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Enhancing the Carbon Monoxide Oxidation Performance through Surface Defect Enrichment of Ceria-Based Supports for Platinum Catalyst

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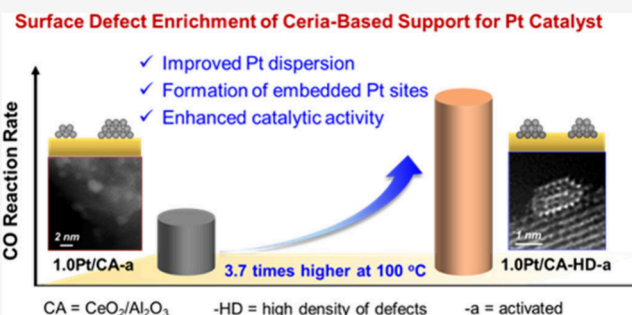
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ABSTRACT: Effective synthesis and application of single-atom catalysts on supports lacking enough defects remain a significant challenge in environmental catalysis. Herein, we present a universal defect-enrichment strategy to increase the surface defects of CeO₂-based supports through H₂ reduction pretreatment. The Pt catalysts supported by defective CeO₂-based supports, including CeO₂, CeZrO_x, and CeO₂/Al₂O₃ (CA), exhibit much higher Pt dispersion and CO oxidation activity upon reduction activation compared to their counterpart catalysts without defect enrichment. Specifically, Pt is present as embedded single atoms on the CA support with enriched surface defects (CA-HD) based on which the highly active catalyst showing embedded Pt clusters (Pt_C) with the bottom layer of Pt atoms substituting the Ce cations in the CeO₂ surface lattice can be obtained through reduction activation. Embedded Pt_C can better facilitate CO adsorption and promote O₂ activation at Pt_C-CeO₂ interfaces, thereby contributing to the superior low-temperature CO oxidation activity of the Pt/CA-HD catalyst after activation.

KEYWORDS: surface defect enrichment, Pt single-atom catalyst, embedded Pt cluster, CO adsorption, O₂ activation



1. INTRODUCTION

Nowadays, supported metal single-atom catalysts (SACs) have garnered significant attention as a result of their 100% metal utilization efficiency and great benefits in various catalytic reactions, including organic catalysis, photocatalysis, electrocatalysis, and thermal catalysis.^{1–6} In environmental catalysis, such as the catalytic oxidation of CO,⁷ one of the critical reactions in purifying vehicle emissions, SACs usually exhibit low intrinsic activity. This is primarily attributed to the lack of synergistic effects from neighboring metal atoms,^{8,9} making their direct application highly challenging. In addition to the tuning of local structures of metal sites in SACs,^{10–14} reduction activation has been proven to be a facile and effective approach to activate less active SACs into more efficient oxidation catalysts,^{8,15} with SACs serving as catalyst precursors. Interestingly, the activated catalysts derived from SACs typically show significantly higher catalytic performance compared to those prepared directly using conventional methods, such as for CO and hydrocarbon oxidation reactions.^{15–17} Surface defects of metal oxide supports have been shown to be crucial for anchoring metal atoms,^{15,18,19} but the limited concentration of surface defects on regular metal oxides makes them difficult to afford high loading of metal

single atoms. Therefore, the development of a universal approach to increase the surface defects of metal oxide supports is highly desired for the preparation of SACs with a high metal loading and superior catalytic activity.

Precious metal catalysts are widely used in automotive exhaust control as a result of their excellent performance.^{20,21} However, the high usage amount of precious metals and poor low-temperature performance after long-term operation remain the major challenges in practical applications.²¹ In comparison to more expensive Pd and Rh catalysts nowadays, Pt catalysts have recently attracted huge interest, owing to their favorable cost-effectiveness and superior catalytic performance. In particular, Pt/CeO₂-based catalysts have been extensively investigated and show high potential in vehicle exhaust treatment systems.^{10,22} To further improve their catalytic activity and thermal stability, the preparation of CeO₂ supports

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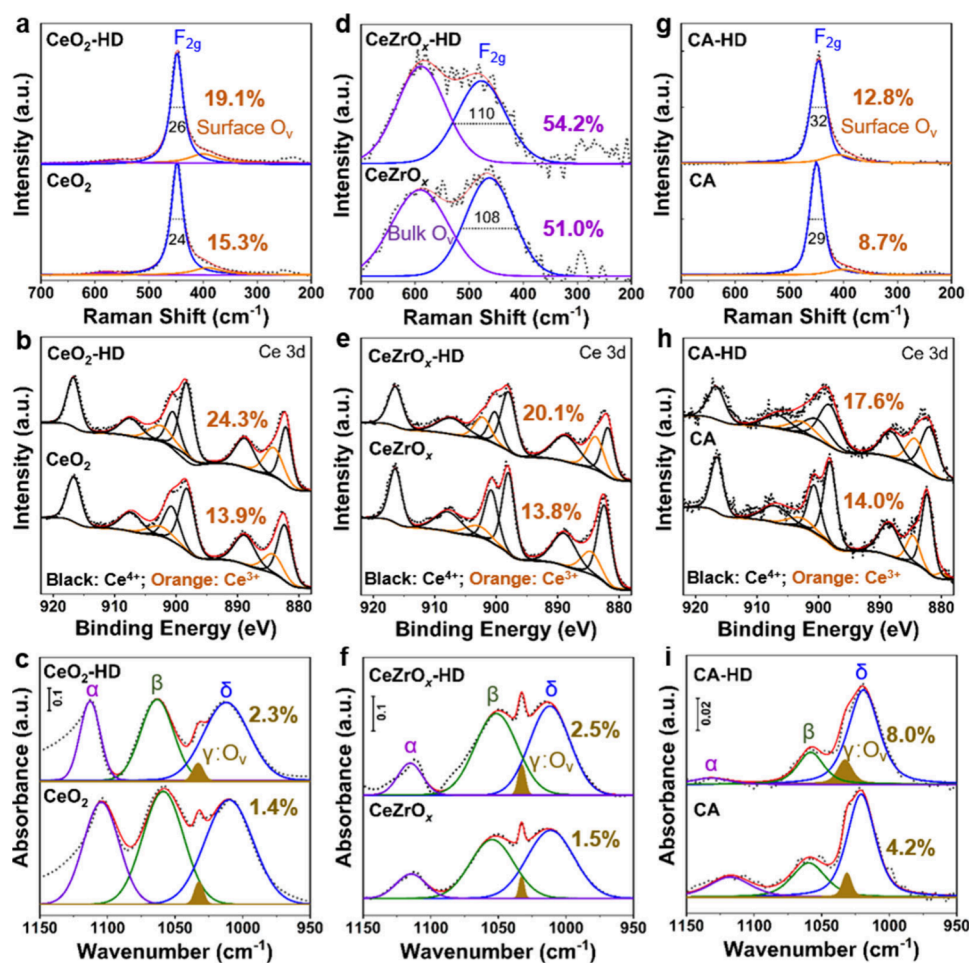


Figure 1. Characterizations of surface defects: (a, d, and g) Raman spectra, (b, e, and h) Ce 3d XPS, and (c, f, and i) *in situ* DRIFTS of methanol adsorption at 25 °C on (a–c) CeO₂, (d–f) CeZrO_x, and (g–i) CA with and without H₂ reduction. The O_v/(O_{latt} + O_v) ratios, Ce³⁺/(Ce³⁺ + Ce⁴⁺) ratios, and surface O_v concentrations are inserted in related figures.

with abundant surface defects as Pt anchoring sites can be a promising approach.¹⁹ Traditional methods for increasing the surface defects of CeO₂ involve the usage of dopants as structure modifiers or the controllable preparation of CeO₂ with specific exposed crystal planes.^{23–25} However, these methods usually require expensive raw materials (e.g., La, Y, Pr, Nd, Sm, etc.) or complex preparation procedures (such as hydrothermal synthesis and precipitation method),^{26–29} limiting their wide applications.

