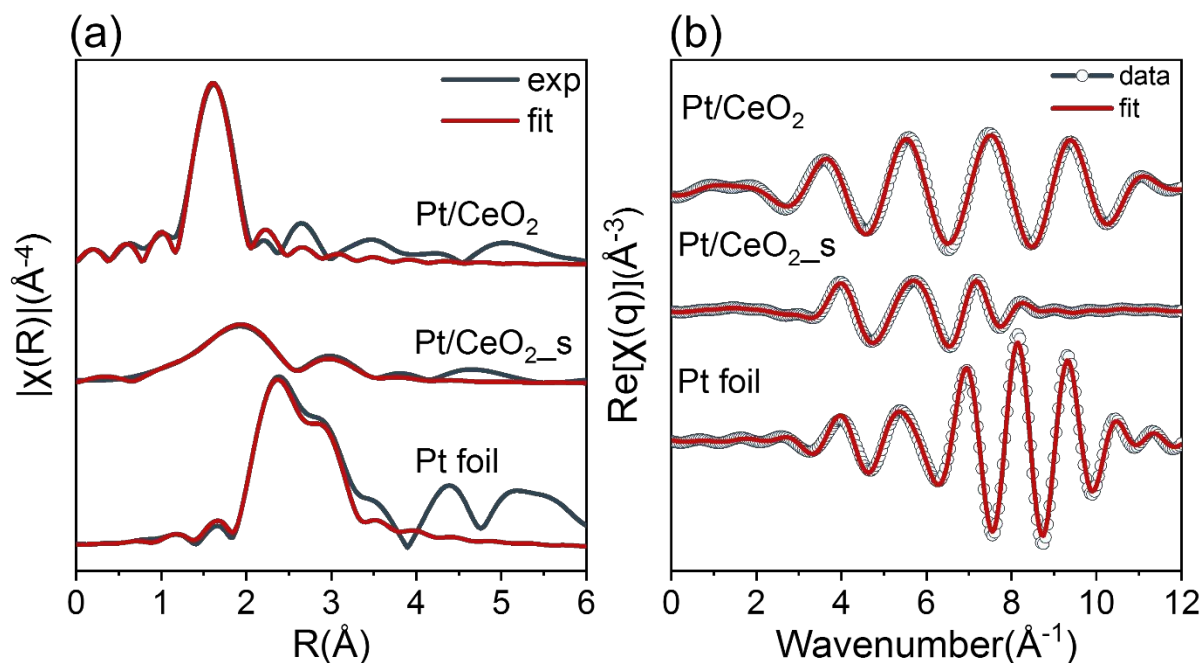


Figure S2. (a) The k^3 -weighted Fourier transform from EXAFS spectra and (b) EXAFS spectra in q -space of Pt L_3 edge for Pt/CeO₂, Pt/CeO_{2_s}, Pt foil and PtO₂. Fits were performed over an R range of 1.25–3.4 \AA for Pt foil in k range 3–10 \AA^{-1} , R range of 1.15–4 \AA for Pt/CeO_{2_s} in k range 3–8 \AA^{-1} , R range of 1.3–2.6 \AA for Pt/CeO₂ in k range 3–10.5 \AA^{-1} . The peaks in the first shell of Pt/CeO₂ and Pt/CeO_{2_s} are fitted to the Pt–O contribution, and the peaks in the second shell of Pt/CeO_{2_s} are fitted to the Pt–Pt coordination. The Pt–O path calculated by atomically dispersed [Pt-4O]/CeO₂(223) model was used to fit the Pt–O contribution in Pt/CeO₂.

