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High-temperature stable hydroxyls tuning the local environment of Pt single atoms for boosting formaldehyde oxidation†

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The relationship between the structure and performance of metal single-atom catalysts remains elusive because it is a challenge to tailor the local environments of single atoms (SAs) while keeping the atomic dispersion. Here, two Pt/CeO₂ catalysts with different Pt coordination environments were prepared at high temperatures, via both atom trapping (Pt₁/CeO₂-AT) and thermal shock (Pt₁/CeO₂-TS), respectively. The Pt SAs in the Pt₁/CeO₂-TS catalyst with an unsymmetrical structure surrounded by stable surface hydroxyls exhibit excellent HCHO oxidation activity. Pt SAs are primarily found at Ce substitution sites in the Pt₁/CeO₂-TS catalyst, which has a Pt₁O₃ configuration with hydroxyls and more active surface lattice oxygen than the Pt₁/CeO₂-AT catalyst. Due to their different coordination and redox properties, Pt₁/CeO₂-TS and Pt₁/CeO₂-AT show different performances in HCHO oxidation (*T*₁₀₀ of HCHO shifts from 60 to 200 °C), confirming that the catalytic performance of Pt SACs can be tailored by optimizing the local environment via high-temperature stable hydroxyls.

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1. Introduction

Environmental catalysis has been attracting much attention because of the emission of pollutants such as aromatics and hydrocarbons. Noble metal catalysts have played a vital role in reducing these environmental pollutants, but their widespread use has been curbed due to their prohibitive cost. Given that each noble metal atom can serve as an active site in catalysis, metal single-atom catalysts (SACs) provide the opportunity for using noble metals with less capital investment. Recently, some metal SACs have been reported to exhibit high reactivity in pollutant mitigation such as the oxidation of volatile organic compounds.^{1–3}

Much progress has been made in the preparation of metal SACs, such as the approaches of coprecipitation, atomic layer deposition (ALD),⁴ atom trapping⁵ and vapor-phase self-assembly.⁶ However, when compared to nano-cluster/particle catalysts, SACs are not always active in catalytic reactions because of the unfavorable coordination structure of metal single atoms. Fine-tuning the oxidation states or local environments of SACs has the potential to significantly improve their performance in catalysis.^{7–12} In CO oxidation, several strategies have been employed to generate metal single atoms with improved catalytic performance. For example, steam-treatment of a Pt₁/CeO₂ catalyst enabled the generation of hydroxyl groups adjacent to Pt single atoms, leading to a dramatic activity increase in CO oxidation due to the generation of surface active lattice oxygen.¹³ The use of a highly defective CeO₂-Al₂O₃ support can tune the oxidation state of Pt₁ and enhance catalytic activity in CO, CH₄, and NO oxidation.¹² Recently, Li *et al.* grafted isolated and defective CeO_x nanoglue islands onto SiO₂, hosting one Pt atom on average. This catalyst exhibits significantly increased activity for CO oxidation.¹⁴ Furthermore, using a simple calcination temperature-control strategy, Tan *et al.* fabricated CeO₂ supported Pt₁ with precisely controlled coordination environments, and its activity trend in CO oxidation and NH₃ oxidation is reversed due to the different property in reactant activation and H₂O desorption.⁸ In addition, O₂ plasma leads to the formation of surface peroxo

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(O₂²⁻) structures that facilitate the formation of strongly bonded Pt²⁺ atoms, rendering them active and resistant to sintering in the CO oxidation reaction.¹⁵ These Pt₁/CeO₂ catalysts were prepared at low temperatures, involving the effect of various kinds of surface functionals such as hydroxyls.¹⁶ The presence of various hydroxyls therefore masked the identification of the structure–performance relationship when investigating the effect of local coordination environments of metal single atoms in catalysis. In addition, the distance between a single metal atom and a hydroxyl group is crucial in determining the formation of active intermediates, which in turn impacts the catalytic performance in catalysis. For example, Wu *et al.* recently discovered that the closeness between the OH group and a single Rh atom on a plane surface significantly influences the catalytic activity of the Rh₁/CeO₂ single-atom catalyst system in CO oxidation.¹⁷

In this work, we focus on the high-temperature preparation of Pt₁/CeO₂ single-atom catalysts to avoid the effect of different kinds of hydroxyl groups because high temperature treatment can remove the weakly adsorbed hydroxyls, only leaving the strongly bonded hydroxyls behind. We employed two high-temperature approaches, *i.e.*, atom trapping (AT) and thermal shock (TS), to prepare Pt₁/CeO₂ catalysts. The Pt/CeO₂ SAC prepared by atom trapping (Pt₁/CeO₂-AT) is achieved by ramping the temperature to 800 °C in air and keeping at that temperature for 10 h, and the Pt/CeO₂ SAC prepared by thermal shock (Pt₁/CeO₂-TS) is achieved by thermally shocking the sample to ~1000 °C for ~0.5 s and repeating the process multiple times. The catalytic performances of the Pt₁/CeO₂ catalysts were then investigated in formaldehyde oxidation and the function of the local environment of the Pt single atoms was studied.

2. Experimental section

2.1 Material preparation

Cerium(III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, ≥99.99%) was purchased from Alfa Aesar. Chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, Pt ≥ 37.5%) was purchased from Sinopharm Chemical Reagent Limited Corporation. Briefly, 1 g of chloroplatinic acid hexahydrate powder was dissolved in 10 mL of deionized water to prepare a chloroplatinic acid solution. Ce(NO₃)₃·6H₂O was calcined in air at 350 °C for 2 h to obtain CeO₂, which was used as the support to prepare Pt₁/CeO₂ catalysts. All the reagents were used as received.