Reducible metal oxides, which have lattice oxygen that can be easily removed by reduction treatment using reductive gases, such as H₂, at specific temperatures, show great potential for enriching the surface defects and serving as effective supports for SACs with increased metal loading. In this study, we demonstrate a general H₂ reduction strategy for enriching the surface defects of CeO₂-based oxide supports, including pure CeO₂, CeZrO_x, and CeO₂/Al₂O₃ (CA). It has been demonstrated that the Pt catalysts on the defect-enriched CeO₂-based supports exhibit much higher Pt dispersion and CO oxidation activity upon reduction activation compared to their counterparts without surface defect enrichment. For example, when 1 wt % Pt catalysts on CA supports are taken as examples, the Pt microstructures within the catalysts before and after reduction activation are systematically investigated using multiple techniques, including *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS),

scanning transmission electron microscopy (STEM), extended X-ray absorption fine structure (EXAFS), etc. Along with kinetics and *in situ* X-ray absorption spectroscopy (XAS) studies, the structure–activity relationship for CO oxidation on these Pt/CA catalysts has been clearly revealed. On the defect-enriched CA support (CA-HD, where -HD is the high density of defects), a unique Pt cluster (Pt_C) site can be fabricated, where the bottom layer of Pt atoms embedded in the CeO₂ surface matrix. Such a unique Pt_C site originated from the reduction activation of Pt single atoms (Pt₁) on CA-HD, which can effectively facilitate the CO adsorption and O₂ activation at Pt_C–CeO₂ interfaces, resulting in superior activity in low-temperature CO oxidation.

2. MATERIALS AND METHODS

2.1. Catalyst Preparation. 2.1.1. Preparation of Ceria-Based Supports with/without Defect Enrichment.

Commercial CeO₂ [Brunauer–Emmett–Teller (BET) surface area of 120 m²/g, Solvay], commercial CeZrO_x (40 wt % CeO₂, Solvay), and CeO₂/Al₂O₃ (30 wt % CeO₂) supports were used in this work for defect enrichment and subsequent Pt loading. The CeO₂/Al₂O₃ support was prepared using a conventional incipient wetness impregnation (IWI) method. Typically, a solution of Ce(NO₃)₃·6H₂O (99.5%, Acros Organics) with a predetermined concentration was added dropwise onto γ-Al₂O₃ (BET surface area of 150 m²/g, Sasol) under stirring.

The CeO₂/Al₂O₃ support was obtained by subsequent calcination in air at 550 °C for 2 h. To enrich surface defects on CeO₂, CeZrO_x, and CeO₂/Al₂O₃ supports, the supports were reduced in 10% H₂/Ar flow at 750 °C for 2 h with a temperature ramping rate of 5 °C/min. These supports with defect enrichment are denoted as CeO₂-HD, CeZrO_x-HD, and CA-HD, respectively. For direct comparison, regular CeO₂, CeZrO_x, and CeO₂/Al₂O₃ (denoted as CA) were further calcined in air at 750 °C for 2 h with the temperature ramping rate of 5 °C/min.

2.1.2. Preparation of Pt Catalysts. The catalysts with 1 wt % of Pt loading on CeO₂, CeO₂-HD, CeZrO_x, and CeZrO_x-HD supports were prepared using the IWI method and tetraammineplatinum nitrate (TAPN) as the precursor. The TAPN solution with a predetermined concentration was added dropwise onto the supports under stirring and then dried at 120 °C for 1 h. After calcination in air at 550 °C for 2 h with a temperature ramping rate of 5 °C/min, the catalysts were obtained and denoted as Pt/CeO₂, Pt/CeO₂-HD, Pt/CeZrO_x, and Pt/CeZrO_x-HD, respectively. The catalysts with *x* wt % of Pt loadings (*x* = 0.5, 1.0, and 5.0) on CA, CA-HD, and pristine γ -Al₂O₃ supports were prepared using IWI method as well with TAPN as the precursor. The obtained catalysts with different Pt loadings were denoted as *x*Pt/CA, *x*Pt/CA-HD, and *x*Pt/Al₂O₃, respectively. To study the effects of reduction activation on CO oxidation activity, all catalysts were reduced in 10% H₂ flow at 400 °C for 1 h with the temperature ramping rate of 10 °C/min and labeled with “-a” (where -a is activated).

2.2. Catalyst Characterizations. The detailed descriptions of catalyst characterizations by X-ray diffraction (XRD), Raman spectroscopy, STEM, *in situ* DRIFTS, X-ray photoelectron spectroscopy (XPS), XAS, H₂ temperature-programmed reduction (H₂-TPR), and dynamic oxygen storage capacity (OSC) techniques can be found in the [Supporting Information](#)

2.3. Catalytic Performance Evaluation. The CO oxidation reaction was conducted in a flow-through fixed bed quartz tubular reactor (inner diameter = 4 mm) system. In each test, 25 mg of catalyst (40–60 mesh) was diluted with inert SiC powder (0.25 g) to prevent temperature gradients. The steady-state CO oxidation activity was measured with a duration time of 30 min at each temperature point. The feeding stream consisted of 1% CO and 1% O₂ balanced with Ar. The total flow rate was fixed at 83.33 mL/min, achieving a weight hourly space velocity (WHSV) of 200 000 mL·g⁻¹·h⁻¹. A catalytic stability test of 1.0Pt/CA-a and 1.0Pt/CA-HD-a catalysts was performed at 100 °C with or without 5% H₂O in the feedstock at a WHSV of 300 000 mL·g⁻¹·h⁻¹. The reactants and products were analyzed online by mass spectrometry (MS, HPR-20 R&D, Hidden Analytical) using the *m/z* ratios of 28, 32, and 44 used for monitoring CO, O₂, and CO₂, respectively. To avoid significant heat or mass transfer limitation, the kinetic study was performed with CO conversion below 16% under a WHSV of 500 000 mL·g⁻¹·h⁻¹.