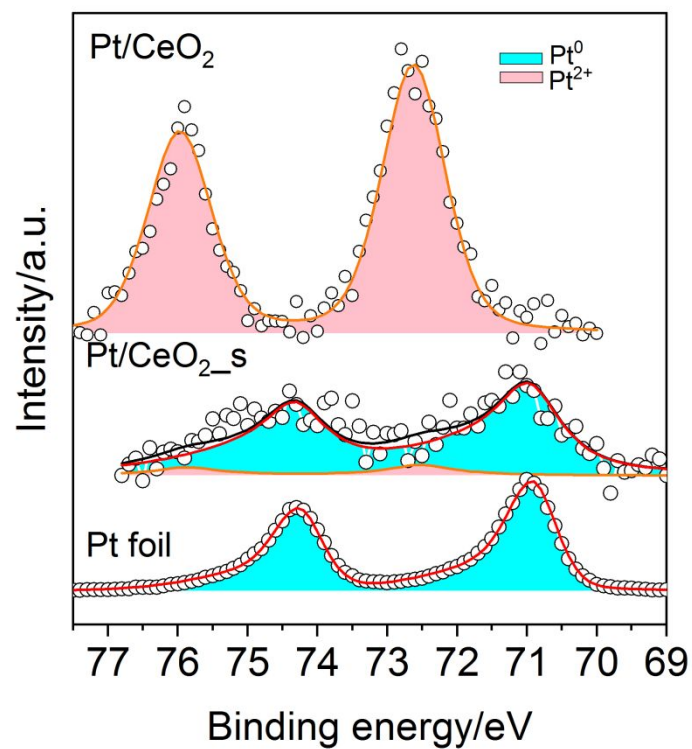


Figure S3. Deconvolution of Pt 4f XPS profile for Pt/CeO₂, Pt/CeO_{2_s} and Pt foil. The spectra of Pt/CeO₂ and Pt/CeO_{2_s} were acquired during activation in 1mbar O₂ at 300°C. Spectra of Pt foil were acquired under high vacuum. The Doniach-Sunjic asymmetric parameters for fitting of Pt/CeO_{2_s} were obtained from the fitting of Pt foil spectra. Pt/CeO₂ was used as a reference of Pt²⁺.

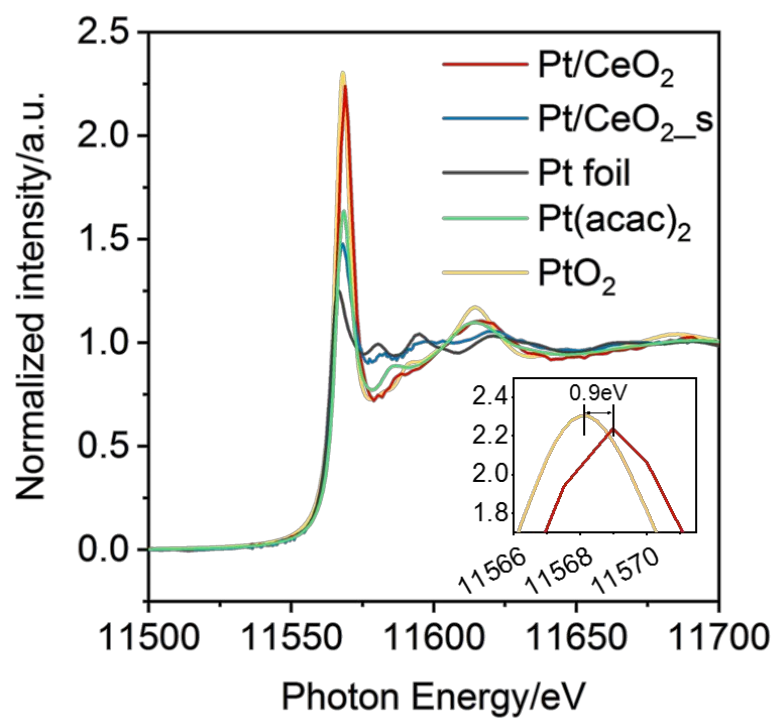


Figure S4. The normalized Pt L₃ edge XANES spectra of Pt/CeO₂, Pt/CeO_{2_s}, PtO₂, Pt(acac)₂ and Pt foil. All the spectra were collected in air at room temperature. There is 0.9eV energy shift between Pt/CeO₂ and PtO₂.