The Pt₁/CeO₂-AT single-atom catalyst was prepared *via* atom trapping (AT).¹³ A 1.0 wt% Pt/CeO₂ catalyst was synthesized by the incipient wetness impregnation method. An appropriate amount of chloroplatinic acid solution was added dropwise to CeO₂ while being kept grinding in a mortar and pestle. Then, the obtained mixture was dried at 80 °C for 12 h in static air and calcined in a muffle furnace at 800 °C for 6 h at a temperature increase rate of 10 °C min⁻¹. The resulting catalyst powder was denoted as Pt₁/CeO₂-AT.

The Pt₁/CeO₂-TS single-atom catalyst was prepared *via* thermal-shock (TS).¹¹ The TS synthesis features a high temperature, but very short heating duration operated in an inert atmosphere. Specifically, a thin layer of the dried Pt/CeO₂ precursor powder was uniformly spread out into a graphite plate and rapidly heated to a high temperature and then quenched through a carbon heater using Joule heating equipment (Hefei *in situ* Technology Co., Ltd. China). The temperature was monitored to be around 1000 °C for ~0.5 s. The pulse power was about 300 Å × 40 V. This thermal shock process was repeated 6 times, and before each heating, the Pt/CeO₂ precursor powder was mixed to ensure uniform heating and single atom formation. The resulting catalyst was denoted as Pt₁/CeO₂-TS.

2.2 Catalytic activity measurements

The HCHO oxidation reaction was carried out in a fixed-bed quartz flow reactor (i.d. = 7.0 mm) under atmospheric pressure. Briefly, 80 mg catalyst (40–60 mesh) was mixed with 120 mg quartz sand. After placing in the quartz tube reactor, the feed gas composition of 400 ppm HCHO/20% O₂/N₂ was introduced and the total flow rate was kept at 50 mL min⁻¹. Water vapor was generated by introducing liquid water into a vaporizer using a Cole Parmer 74900 syringe pump and carried into the reactor by N₂. To investigate the moisture effect, relative humidity (20%) was achieved by adjusting the injection speed of the pump. The products in the effluent gas were analyzed using an online gas chromatograph (GC2060, Shanghai Ruimin GC Instruments Inc.), which was described in previous work.¹⁸

2.3 Characterization

Details of the characterization of the catalysts are described in the ESI.†

3. Results and discussion

3.1 Microstructure characterization of materials

Atom trapping (AT) and thermal shock (TS) methods were used to prepare Pt₁/CeO₂-AT and Pt₁/CeO₂-TS catalysts with a Pt loading of 1.0 wt%. The powder X-ray diffraction (XRD) patterns of the two catalysts (Fig. S1†) only show the diffraction peaks of ceria (JCPDS No.34-0394), without the diffraction peaks of metallic Pt or PtO₂. X-ray photoelectron spectroscopy (XPS) in the Pt 4f region revealed that Pt remained as the ionic form of Pt²⁺ (72.4 eV and 75.8 eV) over both catalysts (Fig. S2†) without the existence of Pt⁰ and Pt⁴⁺ species.^{19,20} High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images revealed the presence of Pt single atoms dispersed on the CeO₂ support in the Pt₁/CeO₂-AT and Pt₁/CeO₂-TS (Fig. 1A and B and Fig. S3†) catalysts, without the presence of Pt clusters or nanoparticles, confirming the high dispersion of Pt single atoms (SAs). This suggests that the atomic



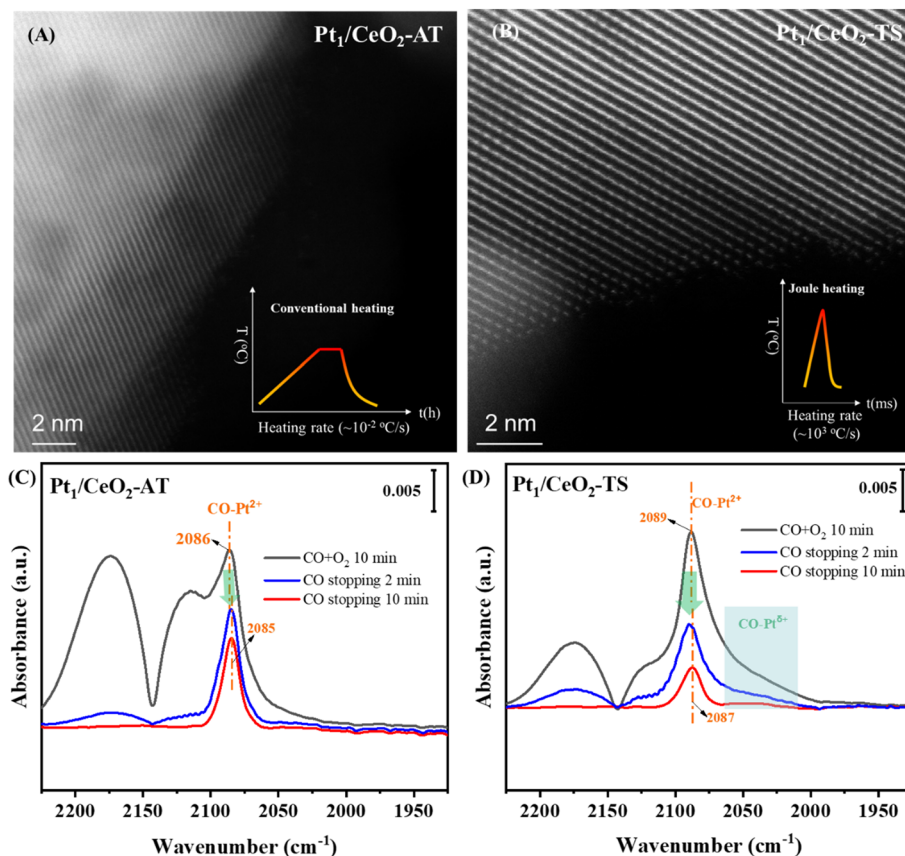


Fig. 1 Representative AC-STEM images of the obtained Pt₁/CeO₂-AT (A) and Pt₁/CeO₂-TS (B) catalysts, and the CO-DRIFT spectra of the Pt₁/CeO₂-AT (C) and Pt₁/CeO₂-TS (D) catalysts at 120 °C (CO-DRIFT experiments were performed by the following steps. Step 1: CO/O₂/He was first introduced into the cell for 10 min; step 2: the CO flow was stopped while O₂/He was kept flowing for 10 min).

