

Supporting information on:

Promotion of Pt/CeO₂ catalyst by hydrogen treatment for low-temperature CO oxidation

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Experimental

Catalyst Preparation

Pt/Ceria composite catalyst was prepared by co-precipitation method. In a typical synthesis, cerium nitrate hexahydrate precursor ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich) was dissolved in deionized water. After the complete dissolution of the precursor, urea as a complexing agent (Sigma-Aldrich) was added to the solution and dissolved completely. Ethyl alcohol was then added to the solution and calcined at 650°C under stagnant air. After the first calcination, pure ceria powder was obtained. The ceria powder was infiltrated with the Pt solution prepared via the same route as ceria solution, but using potassium tetrachloroplatinate (K_2PtCl_4 , Sigma-Aldrich) as the precursor. The amount of the platinum precursor was 0.5 atomic percent. The pure ceria powder infiltrated with the platinum precursor solution was calcined again at 650°C to obtain 0.5 atom% Pt supported on CeO_2 . Furthermore, the Pt/ CeO_2 powder was reduced in hydrogen atmosphere (4% H_2 in Ar) at 200°C , 300°C and 550°C denoted as R2-Pt/ CeO_2 , R3-Pt/ CeO_2 and R5-Pt/ CeO_2 , respectively. In addition, the R5-Pt/ CeO_2 was heat-treated under stagnant air at 500°C to obtain re-oxidized R5-Pt/ CeO_2 sample denoted as O5-R5-Pt/ CeO_2 .

Characterization

XRD

The X-ray diffraction analysis was performed for pure CeO_2 , Pt/ CeO_2 , and R5-Pt/ CeO_2 powders using Rigaku D/max-2500 with X-ray power of 40kV, 200mA in a range from 20° to 110° . Step width was 0.01° and counting time was 1s per each step.

H₂-TPR

The hydrogen temperature programmed reduction (H_2 -TPR) was carried out using AutomChem II 2920 connected to TCD in order to check the reducibility of the pure CeO_2 and

Pt/CeO₂ catalysts. The sample was loaded in a quartz U-tube reactor, and the flow rate of inlet gas (10% H₂ - 90% Ar) was 100sccm. Temperature was raised from 30⁰C to 1000⁰C at a rate of 5⁰/min.

XPS

X-ray photoelectron spectroscopy (XPS) analysis was employed to determine the oxidation state of platinum and cerium in the surface layer of the Pt/CeO₂ catalysts using PHI 5000 Versa Probe (ULVAC-PHI, Japan) model with mono-chromatized Al K α radiation ($h\nu = 1486.6$ eV) as an X-ray anode operated at 25 W. The spectra were calibrated with respect to adventitious C1s peak (284.6 eV).

STEM

High-resolution transmission electron microscopy (HR-TEM) analysis was carried out using a FEI Titan 80-300 microscope operated at 300 keV. The available point resolution is better than 1 Å at an operating accelerating voltage. Images were recorded by a 4k \times 4k CCD (Gatan, Oneview1095) camera. Scanning TEM (STEM) images were collected using a Cs-corrected microscope Titan 80-300 operated at 300 kV equipped with a Gatan Quantum 966 spectrometer.

CO Oxidation

The CO oxidation reaction was conducted in a fixed bed tubular quartz reactor. 75mg of the synthesized catalyst powder was placed in the middle of the reactor on a porous quartz bed fixed by blowtorching. The reactor was placed inside a tube furnace to control the reaction temperature equipped with a thermocouple to monitor the temperature. The reactant gases of CO (3 mol%) and O₂ (20 mol%) in argon balance were supplied with a flow rate of 50sccm. The CO oxidation reaction was carried out in a temperature range of 50⁰C ~ 400⁰C in intervals of 50⁰C. The reaction was held at each temperature for 2 hours to achieve saturation. The concentration of

product gases was monitored by gas chromatography (GC, Agilent, 7890B gas) equipped with a TCD detector. The catalytic activity was evaluated by % CO conversion given by

$$\% \text{ CO Conversion} = ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}) / [\text{CO}]_{\text{in}} \times 100$$