3. RESULTS AND DISCUSSION

3.1. Effects of Reduction on Enriching the Surface Defects of CeO₂-Based Supports. The formation of additional defects on CeO₂-based supports as a result of H₂ reduction was clearly evidenced by Raman spectra, Ce 3d XPS, and *in situ* DRIFTS of methanol adsorption (at 25 °C). When pure CeO₂ was taken as an example, as shown in [Figure 1a](#), two characteristic peaks located at 448 and 400 cm⁻¹ were

observed in Raman spectra, which can be assigned to the typical vibration mode (F_{2g}) of the fluorite-type CeO₂ structure and the near-surface oxygen vacancies (O_v),^{30,31} respectively. In comparison to CeO₂, reduced CeO₂-HD exhibited a much higher O_v/(O_{latt} + O_v) ratio (19.1% for CeO₂-HD versus 15.3% for CeO₂, where O_{latt} is lattice oxygen) and a broader half-width of the F_{2g} peak (26 cm⁻¹ for CeO₂-HD versus 24 cm⁻¹ for CeO₂), suggesting a significant increase in the density of defects (mainly O_v) and a decrease in the crystallinity of CeO₂-HD.³¹ The increase in defect density was further confirmed by Ce 3d XPS and *in situ* DRIFTS of the methanol adsorption results. As depicted in [Figure 1b](#), both surface Ce³⁺ and Ce⁴⁺ species were observed on CeO₂ and CeO₂-HD supports.^{12,32} Notably, CeO₂-HD exhibited a significantly higher concentration of surface Ce³⁺ species (24.3%) compared to CeO₂ (13.9%). Upon methanol adsorption, four types of methoxy species were identified on both CeO₂ and CeO₂-HD ([Figure 1c](#)), including linearly adsorbed methoxy species (peak α), bridgingly adsorbed methoxy species on Ce⁴⁺ cations without O_v (peak β) and with O_v (peak γ) in the neighborhood, and three-coordinated methoxy species (peak δ),³³ respectively. It was clearly observed that more methoxy species adsorbed on Ce⁴⁺ cations with O_v nearby were present on CeO₂-HD than on CeO₂ (2.3% for CeO₂-HD versus 1.4% for CeO₂). Such an effect of H₂ reduction on enriching the surface defects was also observed on CeZrO_x and CA supports. As shown in panels d–i of [Figure 1](#), after H₂ reduction, the half-widths of the F_{2g} peak and the O_v/(O_{latt} + O_v) ratios observed in Raman spectra, the Ce³⁺/(Ce³⁺ + Ce⁴⁺) ratios determined by Ce 3d XPS, and the surface O_v concentrations measured by methanol adsorption on CeZrO_x-HD and CA-HD supports were broader or much higher than those on their counterparts without defect enrichment (CeZrO_x and CA), respectively. It should be noticed that, different from O_v observed on CeO₂ and CA supports (panels a and g of [Figure 1](#)), the bulk O_v defects (589 cm⁻¹) nearby Ce³⁺ species were obviously observed on CeZrO_x supports ([Figure 1d](#)), which was mainly due to the formation of CeZrO_x solid solution.³⁰ These results unambiguously indicate that H₂ reduction is a universally effective method to enhance the surface defects on CeO₂-based supports, thereby enabling their application as highly efficient supports for enhancing metal dispersion upon loading.

3.2. Impact of Defect Enrichment on CO Oxidation Activity. To determine if the supports with enriched defects were beneficial for obtaining highly active metal catalysts, the Pt catalysts supported on CeO₂, CeZrO_x, and CA with and without defect enrichment were prepared and tested for CO oxidation. As depicted in panels a–d of [Figure S1](#) of the Supporting Information, upon Pt loading, a much brighter color of Pt/CeO₂-HD than that of Pt/CeO₂ was observed, suggesting a higher Pt dispersion achieved on CeO₂-HD than on regular CeO₂. As shown in [Figure S1e](#) of the Supporting Information, the as-prepared Pt/CeO₂ catalyst showed higher CO oxidation activity than the Pt/CeO₂-HD catalyst, with a lower T50 (the temperature corresponding to 50% of CO conversion) achieved on the former (188 °C) than on the latter (266 °C). It has been reported that the reduction activation is highly crucial for Pt-CeO₂-based catalysts to achieve excellent catalytic activity for CO oxidation, because it can help generate more active Pt_C species on CeO₂.¹⁶ After H₂ reduction activation in 10% H₂/Ar at 400 °C for 1 h, the light-off curves for CO oxidation on Pt/CeO₂-a and Pt/CeO₂-HD-a

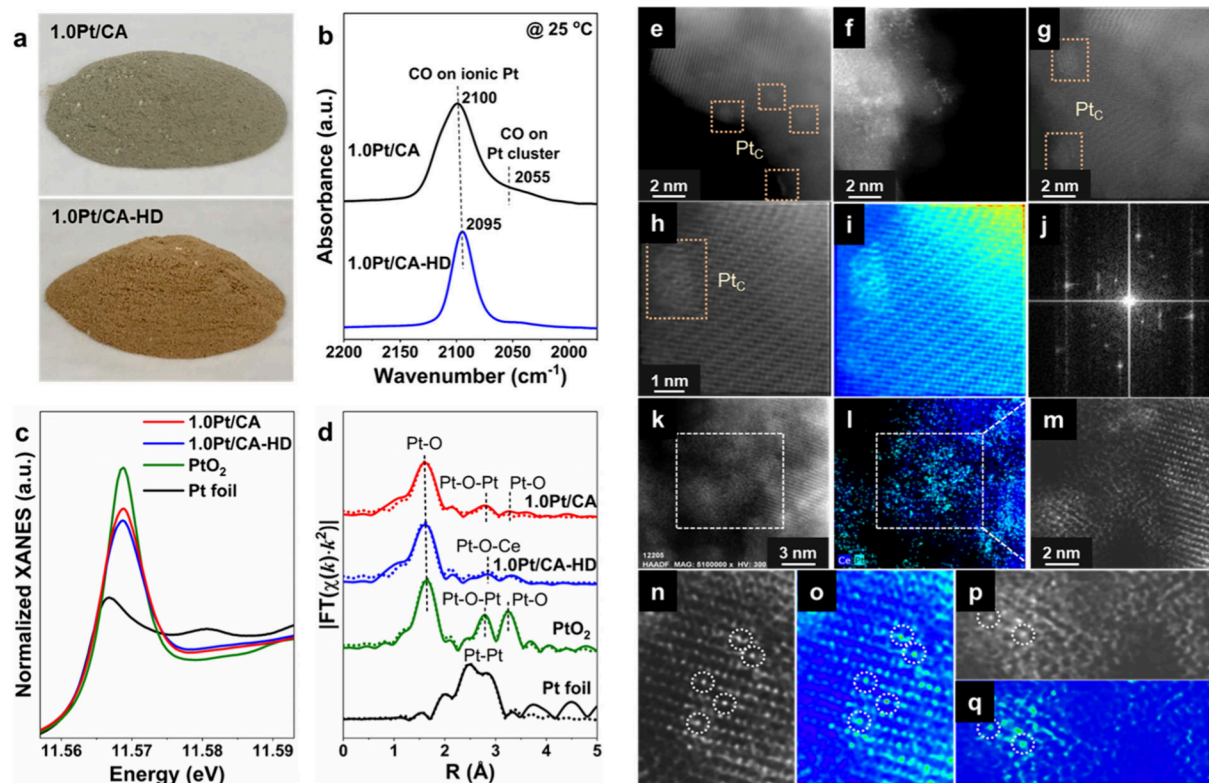


Figure 2. Structure characterizations: (a) photos, (b) *in situ* DRIFTS of CO adsorption, (c) Pt L₃-edge XANES, (d) Pt L₃-edge EXAFS, and (e–q) AC-STEM images for (e–j) 1.0Pt/CA and (k–q) 1.0Pt/CA-HD catalysts.

