

Fine-tuned local coordination environment of Pt single atoms on ceria controls catalytic reactivity

Received: 1 June 2022

Accepted: 7 November 2022

Published online: 18 November 2022

Check for updates

Wei Tan^{1,2,9}, Shaohua Xie^{1,9}, Duy Le^{3,9}, Weijian Diao⁴, Meiyu Wang⁵, Ke-Bin Low⁶, Dave Austin³, Sampyo Hong⁷, Fei Gao², Lin Dong², Lu Ma⁸, Steven N. Ehrlich⁸, Talat S. Rahman³ & Fudong Liu¹✉

Constructing single atom catalysts with fine-tuned coordination environments can be a promising strategy to achieve satisfactory catalytic performance. Herein, via a simple calcination temperature-control strategy, CeO₂ supported Pt single atom catalysts with precisely controlled coordination environments are successfully fabricated. The joint experimental and theoretical analysis reveals that the Pt single atoms on Pt₁/CeO₂ prepared at 550 °C (Pt/CeO₂-550) are mainly located at the edge sites of CeO₂ with a Pt–O coordination number of *ca.* 5, while those prepared at 800 °C (Pt/CeO₂-800) are predominantly located at distorted Ce substitution sites on CeO₂ terrace with a Pt–O coordination number of *ca.* 4. Pt/CeO₂-550 and Pt/CeO₂-800 with different Pt₁-CeO₂ coordination environments exhibit a reversal of activity trend in CO oxidation and NH₃ oxidation due to their different privileges in reactants activation and H₂O desorption, suggesting that the catalytic performance of Pt single atom catalysts in different target reactions can be maximized by optimizing their local coordination structures.

In recent years, different types of single atom catalysts have been applied in many energy and environment-related reactions because of their maximum atomic utilization efficiency, unique electronic states, or higher stability comparing to the nano-cluster/particle catalysts^{1–7}. With the deepening of research in this area, it has been revealed that the performance of single atom catalysts on specified supports for certain reactions such as thermal catalysis and electrocatalysis could be significantly promoted by tuning their oxidation states or coordination environments^{8–14}. Among these single atom catalytic materials, the Pt single atom (Pt₁) catalyst supported on rare earth metal oxide

CeO₂ is one of the most popular catalyst systems, which has been studied extensively for the elimination of environmental pollutants and energy conversion^{15–19}.

Most recently, various synthesis methods have been employed to fabricate Pt single atoms with improved catalytic performance^{18–20}. For instance, by creating stable hydroxyl groups on Pt₁/CeO₂ catalyst using hydrothermal treatment at 750 °C, the CO oxidation activity on Pt₁/CeO₂ could be enhanced dramatically²⁰. Ma et al. reported that modulating Pt₁/CeO₂ with phosphate (PO₄^{3–}) could increase the valence state of Pt and facilitate the reactant adsorption and hydrogen

¹Department of Civil, Environmental, and Construction Engineering, Catalysis Cluster for Renewable Energy and Chemical Transformations (REACT), NanoScience Technology Center (NSTC), University of Central Florida, Orlando, FL 32816, USA. ²State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment; Jiangsu Key Laboratory of Vehicle Emissions Control, School of Chemistry and Chemical Engineering; Center of Modern Analysis, Nanjing University, Nanjing 210023, China. ³Department of Physics, Catalysis Cluster for Renewable Energy and Chemical Transformations (REACT), University of Central Florida, Orlando, FL 32816, USA. ⁴Department of Chemical and Biological Engineering, Villanova University, Villanova, PA 19085, USA. ⁵College of Engineering and Applied Sciences, Nanjing University, Nanjing 210093, China. ⁶BASF Corporation, Iselin, NJ 08830, USA. ⁷Brewton-Parker College, Mount Vernon, GA 30445, USA. ⁸National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory, Upton, NY 11973, USA. ⁹These authors contributed equally: Wei Tan, Shaohua Xie, Duy Le. ✉ e-mail: fudong.liu@ucf.edu

spillover, which accordingly boosted the catalytic activity for styrene hydrogenation²¹. Jeong et al. tuned the oxidation state of Pt single atoms on CeO₂ using hydrogen reduction method for maximizing the catalytic activity in CO, CH₄, and NO oxidation²². Meanwhile, many experimental and theoretical efforts have been devoted to synthesizing Pt₁ catalysts on CeO₂ support with optimal coordination environment or constructing reasonable Pt₁-CeO₂ structural models, which could help better understand the reaction mechanisms and reveal the origin of different catalytic performances on Pt single atom catalysts^{23–28}. For example, Jiang et al. successfully synthesized a Pt₁/CeO₂ catalyst with asymmetric Pt₁-O₄ configuration, which exhibited much higher CO oxidation activity than the reference catalyst with symmetric Pt₁-O₄ configuration²⁷. Wang et al. reported that CO-Pt₁-O₃ was the dominant configuration for CO adsorption on Pt₁ catalyst supported on oxygen plasma-pretreated CeO₂, and such Pt₁ species exhibited higher CO oxidation activity and better resistance towards sintering comparing to that in conventional Pt₁/CeO₂ catalyst²⁸. So far, no comprehensive work has been reported focusing on the precise tuning of local coordination environment for Pt single atoms on CeO₂ support to modulate their activity in different catalytic reactions and at the same time revealing the intrinsic structure-activity relationships. Herein, we proposed a simple strategy for fine-tuning the exact location of Pt single atoms by controlling the calcination temperature of Pt/CeO₂ catalysts prepared by the facile incipient wetness impregnation (IWI) method. The Pt single atoms on Pt₁/CeO₂ catalysts calcined at different temperatures could have different coordination environments. Through systematic experimental characterizations, catalytic performance testing, and density functional theory (DFT) based simulations of Pt₁/CeO₂ catalysts, it was clearly revealed that the CeO₂-supported Pt single atoms with fine-tuned local coordination structures could exhibit strikingly distinct catalytic behaviors in different oxidation reactions such as CO oxidation versus NH₃ oxidation, which needs to be taken into consideration for practical applications of single atom catalysis in the future.

Results

Constructing Pt₁ with different coordination environments

To minimize the potential structural change of pure CeO₂ support after the deposition of Pt followed by calcination, the CeO₂ used in this work was pre-calcined in air at 800 °C for 12 h to obtain pre-stabilized structure. Moreover, the deposition of Pt was reported to have a positive effect on stabilizing the CeO₂ support²⁹. As shown in Supplementary Fig. 1 and Table 1, the pure CeO₂ support and CeO₂ supported Pt catalysts showed almost the same specific surface area and pore structure, suggesting no obvious change in the textural structure of CeO₂ support during the catalyst fabrication process.

Table 1 | Textural properties determined by N₂ physisorption results, band gap determined by UV-Vis spectra, and the average valence states of Pt species determined by XANES linear combination fitting

Samples	S _{BET} (m ² /g)	Pore volume (cm ³ /g) ^a	Band gap (eV) ^b	Average valence state ^c
CeO ₂	62.5	19.2	3.23	–
Pt/CeO ₂ -350	58.3	18.4	3.00	3.6 ± 0.1
Pt/CeO ₂ -550	59.5	16.4	2.96	3.4 ± 0.1
Pt/CeO ₂ -700	57.9	18.0	2.80	2.9 ± 0.1
Pt/CeO ₂ -800	59.5	17.2	2.61	2.7 ± 0.1

^aThe pore volume was determined by BJH method using desorption isotherms.

^bThe band gap was calculated by the intersection of the extrapolated linear portions on plots of (αhν)² vs. photon energy (hν) to the zero absorbance.

^cThe average valence states of Pt species were obtained from the linear combination fitting analysis of Pt L₃-edge XANES.

To determine the states of Pt species on Pt/CeO₂ catalysts, in situ DRIFTS of CO adsorption at 25 °C was first performed (Fig. 1). The IR bands assigned to CO adsorbed on ionic Pt single sites (CO-Pt^{δ+}@Pt₁) were observed on all four catalysts at 2087–2105 cm⁻¹. For Pt/CeO₂-350, a broad band at ca. 2050 cm⁻¹ ascribed to CO adsorbed on metallic Pt sites from Pt clusters (CO-Pt⁰@Pt clusters) was also detected. Although the Pt species on Pt/CeO₂-550, Pt/CeO₂-700, and Pt/CeO₂-800 were mainly in the form of single atoms, the monotonical redshift of CO-Pt^{δ+}@Pt₁ band as the calcination temperature increased indicated the different local coordination environments or oxidation states of Pt single atoms. As concluded from previous works, the center of the IR band assigned to CO linearly adsorbed on Pt₁ supported by CeO₂ usually ranged between 2085 and 2105 cm⁻¹^{124,27,30,31}. The 9 cm⁻¹ redshift of IR band (from 2096 to 2087 cm⁻¹) for CO adsorption as the calcination temperature increased from 550 to 800 °C could be considered as a significant change, indicating the remarkably distinct Pt₁ local structures on Pt/CeO₂-550 and Pt/CeO₂-800. Moreover, the Pt/CeO₂ catalysts calcined at different temperatures showed varied colors (from dark brown to golden brown), suggesting the different states of Pt₁ species as well (inserted photos in Fig. 1a–d).

CO oxidation is a commonly used probe reaction to evaluate the catalytic oxidation performance of Pt–CeO₂-based catalysts and many other catalyst systems^{32–34}. In turn, the difference in the local structure of Pt–CeO₂ catalysts can be reflected by their corresponding CO oxidation activity^{27,35}. As demonstrated in Fig. 1e, with the increase of calcination temperature, the CO oxidation activity on Pt/CeO₂ catalysts decreased monotonically. The presence of Pt clusters on Pt/CeO₂-350 (Fig. 1a) well explained its best CO oxidation activity, as the Pt cluster-CeO₂ interfacial sites were considered as the most active species for CO oxidation^{30,36–38}. Although the Pt species on Pt/CeO₂-550, Pt/CeO₂-700, and Pt/CeO₂-800 were all in Pt single atom form, the significant difference in the CO oxidation activity on Pt/CeO₂-550, Pt/CeO₂-700, and Pt/CeO₂-800 revealed that the Pt single atoms with varied states were successfully created on these three catalysts.

H₂-TPR technique is a powerful tool to evaluate the dispersion of Pt species as well as the strength of Pt–O–Ce interaction on Pt/CeO₂ based catalysts^{39,40}. Herein, the H₂-TPR profiles of Pt/CeO₂-550, Pt/CeO₂-700, Pt/CeO₂-800 were collected to investigate the interaction between Pt single atoms and CeO₂ support (Fig. 2a, b). The H₂-consumption peaks centered around 150 °C could be attributed to the reduction of Pt–O–Ce structure, while the H₂-consumption peaks at ca. 420 and 785 °C could be ascribed to the reduction of surface Ce⁴⁺ species and bulk CeO₂, respectively⁴¹. Interestingly, as the calcination temperature increased from 550 to 800 °C, the H₂-consumption peak assigned to the reduction of Pt–O–Ce structure shifted to higher temperatures (126 °C → 173 °C) with enhanced intensity, indicating the different strength of Pt–O–Ce interaction as well as the different locations of Pt single atoms on Pt/CeO₂-X catalysts. For Pt/CeO₂-700, the Pt single atoms should be in a mixed state of the Pt species in Pt/CeO₂-550 and Pt/CeO₂-800. Based on the CO oxidation evaluation results, Pt/CeO₂-800 catalyst showed very similar CO oxidation activity to the pure CeO₂ support. Therefore, the much more intensive H₂-consumption peak of Pt–O–Ce species at higher reduction temperature on Pt/CeO₂-800 suggested that the Pt single atoms on this catalyst might have migrated into the surface lattice of CeO₂ support and the isolated Pt atoms were strongly bonded to CeO₂ through more Pt–O–Ce linkages.

UV-Vis spectroscopy analysis was also conducted to study the interaction between Pt single atoms and CeO₂ support. As shown in Fig. 2c, the band below 400 nm on CeO₂ and Pt/CeO₂-X catalysts (X = 550, 700, and 800) could be attributed to the charge transfer for O_{2p} → Ce_{4f} transition⁴². Interestingly, after the deposition of Pt, an additional strong absorption assigned to the absorption tail or Urbach tail was observed at 400–600 nm, which was related to the band gap