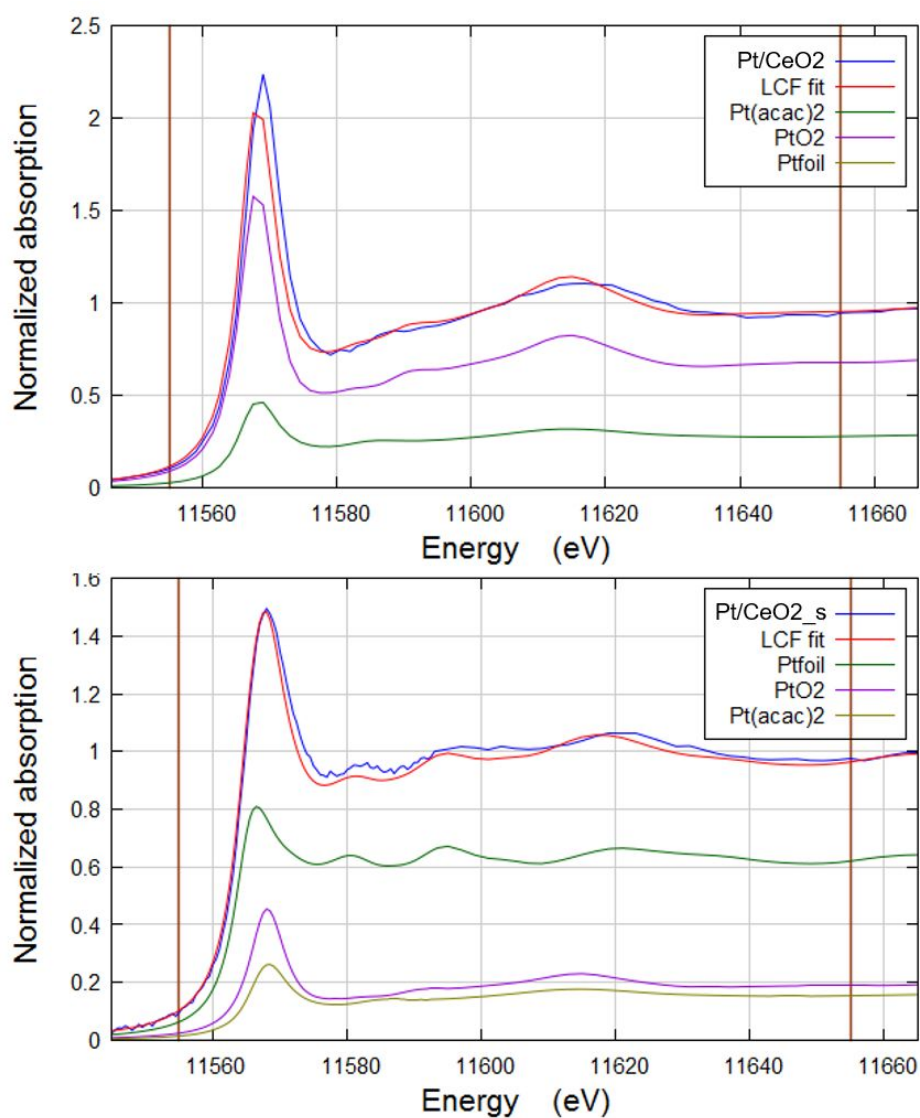


Figure S5. XANES Linear combination fitting details of Pt/CeO₂ and Pt/CeO_{2_s}. The reference spectra for LCF are acquired from Pt foil, Pt(acac)₂ and PtO₂. The energy range for fitting is 11555.8 eV – 11655.8 eV. All weights are constrained between 0 and 1, and weights are forced to sum to 1.