catalysts (where -a is activated) significantly shifted to a lower temperature range, with a much lower T50 achieved on Pt/CeO₂-HD-a (85 °C) than on Pt/CeO₂-a (108 °C). These results clearly show that the defect enrichment of the pure CeO₂ support greatly improved the dispersion of loaded Pt species and significantly enhanced the CO oxidation performance upon reduction activation. Similarly, the activated Pt catalysts on defect-enriched CeZrO_x-HD also showed higher CO oxidation activity than that on CeZrO_x (Figure S2 of the Supporting Information). Such results demonstrate that the defect enrichment strategy for CeO₂-based supports by H₂ reduction is universal for improving the low-temperature CO oxidation activity of supported Pt catalysts after activation and is worthy of systematic investigation, especially for the widely used CA support in industry. Accordingly, the CO oxidation activity of *x*Pt/CA, *x*Pt/CA-HD, and *x*Pt/Al₂O₃ (*x* = 0.5, 1.0, and 5.0 wt %) before and after H₂ reduction activation was investigated (Figure S3 of the Supporting Information). Not surprisingly, the as-prepared *x*Pt/CA catalysts always showed higher CO oxidation activity than *x*Pt/CA-HD and *x*Pt/Al₂O₃ at the same level of Pt loading, mainly as a result of the presence of more active Pt_c species on CeO₂ within *x*Pt/CA catalysts, as confirmed in the subsequent sections. Upon activation, significant enhancement of CO oxidation activity was observed on both *x*Pt/CA-a and *x*Pt/CA-HD-a catalysts in comparison to the less pronounced or no activity promotion on *x*Pt/Al₂O₃. Interestingly, the defect-enriched *x*Pt/CA-HD-a catalysts constantly performed much higher CO oxidation activity than *x*Pt/CA-a and *x*Pt/Al₂O₃-a at the same Pt loading level. Even with the Pt loading as high as 5.0 wt %, the benefit of the support defect enrichment for improving the CO oxidation performance still obviously existed.

3.3. Impact of Defect Enrichment on the Pt Local Structures. The dispersion of precious metals is inherently linked to the density of surface defects on the supports. It was expected that CA-HD with a higher concentration of surface defects could be able to anchor more Pt₁ than CA. To understand the Pt structures in detail, *in situ* DRIFTS of CO adsorption, X-ray absorption near edge structure (XANES), EXAFS, and aberration corrected scanning transmission electron microscopy (AC-STEM) measurements were conducted for 1.0Pt/CA and 1.0Pt/CA-HD. Similar to the observations for Pt/CeO₂-HD and Pt/CeZrO_x-HD catalysts, which showed brighter color than Pt/CeO₂ and Pt/CeZrO_x counterpart catalysts, respectively, as a result of higher Pt dispersion benefiting from defect enrichment, the 1.0Pt/CA-HD catalyst also displayed brighter golden color compared to 1.0Pt/CA, which showed a gray greenish color (Figure 2a). *In situ* DRIFTS of CO adsorption (Figure 2b) clearly revealed that only Pt₁ (with CO@Pt₁ at 2095 cm⁻¹) was present on 1.0Pt/CA-HD, while both Pt₁ sites (with CO@Pt₁ at 2100 cm⁻¹) and Pt_c sites (with CO@Pt_c at 2055 cm⁻¹) were present on 1.0Pt/CA.^{8,34} The Pt L₃-edge XANES results showed that the Pt species within 1.0Pt/CA and 1.0Pt/CA-HD were both in oxidized states (Figure 2c), which were between Pt⁰ and Pt⁴⁺ but closer to Pt⁴⁺ based on the white line intensity. As evidenced by the XANES linear combination fitting results (Figure S4 and Table S1 of the Supporting Information), a lower average oxidation state of Pt species was present on 1.0Pt/CA-HD (+2.8) compared to 1.0Pt/CA (+3.1), which was mainly due to the presence of more interaction between Pt⁴⁺ + 2Ce³⁺ → Pt²⁺ + 2Ce⁴⁺ on 1.0Pt/CA-HD.¹⁴ The EXAFS results in R space (Figure 2d) showed the presence of the Pt–O bond (first shell) and Pt–O–Pt and Pt–O bonds (second

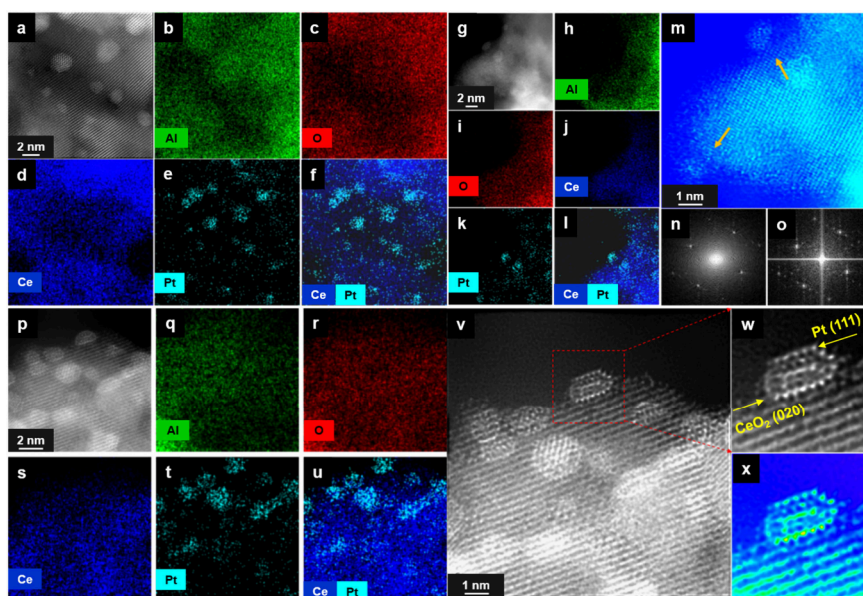


Figure 3. AC-STEM and EDS mapping images for (a–o) 1.0Pt/CA-a and (p–x) 1.0Pt/CA-HD-a catalysts.

shell) in 1.0Pt/CA. In contrast, only Pt–O bonds (first shell) and Pt–O–Ce bonds (second shell) were observed on 1.0Pt/CA-HD. This is notable because the Pt–O–Pt bond appears slightly shorter compared to Pt–O–Ce bonds in phase-uncorrected EXAFS,^{35,36} although the length of the latter also depends upon the local structure of Pt on CeO₂. These results suggest the presence of Pt_C species within 1.0Pt/CA and exclusive Pt₁ species within 1.0Pt/CA-HD. The EXAFS curve-fitting results (Table S2 of the Supporting Information) confirmed that the Pt species in 1.0Pt/CA-HD showed a slightly lower coordination number (CN) of Pt–O (4.6) than that in 1.0Pt/CA (4.8), which was in accordance with the Pt oxidation state sequence within the two catalysts. Such Pt L₃-edge XANES and EXAFS results overall suggested that a much stronger interaction between Pt and CeO₂ was present in 1.0Pt/CA-HD than in regular 1.0Pt/CA.