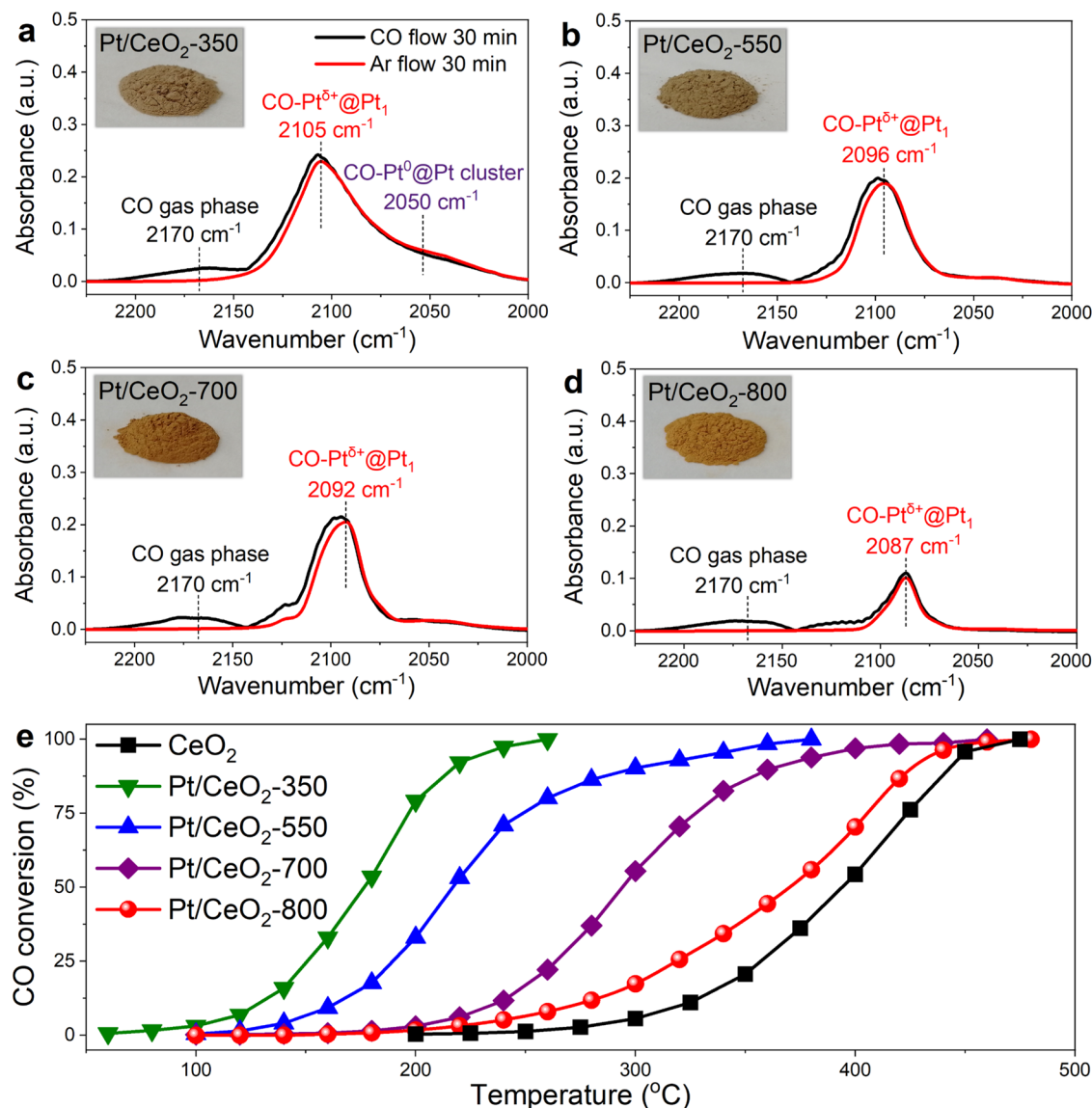


Fig. 1 | Pt status determined by CO adsorption and corresponding CO oxidation activity. In situ DRIFTS of CO adsorption at 25 °C on a **a** Pt/CeO₂-350, **b** Pt/CeO₂-550, **c** Pt/CeO₂-700 and **d** Pt/CeO₂-800 (inserted are the photos of different catalysts);

e CO oxidation performance on Pt/CeO₂-350, Pt/CeO₂-550, Pt/CeO₂-700 and Pt/CeO₂-800 (Reaction condition: [CO] = [O₂] = 1%, balanced with Ar, WHSV = 400,000 mL·g_{cat}⁻¹·h⁻¹).

smearing induced by defect accumulation⁴³. For Pt/CeO₂-X catalysts, such absorption tail could be due to the structural disorders induced by the highly dispersed Pt species. Moreover, with the increase of the calcination temperature, the absorption intensity at 400–600 nm enhanced accordingly, suggesting that the Pt/CeO₂ catalyst calcined at higher temperature possessed higher surface structural disorder and more surface defects, possibly resulted from the migration of Pt single atoms into CeO₂ lattice and the stronger interaction between Pt and CeO₂ support^{44,45}. The formation of more surface defects on Pt/CeO₂-800 was further confirmed by the in situ DRIFTS of methanol adsorption experiments (Supplementary Fig. 2), in which the band at 1034 cm⁻¹ assigned to bridging methoxy species on two Ce⁴⁺ cations with an oxygen vacancy on Pt/CeO₂-800 showed much higher intensity than that on pristine CeO₂ and Pt/CeO₂-550⁴⁶. The indirect band gap was also calculated by Davis and Mott equation for further understanding the interaction between Pt species and CeO₂ support within Pt/CeO₂-X catalysts (Fig. 2d and Table 1)^{43,47}. The band gap for Pt/CeO₂-X catalysts was much lower than that for CeO₂ support (3.23 eV), indicating the insertion of metal levels between the valence and conduction bands of CeO₂ as well as the strong interaction through

Pt–O–Ce linkage⁴⁸. The lower band gap for Pt/CeO₂-800 (2.61 eV) than those for Pt/CeO₂-550 (2.96 eV) and Pt/CeO₂-700 (2.80 eV) well supported the viewpoint that stronger Pt–O–Ce interaction was formed on Pt/CeO₂-800 catalyst.

Location and coordination environment of Pt single atoms

AC-HAADF-STEM images of Pt/CeO₂-550 and Pt/CeO₂-800 were collected to determine the location of Pt species (Fig. 3). CeO₂ support was found to selectively expose (110) crystal plane. As expected, no identifiable Pt clusters were found on Pt/CeO₂-550 and Pt/CeO₂-800, and only bright dots assigned to isolated Pt atoms were observed. It was also shown by the high-resolution EDS mapping results that the Pt species were in highly dispersed state on both Pt/CeO₂-550 and Pt/CeO₂-800 (Supplementary Fig. 3). Moreover, the isolated Pt single atoms on both catalysts were found to fit well into the Ce columns on CeO₂ (110) plane. Based on the results of in situ DRIFTS of CO adsorption, CO oxidation activity evaluation, H₂-TPR and UV-Vis spectra, it could be deduced that the Pt single atoms on Pt/CeO₂-550 and Pt/CeO₂-800 should be in different status including the locations and coordination environments. Considering that the AC-HAADF-

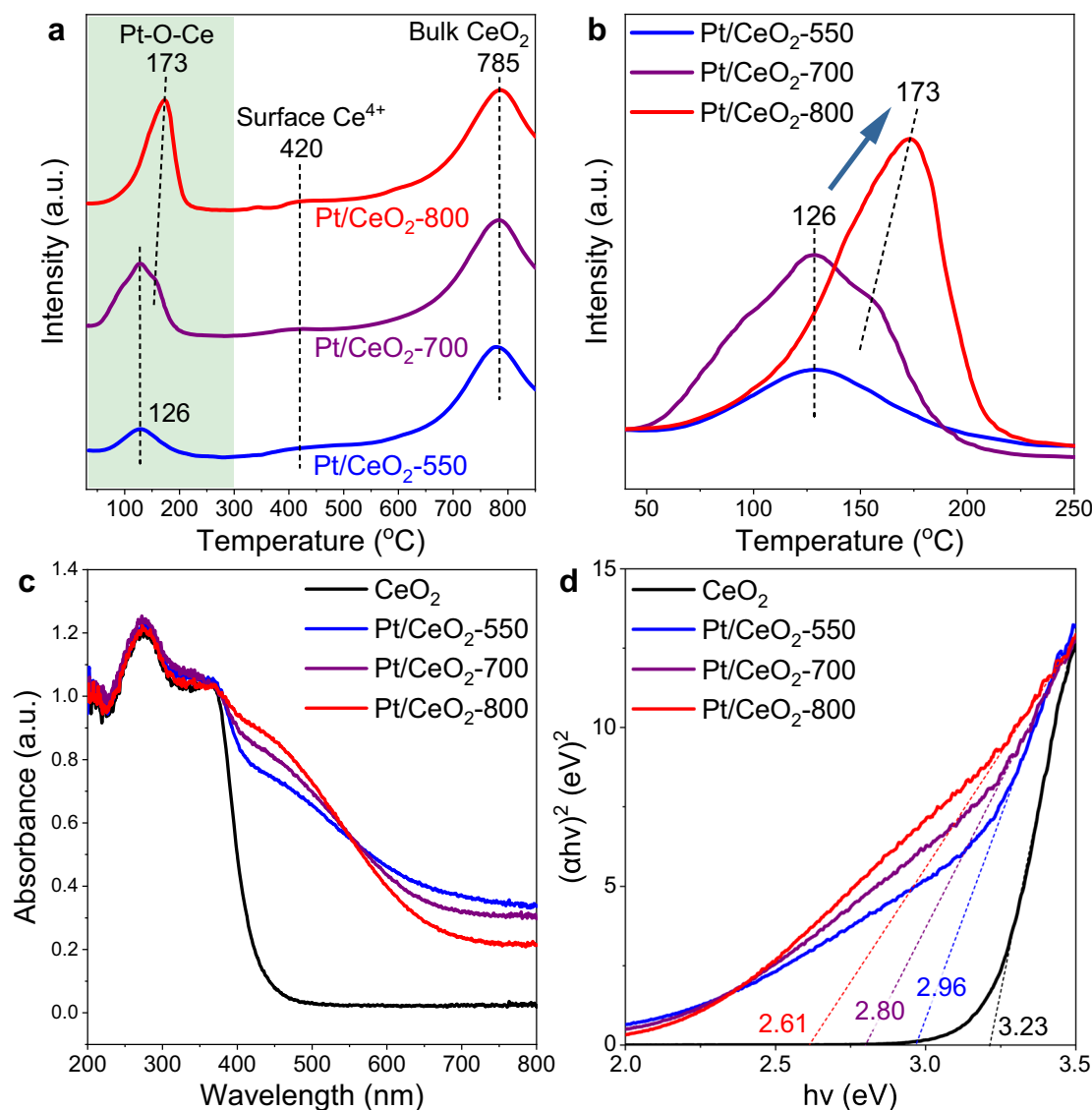


Fig. 2 | Pt-CeO₂ interaction determined by H₂-TPR and UV-Vis spectra. **a, b** H₂-TPR profiles for Pt/CeO₂-X catalysts; **c** UV-Vis spectra of CeO₂ support and Pt/CeO₂-X catalysts; **d** the plots of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) for CeO₂ support and Pt/CeO₂-X catalysts (X = 550, 700 and 800).

STEM images were just projection drawings, the Pt single atoms on Pt/CeO₂-550 and Pt/CeO₂-800 could be located at different substitution sites or epitaxial growth sites of Ce on CeO₂ support, which enabled the Pt single atoms to be in different status but all observed in the Ce columns on CeO₂ (110) plane. With the aid of line profiles of AC-HAADF-STEM images (Fig. 3a, b and Supplementary Fig. 4), the different locations of Pt single atoms on Pt/CeO₂-550 and Pt/CeO₂-800 could be well discerned. For Pt/CeO₂-550, the Pt atoms were mainly located at the edge or step sites on the surface of CeO₂, while the Pt atoms on Pt/CeO₂-800 were possibly located at the Ce substitution sites on the CeO₂ terrace (e.g., embedded into the surface lattice of CeO₂).

To further reveal the location of Pt atoms on CeO₂ support, two sets of in situ XRD experiments were designed, in which the XRD patterns were collected continuously throughout the sample heating (to 550 or 800 °C) and cooling process (Supplementary Fig. 5 and Fig. 3c, d). Before the measurements, the CeO₂ powder newly impregnated with Pt nitrate solution was dried in air at 120 °C for 30 min to remove excess H₂O (denoted as Pt/CeO₂). During the calcination process to obtain Pt/CeO₂-550, the XRD peaks shifted to lower angles in the heating stage from RT to 550 °C, and shifted back to

higher angles in the cooling stage, which should be related to the lattice expansion and lattice contraction, respectively⁴⁹. During the calcination process to obtain Pt/CeO₂-800, the XRD peaks also shifted to lower angles in the heating stage (< 620 °C) due to the lattice expansion of CeO₂ as well. However, an abrupt shift of XRD peaks back to high angles was observed for Pt/CeO₂-800 at higher temperature of ca. 620 °C, which should be resulted from the desorption of O₂ to form surface Ce₂O₃ species at elevated temperatures⁵⁰. The XRD peaks for bare CeO₂ support showed a similar shift trend during the heating and cooling stages as those for Pt/CeO₂-550 and Pt/CeO₂-800 catalysts (Supplementary Fig. 6). After calcination at 550 and 800 °C, the XRD diffraction peaks of Pt/CeO₂ catalysts shifted to higher angles in varying degrees. Considering that the CeO₂ support has already been pre-stabilized by calcination at 800 °C for 12 h, the shift in the diffraction peaks of Pt/CeO₂ should be due to the lattice expansion or contraction of CeO₂ induced by Pt species⁵¹. By conducting the Rietveld refinements of XRD patterns for Pt/CeO₂, Pt/CeO₂-550, and Pt/CeO₂-800, the refined lattice parameters of CeO₂ on these samples were calculated (Fig. 3e). It was noticeable that the lattice parameter of uncalcined Pt/CeO₂ and Pt/CeO₂-550 was slightly higher than that of standard CeO₂ reference, which should result from the perturbation