DRIFTS

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was employed to examine the species adsorbed on the catalyst surface during the CO oxidation reaction. The DRIFTS system was composed of an FT-IR spectrometer (Nicolet 6700, Thermo Scientific) and high temperature reaction chamber (DiffusIR, PIKE Technologies). All IR spectra were recorded using HgCdTe detector over wavelength range 4000 to 650 cm^{-1} at a 4 cm^{-1} resolution, and 128 scans were collected at each wavenumber step. Before measuring the spectra, the sample was cleaned with high purity He gas to removed residual air, thereafter pre mixed reactant gases were introduced into the chamber with increasing temperature. For CO desorption, the chamber was initially flushed in with He in order to remove all the contaminants. Secondly, CO gas was flown in at 25°C and kept for 90 minutes to achieve saturation. Finally, CO flow was switched to He flow, and the spectra was recorded right after swing the gases and after 15 minutes. At 50°C and 100°C, the spectra were collected after holding for 15 minutes, respectively. For CO oxidation, the first and second steps of CO desorption were replicated, but in the final step O₂ was flown in instead of He and the spectra was recorded along the identical schedule.

X-ray Absorption Spectroscopy

X-ray absorption around the Pt L3 edge was measured using the fluorescence mode at 1D XRS KIST-PAL beamline of Pohang Light Source (PLS). A reference Pt foil was concurrently measured to calibrate each sample. PtO₂ (Platinum (IV) oxide, > 60 m²/g, Sigma-Aldrich) was

measured as a reference for Pt oxide. The X-ray absorption spectra were processed using ATHENA and ARTEMIS software.