Figure S5 of the Supporting Information shows the energy-dispersive X-ray spectroscopy (EDS) mapping images for the 1.0Pt/CA and 1.0Pt/CA-HD catalysts. A highly consistent distribution of Pt and Ce was observed on both catalysts, suggesting that CeO₂ was beneficial for anchoring the Pt species rather than Al₂O₃. This finding was further supported by the AC-STEM images (panels e–q of Figure 2), which clearly showed both Pt₁ (Figure 2f) and Pt_C (panels g–i of Figure 2) on CeO₂ within 1.0Pt/CA, whereas only Pt₁ (panels n–q of Figure 2) was observed on CeO₂ within 1.0Pt/CA-HD, with Pt₁ substituting Ce sites in the CeO₂ lattice matrix. As expected, the defect enrichment strategy via pre-reduction resulted in a significant benefit in enhancing the dispersion of Pt on CeO₂-based supports. Afterward, the H₂-TPR technique was used to evaluate the reducibility of 1.0Pt/CA and 1.0Pt/CA-HD catalysts with totally distinct Pt species and local structures. As depicted in Figure S6 of the Supporting Information, for both catalysts, three H₂ consumption peaks attributed to the reduction of surface-adsorbed oxygen species (O_{ads}) (85 or 100 °C), Pt–O species (130 or 141 °C), and Pt–O–Ce species (200 or 205 °C) could be observed. In comparison to 1.0Pt/CA, higher reduction temperatures and a larger total H₂ consumption amount were observed for 1.0Pt/CA-HD (268 μmol/g for 1.0Pt/CA-HD versus 123 μmol/g for

1.0Pt/CA below 300 °C), suggesting the much stronger interaction between Pt and CeO₂ in the 1.0Pt/CA-HD catalyst as a result of the presence of more Pt–O–Ce linkages, as evidenced by the EXAFS results.

The Pt structures in the reduction-activated catalysts, including 1.0Pt/CA-a and 1.0Pt/CA-HD-a, were also systematically characterized using *in situ* DRIFTS, XAS, and AC-STEM techniques. As shown in Figure S7a of the Supporting Information, upon H₂ reduction activation and CO adsorption, similar and broad infrared (IR) bands consisting of several subpeaks showed up on both 1.0Pt/CA-a and 1.0Pt/CA-HD-a catalysts. The IR peaks at 2087, 2069, and 2045 cm⁻¹ were attributed to the CO linearly adsorbed on terrace sites, step sites, and corner sites (under-coordinated Pt) of formed Pt_C, respectively.^{16,37,38} The similar CO adsorption behavior observed on 1.0Pt/CA-a and 1.0Pt/CA-HD-a probably suggested a comparable Pt_C average size within both catalysts.³⁹ As observed from Pt L₃-edge XANES results (Figures S7b and S4 and Table S1 of the Supporting Information), the reduction activation resulted in a significant decline in the oxidation states of Pt species within 1.0Pt/CA-a (1.5) and 1.0Pt/CA-HD-a (1.7), with the latter catalyst showing a slightly higher Pt oxidation state. This decline was mainly due to the formation of Pt–PtO_x clusters with mixed oxidation states between Pt metal and Pt oxide, as verified by the Pt L₃-edge EXAFS results (Figure S7c and Table S2 of the Supporting Information). These results clearly showed the presence of Pt–Pt bonds (2.63–2.69 Å) from the Pt metallic phase and Pt–O bonds (2.00 Å) from the PtO_x phase within 1.0Pt/CA-a and 1.0Pt/CA-HD-a. The varied Pt–Pt bonds suggest distinct Pt structures within the catalysts. In addition, the higher CN of the Pt–O bond (3.5 versus 2.5) and lower CN of the Pt–Pt bond (2.2 versus 4.3) in 1.0Pt/CA-HD-a compared to that in 1.0Pt/CA-a well elucidated the higher average oxidation state of Pt observed on 1.0Pt/CA-HD-a (1.7 versus 1.5). These phenomena could be attributed to either the formation of smaller Pt–PtO_x clusters or the presence of a stronger interaction between Pt species and CeO₂ within 1.0Pt/CA-HD-a compared to 1.0Pt/CA-a. Further clarification can be obtained by the following AC-STEM analysis.

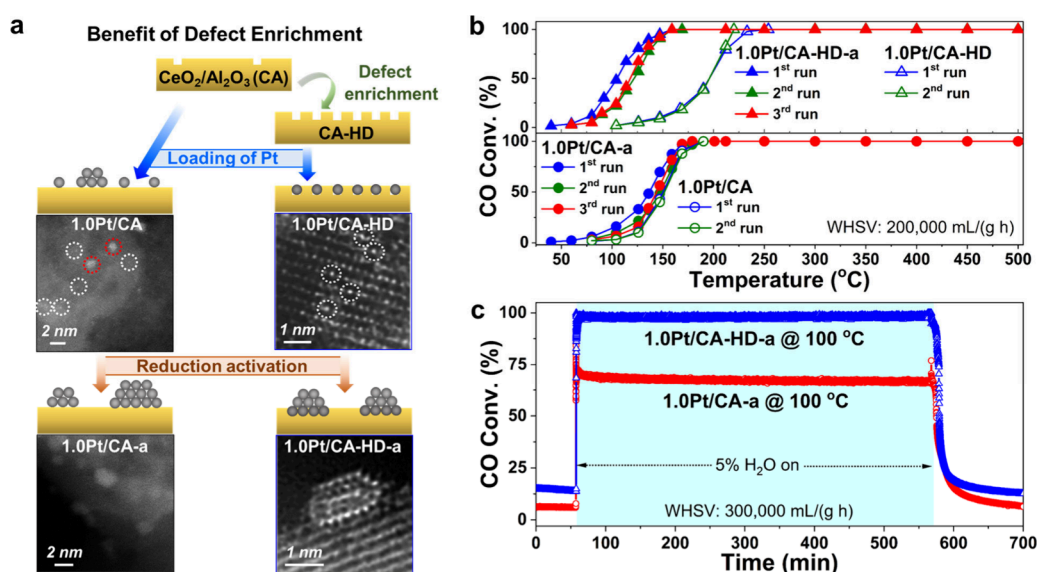


Figure 4. Effect of defect enrichment on CO oxidation activity: (a) scheme for the benefit of defect enrichment and AC-STEM images of 1.0Pt/CA, 1.0Pt/CA-HD, 1.0Pt/CA-a, and 1.0Pt/CA-HD-a catalysts and CO oxidation activity on 1.0Pt/CA-a and 1.0Pt/CA-HD-a catalysts (b) during the cycling test (from 40 to 500 °C) and (c) with H₂O in the feedstock. Reaction conditions: steady-state testing, $[\text{CO}] = [\text{O}_2] = 1\%$, 5% H₂O (when used), and balanced with Ar, at WHSV of 200 000 or 300 000 mL·g_{cat}⁻¹·h⁻¹.