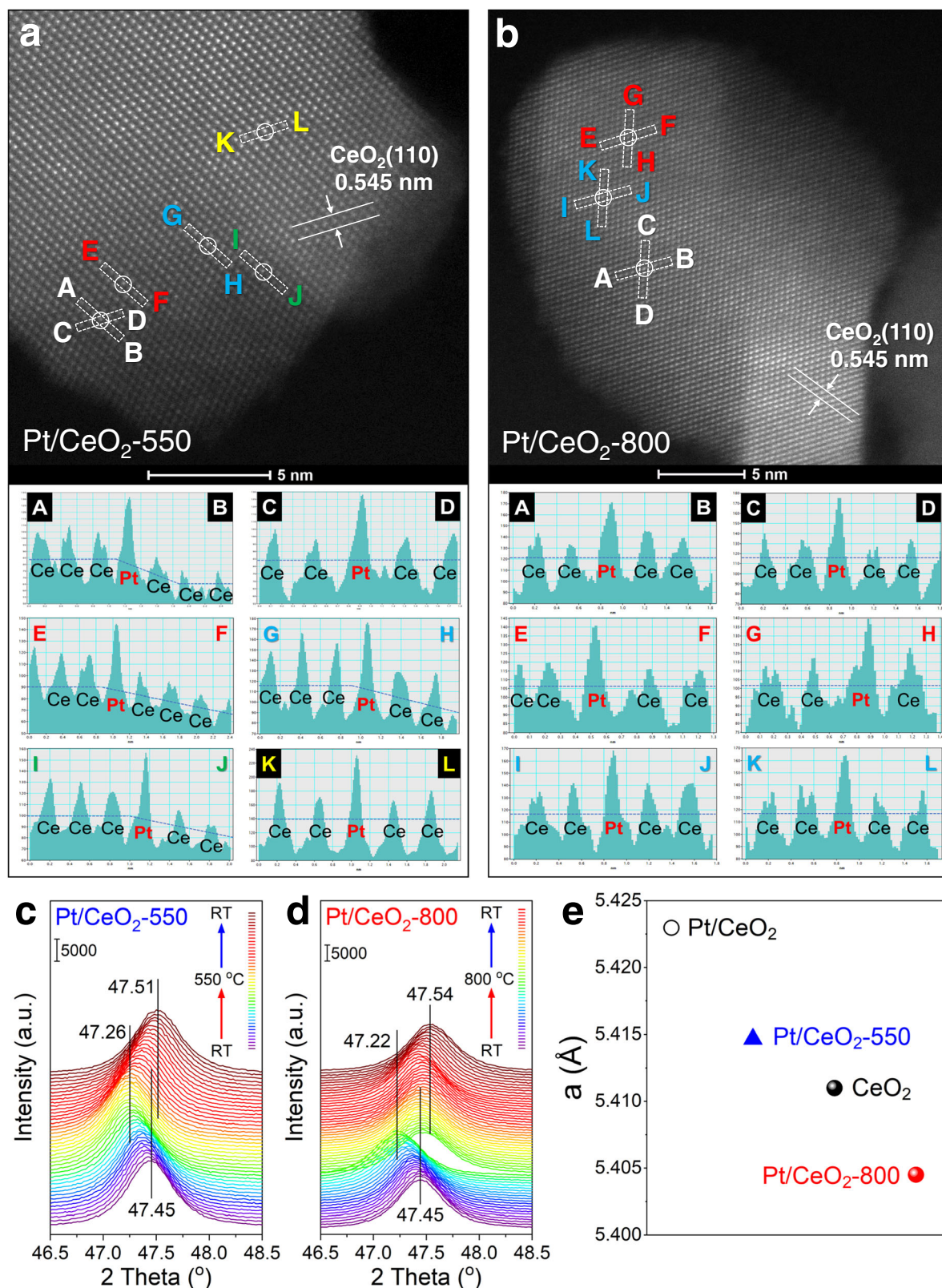


Fig. 3 | Location of Pt single atoms on CeO₂. AC-HAADF-STEM images and the line profiles of **a** Pt/CeO₂-550 and **b** Pt/CeO₂-800 (additional line profiles of Pt/CeO₂-800 can be found in Supplementary Fig. 4). In situ XRD patterns for **c** Pt/CeO₂-550

and **d** Pt/CeO₂-800; **e** the refined lattice parameters of Pt/CeO₂ (without calcination), standard CeO₂, Pt/CeO₂-550 and Pt/CeO₂-800 obtained by Rietveld refinements.

effect of Pt deposition on CeO₂ surface. Interestingly, when the calcination temperature increased to 800 °C, a dramatic decrease in the lattice parameter was observed, which might be related to the substitution of Ce ions by Pt ions with smaller ionic radius (Ce⁴⁺ = 0.970 Å,

Ce³⁺ = 1.280 Å, Pt⁴⁺ = 0.625 Å, Pt²⁺ = 0.800 Å) and further distortion^{43,52}, in line with the previous report that the Pt²⁺ might diffuse into CeO₂ lattice during the high temperature calcination process⁴³. The in situ XRD results further suggested that the Pt atoms might have been

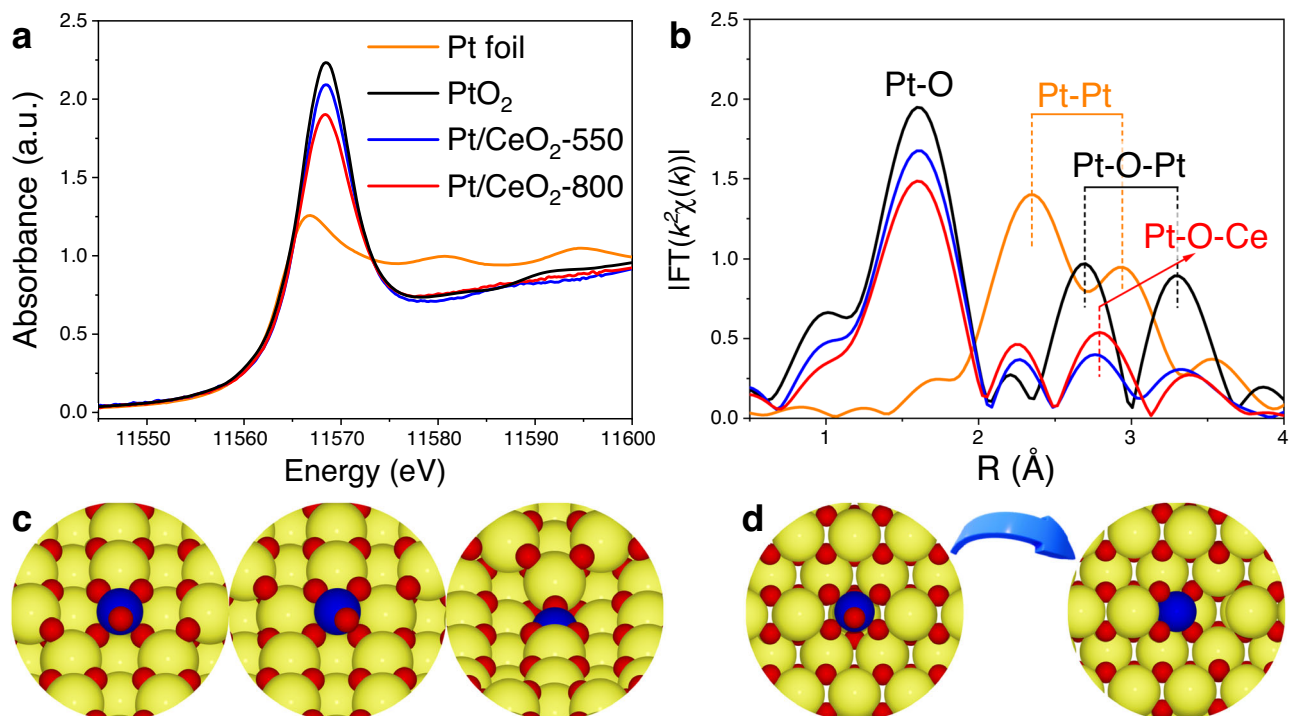


Fig. 4 | Coordination environment of Pt single atoms determined by XAS analysis. **a** Normalized XANES and **b** EXAFS magnitude of the Fourier transformed k^2 -weighted $\chi(k)$ data for Pt/CeO₂-550 (blue) and Pt/CeO₂-800 (red) at the Pt-L₃ edge. Pt foil (orange) and PtO₂ (black) references were used for XANES linear

combination fitting and EXAFS comparison. **c** Three possible geometries of Pt single atoms at the edge or step sites on CeO₂ (110) within Pt/CeO₂-550. **d** The reconstruction of Pt single atoms on CeO₂ (110) terrace from six-coordination sites to square-planar like coordination sites within Pt/CeO₂-800.

incorporated into the surface lattice on CeO₂ terrace within Pt/CeO₂-800 catalyst.

X-ray absorption spectroscopy (XAS) analysis was conducted to further elucidate the valence states and the coordination environments of Pt single atoms on Pt/CeO₂-X catalysts. As shown in Fig. 4a and Supplementary Fig. 7a, the white line (the intense absorption in the near-edge region) intensities of Pt-L₃ XANES for the Pt/CeO₂ catalysts were always much higher than that for Pt foil but lower than that for PtO₂, indicating the intermediate valence state of Pt species between 0 and +4 on Pt/CeO₂-X catalysts. Interestingly, the white line intensity of Pt-L₃ XANES on Pt/CeO₂ catalysts decreased monotonically as the calcination temperature increased, indicating the decreased Pt valence state accordingly. The XANES linear combination fitting was performed to further determine the average valence state of Pt species (Supplementary Fig. 8, Table 1 and Supplementary Table 1). As expected, the Pt species on Pt/CeO₂-800 indeed showed much lower valence state (2.7 ± 0.1) than those on Pt/CeO₂-550 (3.4 ± 0.1), which was further supported by the Pt 4f XPS results that more Pt²⁺ species were created on Pt/CeO₂-800 comparing to those on Pt/CeO₂-550 (Supplementary Table 2 and Supplementary Fig. 9).

Herein, to further reveal the local coordination structure of Pt single atoms on Pt/CeO₂-550 and Pt/CeO₂-800 catalysts, the EXAFS curve fitting was conducted and the results are plotted in both R space and k space (Fig. 4b, Supplementary Fig. 7b, Supplementary Fig. 10 and Supplementary Table 3). The absence of Pt–O–Pt and Pt–Pt coordination shells and the exclusive observation of Pt–O and Pt–O–Ce coordination shells further evidenced the formation of Pt single atoms on Pt/CeO₂-550 and Pt/CeO₂-800. Although Pt/CeO₂-800 indeed showed a lower coordination number (CN) of Pt–O ($\text{CN}_{\text{Pt-O}} = 4.4 \pm 0.3$) than Pt/CeO₂-550 ($\text{CN}_{\text{Pt-O}} = 5.1 \pm 0.4$), a higher CN of Pt–O–Ce was observed on Pt/CeO₂-800 ($\text{CN}_{\text{Pt-O-Ce}} = 4.2 \pm 0.3$) comparing to that on Pt/CeO₂-550 ($\text{CN}_{\text{Pt-O-Ce}} = 3.7 \pm 0.3$), further validating the formation of more Pt–O–Ce linkages within Pt/CeO₂-800, which could be further proved by Raman spectra (Supplementary Fig. 11). As discussed above,

for Pt/CeO₂-550, the Pt single atoms should be mainly located at the edge or step sites of CeO₂ (110), which did not induce any lattice shrinkage of CeO₂ (Fig. 4c). In contrast, for Pt/CeO₂-800, the significant lattice shrinkage of CeO₂ support could be related to the incorporation of Pt atoms into the surface lattice of CeO₂ (110). For Pt atoms substituting the surface Ce sites on CeO₂ (110) in an ideal model, the $\text{CN}_{\text{Pt-O}}$ should be 6, which was higher than the $\text{CN}_{\text{Pt-O}}$ on Pt/CeO₂-800 ($\text{CN}_{\text{Pt-O}} = 4.4 \pm 0.3$). However, since Pt²⁺ species possessed smaller ionic radius (*ca.* 0.800 Å) than Ce⁴⁺ (*ca.* 0.970 Å), a significant reconstruction of Pt single atoms from six-coordination sites to square-planar like coordination sites could occur on Pt/CeO₂-800 to balance the space and charge, thus leading to the decrease in the $\text{CN}_{\text{Pt-O}}$ from 6 to 4 (Fig. 4d and Supplementary Fig. 12). Similar reconstruction of Pt single atoms was also reported to occur on CeO₂ (111)²⁶.

DFT calculations on the coordination environment of Pt₁

To confirm the conjecture about the location, as well as the coordination environment of Pt single atoms on Pt/CeO₂-550 and Pt/CeO₂-800, DFT calculations were performed. For Pt/CeO₂-550, based on the experimental evidence showing that Pt single atoms were mainly located at or near the edge/step sites on CeO₂ (110) surface, ten configurations were proposed (Fig. 5a1–a10 and Supplementary Fig. 13). Among them, five configurations in which one Ce atom at the edge sites was replaced by one Pt atom were constructed (Fig. 5a1–a5). In Pt@CeEdge configuration, Pt replaced Ce atom at the edge sites and coordinated with 6 oxygen atoms to form octahedral Pt–O₆ (Fig. 5a1 and Supplementary Fig. 13a). Once one or two O atoms on Pt@CeEdge were removed, the Pt@CeEdge configuration evolved into Pt@CeEdge–O or Pt@CeEdge–2O (Fig. 5a2–a3 and Supplementary Fig. 13b, c), in which Pt coordinated with 5 or 4 oxygen atoms to form Pt–O₅ or square planar Pt–O₄, respectively. Further removal of another oxygen atom led to the formation of Pt@CeEdgeO_v⁽¹⁾ (Fig. 5a4 and Supplementary Fig. 13d) or Pt@CeEdgeO_v⁽²⁾ (Fig. 5a5 and Supplementary Fig. 13e) with a Pt–O₃ coordination. Furthermore, another five

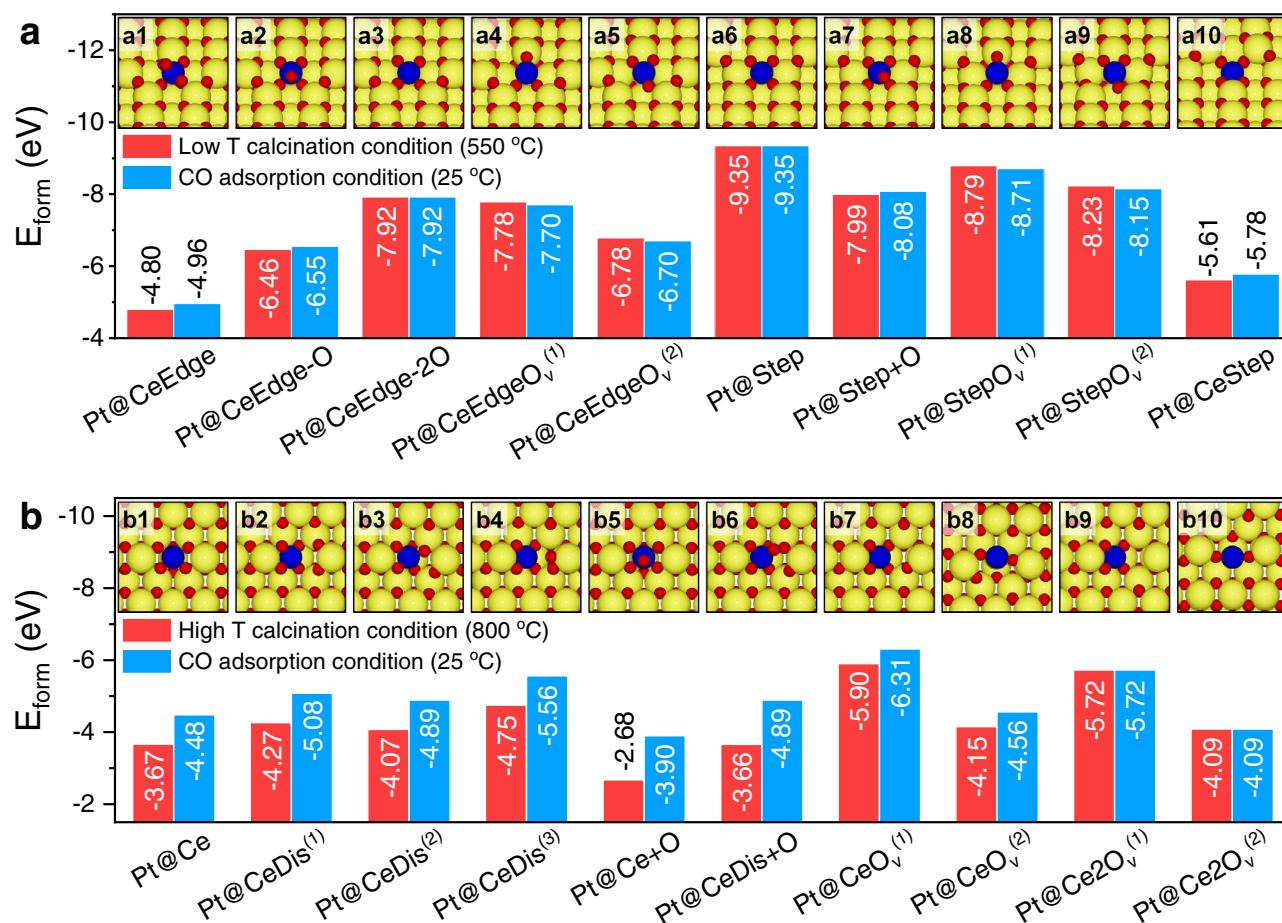


Fig. 5 | Determination of Pt₁ configurations on CeO₂ through DFT calculations. The formation energy (E_{form}) of the considered Pt₁ configurations on CeO₂ (110) under different conditions, i.e., low-temperature (Low T) calcination condition (550 °C, 0.21 atm O₂ pressure), high-temperature (High T) calcination condition (800 °C, 0.21 atm O₂ pressure), and CO adsorption condition (25 °C, 10⁻²⁰ atm O₂