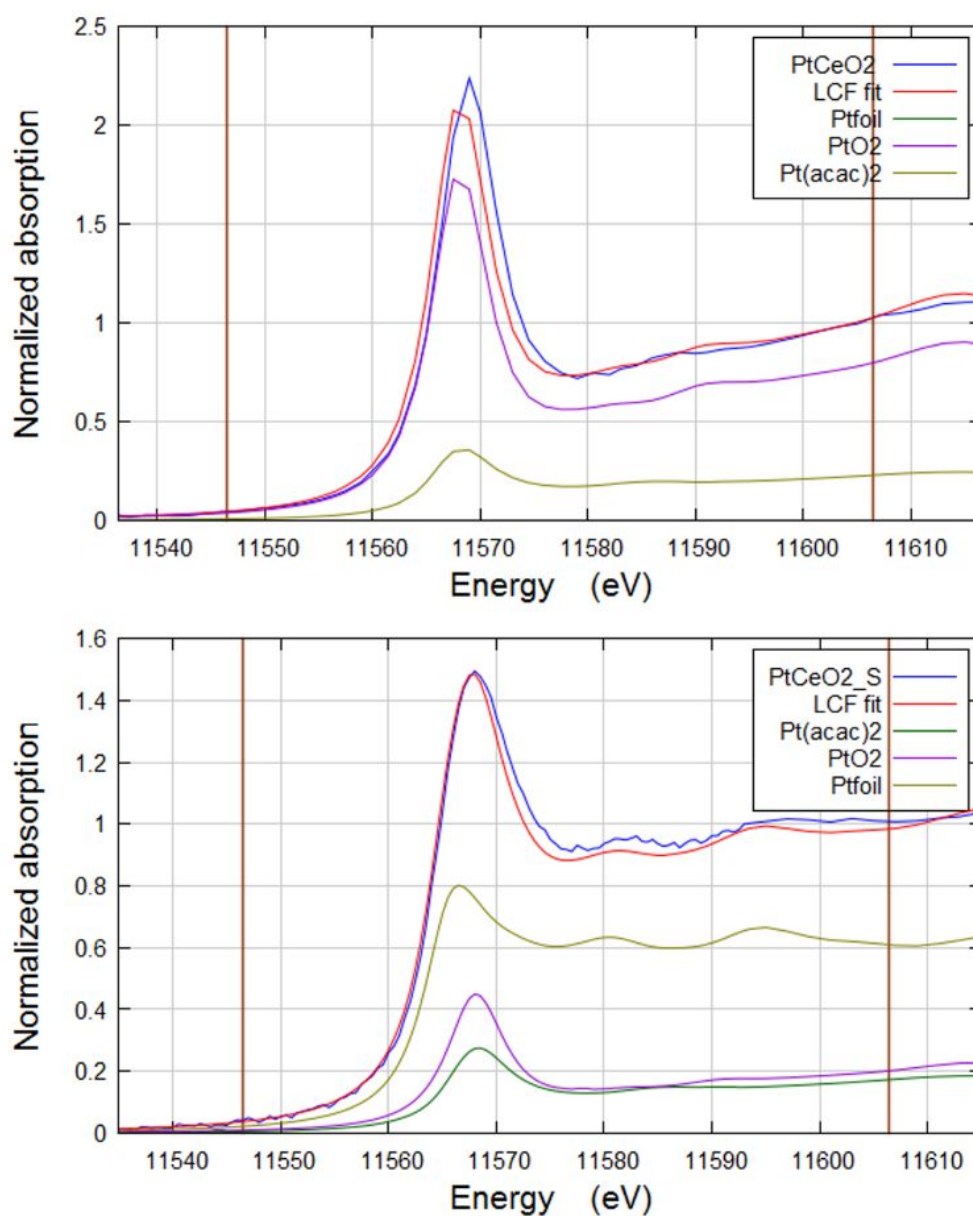


Figure S6. XANES Linear combination fitting details of Pt/CeO₂ and Pt/CeO₂_s. The reference spectra for LCF are acquired from Pt foil, Pt(acac)₂ and PtO₂. The energy range for fitting is -20 to 40 eV. All weights are constrained between 0 and 1, and weights are forced to sum to 1.