Figure S8 of the Supporting Information shows the EDS mapping images for 1.0Pt/CA-a and 1.0Pt/CA-HD-a. It was observed that there were no apparent changes on the morphology of the catalysts after reduction activation, and the Pt distribution was still closely associated with Ce distribution. Consistent with the observation from *in situ* DRIFTS of CO adsorption and EXAFS results, in AC-STEM images (Figure 3 and Figure S9 of the Supporting Information), Pt_C was present on both catalysts with similar size distributions but totally different interactions with CeO₂. Specifically, on 1.0Pt/CA-a, Pt_C species with an average size of ca. 1.8 nm were observed, primarily in the adsorbed state on the CeO₂ surface without crystal plane matching between Pt_C and CeO₂ (panels a–o of Figure 3 and Figures S9a and S10a of the Supporting Information). In clear contrast, on 1.0Pt/CA-HD-a, Pt_C species with an average size of ca. 1.7 nm and the crystal plane matching between Pt_C (111) and CeO₂ (020) were clearly observed (panels p–x of Figure 3 and Figures S9b and S10b of the Supporting Information), with the bottom layer of Pt atoms embedded in the CeO₂ surface matrix. Such a unique Pt_C structure embedded in the CeO₂ surface matrix, which originated from the reduction activation of Pt₁ species on CA-HD with an enhanced Pt–CeO₂ interaction, could be responsible for the superior CO oxidation activity of the 1.0Pt/CA-HD-a catalyst. In our previous study, we concluded that the CeO₂ surface-embedded Pt single-layer structure could more effectively activate the oxygen species at the Pt–CeO₂ interface than the CeO₂ surface-adsorbed Pt single-layer structure,⁴⁰ and this phenomenon should also be applicable to the case of multilayer Pt_C in this study, which can be verified in the following characterization sections.

As summarized in Figure 4a, the surface defects of the CA support could be significantly increased by H₂ reduction treatment, leading to the exclusive formation of Pt₁ species on the Pt/CA-HD catalyst with Pt₁ embedded in the CeO₂ surface matrix substituting the Ce site, in clear contrast to the mixture state of Pt₁ and Pt_C species on regular Pt/CA without defect enrichment. Reduction activation was con-

firmed to be an effective way to transform the less active Pt₁ species into more active Pt_C species on both catalysts. The unique Pt_C structures with the bottom layer of Pt atoms embedded in the CeO₂ surface matrix could be formed after the reduction activation of Pt/CA-HD, while only randomly adsorbed Pt_C structures could be formed on activated Pt/CA. Considering that the 1.0Pt/CA-HD-a catalyst showed much higher activity and a similar Pt cluster size compared to 1.0Pt/CA-a, it can be concluded that the bottom-layer-embedded Pt_C structures in the CeO₂ lattice matrix were more active for the CO oxidation reaction than the adsorbed Pt_C structures on the CeO₂ surface.

3.4. Catalytic Stability. The catalytic stability of the 1.0Pt/CA and 1.0Pt/CA-HD catalysts before and after reduction activation was measured at temperatures up to 500 °C for CO oxidation (Figure 4b). It was observed that there was no apparent change in the CO oxidation activity for both 1.0Pt/CA and 1.0Pt/CA-HD catalysts during the cycling test, suggesting that the Pt sites in these two as-prepared catalysts were stable under the reaction conditions. On 1.0Pt/CA-a and 1.0Pt/CA-HD-a catalysts, the CO oxidation activity only slightly declined after the first run and then remained stable during the following test cycles. Notably, the 1.0Pt/CA-HD-a catalyst consistently showed much higher CO oxidation activity than the 1.0Pt/CA-a catalyst, with the stabilized T₅₀ at 118 °C on 1.0Pt/CA-HD-a compared to that at 145 °C on 1.0Pt/CA-a. With the presence of H₂O in the reaction flow, significant improvement of CO oxidation activity was observed on both 1.0Pt/CA-a and 1.0Pt/CA-HD-a catalysts (Figure 4c and Figure S11 of the Supporting Information), which was in line with the observation that H₂O has a positive effect on CO oxidation over Pt–CeO₂ based catalysts.^{8,41,42} It is noteworthy that the 1.0Pt/CA-HD-a catalyst always outperformed the 1.0Pt/CA-a catalyst under the wet reaction conditions, at either the fixed reaction temperature (Figure 4c) or the varied reaction temperatures (Figure S11 of the Supporting Information). These results confirmed that the Pt/CA catalysts were catalytically stable and exhibited excellent H₂O tolerance,

with the 1.0Pt/CA-HD-a catalyst performing the best. The CO oxidation rate and turnover frequency (TOF) on 1.0Pt/CA-HD-a were further calculated and compared to other Pt-CeO₂-based catalysts reported in the literature. As listed in Table S3 of the Supporting Information, at 125 °C, the reaction rate (418 mmol·g_{Pt}⁻¹·s⁻¹) and TOF (0.601 s⁻¹) on 1.0Pt/CA-HD-a surpassed those on most Pt-CeO₂-based catalysts, showing high potential for practical applications.

3.5. Crystal Structure and Surface Elemental Composition. As shown in Figure S12 of the Supporting Information, all 1.0Pt/CA and 1.0Pt/CA-HD catalysts exhibited similar crystal structures, containing a mixture of γ -Al₂O₃ and cubic fluorite CeO₂, before and after reduction activation. No Pt species was detected in these catalysts, which should be due to the low Pt loading and relatively high Pt dispersion. The crystallite sizes of CeO₂ were calculated using the Scherrer equation and were found to be smaller in the 1.0Pt/CA-HD (9.5 nm) and 1.0Pt/CA-HD-a (6.7 nm) catalysts compared to those in the 1.0Pt/CA (10.3 nm) and 1.0Pt/CA-a (7.6 nm) catalysts, respectively, as inserted in Figure S12 of the Supporting Information. In addition, it is interesting to see that the reduction activation led to a significant decrease of the CeO₂ crystallite size in 1.0Pt/CA-a and 1.0Pt/CA-HD-a catalysts compared to their unreduced 1.0Pt/CA and 1.0Pt/CA-HD precursor catalysts, respectively, possibly as a result of the disruption of the long-range order of CeO₂ and the formation of rich Ce³⁺ species in the activation process. The Ce 3d XPS results, as depicted in Figure S13 of the Supporting Information, revealed the presence of both surface Ce³⁺ and Ce⁴⁺ species in all of the 1.0Pt/CA and 1.0Pt/CA-HD catalysts before and after activation. As expected, the 1.0Pt/CA-a and 1.0Pt/CA-HD-a catalysts indeed exhibited much higher concentrations of surface Ce³⁺ species (Figure S13 and Table S1 of the Supporting Information) compared to those of their precursor catalysts before activation. Previous work reported that the formation of richer Ce³⁺ species was usually associated with the generation of more oxygen defects on the CeO₂ surface, which was beneficial for O₂ activation.³⁰ The slightly higher concentration of surface Ce³⁺ species observed on 1.0Pt/CA-HD-a than on 1.0Pt/CA-a could have contributed to the higher CO oxidation activity achieved on 1.0Pt/CA-HD-a.