pressure) within **a** Pt/CeO₂-550 and **b** Pt/CeO₂-800. The insert figures are the top view of considered configurations of isolated Pt atoms at or near the edge/step sites on CeO₂ (110) surface within Pt/CeO₂-550 (**a1–10**), and at the Ce substitution sites of CeO₂ (110) surface within Pt/CeO₂-800 (**b1–10**). Large yellow, medium blue, and small red balls represented Ce, Pt, and O atoms.

configurations where Pt atoms located at or near the step sites were constructed. In the configuration of Pt@Step, Pt atom was adsorbed at the step on CeO₂ (110) surface with a Pt–O₄ coordination (Fig. 5a6 and Supplementary Fig. 13f). Similar to Pt@CeEdge configuration, as shown in Fig. 5a7–a9 and Supplementary Fig. 13g–i, after adding or removing O atoms, three new configurations were obtained (Pt@Step+O, Pt@StepO_v⁽¹⁾ and Pt@StepO_v⁽²⁾). One configuration in which Pt replaced Ce step atom (Pt–O₄ coordination) was also proposed (Fig. 5a10 and Supplementary Fig. 13j).

To compare the relative stability of the Pt structures, the formation energy of the above-mentioned configurations was calculated under two different conditions, i.e., calcination condition (550 °C, 0.21 atm O₂ pressure) and condition at which the CO adsorption experiments were performed (25 °C, 10⁻²⁰ atm O₂ pressure). As illustrated in Fig. 5a, the formation energies of each configuration under the two conditions were similar, suggesting that the Pt₁/CeO₂ structures were almost the same after calcination and during CO adsorption process. Furthermore, other than Pt@CeEdge and Pt@CeStep, the rest eight configurations showed low formation energy, suggesting that the isolated Pt atoms could be stably anchored at edge or step sites on CeO₂ (110) with different possible O-coordination environments.

For Pt/CeO₂-800, based on the characterization results indicating that Pt atoms substituted the surface Ce sites on CeO₂ (110), ten configurations of Pt₁ on CeO₂ (110) terrace were proposed (Fig. 5b and Supplementary Fig. 14). The most trivial configuration was the one in

which Pt substituted Ce on the CeO₂ (110) surface without any change in the arrangement of O atoms (Fig. 5b1 and Supplementary Fig. 14a), forming an asymmetrical Pt–O₅-like coordination (Pt@Ce). However, the Pt–O₅ structure could transform to a distorted configuration of Pt@CeDis⁽¹⁾ without enforcing symmetry during the ionic relaxation process (Fig. 5b2 and Supplementary Fig. 14b), thus forming a Pt–O₄ planar type of coordination. Two other distorted configurations (Pt@CeDis⁽²⁾ and Pt@CeDis⁽³⁾) were also considered. Pt@CeDis⁽²⁾ was similar to Pt@CeDis⁽¹⁾ with an O atom displaced towards the top of Pt to form Pt–O₅ configuration (Fig. 5b3 and Supplementary Fig. 14c). In Pt@CeDis⁽³⁾ configuration, an O atom was displaced towards a nearby O atom to form O₂ species (Fig. 5b4 and Supplementary Fig. 14d), yielding a configuration similar to the one suggested by Tang et al.²⁵. By adding an additional O atom on top of Pt in Pt@Ce and Pt@CeDis, two configurations of Pt@Ce+O (Fig. 5b5 and Supplementary Fig. 14e) and Pt@CeDis+O (Fig. 5b6 and Supplementary Fig. 14f) were achieved, with the formation of Pt–O₆ coordination and Pt–O₅ coordination, respectively. When one O atom was removed from Pt@CeDis, two configurations with O vacancies nearby Pt atoms were constructed, referred as Pt@CeO_v⁽¹⁾ (Fig. 5b7 and Supplementary Fig. 14g) and Pt@CeO_v⁽²⁾ (Fig. 5b8 and Supplementary Fig. 14h), thus forming Pt–O₄ coordination and Pt–O₃ coordination, respectively. The further removal of one O atom from Pt@CeO_v⁽¹⁾ and Pt@CeO_v⁽²⁾ would result in the formation of configurations with two O vacancies, which were denoted as Pt@Ce2O_v⁽¹⁾ (Fig. 5b9 and Supplementary Fig. 14i) and Pt@Ce2O_v⁽²⁾ (Fig. 5b10 and Supplementary Fig. 14j), respectively.

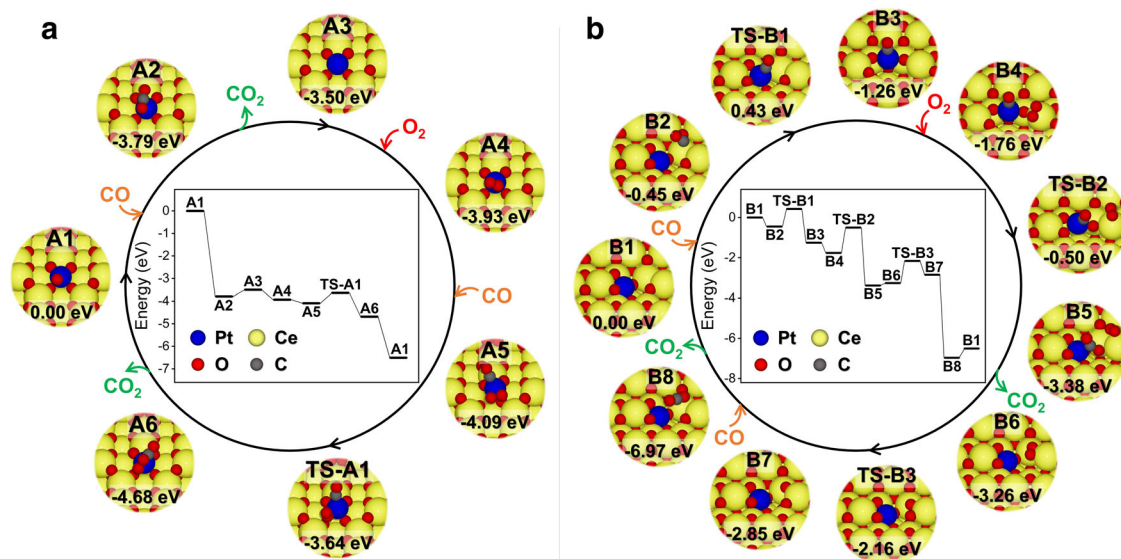


Fig. 6 | CO oxidation mechanisms on different Pt₁/CeO₂ catalysts. Proposed mechanisms of CO oxidation on **a** Pt@CeEdge-O (representing Pt/CeO₂-550 catalyst) and **b** Pt@CeO_v⁽¹⁾ (representing Pt/CeO₂-800 catalyst). “TS” indicates transition states. Potential energies were calculated with respect to CO and O₂ in gas phase.

The formation energy of the above-mentioned configurations was also calculated under both calcination condition and CO adsorption condition (Fig. 5b). Pt@CeDis⁽¹⁾, Pt@CeDis⁽³⁾, Pt@CeO_v⁽¹⁾ and Pt@Ce2O_v⁽¹⁾ showed the lowest formation energy among the ten configurations. Furthermore, the Pt atoms in these four configurations were in Pt–O₄ coordination. According to the results of H₂-TPR, Raman spectra, and XAS analysis, the CN_{Pt–O} on Pt/CeO₂-550 was higher than that on Pt/CeO₂-800 (5.1 vs. 4.4). Thus, the Pt₁ species on Pt/CeO₂-550 should be in Pt–O_{4+x} ($x > 0$) coordination, and the dominant Pt₁/CeO₂ configuration within Pt/CeO₂-550 could be Pt@CeEdge-O or Pt@Step+O with CN_{Pt–O} of 5. It is noteworthy that, because of the large difference in chemical potential of oxygen (–0.41 eV) between High T calcination condition and CO oxidation condition, there was noticeable difference in the formation energy of Pt₁ under the two conditions, except for the cases with two oxygen vacancies (Fig. 5b9–b10) in which the Pt₁ formation energy was independent of oxygen chemical potential. In contrast, there was virtually no difference in the chemical potential of oxygen (–0.08 eV) between Low T calcination condition and CO oxidation condition, resulting in the virtually identical Pt₁ formation energy under the two conditions (Fig. 5a).

To confirm the Pt₁/CeO₂ configurations within Pt/CeO₂-550 and Pt/CeO₂-800, CO adsorption calculations were conducted. As shown in Supplementary Fig. 15a, for Pt@CeEdge-O within Pt/CeO₂-550, CO picked up an O atom to form CO₂ during structural (ionic) relaxation, thus forming the configuration of Pt@CeEdge-2O. CO adsorbed on Pt@CeEdge-2O showed a stretching frequency of 2047 cm^{–1}, with a binding energy (E_B) of –0.36 eV. When CO picked up another O atom, CO–Pt@CeEdgeO_v⁽¹⁾ (E_B = –1.99 eV) or CO–Pt@CeEdgeO_v⁽²⁾ (E_B = –2.17 eV) was formed, which showed stretching frequencies of 2006 and 1949 cm^{–1}, respectively (Supplementary Fig. 15b, c). Similar to the case of Pt@CeEdge-O, CO adsorption would pick up an O atom on Pt@Step+O to form Pt@Step (Supplementary Fig. 15d). CO–Pt@Step showed a stretching frequency of 2012 cm^{–1} (E_B = –0.38 eV). Further removal of another O atom on CO–Pt@Step resulted in the formation of CO–Pt@StepO_v⁽¹⁾ (E_B = –1.99 eV) and CO–Pt@StepO_v⁽²⁾ (E_B = –2.34 eV), showing stretching frequencies of 2012 and 1921 cm^{–1}, respectively (Supplementary Fig. 15e, f).

For Pt/CeO₂-800, it was found that CO could not bind on the Pt atom in Pt@CeDis⁽¹⁾, but could bind on the Ce atom adjacent to Pt atom (E_B = –0.39 eV), with a CO stretching frequency of 2102 cm^{–1} (Supplementary Fig. 16a). As reported by Tang et al.²⁵, the CO adsorbed

on Pt@CeDis⁽³⁾ structure could react with an O atom nearby, thus creating Pt@CeO_v⁽¹⁾ configuration. Interestingly, it was found in this study that the adsorbed CO could pull the Pt atom from the Pt–O₄ planar configuration in Pt@CeO_v⁽¹⁾ to form CO–Pt–O₃ (Supplementary Fig. 16b, E_B = –1.33 eV). The reconstruction of Pt@CeDis⁽³⁾ under CO adsorption condition was demonstrated in Supplementary Fig. 17. Moreover, the adsorption of CO on Pt@Ce2O_v⁽¹⁾ was found rather weak (E_B = –0.07 eV). Therefore, Pt@CeDis⁽³⁾ and Pt@CeO_v⁽¹⁾ were the most possible Pt₁/CeO₂ configurations within Pt/CeO₂-800. Considering the lower formation energy of Pt@CeO_v⁽¹⁾ as compared to that of Pt@CeDis⁽³⁾ (Fig. 5b), Pt@CeO_v⁽¹⁾ should be the dominant configuration within Pt/CeO₂-800. The formation of Pt@CeO_v⁽¹⁾ configuration within Pt/CeO₂-800 was also well supported by the UV–Vis spectra that Pt/CeO₂-800 possessed higher surface structural disorder (Fig. 2c).

Based on the in situ DRIFTS results of CO adsorption showing that the CO stretching frequency on Pt/CeO₂-550 was higher than that on Pt/CeO₂-800, it can be concluded that Pt@CeEdge-O was the dominant configuration within Pt/CeO₂-550, on which the adsorbed CO showed a higher stretching frequency (2047 cm^{–1}) than CO–Pt@CeO_v⁽¹⁾ within Pt/CeO₂-800 (2022 cm^{–1}). Moreover, the calculated E_B of CO–Pt@CeO_v⁽¹⁾ (–1.33 eV) was higher than that of CO–Pt@CeEdge-2O (–0.36 eV), which was well supported by the CO-TPD results showing that the CO adsorption on Pt/CeO₂-800 catalyst was indeed stronger than that on Pt/CeO₂-550 catalyst (Supplementary Fig. 18). The Bader charge analysis was conducted on Pt@CeEdge-O and Pt@CeO_v⁽¹⁾ configurations to further evaluate the electronic structure of Pt₁ sites. As shown in Supplementary Fig. 19, the Pt atom in Pt@CeEdge-O representing Pt/CeO₂-550 catalyst showed a more positive Bader charge (+1.55) than that in Pt@CeO_v⁽¹⁾ (+0.75) representing Pt/CeO₂-800 catalyst, which could be resulted from the higher CN_{Pt–O} of Pt atom in Pt@CeEdge-O. Such results were in consistency with XPS and XANES analysis suggesting that the Pt single atoms in Pt/CeO₂-550 catalyst were in higher valence state than those in Pt/CeO₂-800 catalyst.