dispersion of Pt²⁺ was present on both Pt₁/CeO₂-AT and Pt₁/CeO₂-TS catalysts.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) using CO as a probe molecule (CO-DRIFTS) was used to figure out the local environment of the two Pt₁/CeO₂ SACs. Fig. 1C and D reveal that the two catalysts present isolated Pt species, as confirmed by the CO bands at 2086 and 2089 cm⁻¹, which is consistent with the XPS and HAADF-STEM results. The spectra do not show the lower-wavenumber features (<2000 cm⁻¹) assigned to the bridge or three-fold adsorbed CO on Pt clusters or nanoparticles,^{21,22} further indicating the atomic dispersion of the Pt species on the two Pt₁/CeO₂ catalysts. The different peaks between 2000 and 2090 cm⁻¹ of the two catalysts indicate the different local environments (e.g., location or coordination structure) of Pt single atoms. Pt₁/CeO₂-TS shows a more intense CO-Pt²⁺ (~2089 cm⁻¹) peak and a broader CO-Pt^{δ+} (~2052 cm⁻¹) peak, suggesting the wide distribution of local environments of Pt²⁺ with an unsaturated coordination configuration,^{8,22} which is also evidenced by density functional theory (DFT) simulation below. The simulations in Fig. S4† showed that as the Pt-O coordination number decreased on the Pt₁/CeO₂ (111) model, the vibrational frequency decreased from 2123.7 to 2028.2 cm⁻¹. This corroborates that the Pt atoms on Pt₁/

CeO₂-TS are likely coordinated with less adjacent heteroatoms. Along with the peak at ~2086 cm⁻¹ assigned to CO on Pt²⁺ species with a square-planar PtO₄ configuration, there is no obvious peak at 2052 cm⁻¹ for Pt₁/CeO₂-AT, implying that Pt₁/CeO₂-AT contains very few less-coordinated Pt single atoms, which agrees well with the previous result.^{11,22}

The local coordination environment and the oxidation state of Pt single atoms were further investigated by X-ray absorption spectroscopy (XAS) at the Pt L₃-edge.^{23,24} Fig. 2A shows the XANES spectra of the reference Pt foil and Pt₁/CeO₂ catalysts. The spectral analysis of Pt₁/CeO₂-TS closely resembles that of Pt₁/CeO₂-AT, which has been previously confirmed to consist of isolated platinum species carrying a +2 state.^{11,15,22} Because of the absence of Pt-Pt scattering in the EXAFS spectrum (Fig. 2C), the Pt species on Pt₁/CeO₂-TS is therefore the isolated Pt²⁺ cation, which is also confirmed by XPS (Fig. S2†). It is noted that Pt₁/CeO₂-TS shows a slightly lower white line intensity as compared to Pt₁/CeO₂-AT (Fig. 2B), indicating that the ionic Pt²⁺ on the former is a less saturated coordination.¹³ Furthermore, in the XANES absorption edge of Pt₁/CeO₂-TS, a rising-edge feature was observed, demonstrated by a bump in the first-order derivative curve (Fig. 2B). Such a rising edge is due to the