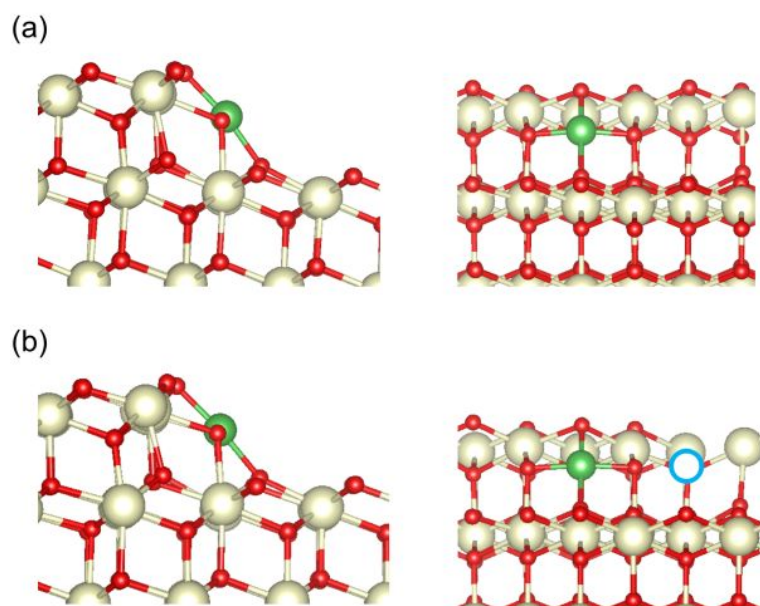
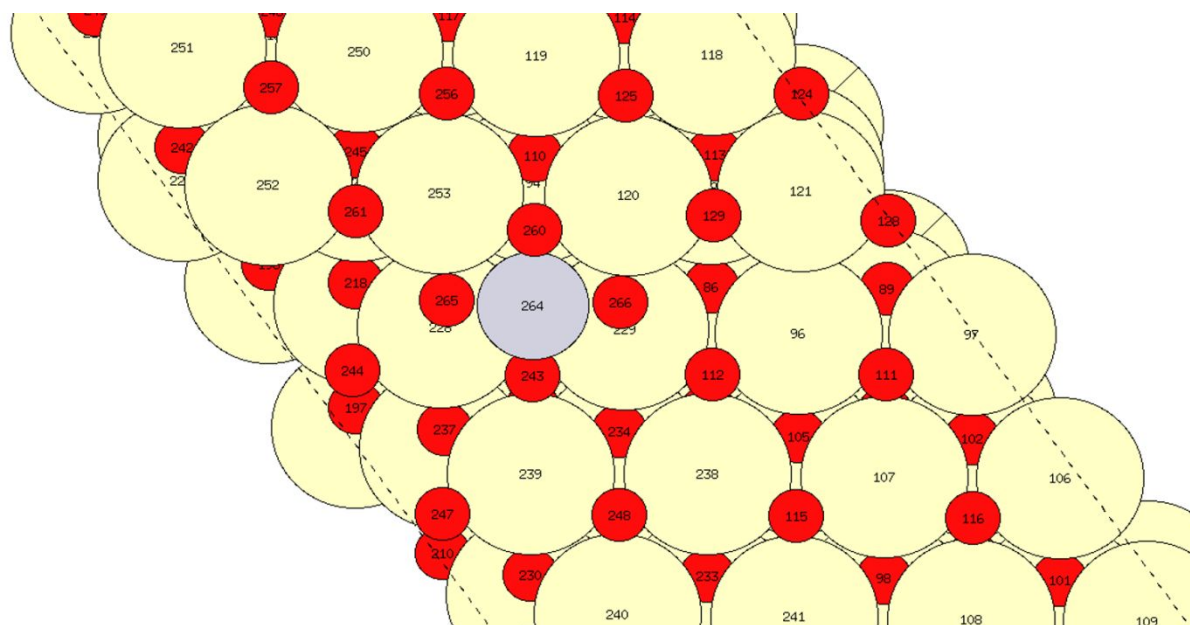


Figure S7. The most stable geometry of atomically dispersed platinum species on CeO₂ (223) surface in side and top views. (a) Pt^{IV}O₂, (b) Pt^{II}O. Green spheres: Pt atoms, gray spheres: Ce atoms, red spheres: O atoms, and the blue circle represent an oxygen vacancy.



Relative stability of [Pt-4O]
with one oxygen vacancy

Ov index	Relative stability (eV)	Bader charge
O-129	0.00	0.74
O-112	+1.06	0.75
O-128	+0.44	0.76
O-115	+1.44	0.76
O-111	+1.58	0.76
O-247	+1.28	0.76
O-244	+1.07	0.76

Relative stability of [Pt-4O]
with two oxygen vacancies

Ov index	Relative stability (eV)	Bader charge
265-266	+1.87	-0.03
129-243	+3.41	-0.05
129-260	+3.14	0.005
129-265	+2.56	0.027
129-266	+3.13	0.029

Figure S8. Structures and relative stability of [Pt-4O] with one and two oxygen vacancies in different locations on ceria 223 face.