CO oxidation mechanism on Pt/CeO₂-550 and Pt/CeO₂-800

To understand the rationale for different CO oxidation activity on Pt/CeO₂-550 and Pt/CeO₂-800, the CO oxidation mechanisms on Pt@CeEdge-O and Pt@CeO_v⁽¹⁾ were studied by DFT calculations. As shown in Fig. 6a, on Pt@CeEdge-O (the dominant configuration of Pt/CeO₂-550), CO first picked up the O atom on top of Pt (A1) to form CO₂

that was physisorbed on the surface (A2), with a reaction energy of -3.79 eV. The CO_2 was found to desorb from the surface with a desorption energy of 0.29 eV to form Pt@CeEdge-2O configuration (A3), followed by the adsorption of O_2 on Pt atom with an adsorption energy of -0.43 eV (A4). Another CO was found to co-adsorb with O_2 on Pt atom (adsorption energy = -0.16 eV) to form A5 configuration. After a transition state of TS-A1 with an activation barrier of 0.45 eV, configuration A5 could transform into A6 (reaction energy = -0.59 eV), during which CO could pick up an O atom from the adsorbed O_2 to form CO_2 . The CO_2 subsequently desorbed from the surface with a desorption energy of -1.82 eV, resulting in the original Pt@CeEdge-O structure.

As shown in Fig. 6b, on Pt@CeO_v⁽¹⁾, CO was found to adsorb on Ce atom with an oxygen vacancy (B1) to form configuration B2, with an adsorption energy of -0.45 eV. The adsorbed CO could react with Pt to pull it up forming a CO–Pt–O₃ coordination (B3). This process was exothermic with a reaction energy of -0.81 eV and but not spontaneous with an activation barrier of 0.88 eV (TS-B1). Then, O_2 could adsorb on a Ce atom nearby (B4) with an adsorption energy of -0.50 eV. The adsorbed CO could react with a lattice O to form CO_2 (B5), with a reaction energy of -1.62 eV and an activation barrier of 1.26 eV (TS-B2). After the desorption of CO_2 (desorption energy = 0.12 eV), configuration B6 with two oxygen vacancies and adsorbed O_2 molecule was formed. O_2 could dissociate to fill these two oxygen vacancies (B7) after overcoming an activation barrier of 1.10 eV (TS-B3). Another CO could react with one of the dissociated O atoms to form a physisorbed CO_2 molecule (B8). This step was highly exothermic with a reaction energy of -4.12 eV and the CO_2 could then desorb with a desorption energy of 0.46 eV to form original Pt@CeO_v⁽¹⁾ structure (B1).

Comparing the above two proposed mechanisms for CO oxidation, it can be concluded that the oxidation of CO required three steps with sizable activation barrier on Pt@CeO_v⁽¹⁾ (the dominant structure on Pt/CeO₂-800), while only one with a relatively lower barrier on Pt@CeEdge-O (the dominant structure on Pt/CeO₂-550), well explaining why Pt/CeO₂-800 showed markedly lower CO oxidation activity than Pt/CeO₂-550. The results of dynamic oxygen storage capacity (OSC) test further confirmed that O_2 could be better activated and consumed by CO on Pt/CeO₂-550 than on Pt/CeO₂-800 (Supplementary Fig. 20), well supporting the DFT calculation results that the CO oxidation and O_2 dissociation (A5 → TS-A1 → A6) on Pt/CeO₂-550 only needed to overcome much lower activation barrier comparing to those on Pt/CeO₂-800 (B4 → TS-B2 → B5 and B6 → TS-B3 → B7). The lower apparent activation energy (E_a) for CO oxidation on Pt/CeO₂-550 (43 kJ·mol⁻¹) than that on Pt/CeO₂-800 (52 kJ·mol⁻¹) (Supplementary Fig. 21) should also be resulted from the more efficient activation of reactants.

The stability of Pt/CeO₂-550 and Pt/CeO₂-800 under reaction conditions was evaluated in a two-round CO oxidation activity test and through comparison to Pt cluster and nanoparticle catalysts on CeO₂. Almost no change in CO oxidation activity was observed on both Pt/CeO₂-550 and Pt/CeO₂-800 during the two rounds of tests up to 500 °C (both with constantly lower activity than Pt cluster and nanoparticle catalysts) (Supplementary Fig. 22), suggesting the high stability of Pt₁ catalysts under CO oxidation atmosphere in this study. Considering the inevitable presence of water vapor in vehicle exhaust, the CO oxidation on both catalysts was also performed under wet condition. As shown in Supplementary Fig. 23, Pt/CeO₂-550 still exhibited much higher CO oxidation activity than Pt/CeO₂-800 under wet condition.

NH₃ oxidation behavior on Pt/CeO₂-550 and Pt/CeO₂-800

As discussed above, through simply controlling the calcination temperatures, Pt single atoms with different coordination environments were successfully constructed on CeO₂. It has been demonstrated that Pt single atoms with a CN_{Pt-O} of ca. 5 on Pt/CeO₂-550 could better

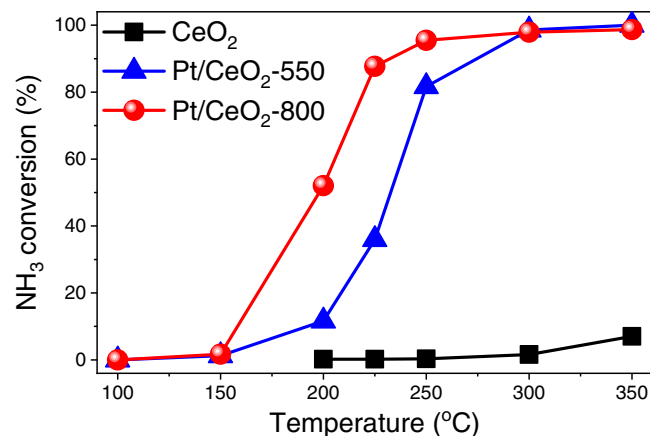


Fig. 7 | NH₃ oxidation activity. NH₃ oxidation performance on Pt/CeO₂-550 and Pt/CeO₂-800 catalysts as well as CeO₂ support (Reaction condition: [NH₃] = 500 ppm, [O₂] = 5%, balanced with Ar, WHSV = 200,000 mL·g_{cat}⁻¹·h⁻¹).

catalyze CO oxidation than those on Pt/CeO₂-800 with a CN_{Pt-O} of ca. 4. To further evaluate the catalytic performance of Pt/CeO₂-550 and Pt/CeO₂-800 in other oxidation reactions, NH₃ oxidation, a relatively less studied but important catalytic oxidation reaction in emission control field^{53,54}, was selected as a probe reaction. As shown in Fig. 7, contrary to the trend observed in CO oxidation reaction, surprisingly, Pt/CeO₂-800 exhibited much superior NH₃ oxidation performance than Pt/CeO₂-550. The NH₃ oxidation reaction on Pt/CeO₂-800 even showed slightly higher N₂ selectivity than that on Pt/CeO₂-550 especially at 350 °C (Supplementary Fig. 24), and such discrepancy was mainly due to the reduced formation of non-selective oxidation products including N₂O, NO, NO₂ at high temperatures on Pt/CeO₂-800 (Supplementary Fig. 25). The NH₃ oxidation activity on CeO₂, Pt/CeO₂-550 and Pt/CeO₂-800 was also tested in the presence of H₂O. After adding 5% H₂O to the feed gas, Pt/CeO₂-800 still exhibited better NH₃ oxidation activity than Pt/CeO₂-550 (Supplementary Fig. 26).

To reveal the intrinsic reasons for the higher NH₃ oxidation activity on Pt/CeO₂-800, NH₃-TPD was first conducted to investigate the NH₃ adsorption capacity on pure CeO₂ support and Pt/CeO₂ catalysts (Fig. 8a). Three NH₃-desorption peaks at ca. 130, 170 and 220 °C were observed on Pt/CeO₂-550 (denoted as peaks α, β, and γ) similar to those observed on CeO₂ support, which could be assigned to the desorption of NH₃ species adsorbed on CeO₂ sites and Pt sites with weak (α and β) or strong (γ) adsorption strength⁵⁵. Interestingly, the peak γ on Pt/CeO₂-550 showed a much higher relative intensity than that on CeO₂ support, indicating that the interaction between Pt single atoms and CeO₂ support could generate extra sites for stronger NH₃ adsorption. More importantly, on Pt/CeO₂-800, a new intensive NH₃-desorption peak (δ) was clearly observed, which could be attributed to NH₃ species more strongly bound to Pt single atoms or Ce atoms adjacent to Pt atoms on Pt/CeO₂-800 with another unique coordination environment (i.e., Pt atoms substituting Ce sites at CeO₂ (110) terrace). Due to the limited NH₃ conversion below 150 °C on Pt/CeO₂-550 and Pt/CeO₂-800, the NH₃ oxidation activity on both catalysts should be mainly related to the NH₃ species strongly adsorbed on Pt sites (peaks γ and δ). As listed in Supplementary Table 4, from the deconvolution results of NH₃-TPD profiles, a much higher ratio of NH₃ species more strongly adsorbed on Pt sites was observed on Pt/CeO₂-800. Given the near zero order of NH₃ in NH₃ oxidation reaction (Supplementary Fig. 27), the adsorption capacity of NH₃ at the investigated temperature regime would strongly determine the NH₃ oxidation activity on Pt/CeO₂-550 and Pt/CeO₂-800 catalysts. More strongly adsorbed NH₃ species on Pt/CeO₂-800 catalyst could be one of the main reasons for its much higher catalytic performance in NH₃ oxidation reaction.

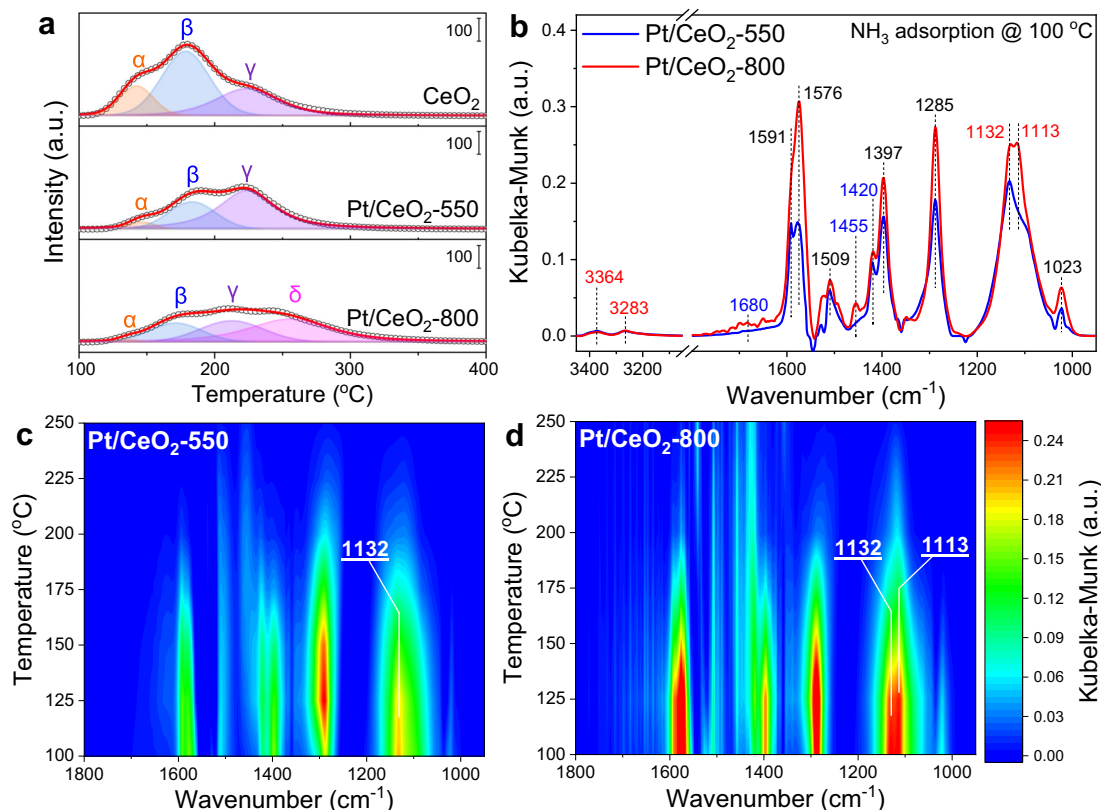


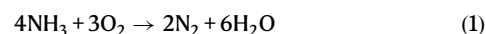
Fig. 8 | **NH₃ adsorption properties of Pt/CeO₂ catalysts.** **a** NH₃-TPD profiles on CeO₂, Pt/CeO₂-550, and Pt/CeO₂-800; **b** in situ DRIFTS of NH₃ adsorption at 100 °C; in situ DRIFTS of NH₃ adsorption and desorption on **c** Pt/CeO₂-550 and **d** Pt/CeO₂-800.

To further investigate the surface acidity of Pt/CeO₂-550 and Pt/CeO₂-800, in situ DRIFTS of NH₃ adsorption at 100 °C was conducted (Fig. 8b). The bands at 1113, 1132, 3283 and 3364 cm⁻¹ could be assigned to NH₃ adsorbed on Lewis acid sites. The bands at 1420 and 1680 cm⁻¹ could be attributed to NH₄⁺ bound to Brønsted acid sites^{55,56}. The other bands at 1023, 1285, 1397, 1509, 1576, and 1591 cm⁻¹ could be assigned to nitrate species generated by the oxidation of adsorbed NH₃^{57,58}. Considering the same initial CeO₂ support and Pt loading of Pt/CeO₂-550 and Pt/CeO₂-800 catalysts, the more intensive bands of nitrates on Pt/CeO₂-800 suggested that the adsorbed NH₃ on this catalyst could be better activated and oxidized mainly due to its unique local surface microstructure. In situ DRIFTS of NH₃ adsorption–desorption was also conducted to further evaluate the strength of surface acid sites on Pt/CeO₂-550 and Pt/CeO₂-800 (Fig. 8c, d). It was clearly demonstrated that the NH₃ bands located at 1113–1132 cm⁻¹ on Pt/CeO₂-800 were much more intensive than those on Pt/CeO₂-550 and also showed much higher stability in Ar flow during the temperature elevation. The formation of Pt₁ sites with different configurations on Pt/CeO₂-550 and Pt/CeO₂-800 should account for the distinct strength of NH₃ adsorption on these two catalysts. Based on DFT calculations, higher adsorption energy of NH₃ on Pt@CeO_v⁽¹⁾ ($E_B = -1.10$ eV) was observed than on Pt@CeEdge-O ($E_B = -0.73$ eV) (Supplementary Fig. 28), further confirming this viewpoint. Besides, it was found that NH₃ could be preferentially adsorbed on Ce atoms adjacent to Pt atoms on both structures rather than on Pt single atoms directly.