3.6. Structure–Activity Relationship for CO Oxidation. The reaction orders for CO and O₂ in CO oxidation were determined on all catalysts before and after activation, and the results are shown in panels a and b of Figure 5. For CO oxidation on 1.0Pt/CA, 1.0Pt/CA-a, 1.0Pt/CA-HD, and 1.0Pt/CA-HD-a, the CO reaction orders were determined as 0.20, 0.20, 1.49, and 0.11, respectively, while the O₂ reaction orders were determined as 0.30, 0.31, 0.56, and 0.19, respectively. The high CO reaction order on the 1.0Pt/CA-HD catalyst could be explained by the difficult CO adsorption on embedded Pt₁ sites without oxygen vacancies nearby, as already evidenced in our previous work.⁴⁰ On other catalysts with Pt_C sites, CO could be easily adsorbed and involved in CO oxidation, resulting in low CO reaction orders (≤ 0.20). The lowest CO reaction order achieved on the 1.0Pt/CA-HD-a catalyst suggests that the embedded Pt_C sites were more beneficial for CO adsorption than adsorbed Pt_C and Pt₁ sites. The O₂ reaction orders showed a sequence similar to that of the CO reaction orders on all catalysts, decreasing in the sequence of 1.0Pt/CA-HD (0.56) > 1.0Pt/CA-a (0.31) \approx 1.0Pt/CA (0.30) > 1.0Pt/CA-HD-a (0.19). On 1.0Pt/CA-HD-

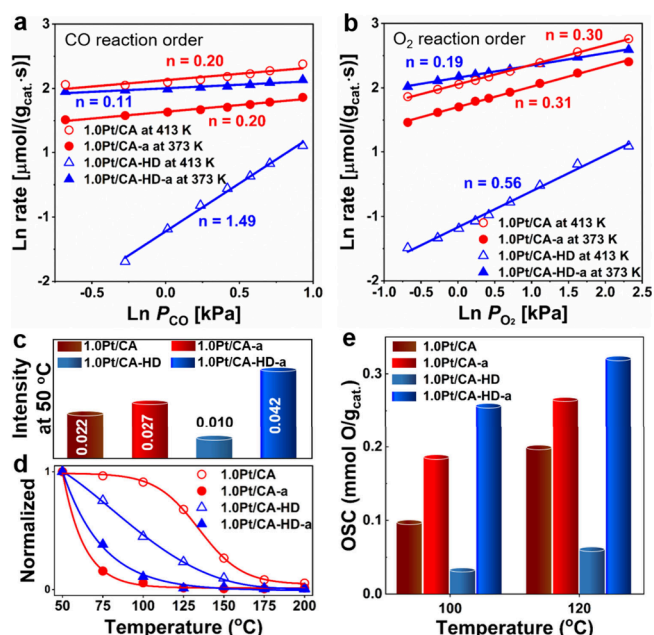


Figure 5. Kinetic study results: (a) CO reaction orders and (b) O₂ reaction orders in CO oxidation, (c) intensity for CO adsorption detected by DRIFTS at 50 °C and (d) normalized intensity for CO adsorption at different temperatures, and (e) OSC of 1.0Pt/CA, 1.0Pt/CA-a, 1.0Pt/CA-HD, and 1.0Pt/CA-HD-a catalysts at 100 and 120 °C. The kinetic study experiments were conducted under the CO conversions below 16% and the WHSV of 500 000 mL·g_{cat}⁻¹·h⁻¹. The intensity for CO adsorption was referring to the main CO adsorption peak detected by *in situ* DRIFTS experiments, and the normalized intensity for CO adsorption at different temperatures was determined by dividing the corresponding CO adsorption intensity at 50 °C.

a, the lowest O₂ order for CO oxidation could be achieved, suggesting that the embedded Pt_C sites favored the O₂ adsorption/activation compared to the adsorbed Pt_C and Pt₁ sites. In summary, the embedded Pt_C sites could better facilitate both CO adsorption and O₂ adsorption/activation, contributing to the superior CO oxidation activity of the 1.0Pt/CA-HD-a catalyst. It should be noted that the similar CO and O₂ reaction orders obtained on 1.0Pt/CA-a and 1.0Pt/CA were due to the presence of adsorbed Pt_C sites in both catalysts, and the higher CO oxidation activity achieved on 1.0Pt/CA-a was mainly due to its higher density of Pt_C sites.

To further investigate the CO adsorption capability of different Pt structures, *in situ* DRIFTS experiments of CO adsorption (at 25 °C)–desorption (from 50 to 200 °C) were conducted on all catalysts before and after reduction activation (panels c and d of Figure 5 and Figure S14 of the Supporting Information). At 50 °C, the CO adsorption intensity on all catalysts (Figure 5c) increased in the following order: 1.0Pt/CA-HD (0.010) < 1.0Pt/CA (0.022) < 1.0Pt/CA-a (0.027) < 1.0Pt/CA-HD-a (0.042). This trend was in accordance with the kinetic study results (CO reaction order), confirming again that the 1.0Pt/CA-HD-a catalyst with embedded Pt_C sites showed higher CO adsorption capacity, while the CO adsorption on the 1.0Pt/CA-HD catalyst with embedded Pt₁ sites was rather difficult. Furthermore, the higher CO adsorption capacity on the 1.0Pt/CA-a catalyst than 1.0Pt/CA was mainly attributed to the presence of more adsorbed Pt_C sites in the former catalyst. As shown in Figure S14 of the Supporting Information, the CO adsorption intensity on all

catalysts decreased monotonically with the increased temperature. The normalized CO adsorption intensities (on the basis of the corresponding reference CO intensity at 50 °C) as a function of the desorption temperature are shown in Figure Sd, to reveal the CO desorption rates on different catalysts. It can be clearly seen that the decline degree of CO adsorption intensity followed the order of 1.0Pt/CA-a > 1.0Pt/CA-HD-a > 1.0Pt/CA-HD > 1.0Pt/CA. In combination with the CO oxidation activity, these results suggest that the amount of Pt sites for CO adsorption was more critical than the strength of CO–Pt bonding for the CO oxidation on different catalysts. To further investigate the O₂ activation and oxygen mobility within all catalysts, the dynamic OSC was determined by CO/O₂ pulse cycling experiments for 1.0Pt/CA and 1.0Pt/CA-HD catalysts before and after activation (Figure 5e). It can be observed that the OSC values for all catalysts followed the sequence of 1.0Pt/CA-HD < 1.0Pt/CA < 1.0Pt/CA-a < 1.0Pt/CA-HD-a at different temperatures. Consistent with the kinetic study results (O₂ reaction order), the 1.0Pt/CA-HD-a catalyst with embedded Pt_C sites indeed exhibited superior O₂ activation ability. To better reveal the relationship between the CO adsorption capacity, OSC function, and CO oxidation activity on these catalysts, the plots of the CO adsorption intensity and OSC values versus T50 for the CO oxidation light-off are presented in Figure 6. It was evident that the CO