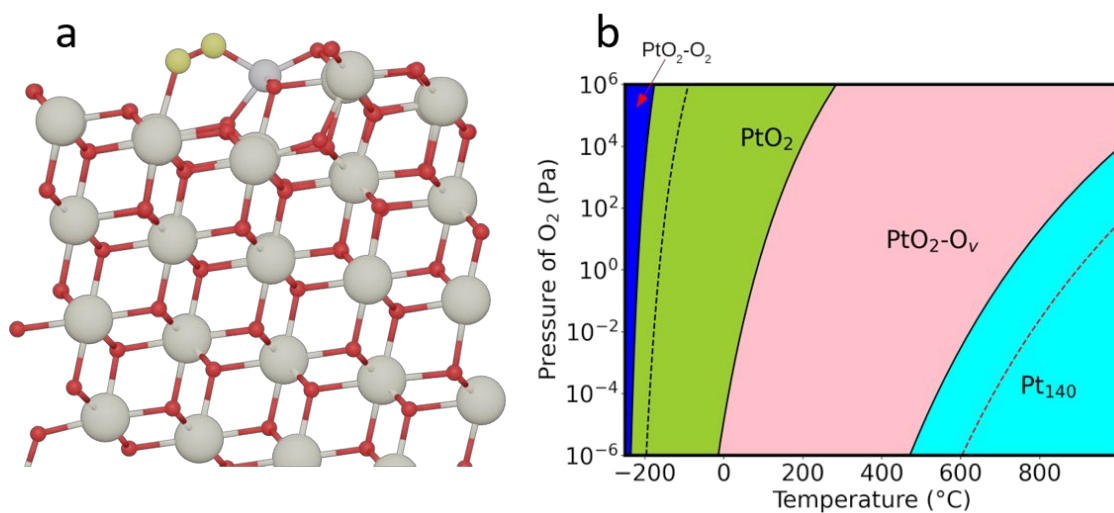


Figure S9. (a) Optimized structure for adsorbed O₂ on [Pt^{IV}O₂] and (b) Phase diagram of platinum species as a function of temperature and pressure of O₂. Black dashed line is plotted using the adsorption energy reported in the paper (ACS Catalysis, 2021, 11, 8701-8715). Red dashed line is the equilibrium line between the atomically dispersed Pt⁰ species and PtO₂-O_v species.