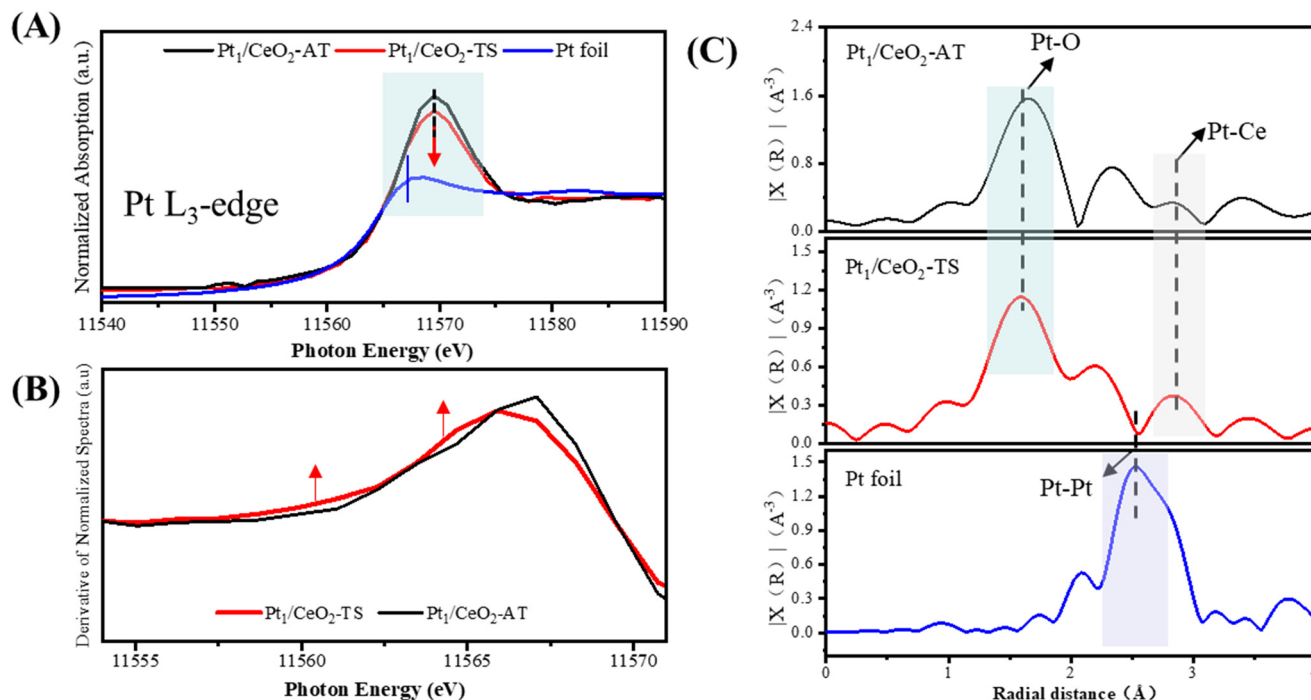


Fig. 2 The XAS analysis of the Pt samples demonstrating the different coordination environments of Pt single atoms over the Pt₁/CeO₂ SACs. (A) Normalized XANES spectra, (B) the first derivative of the normalized XANES spectra in (A) and (C) EXAFS magnitude of the Fourier transformed k^2 -weighted $\chi(k)$ data for Pt₁/CeO₂-AT (black) and Pt₁/CeO₂-TS (red) at the Pt-L₃ edge. The reference Pt foil (blue) was used for XANES analysis.

decreased local coordination symmetry of the Pt.²⁵ This confirms that the TS technique produces the Pt₁/CeO₂-TS catalyst having isolated Pt²⁺ species with an unsaturated coordination configuration, which were analyzed by fitting the EXAFS spectra (Fig. S5 and Table S2†). The Pt₁/CeO₂-AT catalyst presents a square-planar Pt₁O₄ configuration with four equivalent Pt–O bonds, as revealed in previous work.^{26,27} However, Pt₁/CeO₂-TS has a relatively low Pt–O coordination number (CN) of approximately 3.6 (Table S2†), indicating a defective Pt₁O_x ($x < 4$) configuration. It is known that the

square-planar PtO₄ has high thermal stability, whereas the low-coordinated Pt₁O_x in the air-exposed state is less stable. The improved stability of Pt₁O_x is therefore proposed to be related to the hydroxyl existing on the surface at high temperature.^{13,16} To verify the existence of the high-temperature stable hydroxyl, we performed the deconvolution of the O 1s XPS spectra for both samples, which included three peaks (Fig. S6†). The peaks at ~528.9, 530.8 and 531.6 eV are assigned to the lattice oxygen (O_L), defect-related oxygen (O_D) and surface hydroxyl oxygen (O_{OH}), respectively.

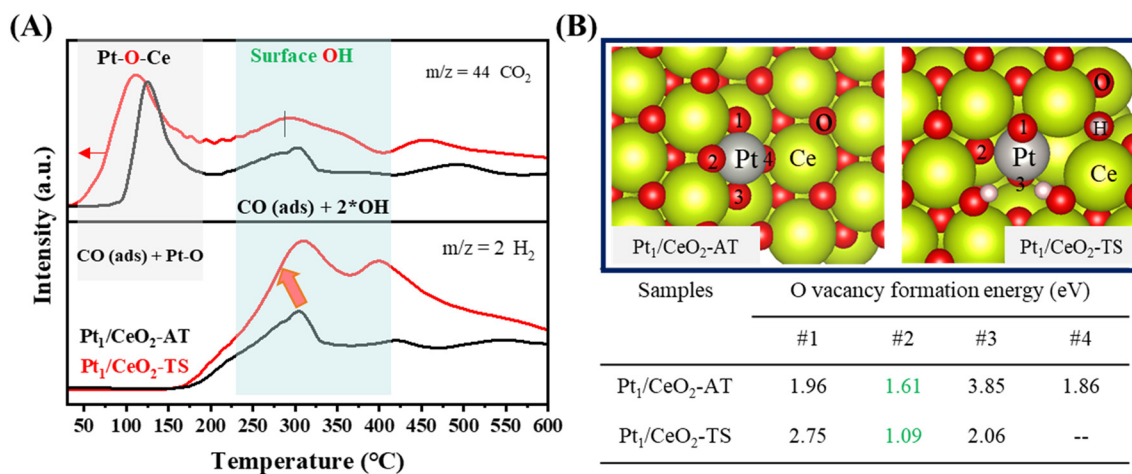


Fig. 3 (A) CO-TPR profiles of the Pt₁/CeO₂-AT and Pt₁/CeO₂-TS catalysts, CO₂ ($m/z = 44$) and H₂ ($m/z = 2$) signals. (B) A top-down view of the PtO_x active site on the surface of CeO₂ (111), with atoms close to the Pt atom and the corresponding formation energy of the O-vacancy.

Therefore, we deduced that compared to the Pt₁/CeO₂-AT sample with a square-planar Pt₁O₄ coordination, a non-equilibrium Pt₁O_x configuration stabilized by the surface hydroxyl on the CeO₂ (111) facet was formed on the Pt₁/CeO₂-TS catalyst during the TS treatment, which is confirmed by the FTIR result (Fig. S7†). The data shown in Fig. S7† clearly indicate that the Pt₁/CeO₂-TS catalyst exhibits unique vibrational peaks around 3500 cm⁻¹, which we can associate with surface hydroxyl groups. This finding further supports and confirms our initial theory.