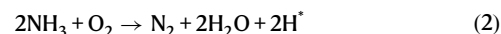
To evaluate the reactivity of adsorbed NH₃ on Pt/CeO₂-550 and Pt/CeO₂-800 catalysts, in situ DRIFTS of O₂ reacting with pre-adsorbed NH₃ at 175 °C was performed (Supplementary Fig. 29). As expected, more NH₃ adsorbed on Lewis acid sites (1067, 1105 and 1132 cm⁻¹) were observed on Pt/CeO₂-800 than on Pt/CeO₂-550 at 175 °C. With the introduction of O₂, the NH₃ species adsorbed on Brønsted acid sites (1424/1435 and 1650 cm⁻¹) showed almost no reactivity. In contrast, the

NH₃ species coordinated to Lewis acid sites could effectively react with O₂, and such NH₃ species on Pt/CeO₂-800 catalyst were consumed much faster than those on Pt/CeO₂-550 (Supplementary Fig. 30).

To better reveal the intrinsic reason for the higher NH₃ oxidation activity on Pt/CeO₂-800, DFT calculations for mechanism study were also performed. It is worth noting that the overall stoichiometric reaction of NH₃ oxidation is



involving a number of steps, full consideration of which is beyond the scope of this work. Instead, we have resorted to consideration of the initial reaction



to provide some insights into the NH₃ oxidation process. In the above reaction, there are two H atoms (H*) remaining adsorbed on the catalyst surface after N₂ desorption. H₂O molecules formed from the –OH groups can subsequently desorb and a surface oxygen vacancy will be created, which can be healed by the adsorption and dissociation of O₂. More details of mechanisms and their energetics can be found in Supplementary Figs. 31 and 32, and the simplified pictures presented in Fig. 9 capture the gist of our argument.

On Pt@CeEdge-O (Fig. 9a), the NH₃ oxidation started with the adsorption of NH₃ on the Ce atom adjacent to Pt atom, on the upper terrace (C2). After dissociation of two N–H bonds, the resulting H atoms combined with O atom on top of Pt to form H₂O (C3), which then desorbed from the surface leaving –NHO group behind (C4). Afterwards, the adsorption of the second NH₃ molecule on the same Ce atom could occur (C5). After the dissociation of two N–H bonds of the second NH₃ molecule and the diffusion of resulting H atoms, two

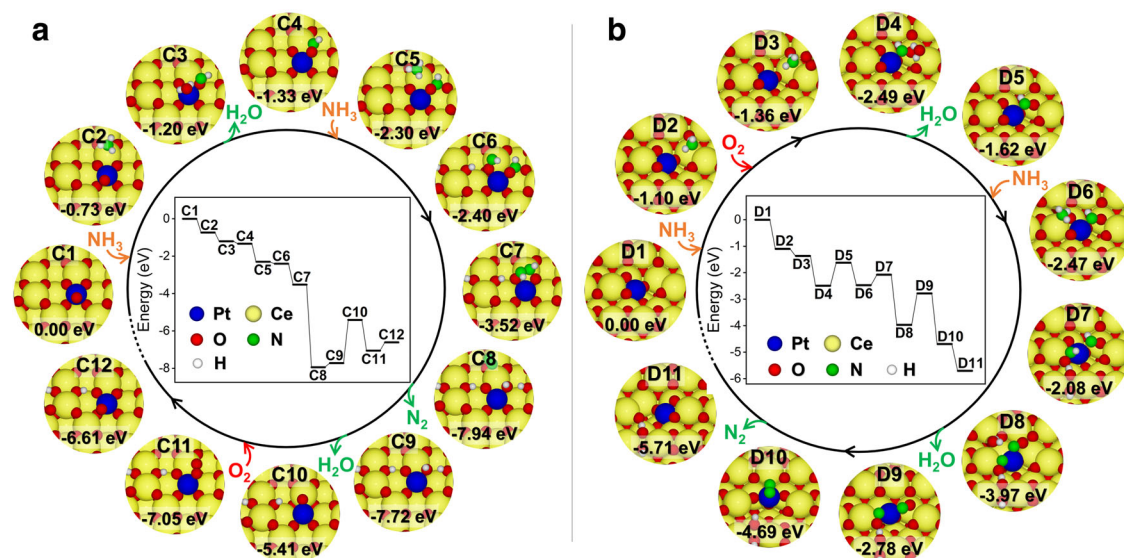


Fig. 9 | NH₃ oxidation mechanisms on different Pt₁/CeO₂ catalysts. Proposed mechanisms of NH₃ oxidation on **a** Pt@CeEdge-O (representing Pt/CeO₂-550 catalyst) and **b** Pt@CeO_v⁽¹⁾ (representing Pt/CeO₂-800 catalyst). Potential energies were calculated with respect to NH₃ and O₂ in gas phase.

-NHO groups were formed (C6), which could then react with each other to form N₂H₂ adsorbed on the surface (C7). Subsequently, N₂ could be formed after the dissociation of the two N-H bonds (C8) and then desorbed from the surface leaving four H atoms on the catalyst (C9). The followed step was the formation and desorption of second H₂O molecule, thus creating an oxygen vacancy (C10). The vacancy could be filled by the adsorption of O₂ (C11). After reconstruction, the original structure with the addition of two H atoms on the upper terrace was achieved (C12).

A similar process was observed on Pt@CeO_v⁽¹⁾ as well (Fig. 9b). The oxidation of NH₃ on Pt@CeO_v⁽¹⁾ started with the adsorption of NH₃ on the Ce atom adjacent to Pt atom with an oxygen vacancy (D2), followed by the co-adsorption of O₂ to form D3 configuration. After the dissociation of two N-H bonds and O₂ molecule, a H₂O molecule was formed (D4), which could desorb from surface leaving -NHO group behind (D5). Then, the second NH₃ molecule could adsorb on another Ce atom nearby the Pt atom (D6). After the dissociation of two N-H bonds of the second NH₃ molecule, two -NHO groups were formed on Pt@CeO_v⁽¹⁾ (D7). The two H atoms from these two -NHO groups could recombine with surface O atom to form second H₂O (D8), which could desorb from surface leaving two -NO groups and an oxygen vacancy (D9). The formed N₂ from these two -NO groups could then desorb from surface (D10). After a surface structural reconstruction, the catalyst could return to its starting configuration with two additional H atoms on the terrace of the CeO₂ (110) surface (D11).

When comparing the two reaction mechanisms mentioned above, it can be observed that the N atoms in -NHO or -NO groups on Pt@CeO_v⁽¹⁾ (representing Pt/CeO₂-800 catalyst) were coordinated to Pt atom, which could weaken the strength of Pt-O bond and accordingly facilitate the formation (D7 → D8) and desorption (D8 → D9) of the second H₂O molecule. The desorption energy of the second H₂O formed on Pt@CeO_v⁽¹⁾ was determined as 1.19 eV, much lower than that on Pt@CeEdge-O representing Pt/CeO₂-550 catalyst (2.31 eV) on which the N atoms in -NHO or -NO groups were coordinated to Ce atoms. For the NH₃ oxidation on both Pt@CeEdge-O and Pt@CeO_v⁽¹⁾, the desorption of the second H₂O molecule (C9 → C10 and D8 → D9, respectively) was the rate limiting step. Therefore, the lower desorption energy of the second H₂O molecule on Pt@CeO_v⁽¹⁾ was one of the main reasons for the much higher NH₃ oxidation activity obtained on Pt/CeO₂-800.

Discussion

Pt single atom catalysts with different local coordination environments on CeO₂ support were finely fabricated by a simple calcination temperature control strategy. With the calcination temperature increased from 350 to 800 °C, the Pt clusters could first disperse into Pt single atoms, and then the Pt single atoms with much stronger interaction with CeO₂ through Pt-O-Ce linkages were created. Different from Pt/CeO₂-550 catalyst in which the Pt single atoms were mainly located at the edge sites of CeO₂ support, for Pt/CeO₂-800 catalyst, the Pt single atoms were mainly incorporated into the surface lattice of CeO₂ with further structural reconstruction to form a square-planar like coordination environment on CeO₂ terrace. Although the Pt single atoms on Pt/CeO₂-800 catalyst showed rather limited catalytic activity in CO oxidation reaction due to its inferior ability to activate O₂, the enhanced surface acidity for NH₃ adsorption/activation and the easier desorption of H₂O produced during the reaction enabled Pt/CeO₂-800 to exhibit much higher NH₃ oxidation activity than that on Pt/CeO₂-550. It is suggested that the precise control of the coordination environments of Pt single atoms is beneficial for maximizing their catalytic performance in different oxidation reactions. This work can provide instructive insights into the flexible tuning of local coordination environments of single atom catalysts for more efficient application in different target reactions.

Methods

Catalyst preparation

Before being used as a support, commercial CeO₂ (high surface area ceria with the BET surface area as ca. 120 m²/g) was pre-calcined in air at 800 °C for 12 h to minimize its potential structural changes in the subsequent catalyst preparation process. To prepare CeO₂ supported Pt catalysts, 1.00 wt.% Pt using Pt(NO₃)₂ as precursor was loaded onto the pretreated CeO₂ support by incipient wetness impregnation (IWI) method. After impregnation of Pt(NO₃)₂ onto CeO₂, the wet powder was dried in air at 120 °C for 1 h. Afterwards, the obtained powder was calcined in air at 350, 550, 700, or 800 °C for 2 h. The obtained catalysts were denoted as Pt/CeO₂-X, with X °C as calcination temperature. The practical mass loadings of Pt in the selected catalysts were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). As expected, Pt/CeO₂-550 (0.92 wt.%) and Pt/CeO₂-800 (0.90 wt.%) showed almost the same Pt loadings, which were very close to the nominal Pt loading (1.00 wt.%).

Characterizations

The specific surface area and pore volume were measured by N_2 physisorption at -196°C using a Micromeritics ASAP-2020 analyzer. Before each test, the samples were degassed at 300°C for 4 h. The specific surface area was calculated using Brunauer-Emmett-Teller method, and the pore volume and pore size distribution were determined by BJH method using the desorption isotherms.

In situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) study was carried out on a Thermo Nicolet iS50 FTIR spectrometer equipped with a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector. In each test, 50 mg of catalyst powder was placed in the DRIFTS cell (PIKE Technologies DiffusIR), pressed, and mounted. The catalysts were first pretreated in air at 300°C for 1 h. Afterwards, the catalysts were cooled down stepwise to room temperature. During this process, the background spectra were collected at target temperatures for different experiments (e.g., 25°C for CO adsorption, 25°C for methanol adsorption, $100/125/150/175/200/225/250^\circ\text{C}$ for NH_3 adsorption/desorption, and 175°C for NH_3 oxidation). For CO adsorption, methanol adsorption, or NH_3 adsorption/desorption/oxidation experiments, the feed gas consisted of 1% CO, 15% methanol, or 500 ppm NH_3 and/or 5 vol% O_2 (when used), respectively, using Ar as balance. The total flow rate was controlled at $83.33\text{ mL}\cdot\text{min}^{-1}$. All the spectra were collected from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} for 100 scans.

H_2 -temperature-programmed reduction (H_2 -TPR) was conducted on a Quantachrome Autosorb-iQ instrument. Typically, 30 mg of sample was loaded in a U-type quartz tube reactor and pretreated with air at 400°C for 1 h. When the sample was cooled down to room temperature in air, the feeding gas was switched to 10 vol% H_2 balanced with Ar ($30\text{ mL}\cdot\text{min}^{-1}$). Then, the reactor was heated linearly to 900°C with a ramping rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. The signal of H_2 consumption was monitored by a thermal conductivity detector (TCD). H_2O moisture in the gas mixture was removed by a cold trap filled with liquid N_2 before passing into the TCD.

Ultraviolet-visible (UV-Vis) spectra were collected on a Shimadzu UV-2401 PC instrument in diffuse mode. BaSO_4 was used as a reference and the spectra collection range was 200–800 nm. Samples were exposed to air at room temperature throughout the experiments.

Atomic-resolution aberration-corrected high angle annular dark field scanning transmission electron microscopic (AC-HAADF-STEM) images were collected on a FEI Titan Cubed G2 60-300 aberration-corrected S/TEM instrument at 300 kV accelerating voltage. The observations were performed in the HAADF mode, which allowed Z-contrast imaging. The probe convergence angle on the Titan electron microscope was 22 mrad, and the angular range of the HAADF detector was from 79.5 to 200 mrad. To prepare the TEM samples, an appropriate amount of sample powder was dispersed in ethanol and then dropped on a 3 mm TEM Mo grid. The images of energy dispersive spectroscopy (EDS) elemental mapping in the STEM mode were obtained from the Titan electron microscope using SuperX system.