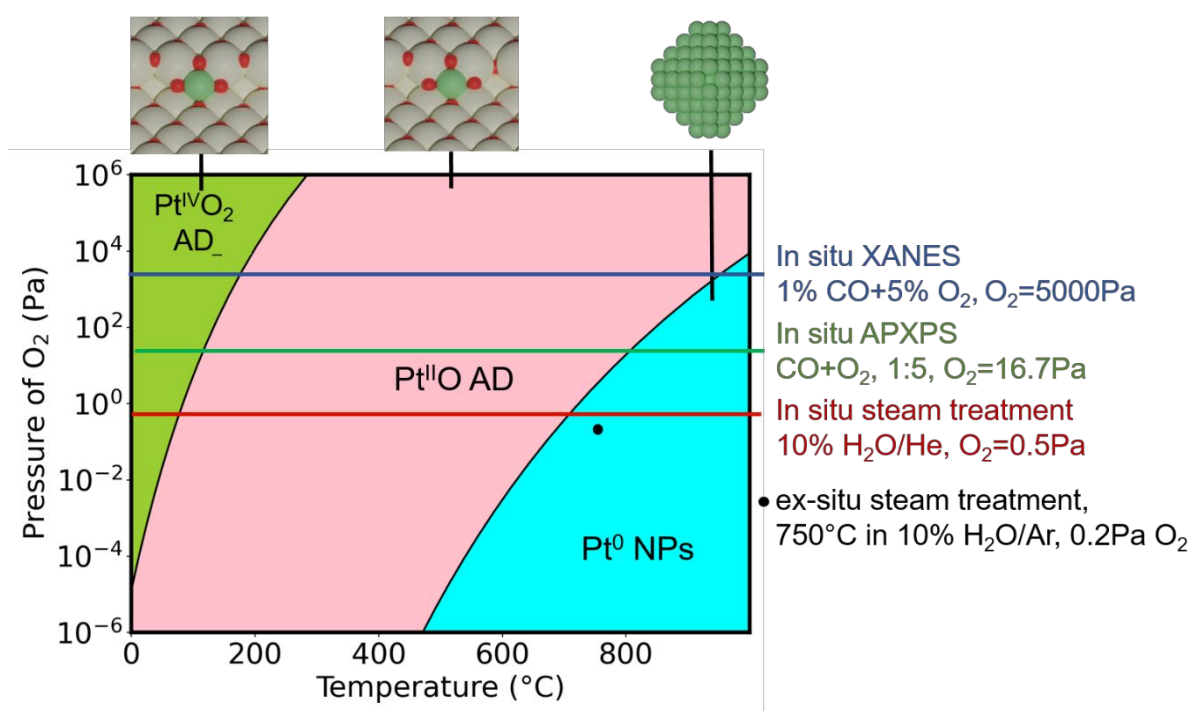


Figure S10. In situ experiments, i.e. in situ XAS, in situ XPS and in situ steam treatment conditions labeled in the phase diagram.

