Supporting information

Unravelling the gas condition-dependent aggregation and fragmentation of atomically dispersed Pt catalyst on ceria support

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Content

1. Sample Preparation and Characterization

Sample Preparation

Pt/ceria sample was prepared by dispersing 0.5 g cerium (IV) oxide nanopowder (<25 nm) in a solution of 0.42 g of cerium (III) nitrate hexahydrate, 2.0 g urea, and 8 mL of water. The weight loading of Pt was controlled by adding the desired amount of Pt precursor solution (chloroplatinic acid hydrate in water, approximately 1 wt.% Pt). All chemicals were purchased from Sigma-Aldrich. Ultrapure water was provided by Millipore purification system. The mixture was sealed in a glass vial and stirred for 24 hours in an oil bath at 90 °C. Afterward, the samples were washed with deionized water and centrifuged three times. After drying overnight in an oven at 80 °C, the sample was crushed into powders and calcined at 500 °C (5 °C/min heating ramp) for 5 h. The resulting platinum loading of the Pt/ceria sample was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) by Galbraith Laboratories. The instrument measures characteristic emission spectra by optical spectrometry and describes multi-elemental determinations.

Diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS)

The spectra were collected using an iS50 FTIR spectrometer equipped with a rapid-scanning liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector and a Praying Mantis High Temperature Reaction Chamber (Harrick Scientific Products). Prior to measurement, each sample was heated at 150 °C for 30 minutes under He with a flow rate of 20 ml/min to remove surface adsorbed species followed by collection of background spectra at each temperature. The sample was then cooled to room temperature. The sample was exposed to a mixture of 5%CO_2 and 5%H_2 (balanced with He, with a total flow rate of 31.5 ml/min) at 300 °C to collect reaction spectra. After that, the sample was cooled down to room temperature and collected RT spectra. For cooling down at CO, a mixture of 5% CO (balanced with He, the flow rate is 31.5 ml/min) and He with a flow rate of 10 ml/min was flowed through the reaction chamber for 30 minutes to acquire CO adsorption spectra.

X-ray absorption spectroscopy (XAS)

XAS measurements were performed at the QAS beamline (7-BM) of National Synchrotron Light Source II (NSLS II), Brookhaven National Laboratory. For in-situ measurement, the sample was prepared in a pellet using a hydraulic press and mounted in a Nashner-Adler cell. In-situ data were collected before the reaction, at the reaction condition (5%CO_2+5%H_2, 300 °C), and room temperature (5%CO_2+5%H_2). At each regime, 30 scans of XAS data at the Pt L_3 edge were collected in fluorescence mode.

High Angle Annular Dark Field – Scanning Transmission Electron Microscopy (HAADF-STEM)

HAADF-STEM imaging was carried out on Hitachi HD2700 STEM equipped with a probe aberration corrector, at Center for Functional Nanomaterials, Brookhaven National Laboratory. The powder sample was deposited onto a 3mm Cu grid covered with a ultra-thin carbon layer.

2. DFT calculations

We optimized the $CeO_2(100)$ surface using a 4×4 supercell with two O-Ce-O layers to describe the ceria nanodomes in the experimental catalyst system, as in our previous results.[1] The vacuum layer was applied to 15Å to avoid electronic interference between the periodic supercells. We performed spin-polarized DFT calculations using a plane-wave basis with the VASP code[2] and the Perdew-Burke-Ernzerhof (PBE) [3] of functional. The DFT+U scheme[4] with U_{eff} = 4.5 eV [5,6] was applied for Ce ions to appropriately consider the localized Ce-f orbitals. The projector-augmented wave method[7] described the interaction between the ionic core and the valence electrons. Valance electron wave functions were expanded on a plane-wave basis up to an energy cutoff of 400 eV. The Brillouin zone was sampled at the Γ-point for all calculations. The convergence criteria for the electronic structure and the atomic geometry were 10^{-4} eV and 0.03 eV/Å, respectively. We used a Gaussian smearing function with a finite temperature width of 0.05 eV to improve the convergence of states near the Fermi level. The location and energy of transition states (TSs) were calculated with the climbing-image nudged-elastic-band method.[8]