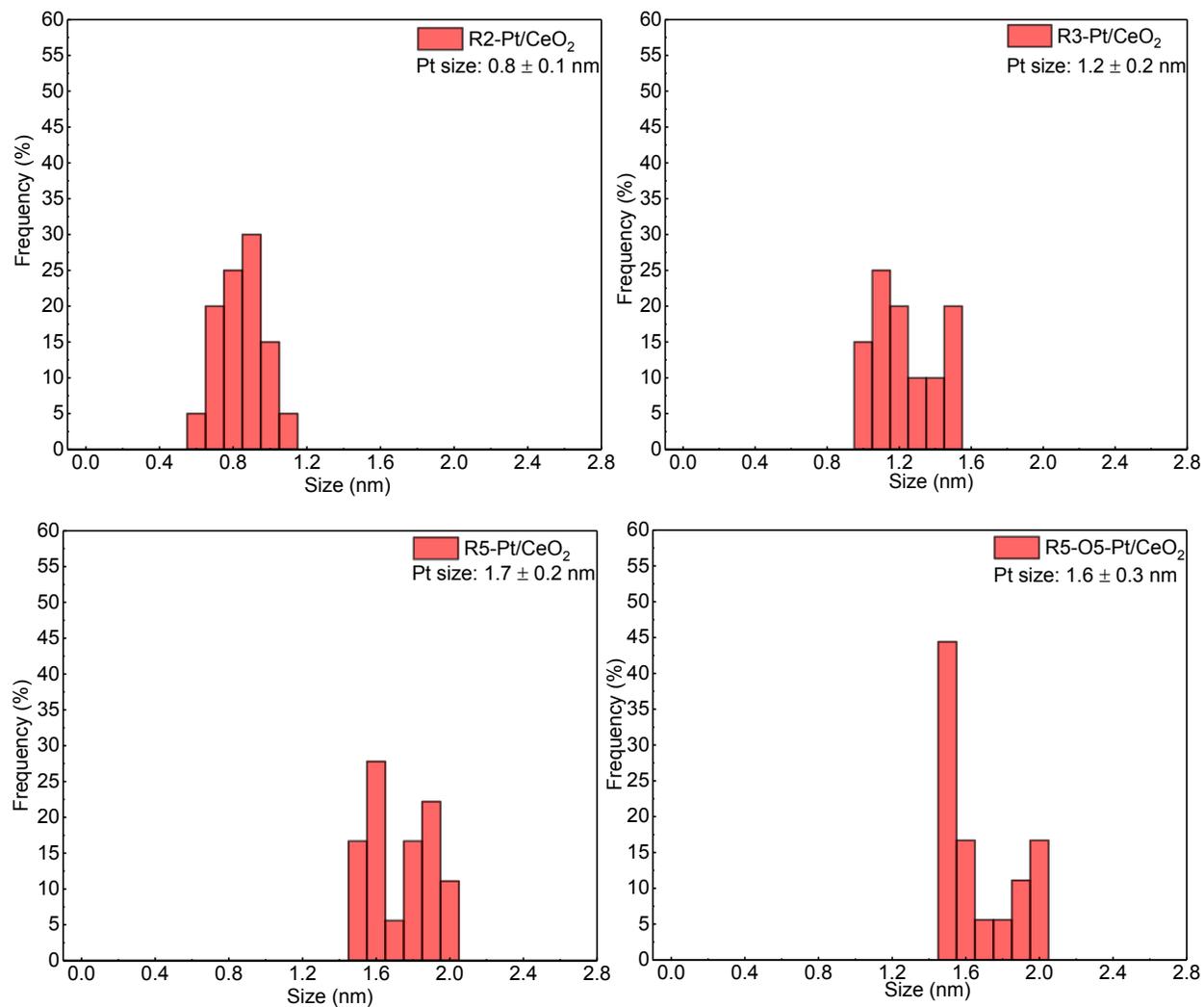


Figure S1. Pt particle size distributions for R2-Pt/CeO₂, R3-Pt/CeO₂, R5-Pt/CeO₂, and R5-O5-Pt/CeO₂.

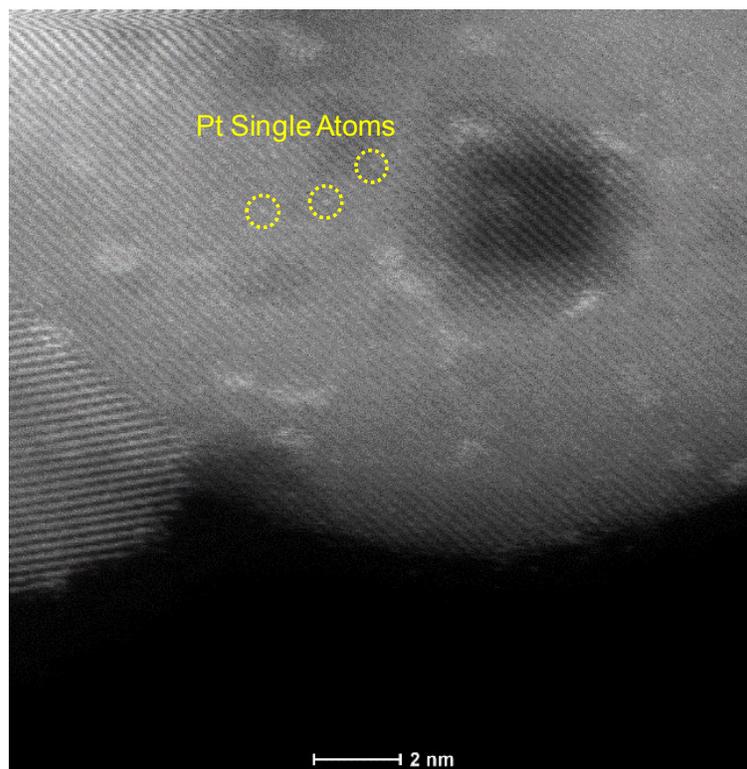


Figure S2. STEM image of R2-Pt/CeO₂ showing Pt²⁺ single atoms coexisting with Pt⁰ nanoparticles.