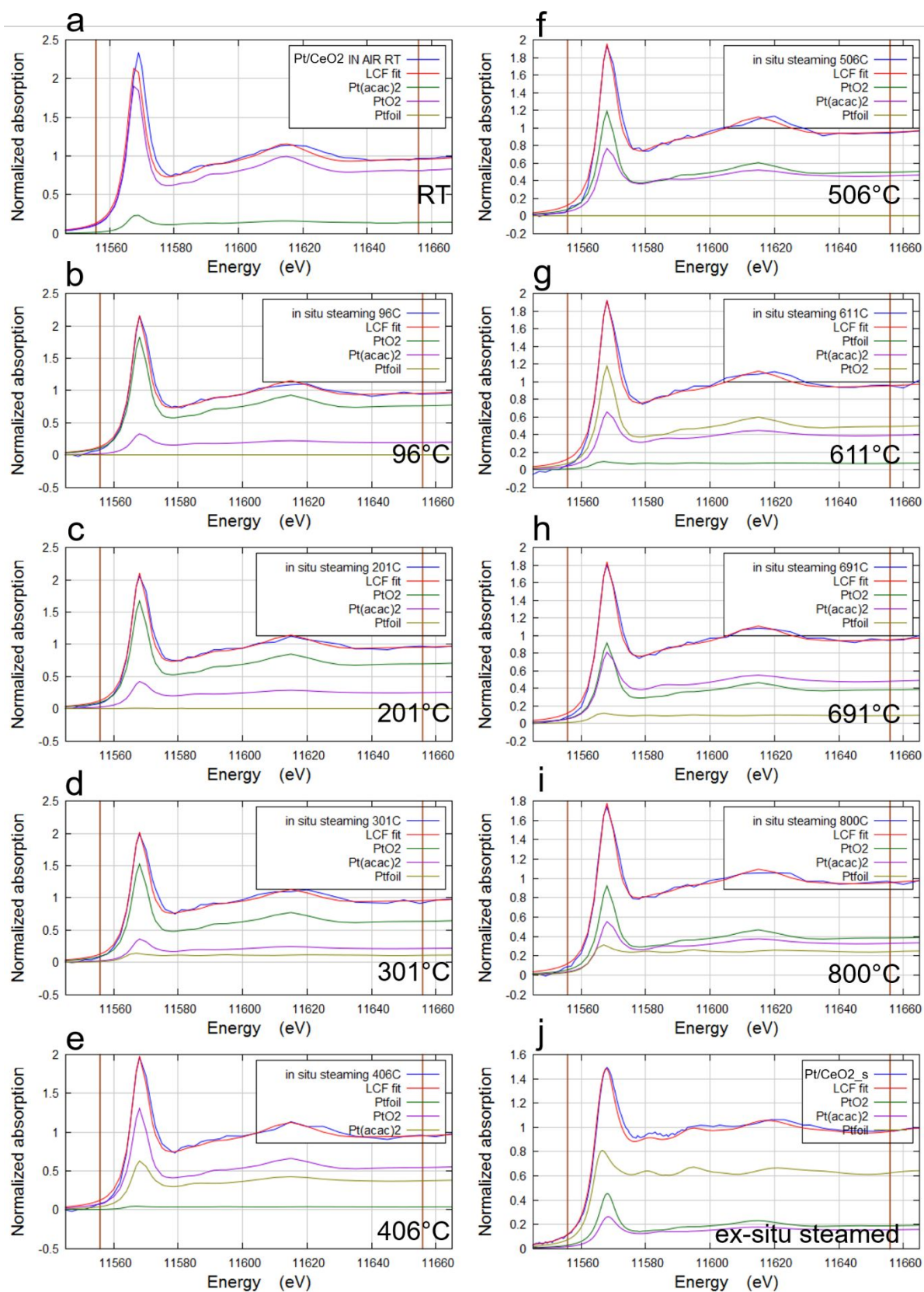


Figure S11. Linear combination fitting details of XANES spectra acquired during in situ steam treatment. Raw and LCF XANES spectra during ramp up: (a) room temperature; (b) 96°C; (c)

201°C; (d) 301°C; (e) 406°C; (f) 506°C; (g) 611°C; (h) 691°C; (i) 800°C and (j) after ex situ steam treatment. The reference spectra for LCF are acquired from Pt foil, Pt(acac)₂ and PtO₂. The energy range for fitting is 11555.8 eV – 11655.8 eV. All weights are constrained between 0 and 1, and weights are forced to sum to 1.

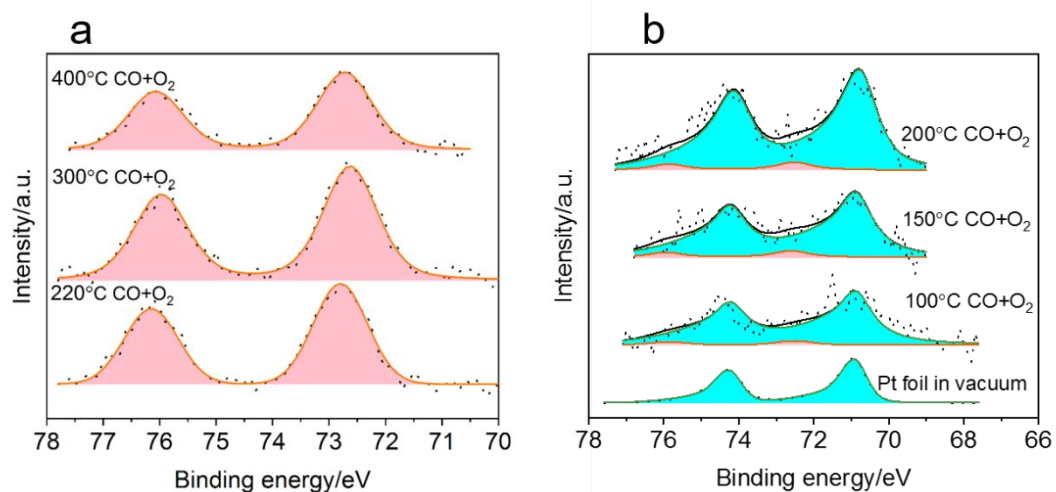


Figure S12. Deconvolution of Pt 4f XPS profile for Pt/CeO₂ (a) and Pt/CeO_{2_s} (b) during in situ reaction.

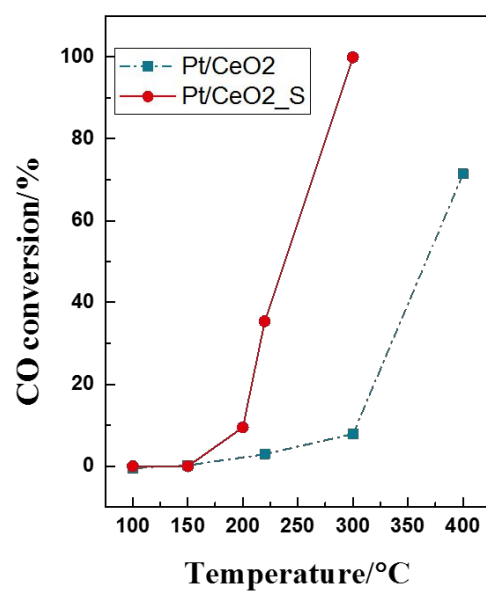


Figure S13. CO oxidation conversion of Pt/CeO₂ and Pt/CeO₂_s under the same conditions during in situ XANES experiments.