In situ XRD experiments were conducted on a Rigaku SmartLab SE XRD instrument equipped with a high speed 1D silicon strip detector (D/teX Ultra 250, Rigaku, Japan) and an in situ cell (Reactor X, Rigaku, Japan). X-rays were generated from a Cu source, with a tube operational power of 2.2 kW (Cu $K\alpha$). Additional PXRD parameters were as follows: goniometer radius = 300 mm, incident and receiving Soller slits = 2.5° , length limiting slit = 10 mm, with a receiving slit Ni filter mitigating the Cu $K\beta$ signal. The temperature of the sample was controlled by IR heating of the quartz sample holder (sample indentation dimensions: $13 \times 20 \times 0.4\text{ mm}$) from below, and the gas composition in the cell was controlled by a bank of mass flow controllers (Brooks 5850e, Brooks Instrument, Hatfield, PA, USA). During the experiments, dry air flowed through the in situ cell ($100\text{ mL}\cdot\text{min}^{-1}$). Samples were held on at 25°C for 5 min, and then the XRD scans were performed

continuously throughout the temperature ramping, holding and cooling steps. In more detail, the samples were heated from 25°C to the target temperatures (550 or 800°C) with a ramping rate of $2^\circ\text{C}\cdot\text{min}^{-1}$, held at the target temperatures (550 or 800°C) for 2 h, and finally cooled to 25°C at a rate of $2^\circ\text{C}\cdot\text{min}^{-1}$. The XRD scans were taken from 25 to 50° at a scan rate of $2^\circ\text{C}\cdot\text{min}^{-1}$, with a step size of 0.01° .

ICP-OES measurement was conducted on an Optima 8300 instrument (PerkinElmer). The incident power was set at 13,000 W and the wavelength for Pt detection was 265.945 nm.

XAS for Pt $L_{3\text{-edge}}$ in fluorescence mode was measured at beamline 7-BM QAS of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory. The energy range of the X-ray provided by this beamline was 4.7–31 keV. Its monochromator is equipped with a Si(111) channel-cut crystal and runs at continuous scan mode. The duration of a typical scan was 30 s and each sample was scanned 40 times. Samples were exposed to air at room temperature throughout the experiments. The XAS data including X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were analyzed using Demeter software package.

X-ray photoelectron spectroscopy (XPS) was collected on a VG CLAM 4 MCD analyzer. Before the analysis, the samples were degassed in a preparation chamber (10^{-5} Torr) for 0.5 h. Then, the samples were put into the analysis chamber (3×10^{-9} Torr) for further analysis. The binding energies (BE) were calibrated with C1s line at 284.6 eV.

Raman spectra were collected on a Renishaw Laser Raman spectrometer (Renishaw plc) with an Ar^+ laser beam. The emission line was 532 nm and the output power was 10 mW. Samples were exposed to air at room temperature throughout the experiments.

CO-temperature programmed desorption (CO-TPD) was conducted in a fixed-bed quartz tube flow reactor with an online mass spectrometer (Hiden Analytical, HPR20 R&D). The mass-to-charge ratio (m/z) of 28 was used to monitor CO. In each test, 100 mg sample was pretreated by air at 300°C for 1 h and then saturated with CO at 30°C . Then, Ar was introduced into the quartz tube reactor to remove the weakly adsorbed CO. Finally, the sample was heated linearly to 300°C at a rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ in flowing Ar.

The dynamic oxygen storage capacity (OSC) was measured by a multi-pulse experiment under alternating pulses of 2% CO/4% O_2 with a total flow rate of $100\text{ mL}\cdot\text{min}^{-1}$. Before testing, all samples were pretreated in air at 300°C for 1 h. A single cycle lasted 1 min, with 30 s CO/30 s O_2 cycling switch controlled by automatic mass flow controller (MFC) systems. The OSC values were calculated from the averaged CO_2 formation in a cycle (30 s + 30 s) detected by an online mass spectrometer (Hiden Analytical, HPR20 R&D).

NH_3 -temperature-programmed desorption (NH_3 -TPD) was carried out in a fixed-bed quartz flow reactor connected with an online Thermo Nicolet iS10 FTIR spectrometer equipped with a 2 m path-length gas cell (200 mL volume). In each test, 100 mg sample was pretreated by pure Ar at 200°C for 1 h and then saturated with NH_3 at 100°C . Then, Ar was introduced into the quartz tube reactor again to remove the weakly adsorbed NH_3 . Finally, the sample was heated linearly to 500°C at a rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ in the flowing Ar ($100\text{ mL}\cdot\text{min}^{-1}$).

Details of density functional theory (DFT) based calculations

DFT calculations were performed using the Vienna ab initio Simulation Package (VASP)⁵⁹, employing the projector-augmented wave (PAW)^{60,61} and plane-wave basis set. The generalized-gradient approximation (GGA) was used in the form of the Perdew-Burke-Ernzerhof (PBE)⁶² functional together with the DFT-D3 correction⁶³ to describe electronic exchange-correlation. The DFT + U method with $U = 5\text{ eV}$ for Ce 5f orbitals⁶⁴ was used to properly describe the electronic structure of CeO_2 . The electron kinetic energy cut-off for plane-wave expansion was set to 500 eV. For modeling the CeO_2 (110) surface, a 5 layer 4×3 CeO_2 (110) slab was constructed, i.e., 12 Ce and 24 O atoms per layer, using the optimized lattice constant of 5.479 \AA . For modeling the

stepped CeO₂ (110) surface, a twice-large slab was removed with half of the top CeO₂ layer to create the step. 15 Å vacuum added along the surface normal direction was used to decouple periodical images along the surface normal direction. Given the large size of the supercell, the Brillouin zone was sampled with one point at the zone center, using a Gaussian smearing with $\sigma = 0.1$ eV for structural relaxation. All electronic cycles converged to 10⁻⁵ eV. All structures were relaxed to minimize the stress until all components of forces acting on each atom were less than 10⁻² eV/Å.

To search the preferable location of Pt atom on surface, various surface Ce atoms were replaced with Pt atoms. To mimic the cases that Pt atom was next to O-vacancies, one or two O atoms nearby Pt were removed to create a scenario. To mimic the cases that Pt atom was coordinated with 5 or 6 O atoms, one O atom was added on top of Pt. For step surface, Pt atoms adsorbed at the step sites were also considered.

To evaluate the relative formation energy of Pt₁ configurations, the formation energy of Pt₁/CeO₂ was defined as

$$E_{\text{form}} = F_{\text{Pt}_1/\text{CeO}_2} - F_{\text{CeO}_2}, \quad (3)$$

where $F_{\text{Pt}_1/\text{CeO}_2}$ and F_{CeO_2} were the free energy of Pt₁/CeO₂ system and CeO₂ surface. The free energy of a system was defined as

$$F = E + F_{\text{vib}} + PV - N_{\text{Ce}}\mu_{\text{Ce}}^{\circ} - N_{\text{O}}\mu_{\text{O}} - N_{\text{Pt}}\mu_{\text{Pt}}, \quad (4)$$

where E , F_{vib} , and PV were the total energy (calculated from DFT), the vibrational contribution to free energy, and the contribution to free energy of the change of pressure and volume, respectively. The difference between PV term of Pt₁/CeO₂ and clean CeO₂ surface was small and could be ignored. In this work, the difference in F_{vib} between Pt₁/CeO₂ and clean CeO₂ surface was not included for computational feasibility, as 20 Pt₁/CeO₂ configurations with large simulation supercell were considered. Nevertheless, such contribution was expected to play a minor role because of the large difference between the formation energy of considered Pt₁/CeO₂ configurations, as shall be seen. N_X and μ_X were the number of X atoms in the considered system and chemical potential of X atom ($X = \text{Ce}, \text{O}, \text{or Pt}$), respectively. As Ce was in equilibrium with Ce atoms in bulk CeO₂ (i.e., if Ce atoms moved away from the surface, they would go to bulk CeO₂), μ_{Ce} and μ_{O} were not independent and

$$\mu_{\text{Ce}} + 2\mu_{\text{O}} = E_{\text{CeO}_2}, \quad (5)$$

where E_{CeO_2} was the total energy per bulk CeO₂ unit. As oxygen was in equilibrium with the O₂ reservoir surrounding the surface, the chemical potential of oxygen at temperature T and partial pressure p_{O_2} was calculated as

$$\mu_{\text{O}}(T, p) = 1/2(E_{\text{Tot}}^{\text{O}_2} + E_{\text{ZPE}}^{\text{O}_2}) + \tilde{\mu}_{\text{O}}(T, p^{\circ}) + 1/2k_{\text{B}}T \ln(p_{\text{O}_2}/p^{\circ}), \quad (6)$$

where $E_{\text{Tot}}^{\text{O}_2}$ and $E_{\text{ZPE}}^{\text{O}_2}$ were the total energy and zero point energy of an O₂ molecule calculated with DFT, k_{B} was Boltzmann constant, p° was a reference pressure, and $\tilde{\mu}_{\text{O}}(T, p^{\circ})$ was the temperature dependent part that could be calculated from experimental data^{65,66}. As Pt was often deposited on the surface at the beginning of the calcination process, there was no reservoir for Pt during or after calcination, thus the chemical potential of Pt was approximated as the total energy of the isolated Pt atom.

The adsorption energy of CO on Pt₁/CeO₂ was calculated as

$$E_{\text{Ads}} = E_{\text{CO-Pt}_1/\text{CeO}_2} - E_{\text{Pt}_1/\text{CeO}_2} - E_{\text{CO}}, \quad (7)$$

where $E_{\text{CO-Pt}_1/\text{CeO}_2}$, $E_{\text{Pt}_1/\text{CeO}_2}$ and E_{CO} were the total energy of CO adsorption configuration, Pt₁/CeO₂ system, and an isolated CO

molecule which was evaluated inside a cubic 15 × 15 × 15 Å³ box, respectively. CO stretching frequencies were calculated using the finite-difference method as implemented in the Phonopy code (a 0.01 Å displacement was used, and electronic cycles were converged to 10⁻⁶ eV)⁶⁷. It was found that displacements applied to about 30 atoms around the adsorbed CO molecule were sufficient to obtain converged CO stretching frequencies.

Since the study here involved considerations of a large number of configurations of adsorbed reactants and their intermediates as appropriate for CO oxidation and NH₃ oxidation on Pt@CeO_v⁽¹⁾ and Pt@CeEdge-O, for computational feasibility, a CeO₂ (110) slab with 4 layers of 4 × 3 CeO₂ (110), i.e., 12 Ce and 24 O atoms per layer, was used for the investigations on Pt@CeO_v⁽¹⁾. A CeO₂ (110) slab with 5 layers of 1 × 3 CeO₂ (230) stepped surface, i.e., 12 Ce and 24 O atoms per layer, was used for CO oxidation study on Pt@CeEdge-O. A CeO₂ (110) slab with 4 layers of 6 × 3 CeO₂ (110) with 50% of the top layer removed, creating the step in the Pt@CeEdge-O model, was used for NH₃ oxidation study. Transition state (TS) for a reaction was determined using the nudged-elastic band (NEB) and the climbing-image (CI)-NEB methods^{68,69}.

Catalytic activity test

The CO oxidation and NH₃ oxidation activities of the catalysts were evaluated in a fixed-bed quartz tube reactor. Samples (40–60 mesh) were mixed with SiC to minimize the heat effect (with a mass ratio of 1:10). For CO oxidation activity test, the reactants consisted of 1% CO, 1% O₂ and 5% H₂O (if used) in Ar balance. The total flow rate was 83.33 mL·min⁻¹ with a weight hourly space velocity (WHSV) of 400,000 mL·g_{cat}⁻¹·h⁻¹. The outlet gas was detected by an online mass spectrometer (Hiden Analytical, HPR20 R&D). The mass-to-charge ratio (m/z) of 28 and 44 were used to monitor CO and CO₂, respectively. For NH₃ oxidation activity test, the reactants consisted of 500 ppm NH₃, 5% O₂, and 5% H₂O (if used) in Ar balance. The WHSV was controlled at 200,000 mL·g_{cat}⁻¹·h⁻¹. The concentrations of NH₃, NO, NO₂, and N₂O in the outlet gas were measured by Thermo Nicolet iS10 FTIR spectrometer equipped with a 2 m path-length gas cell with 200 mL volume. All reactions were performed under steady state conditions. The CO conversion in CO oxidation reaction, and the NH₃ conversion and N₂ selectivity in NH₃ oxidation reaction were determined according to the following equations:

$$\text{CO conversion (\%)} = \{([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}})/[\text{CO}]_{\text{in}}\} \times 100\% \quad (8)$$

$$\text{NH}_3 \text{ conversion (\%)} = \{([\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}})/[\text{NH}_3]_{\text{in}}\} \times 100\% \quad (9)$$

$$\text{N}_2 \text{ selectivity (\%)} = \{1 - ([\text{NO}]_{\text{out}} + [\text{NO}_2]_{\text{out}} + 2[\text{N}_2\text{O}]_{\text{out}})/([\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}})\} \times 100\% \quad (10)$$

In the reaction kinetics study, to avoid the heat and mass transfer effects, the reaction rates were determined with CO or NH₃ conversions below 15%, and samples (40–60 mesh) were mixed with SiC to minimize the heat effect (with a mass ratio of 1:20) before the test. For CO oxidation reaction, the feed gas consisted of 1% CO and 1% O₂ in Ar balance. The WHSV was controlled at 800,000 mL·g_{cat}⁻¹·h⁻¹ and 400,000 mL·g_{cat}⁻¹·h⁻¹ for Pt/CeO₂-550 and Pt/CeO₂-800, respectively. For NH₃ oxidation reaction, the feed gas consisted of 500 ppm NH₃ and 5% O₂ in Ar balance, with a WHSV of 600,000 mL·g_{cat}⁻¹·h⁻¹.

Data availability

Source data are provided with this paper.

References

- Liu, L. & Corma, A. Metal catalysts for heterogeneous catalysis: From single atoms to nanoclusters and nanoparticles. *Chem. Rev.* **118**, 4981–5079 (2018).