4. Supplementary Figures

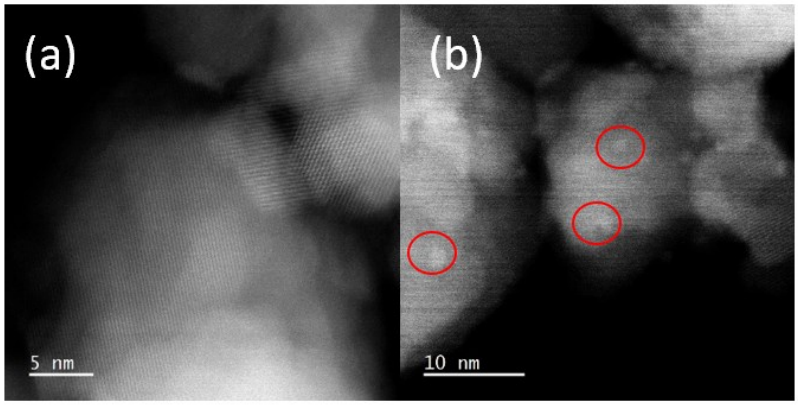

Figure S1. HAADF-STEM images of the Pt/ceria sample (a) as prepared and (b) after RWGS reaction.

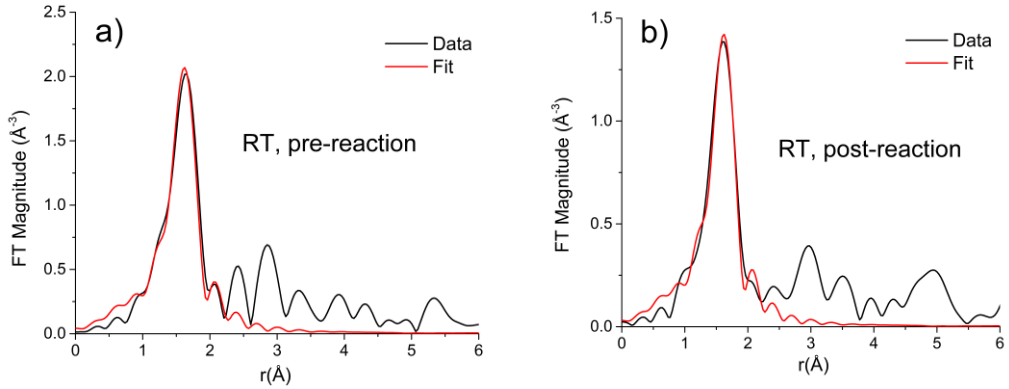

Figure S2. Fourier transform magnitudes of the k^2-weighted EXAFS data and theoretical (FEFF) fits of the pre-reaction (a) and post-reaction (b) states of the experiment, measured at room temperature.

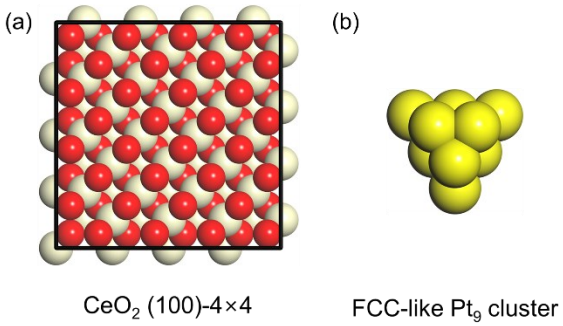

Figure S3. The DFT-constructed models of (a) CeO_2 (100) and (b) Pt_9 nanocluster.