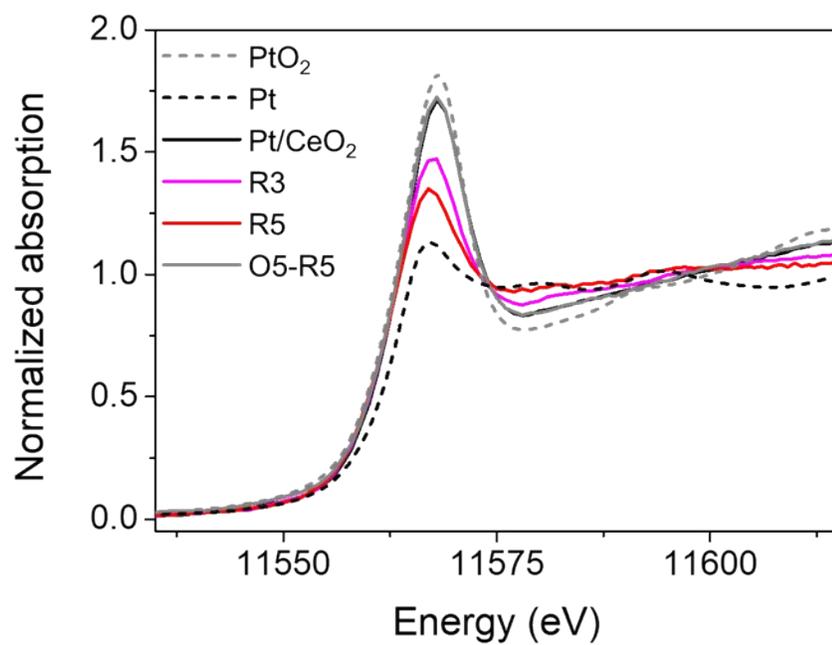


Figure S3. X-ray absorption near edge structure (XANES) spectra on Pt L3 edge of Pt/CeO₂ samples (solid lines) with reference Pt samples (Pt foil and PtO₂; dashed lines).

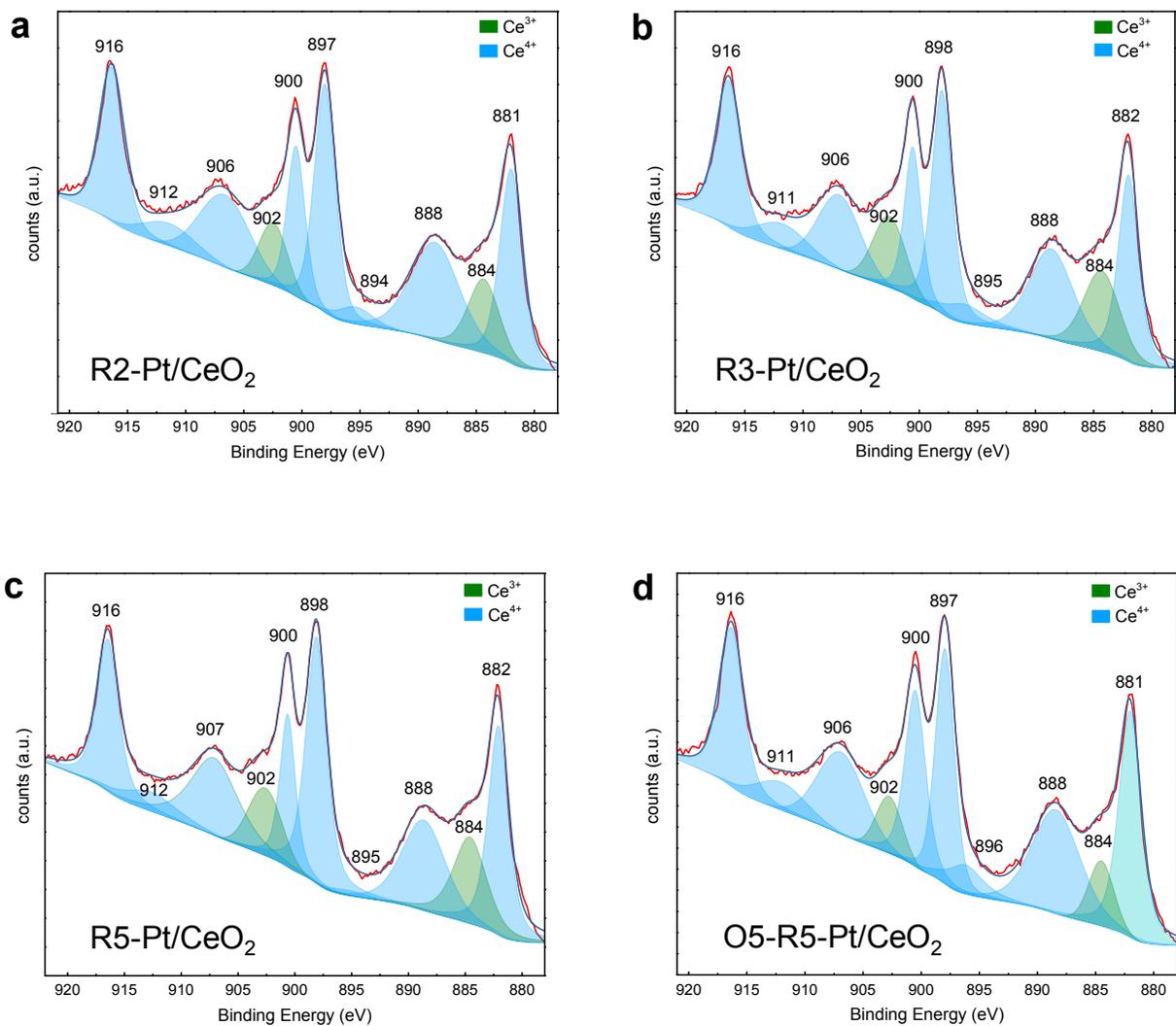
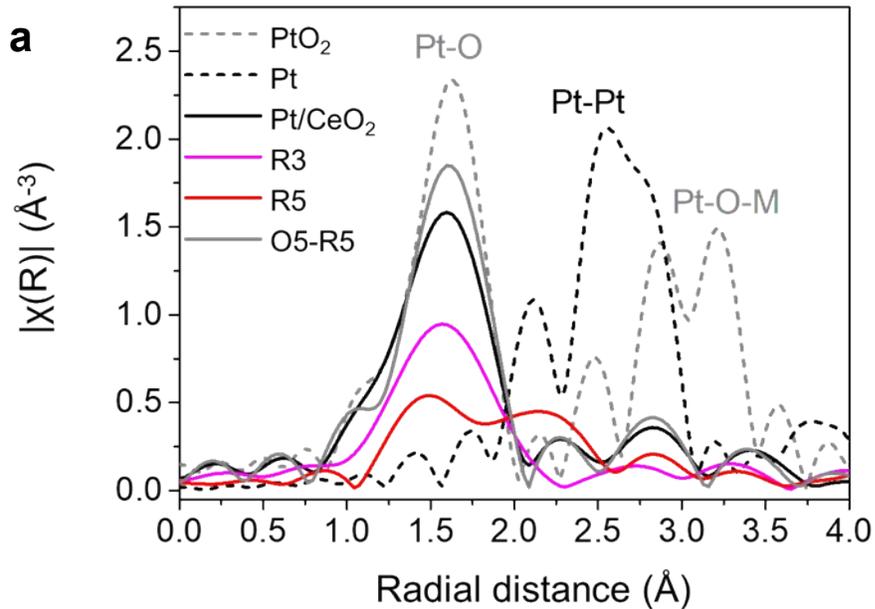