2. Kaiser, S. K., Chen, Z., Faust Akl, D., Mitchell, S. & Pérez-Ramírez, J. Single-atom catalysts across the periodic table. *Chem. Rev.* **120**, 11703–11809 (2020).
3. Lang, R. et al. Single-atom catalysts based on the metal-oxide interaction. *Chem. Rev.* **120**, 11986–12043 (2020).
4. Lu, Y. et al. Identification of the active complex for CO oxidation over single-atom Ir-on-MgAl₂O₄ catalysts. *Nat. Catal.* **2**, 149–156 (2019).
5. Wang, J. et al. Catalytic CO oxidation on MgAl₂O₄-supported Iridium single atoms: Ligand configuration and site geometry. *J. Phys. Chem. C* **125**, 11380–11390 (2021).
6. Liang, J.-X. et al. Dual metal active sites in an Ir₁/FeO_x single-atom catalyst: A redox mechanism for the water-gas shift reaction. *Angew. Chem. Int. Ed.* **59**, 12868–12875 (2020).
7. Chen, Y. et al. Identifying size effects of Pt as single atoms and nanoparticles supported on FeO_x for the water-gas shift reaction. *ACS Catal.* **8**, 859–868 (2018).
8. Yin, P. et al. Single cobalt atoms with precise N-coordination as superior oxygen reduction reaction catalysts. *Angew. Chem. Int. Ed.* **55**, 10800–10805 (2016).
9. Pan, Y. et al. Regulating the coordination structure of single-atom Fe-N_xC_y catalytic sites for benzene oxidation. *Nat. Commun.* **10**, 4290 (2019).
10. Huang, D. et al. Conflicting roles of coordination number on catalytic performance of single-atom Pt catalysts. *ACS Catal.* **11**, 5586–5592 (2021).
11. Xu, Y. et al. Revealing the correlation between catalytic selectivity and the local coordination environment of Pt single atom. *Nano Lett.* **20**, 6865–6872 (2020).
12. Zhang, Y., Jiao, L., Yang, W., Xie, C. & Jiang, H.-L. Rational fabrication of low-coordinate single-atom Ni electrocatalysts by MOFs for highly selective CO₂ reduction. *Angew. Chem. Int. Ed.* **60**, 7607–7611 (2021).
13. Zhang, J. et al. Tuning the coordination environment in single-atom catalysts to achieve highly efficient oxygen reduction reactions. *J. Am. Chem. Soc.* **141**, 20118–20126 (2019).
14. Yang, W. et al. The effect of coordination environment on the kinetic and thermodynamic stability of single-atom Iron catalysts. *Phys. Chem. Chem. Phys.* **22**, 3983–3989 (2020).
15. Zhang, S. et al. Insights into the mechanism of n-Hexane reforming over a single-site platinum catalyst. *J. Am. Chem. Soc.* **142**, 16533–16537 (2020).
16. Xiao, Y., Li, H. & Xie, K. Activating lattice oxygen at the twisted surface in a mesoporous CeO₂ single crystal for efficient and durable catalytic CO oxidation. *Angew. Chem. Int. Ed.* **60**, 5240–5244 (2021).
17. Liu, X. et al. Revealing the catalytic kinetics and dynamics of individual Pt atoms at the single-molecule level. *Proc. Natl Acad. Sci. USA* **119**, e2114639119 (2022).
18. Chen, L.-N. et al. Efficient hydrogen production from methanol using a single-site Pt₁/CeO₂ catalyst. *J. Am. Chem. Soc.* **141**, 17995–17999 (2019).
19. Jiang, Z. et al. Stabilizing platinum atoms on CeO₂ oxygen vacancies by metal-support interaction induced interface distortion: Mechanism and application. *Appl. Catal., B* **278**, 119304 (2020).
20. Nie, L. et al. Activation of surface lattice oxygen in single-atom Pt/CeO₂ for low-temperature CO oxidation. *Science* **358**, 1419 (2017).
21. Ma, Y. et al. Tailoring of the proximity of platinum single atoms on CeO₂ using phosphorus boosts the hydrogenation activity. *ACS Catal.* **9**, 8404–8412 (2019).
22. Jeong, H. et al. Controlling the oxidation state of Pt single atoms for maximizing catalytic activity. *Angew. Chem. Int. Ed.* **59**, 20691–20696 (2020).
23. Bruix, A. et al. Maximum noble-metal efficiency in catalytic materials: Atomically dispersed surface platinum. *Angew. Chem. Int. Ed.* **53**, 10525–10530 (2014).
24. Wang, C. et al. Water-mediated Mars-van Krevelen mechanism for CO oxidation on ceria-supported single-atom Pt₁ catalyst. *ACS Catal.* **7**, 887–891 (2017).
25. Tang, Y., Wang, Y.-G. & Li, J. Theoretical investigations of Pt₁@CeO₂ single-atom catalyst for CO oxidation. *J. Phys. Chem. C* **121**, 11281–11289 (2017).
26. Su, Y.-Q. et al. Theoretical approach to predict the stability of supported single-atom catalysts. *ACS Catal.* **9**, 3289–3297 (2019).
27. Jiang, D. et al. Tailoring the local environment of platinum in single-atom Pt₁/CeO₂ catalysts for robust low-temperature CO oxidation. *Angew. Chem. Int. Ed.* **60**, 26054–26062 (2021).
28. Wan, W. et al. Highly stable and reactive platinum single atoms on oxygen plasma-functionalized CeO₂ surfaces: Nanostructuring and peroxo effects. *Angew. Chem. Int. Ed.* **61**, e202112640 (2022).
29. Lee, J., Ryou, Y., Chan, X., Kim, T. J. & Kim, D. H. How Pt interacts with CeO₂ under the reducing and oxidizing environments at elevated temperature: The origin of improved thermal stability of Pt/CeO₂ compared to CeO₂. *J. Phys. Chem. C* **120**, 25870–25879 (2016).
30. Pereira-Hernández, X. I. et al. Tuning Pt–CeO₂ interactions by high-temperature vapor-phase synthesis for improved reducibility of lattice oxygen. *Nat. Commun.* **10**, 1358 (2019).
31. Chen, J. et al. Surface engineering protocol to obtain an atomically dispersed Pt/CeO₂ catalyst with high activity and stability for CO oxidation. *ACS Sustain. Chem. Eng.* **6**, 14054–14062 (2018).
32. Gänzler, A. M. et al. Unravelling the different reaction pathways for low temperature CO oxidation on Pt/CeO₂ and Pt/Al₂O₃ by spatially resolved structure-activity correlations. *J. Phys. Chem. Lett.* **10**, 7698–7705 (2019).
33. Freund, H.-J., Meijer, G., Scheffler, M., Schlögl, R. & Wolf, M. CO oxidation as a prototypical reaction for heterogeneous processes. *Angew. Chem. Int. Ed.* **50**, 10064–10094 (2011).
34. Qiao, B. et al. Single-atom catalysis of CO oxidation using Pt₁/FeO_x. *Nat. Chem.* **3**, 634–641 (2011).
35. Ke, J. et al. Strong local coordination structure effects on sub-nanometer PtO_x clusters over CeO₂ nanowires probed by low-temperature CO oxidation. *ACS Catal.* **5**, 5164–5173 (2015).
36. Lu, Y., Thompson, C., Kunwar, D., Datye, A. K. & Karim, A. M. Origin of the high CO oxidation activity on CeO₂ supported Pt nanoparticles: Weaker binding of CO or facile oxygen transfer from the support? *Chem. Cat. Chem.* **12**, 1726–1733 (2020).
37. Wei, D.-Y. et al. In situ Raman observation of oxygen activation and reaction at platinum-ceria interfaces during CO oxidation. *J. Am. Chem. Soc.* **143**, 15635–15643 (2021).
38. Gänzler, A. M. et al. Tuning the Pt/CeO₂ interface by in situ variation of the Pt particle size. *ACS Catal.* **8**, 4800–4811 (2018).
39. Gao, Y., Wang, W., Chang, S. & Huang, W. Morphology effect of CeO₂ support in the preparation, metal-support interaction, and catalytic performance of Pt/CeO₂ catalysts. *Chem. Cat. Chem.* **5**, 3610–3620 (2013).
40. Tan, W. et al. Transformation of highly stable Pt single sites on defect engineered ceria into robust Pt clusters for vehicle emission control. *Environ. Sci. Technol.* **55**, 12607–12618 (2021).
41. Tan, W. et al. Tuning single-atom Pt₁-CeO₂ catalyst for efficient CO and C₃H₆ oxidation: Size effect of ceria on Pt structural evolution. *ChemNanoMat* **6**, 1797–1805 (2020).
42. Zhu, C. et al. Crystal-plane effects of CeO₂{110} and CeO₂{100} on photocatalytic CO₂ reduction: Synergistic interactions of oxygen defects and hydroxyl groups. *ACS Sustain. Chem. Eng.* **8**, 14397–14406 (2020).
43. Bugrova, T. A. et al. Insights into formation of Pt species in Pt/CeO₂ catalysts: Effect of treatment conditions and metal-support interaction. *Catal. Today* **375**, 36–47 (2021).
44. Yaghoubi, H. et al. Toward a visible light-driven photocatalyst: The effect of midgap-states-induced energy gap of undoped TiO₂ nanoparticles. *ACS Catal.* **5**, 327–335 (2015).

45. Hu, Y., Song, X., Jiang, S. & Wei, C. Enhanced photocatalytic activity of Pt-doped TiO₂ for NO_x oxidation both under UV and visible light irradiation: A synergistic effect of lattice Pt⁴⁺ and surface PtO. *Chem. Eng. J.* **274**, 102–112 (2015).
46. Wu, Z., Li, M., Mullins, D. R. & Overbury, S. H. Probing the surface sites of CeO₂ nanocrystals with well-defined surface planes via methanol adsorption and desorption. *ACS Catal.* **2**, 2224–2234 (2012).
47. Masui, T. et al. Characterization of Cerium(IV) oxide ultrafine particles prepared using reversed micelles. *Chem. Mater.* **9**, 2197–2204 (1997).
48. Pastor-Pérez, L., Ramos-Fernández, E. V. & Sepúlveda-Escribano, A. Effect of the CeO₂ synthesis method on the behaviour of Pt/CeO₂ catalysis for the water-gas shift reaction. *Int. J. Hydrog. Energy* **44**, 21837–21846 (2019).
49. Parvulescu, V. I. & Tiseanu, C. Local structure in CeO₂ and CeO₂-ZrO₂ nanoparticles probed by Eu luminescence. *Catal. Today* **253**, 33–39 (2015).
50. Ma, R., Jahurul Islam, M., Amaranatha Reddy, D. & Kim, T. K. Transformation of CeO₂ into a mixed phase CeO₂/Ce₂O₃ nanohybrid by liquid phase pulsed laser ablation for enhanced photocatalytic activity through Z-scheme pattern. *Ceram. Int.* **42**, 18495–18502 (2016).
51. D'Angelo, A. M., Webster, N. A. S. & Chaffee, A. L. Vacancy generation and oxygen uptake in Cu-doped Pr-CeO₂ materials using neutron and in situ X-ray diffraction. *Inorg. Chem.* **55**, 12595–12602 (2016).
52. Mukri, B. D., Waghmare, U. V. & Hegde, M. S. Platinum ion-doped TiO₂: High catalytic activity of Pt²⁺ with oxide ion vacancy in Ti^{4+1-x}Pt^{2+x}O_{2-x} compared to Pt⁴⁺ without oxide ion vacancy in Ti^{4+1-x}Pt^{4+x}O₂. *Chem. Mater.* **25**, 3822–3833 (2013).
53. Wang, F. et al. Resolving the puzzle of single-atom silver dispersion on nanosized γ -Al₂O₃ surface for high catalytic performance. *Nat. Commun.* **11**, 529 (2020).
54. Pignet, T. & Schmidt, L. D. Kinetics of NH₃ oxidation on Pt, Rh, and Pd. *J. Catal.* **40**, 212–225 (1975).
55. Liu, F., Shan, W., Lian, Z., Liu, J. & He, H. The smart surface modification of Fe₂O₃ by WO_x for significantly promoting the selective catalytic reduction of NO_x with NH₃. *Appl. Catal., B* **230**, 165–176 (2018).
56. Wang, F. et al. Nanosize effect of Al₂O₃ in Ag/Al₂O₃ catalyst for the selective catalytic oxidation of ammonia. *ACS Catal.* **8**, 2670–2682 (2018).
57. Tan, W. et al. Gas phase sulfation of ceria-zirconia solid solutions for generating highly efficient and SO₂ resistant NH₃-SCR catalysts for NO removal. *J. Hazard. Mater.* **388**, 121729 (2020).
58. Wang, F. et al. Insights into the activation effect of H₂ pretreatment on Ag/Al₂O₃ catalyst for the selective oxidation of ammonia. *ACS Catal.* **9**, 1437–1445 (2019).
59. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**, 15–50 (1996).
60. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953–17979 (1994).
61. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758–1775 (1999).
62. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
63. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **132**, 154104–154122 (2010).
64. Plata, J. J., Márquez, A. M. & Sanz, J. F. Communication: Improving the density functional Theory+*U* description of CeO₂ by including the contribution of the O 2p electrons. *J. Chem. Phys.* **136**, 041101 (2012).
65. Reuter, K. & Scheffler, M. Composition and structure of the RuO₂(110) surface in an O₂ and CO environment: Implications for the catalytic formation of CO₂. *Phys. Rev. B* **68**, 045407 (2003).
66. Chase, M. W. et al. *NIST-JANAF Thermochemical Tables* (Standard Reference Data Program National Institute of Standards and Technology, 1985).
67. Togo, A. & Tanaka, I. First principles phonon calculations in materials science. *Scr. Mater.* **108**, 1–5 (2015).
68. Henkelman, G. & Jonsson, H. Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *J. Chem. Phys.* **113**, 9978–9985 (2000).
69. Henkelman, G., Uberuaga, B. P. & Jonsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.* **113**, 9901–9904 (2000).

Acknowledgements

This work was supported by the National Science Foundation grant (CHE-1955343) received by F.L., T.R., and S.H., and Startup Fund (F.L.) from the University of Central Florida (UCF). S.X. thanks the support from the Preeminent Postdoctoral Program (P3) at UCF. This research used beamline 7-BM (QAS) of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704. DFT calculations were performed using the computing resources at the Advanced Research Computing Center at the University of Central Florida and the Extreme Science and Engineering Discovery Environment (XSEDE).

Author contributions

F.L. conceived the idea, directed the project, and mentored the manuscript writing and revision. W.T. designed the experiments, analyzed the data, and wrote the manuscript. S.X. performed the experiments and analyzed the data. D.L., D.A., S.H., and T.R. were responsible for the DFT calculations. W.D. performed the in situ XRD. M.W. and K.L. carried out the AC-HAADF-STEM characterization and data analysis. F.G. and L.D. provided experimental resource. L.M. and S.E. conducted XAS measurements. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41467-022-34797-2>.

Correspondence and requests for materials should be addressed to Fudong Liu.

Peer review information *Nature Communications* thanks Rong Chen and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

Reprints and permissions information is available at <http://www.nature.com/reprints>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2022