The oxygen-containing surface species on the catalysts were further characterized by CO temperature-programmed reduction (CO-TPR) (Fig. 3A). As for Pt₁/CeO₂-AT, the surface lattice oxygen in the vicinity of Pt (Pt–O–Ce bond) can react with CO at ~90 °C, while on the Pt₁/CeO₂-TS catalyst, it can not only react with CO at a lower temperature (~50 °C) but also produce more CO₂, suggesting that surface oxygen species are more active and abundant on the latter. Meanwhile, more surface hydroxyl groups were generated on the Pt₁/CeO₂-TS catalyst, which can react with CO at ~175 °C. The effect of surface hydroxyls was rarely considered in previous studies on Pt₁/CeO₂-AT,^{23,28,29} primarily because those formed by AT are far away from the active sites and have little influence on the local environment of the active single atoms.^{13,16} Surface hydroxyls were found to be more abundant in Pt₁/CeO₂-TS, correlating with the XPS results. Simultaneously, these surface hydroxyls had a lower reaction temperature than those formed from AT and a similar reaction temperature to hydroxyls formed by high-temperature steam treatment,^{13,16,30} implying that the hydroxyl groups on Pt₁/CeO₂-TS could affect the local environment of Pt single atoms. This lends credence to the hypothesis that surface hydroxyls produced from TS can stabilize single atoms. We also found the presence of more oxygen defects at Pt₁/CeO₂-TS (Fig. S8†), which agrees well with the results of EXAFS and CO-DRIFTS. Raman spectroscopy (Fig. S9†) revealed the formation of the Pt–O–Ce bond, as evidenced by the feature of the peak at 550 cm⁻¹ (the one at 657 cm⁻¹ corresponding to Pt–O). The significant decrease in the peak strength of the Pt₁/CeO₂-TS catalyst is due to the looser bonds of Ce–O–Ce and Pt–O–Ce as compared to the Pt₁/CeO₂-AT sample, which also confirms that the surface oxygen is more active *via* TS treatment.^{31,32} Models of Pt₁/CeO₂-TS and Pt₁/CeO₂-AT were built based on the characterization results and are shown in Fig. 3B. The model for the Pt₁/CeO₂-AT catalyst is a symmetric square-planar Pt₁O₄ coordination, whereas the structure model of Pt₁O₃ on CeO₂ (111) stabilized with surface hydroxyls is built for the Pt₁/CeO₂-TS catalyst.¹¹ For the PtO₃ model, the formation energy of the oxygen vacancy is lower than that of the square-planar Pt₁O₄ ensemble (1.09 vs. 1.61 eV). Since the formation energy of the O-vacancy of the low-coordination PtO₂ is greater than that of the square-planar Pt₁O₄ coordination (2.21 vs. 1.61 eV), which contradicts the CO-TPR and EXAFS results, the local environment of the Pt single atoms in the Pt₁/CeO₂-TS catalyst is therefore determined as

the non-equilibrium PtO₃ configuration surrounded with the surface hydroxyls existing at high temperature.

3.2 Evaluation performance of HCHO oxidation

We tested the two Pt₁/CeO₂ catalysts prepared at high temperatures in HCHO oxidation to evaluate their distinct catalytic performance in environmental catalysis. The Pt₁/CeO₂-AT catalyst has a high onset temperature of ~120 °C and achieves only 50% HCHO conversion at 170 °C (Fig. 4A). However, the Pt₁/CeO₂-TS catalyst exhibits low-temperature activity, achieving 100% HCHO conversion at 60 °C. The turnover frequencies (TOFs) of the Pt₁/CeO₂-TS catalyst in formaldehyde catalytic oxidation can reach up to approximately 8.5 per hour at room temperature. This level of activity is relatively impressive compared to other catalytic systems based on Pt for similar reaction conditions, as indicated in Table S3.† Moreover, the Pt₁/CeO₂-TS catalyst demonstrated excellent stability in a time-on-stream run of 50 h in the presence of 400 ppm HCHO at 30 °C (Fig. S10†). The spent Pt₁/CeO₂-TS catalyst after 50 h of HCHO oxidation (Pt₁/CeO₂-TS-spent) was characterized, and the HAADF-STEM (Fig. S11A, B and S13†), XRD (Fig. S11C†), Raman (Fig. S11D†) and XPS results (Fig. S11E and F†) confirmed that there are no significant changes in the CeO₂ morphology and Pt local environments. Furthermore, the surface Ce species (Fig. S11E†), oxygen defects and hydroxyl groups (Fig. S12†) have no obvious changes after the reaction, which is consistent with the *in situ* HCHO-DRIFTS results below (Fig. 5), demonstrating that the surface hydroxyls were maintained.

In addition, the effect of relative humidity (RH) on HCHO catalytic oxidation was investigated. As seen in Fig. 4B, under 20% relative humidity, the reactivity of Pt₁/CeO₂-TS is higher than that under dry conditions (~80% vs. ~65%). The previous studies have reported that the presence of H₂O significantly improves the transformation of dioxymethylene (DOM, H₂COO) into formate species (HCOO) or promotes the adsorption of formaldehyde and the formation of HCOO species. Therefore, the presence of an appropriate amount of water vapor can enhance the oxidation of HCHO, indicating the good tolerance of the Pt₁/CeO₂-TS catalyst against moisture. Therefore, the Pt₁/CeO₂-TS catalyst exhibits superior activity and excellent durability in the mitigation of HCHO.

3.3 Reaction mechanism and theoretical calculation

To investigate the reaction mechanism and the efficient activation of HCHO and O₂ molecules over the Pt₁/CeO₂-TS catalyst, we performed *in situ* HCHO-DRIFTS experiments and DFT calculations. The *in situ* HCHO-DRIFTS experiments were carried out on the Pt₁/CeO₂-TS catalyst in a flow of HCHO/N₂ or HCHO/O₂/N₂ (Fig. 5) at room temperature to gain insight into the formation of intermediates during the reaction. As shown in Fig. 5, with the introduction of HCHO/N₂ or HCHO/O₂/N₂, there was no peak associated with the