Figure S4. Ce3d XP spectra for (a) R2-Pt/CeO₂; (b) R3-Pt/CeO₂; (c) R5-Pt/CeO₂; (d) O5-R5-Pt/CeO₂.



b

Sample	Neighbor	N	R (\AA)	σ^2 (\AA^2)	ΔE_0 (eV)	R-factor
Pt/CeO ₂	O ^a	4.3 ± 0.7	2.02 ± 0.02	0.001 ± 0.003	13.8 ± 1.7	0.013
R3-Pt/CeO ₂	O ^a	2.9 ± 0.8	2.01 ± 0.03	0.003 ± 0.005	12.9 ± 2.8	0.051
R5-Pt/CeO ₂	O ^a	2.0 ± 1.3	1.95 ± 0.04	0.007 ± 0.012	3.1 ± 3.6	0.066
	Pt ^b	5.1 ± 2.9	2.67 ± 0.03	0.008 ± 0.006		
O5-R5-Pt/CeO ₂	O ^a	4.3 ± 0.5	2.01 ± 0.02	0.000 ± 0.001	13.3 ± 2.0	0.021

Figure S5. (a) Fourier transformed Extended X-ray absorption fine structure (EXAFS) spectra on Pt L3 edge of Pt/CeO₂ samples (solid lines) with reference Pt samples (Pt foil and PtO₂; dashed lines), (b) EXAFS fitting results from Pt L3 edge X-ray absorption spectra for Pt/CeO₂ samples.