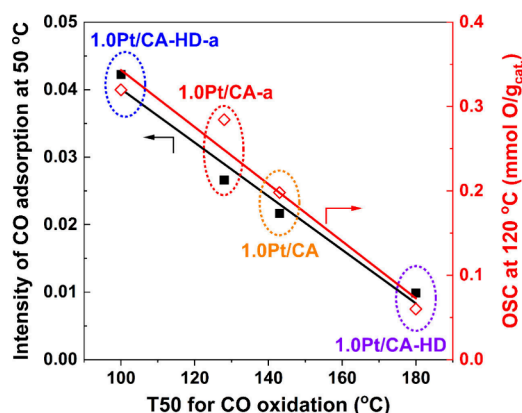


Figure 6. Correlation between the T50 for the CO oxidation reaction and the intensity of CO adsorption at 50 °C as well as the OSC values measured at 120 °C on all Pt/CA catalysts.

oxidation activity on Pt-CeO₂-Al₂O₃ serial catalysts was strongly correlated to the Pt sites with distinct CO adsorption capacity and an O₂ activation ability. The 1.0Pt/CA-HD-a catalyst with embedded Pt_C sites showed significantly enhanced CO adsorption and promoted O₂ activation, thus contributing to its superior CO oxidation activity at low temperatures.

To clarify the role of Pt active sites in CO oxidation, *in situ* XANES analysis of the Pt L₃-edge in 1.0Pt/CA-a and 1.0Pt/CA-HD-a catalysts was conducted under different testing conditions. As shown in Figure 7 and Figure S15 of the Supporting Information, a consistent trend in the changes of white line intensities of Pt L₃-edge XANES and, accordingly, the average Pt oxidation states was observed on both catalysts from experimental steps 1–4. In the reaction flow (CO + O₂), with the temperature increasing from 25 to 100 °C, both catalysts exhibited a decline in the Pt oxidation state, indicating the partial reduction of PtO_x clusters by CO during the reaction. Upon the change from a CO + O₂ flow to a CO flow at 100 °C, a further decrease in the Pt oxidation state occurred as a result of a further reduction of PtO_x clusters. Interestingly, when the reaction flow was switched back to the reaction flow (CO + O₂) at 100 °C, there was no substantial change in the Pt oxidation state on both catalysts. These results suggest that the partially reduced Pt species remained stable and showed high resistance to reoxidation by O₂, underscoring the crucial role of partially reduced Pt species in the CO adsorption and activation, while the O₂ activation should not take place on the Pt surface (but at the Pt_C–CeO₂ interface). In comparison of the Pt oxidation state in 1.0Pt/CA-HD-a to that in 1.0Pt/CA-a under different testing conditions, a consistently higher Pt oxidation state was observed in the former catalyst. These results suggest that the stronger interaction between Pt_C and CeO₂ in the 1.0Pt/CA-HD-a catalyst remained constantly stable under different conditions and could effectively facilitate the oxygen mobility at the Pt_C–CeO₂ interface. Therefore, the 1.0Pt/CA-HD-a catalyst showed both significantly enhanced CO adsorption and promoted O₂ activation, on which the abundant CO species adsorbed on embedded Pt_C sites could readily react with facily mobile O from CeO₂ at the interfaces, thus exhibiting excellent low-temperature CO oxidation performance.

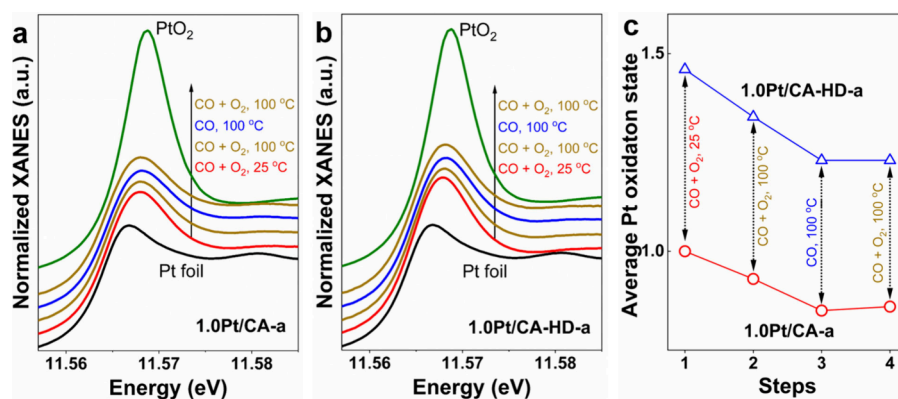


Figure 7. *In situ* XANES of Pt L₃-edge in (a) 1.0Pt/CA-a and (b) 1.0Pt/CA-HD-a catalysts and their corresponding (c) average Pt oxidation states under different testing conditions. The average Pt oxidation states were determined by the linear combination fitting of Pt L₃-edge XANES using Pt foil and PtO₂ as references.

4. ENVIRONMENTAL IMPLICATION

CO gas emitted from diverse sources, including vehicle exhaust and industrial activities, poses significant risks to both the environment and human health. There is a continuous demand for the development of highly efficient catalysts to mitigate CO emissions at low temperatures. Precious metal catalysts, such as Pt-CeO₂, have shown great promise, although further improvement in the low-temperature activity is still needed. In this work, a universal defect enrichment strategy involving reduction pretreatment was developed for CeO₂-based supports, including CeO₂, CeZrO_x, and CeO₂/Al₂O₃ (CA). On these defect-enriched supports, Pt catalysts showed improved Pt dispersion and enhanced low-temperature CO oxidation activity upon reduction activation. Specifically, using the CeO₂/Al₂O₃ support with enriched surface defects (CA-HD), embedded Pt clusters (Pt_C) with the bottom layer of Pt atoms substituting the Ce cations were generated within the 1.0Pt/CA-HD-a catalyst after reduction activation (where -a is activated). These embedded Pt_C sites exhibited superior catalytic activity in CO oxidation in comparison to the adsorbed Pt_C sites on CeO₂ within the 1.0Pt/CA-a catalyst, although they were showing similar cluster sizes. In-depth characterizations and mechanism studies suggested that the uniquely embedded Pt_C sites had a stronger interaction with CeO₂, which not only benefited the CO adsorption on Pt_C sites but also improved the O₂ activation and interfacial oxygen mobility on CeO₂. Collectively, the significantly enhanced low-temperature CO oxidation at the interfaces between Pt_C and CeO₂ could be achieved on the 1.0Pt/CA-HD-a catalyst. This work offers valuable insights into the support defect enrichment and the synthesis of metal catalysts with improved metal dispersion and superior catalytic performance for environmental catalysis applications.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.4c03078>.

Catalyst characterization, curve fitting results of Pt L₃-edge EXAFS, surface atomic concentrations and Pt average oxidation states, CO oxidation activity on 1.0Pt/CeO₂-HD, 1.0Pt/CeZrO_x-HD, and *x*Pt/CA-HD catalysts, linear combination fitting results of Pt L₃-edge XANES, AC-STEM and EDS mapping images, H₂-TPR profiles, XRD patterns, XPS results, and *in situ* DRIFTS study (PDF)

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The authors declare no competing financial interest.

▲Maria Flytzani-Stephanopoulos passed away on October 28, 2019.

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