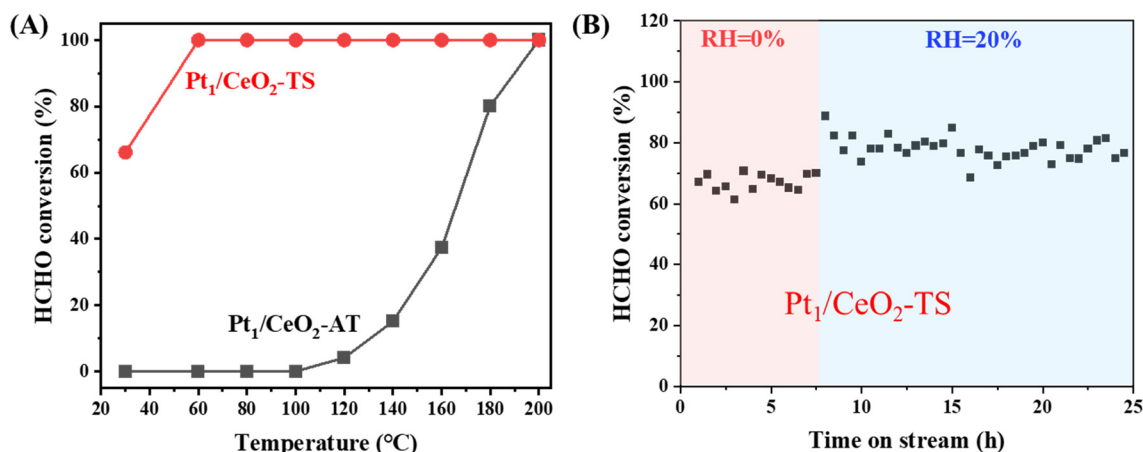


Fig. 4 (A) HCHO conversion as a function of temperature over the Pt₁/CeO₂-AT and Pt₁/CeO₂-TS single-atom catalysts. (B) Relative humidity effect (20%) on the activity of the Pt/CeO₂-TS catalyst at 30 °C. The reaction conditions were described in the Experimental section.

adsorbed HCHO (1722 cm⁻¹) on the Pt₁/CeO₂-TS catalyst.³³ The assignments of other peaks appeared are listed in Table S4.† It should be noted that with the introduction of HCHO/N₂ from 20 to 40 min (Fig. 5), the contents of HCOO and DOM species gradually increase, while the adsorption peak at 3695 cm⁻¹ becomes more negative (Fig. 5), which is assigned to the consumption of the hydroxyl species residing on the catalyst at high temperature.^{34,35} This indicates that the formation of surface DOM and HCOO consumes the surface hydroxyls. At the same time, we found that the intensity of the DOM peak formed during the entire HCHO/N₂ process was significantly higher compared to that of the HCOO species. This result contradicts the previous findings on a steam-treated Pt₁/CeO₂ catalyst having surface hydroxyls,¹⁶ indicating a different reaction mechanism. When the reactant gas was switched to HCHO/O₂/N₂, the DOM and HCOO species were still present, whereas their intensity was much lower than that in HCHO/N₂. The decrease of DOM and HCOO peaks indicates that oxygen is needed for further dehydrogenation. The peak position and intensity of the surface hydroxyl group did not change significantly throughout the catalytic cycle, which suggests that the consumption of the surface hydroxyl group was a reversible process that primarily facilitated the adsorption of intermediate species rather than breaking the C–H bond. We propose that the main reaction path in the Pt₁/CeO₂-TS catalyst is HCHO* → DOM* → HCOO* → COO*. Previous studies have already proposed that the reaction mechanism involves the decomposition of HCOO* into *CO, followed by its subsequent oxidation into *CO₂. To reinforce the credibility and validity of our proposed mechanism, we have obtained additional supporting evidence from our *in situ* infrared analysis, specifically the absence of CO peaks. The activation of the HCHO* molecule is a two-step process, with the first step being the breaking of the C–H bond in DMO to form HCOO, mainly by surface active oxygen species, and the second step being the further breaking of the C–H bond to form COO* with the assistance of O₂ molecules. Based on

the *in situ* experiments, we propose that the high-temperature stable hydroxyl on the Pt₁/CeO₂-TS catalyst promotes the adsorption activation of DMO and HCOO, and the subsequent dehydrogenation of DOM to HCOO is the rate-limiting step of the whole reaction. Furthermore, the O₂ molecule is easily activated by the Pt₁/CeO₂-TS catalyst to rapidly break C–H bonds.

DFT simulation is used to further validate the reaction mechanism and the activation of reactants over the Pt₁/CeO₂-TS catalyst in HCHO oxidation. Based on the characterization, the Pt₁/CeO₂-TS model has a Pt single atom bonding with three oxygen atoms on CeO₂ (111), as well as two neighboring active hydroxyls located adjacently to the Pt atom (PtO₃-Ce(OH)₂), as shown in Fig. S14.† The energy barrier of each step on the optimized Pt₁/CeO₂-TS model in the reaction was calculated and is shown in Fig. 6. HCHO oxidation starts with the adsorption of HCHO at the Pt₁ site over the PtO₃-Ce(OH)₂ ensemble. The adsorbed HCHO reacts with the adjacent active oxygen species from the Pt–O bond to form H₂COO*_{lat} (DMO*), and meanwhile the bridging OH group interacts with O from HCHO, which stabilizes the

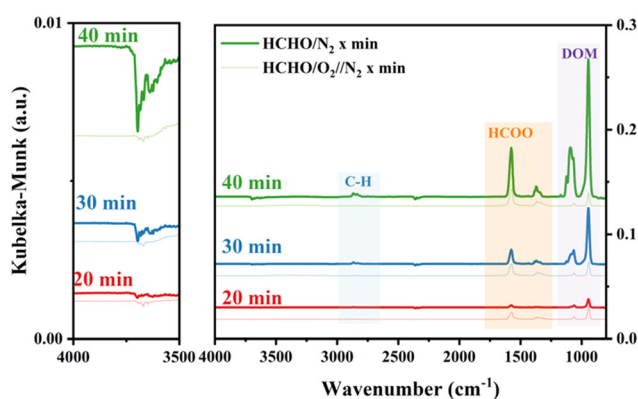


Fig. 5 *In situ* HCHO-DRIFTS of the Pt₁/CeO₂-TS catalyst carried out in a flow of HCHO/N₂ (solid line) or HCHO/O₂/N₂ (dotted line) at 30 °C.