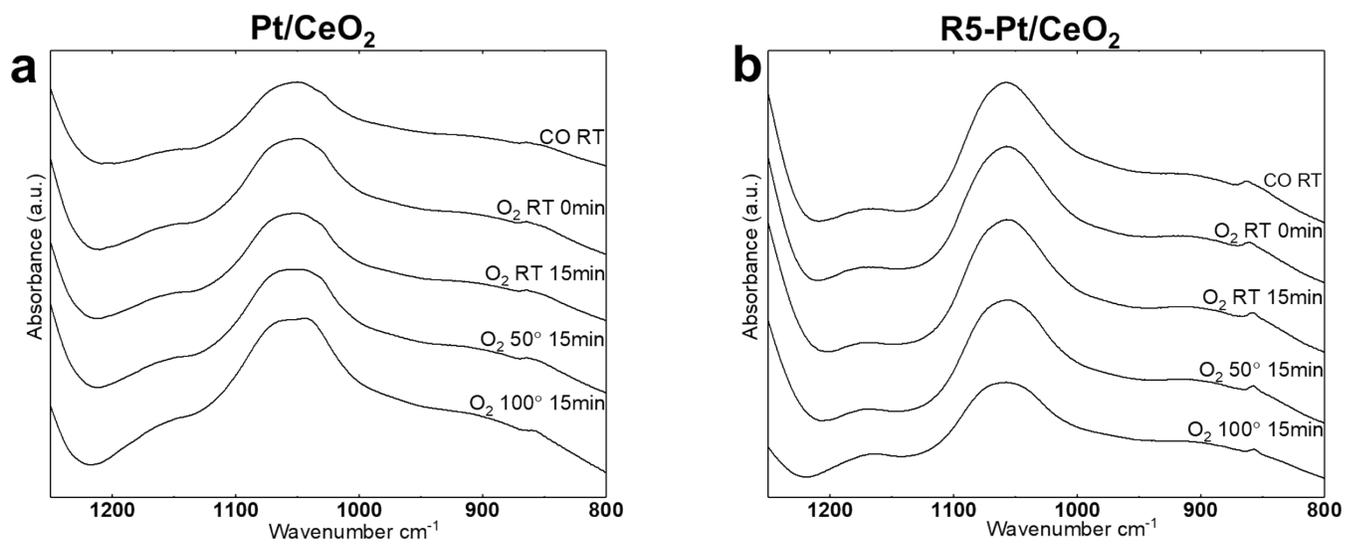


Figure S6. DRIFT spectra of (a) Pt/CeO₂, (b) R5-Pt/CeO₂ to analyze

active oxygen species.

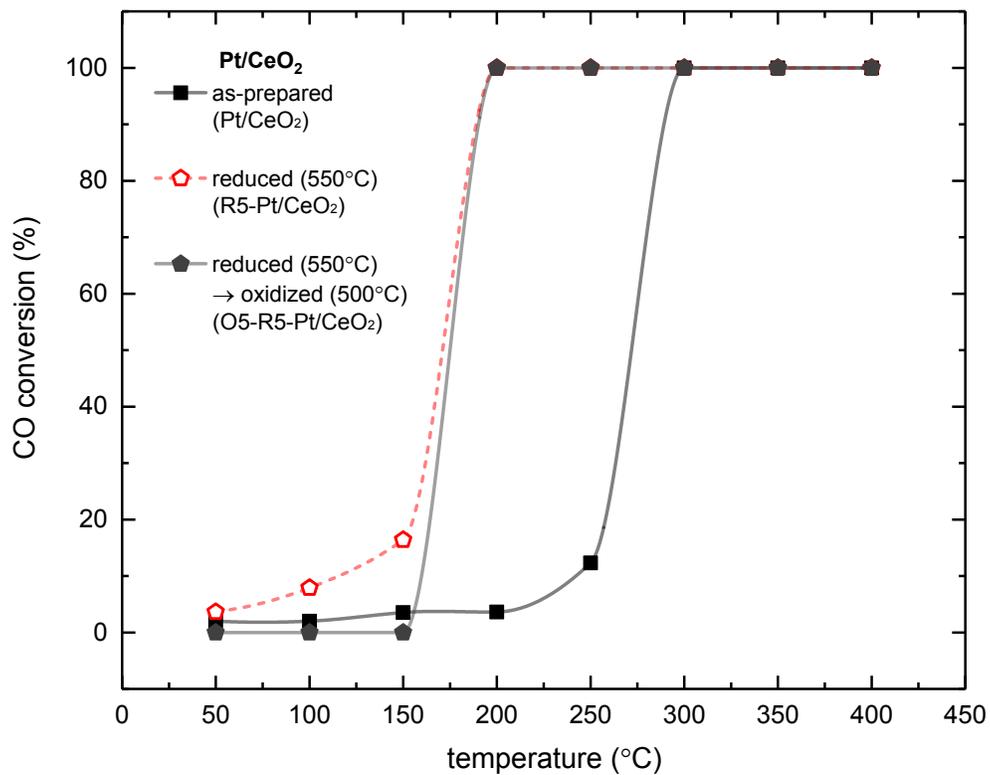


Figure S7. Light-off curves of CO oxidation over Pt/CeO₂, R5-, and O5-R5-Pt/CeO₂. Identical curves in Fig.7 but selected for comparison.