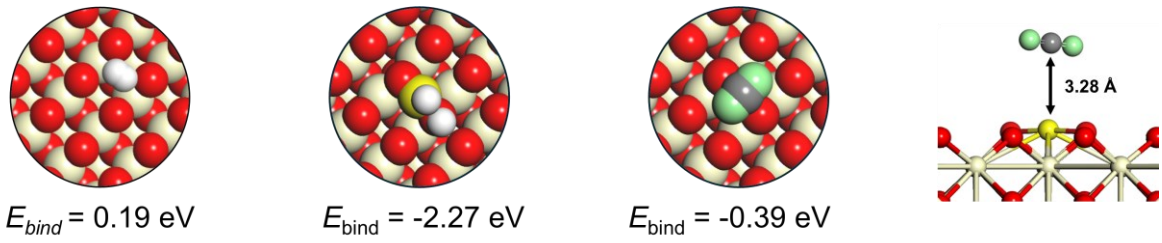

Figure S4. The DFT-calculated binding energy, E_{bind} of H_2 on CeO_2 (0.19 eV), H_2 on Pt_1/CeO_2 (-2.27 eV), and CO_2 (-0.39 eV) on Pt_1/CeO_2.

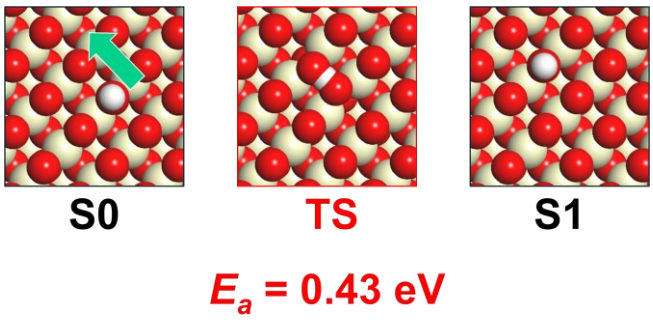

Figure S5. The DFT-calculated diffusion barrier of the H atom along the CeO_2 (100).

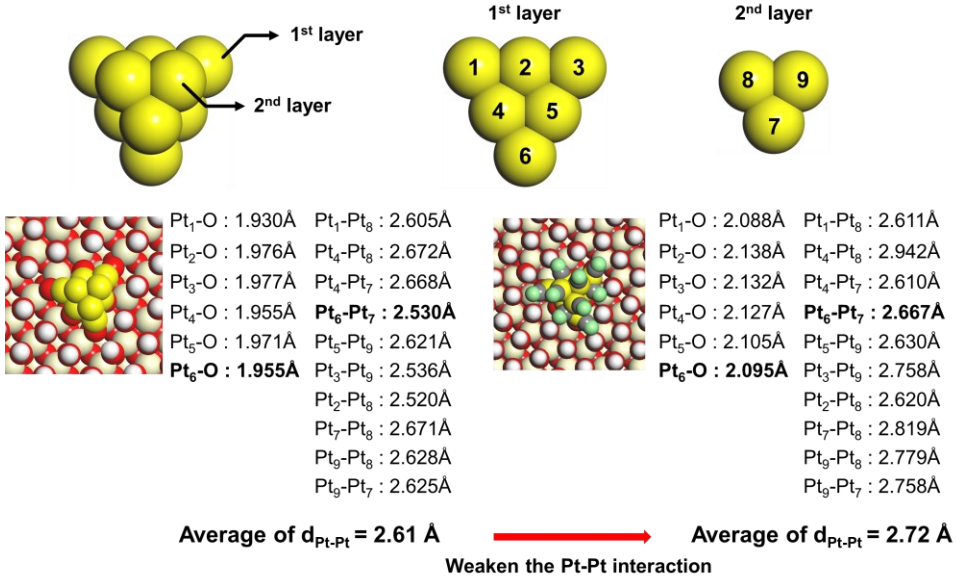

Figure S6. The DFT-estimated interatomic distances of Pt-O and Pt-Pt over the Pt_9/H-CeO_2, and 9CO*-Pt/H-CeO_2.

References

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