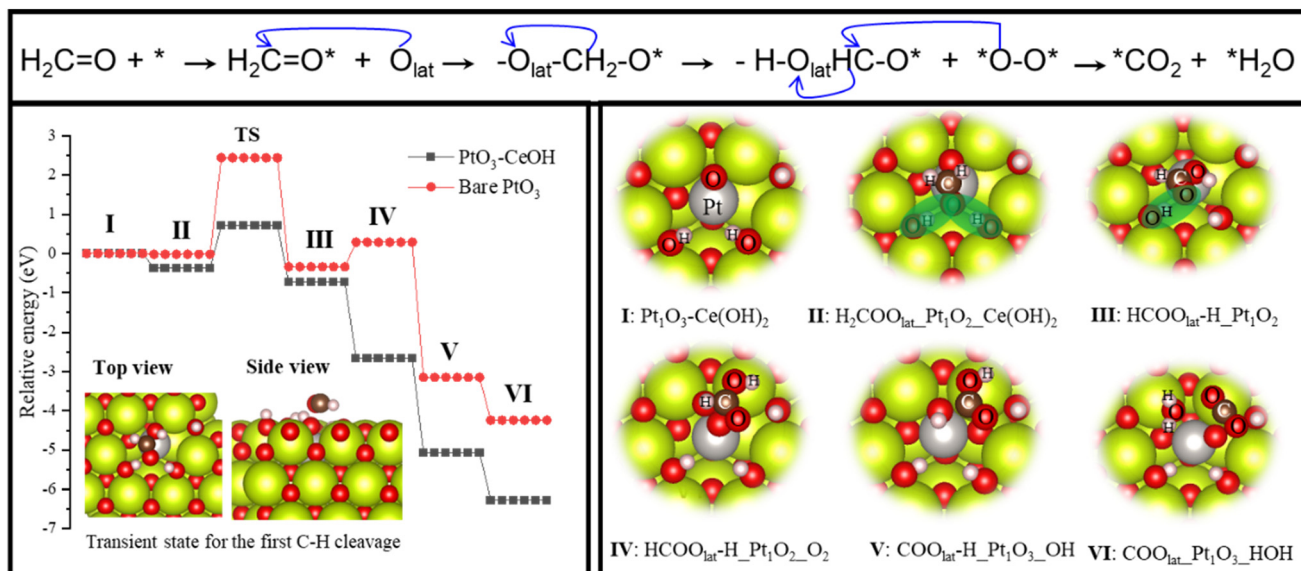


Fig. 6 The calculated energy profile and the corresponding structures of the intermediates and transition states of the key elemental steps on Pt₁O₃-Ce(OH)₂ on the CeO₂ (111) surface in HCHO oxidation.

H₂COO_{lat}^{*} species. This is consistent with the results on the formation of DMO and the consumption of hydroxyls in the *in situ* DRIFTS experiment. The DFT calculation shows that this step is exothermic (−0.38 eV) with no activation barrier. Then, the formed H₂COO_{lat}^{*} starts the first C–H bond breaking reaction, which involves the interaction of C–H with the activated Pt–O_{lat} bond to form HCOO_{lat}^{*} and OH species. Despite being exothermic (−0.36 eV), this step has a high energy barrier of 0.88 eV. This suggests that HCOO_{lat}^{*} species are more difficult to form as compared to H₂COO_{lat}^{*} species, which explains the reason that the peak intensity of DMO is significantly higher than that of HCOO in the *in situ* DRIFTS experiment (Fig. 5). The activation of an oxygen molecule (O₂^{*}) at the surface vacancy is highly exothermic (−1.93 eV), and the O₂^{*} species reacts with HCOO_{lat}^{*} to break the second C–H bond. This is a highly exothermic step (−2.41 eV) with a low energy barrier, indicating that oxygen activation is not the rate-limiting step in the reaction. This finding is consistent with the results of the *in situ* DRIFTS experiment. Finally, the interaction of COO^{*}–H and hydroxyl species results in the formation of COO^{*}, H₂O^{*}, and Pt–O bonds on the CeO₂ surface, completing the reaction cycle. As a comparison, we also examined the PtO₃ structure with no hydroxyls (Fig. 6, red line and S15†). The study discovered that the first step of the C–H bond activity requires a very high activation energy (~2.5 eV), which is similar to the catalyst obtained through the AT method.¹⁶ As confirmed by the *in situ* experiment and DFT calculation, the high-temperature stable surface hydroxyl existing from the TS synthesis primarily facilitated the adsorption activation of DMO and HCOO^{*} and did not participate in the C–H bond breaking. The activation of C–H bonds during the HCHO oxidation reaction is influenced by the activity of surface

oxygen species. The initial C–H bond activation is facilitated by the surface lattice oxygen present in the Pt–O–Ce bond, whereas the subsequent C–H bond activation is facilitated by the adsorbed oxygen species produced by molecular oxygen dissociation.

4. Conclusions

In this work, we tune the local environment of the Pt single atoms on two Pt₁/CeO₂ single-atom catalysts (SACs) prepared at elevated temperatures (>800 °C), *i.e.*, *via* atom trapping (Pt₁/CeO₂-AT) and thermal shock (Pt₁/CeO₂-TS). The use of the high-temperature preparation avoids the effect of various surface hydroxyls existing at low temperatures, exclusively maintaining the high-temperature stable hydroxyls. The Pt single atoms in the Pt₁/CeO₂-TS catalyst present the non-equilibrium local environments surrounded by high-temperature stable hydroxyls, exhibiting excellent activity in HCHO oxidation and lowering the *T*₁₀₀ to 60 °C, as compared to the *T*₁₀₀ of 200 °C for the Pt₁/CeO₂-AT catalyst.

For the Pt₁/CeO₂-TS catalyst, Pt single atoms substituting the Ce site of CeO₂ (111) have a PtO₃ configuration coordinated with hydroxyls (Pt–O CN of 3.6), showing more active surface lattice oxygen than the Pt₁/CeO₂-AT catalyst (symmetric square-planar Pt₁O₄ coordination). The high-temperature stable hydroxyl existing on Pt₁/CeO₂-TS promotes the adsorption of formaldehyde, DMO and HCOO, but does not participate in the C–H bond activation. This confirms that the catalytic performance of Pt SACs can be tailored by tuning the local environment of Pt single atoms with the help of high-temperature stable hydroxyls. This work provides insight into preparing efficient single-atom catalysts for environmental catalysis.



Data availability statement

The data that support this study are available from the corresponding author upon reasonable request.

Author contributions

Jinshu Tian: conceptualization, investigation, methodology, writing – original draft. Mingyi Xiao and Lina Zhang: investigation, formal analysis, methodology, writing – review & editing. Shuzhe Zheng and Ling Fang: investigation, methodology, validation, visualization. Tulai Sun: visualization, investigation, writing – review & editing. Yonghe Li: writing – review & editing. Yihan Zhu: writing – review & editing. Jianghao Zhang: writing – review & editing. Haifeng Xiong: conceptualization, investigation, methodology, writing – review and editing, supervision.

Conflicts of interest

All the authors declare no conflicts of interest.

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References

- 1 S. Zhao, Y. Wen, X. Liu, X. Pen, F. Lü, F. Gao and X. Tang, Formation of active oxygen species on single-atom Pt catalyst and promoted catalytic oxidation of toluene, *Nano Res.*, 2020, **13**, 1544–1551.
- 2 K. Yang, Y. Liu, J. Deng, X. Zhao, J. Yang, Z. Han, Z. Hou and H. Dai, Three-dimensionally ordered mesoporous iron oxide-supported single-atom platinum: Highly active catalysts for benzene combustion, *Appl. Catal., B*, 2019, **244**, 650–659.
- 3 M. Jiang, D. Yan, X. Lv, Y. Gao and H. Jia, Recognition of water-dissociation effect toward lattice oxygen activation on single-atom Co catalyst in toluene oxidation, *Appl. Catal., B*, 2022, **319**, 121962.
- 4 Q. Q. Guan, C. W. Zhu, Y. Lin, E. I. Vovk, X. H. Zhou, Y. Yang, H. C. Yu, L. N. Cao, H. W. Wang, X. H. Zhang, X. Y. Liu, M. K. Zhang, S. Q. Wei, W. X. Li and J. L. Lu, Bimetallic monolayer catalyst breaks the activity-selectivity trade-off on metal particle size for efficient chemoselective hydrogenations, *Nat. Catal.*, 2021, **4**, 840–849.
- 5 R. Alcalá, A. Delariva, E. J. Peterson, A. Benavidez, C. E. Garcia-Vargas, D. Jiang, X. I. Pereira-Hernandez, H. H. Brongersma, R. Ter Veen and J. Stanek, Atomically Dispersed Dopants for Stabilizing Ceria Surface Area, *Appl. Catal., B*, 2021, **284**, 119722.
- 6 H. C. Li, Q. Wan, C. Du, J. Zhao, F. Li, Y. Zhang, Y. Zheng, M. Chen, K. H. L. Zhang, J. Huang, G. Fu, S. Lin, X. Huang and H. Xiong, Layered Pd oxide on PdSn nanowires for boosting direct H₂O(2) synthesis, *Nat. Commun.*, 2022, **13**, 6072.
- 7 J. Yang, Y. Huang, H. Qi, C. Zeng, Q. Jiang, Y. Cui, Y. Su, X. Du, X. Pan, X. Liu, W. Li, B. Qiao, A. Wang and T. Zhang, Modulating the strong metal-support interaction of single-atom catalysts *via* vicinal structure decoration, *Nat. Commun.*, 2022, **13**, 4244.
- 8 W. Tan, S. Xie, D. Le, W. Diao, M. Wang, K. B. Low, D. Austin, S. Hong, F. Gao, L. Dong, L. Ma, S. N. Ehrlich, T. S. Rahman and F. Liu, Fine-tuned local coordination environment of Pt single atoms on ceria controls catalytic reactivity, *Nat. Commun.*, 2022, **13**, 7070.
- 9 F. Dvorak, M. Farnesi Camellone, A. Tovt, N. D. Tran, F. R. Negreiros, M. Vorokhta, T. Skala, I. Matolinova, J. Myslivecek, V. Matolin and S. Fabris, Creating single-atom Pt-ceria catalysts by surface step decoration, *Nat. Commun.*, 2016, **7**, 10801.
- 10 J. Zhang, X. Qin, X. Chu, M. Chen, X. Chen, J. Chen, H. He and C. Zhang, Tuning Metal-Support Interaction of Pt-CeO₂ Catalysts for Enhanced Oxidation Reactivity, *Environ. Sci. Technol.*, 2021, **55**, 16687–16698.
- 11 D. Jiang, Y. Yao, T. Li, G. Wan, X. I. Pereira-Hernandez, Y. Lu, J. Tian, K. Khivantsev, M. H. Engelhard, C. Sun, C. E. Garcia-Vargas, A. S. Hoffman, S. R. Bare, A. K. Datye, L. Hu and Y. Wang, Tailoring the Local Environment of Platinum in Single-Atom Pt₁/CeO₂ Catalysts for Robust Low-Temperature CO Oxidation, *Angew. Chem., Int. Ed.*, 2021, **60**, 26054–26062.
- 12 H. Jeong, D. Shin, B. S. Kim, J. Bae, S. Shin, C. Choe, J. W. Han and H. Lee, Controlling the Oxidation State of Pt Single Atoms for Maximizing Catalytic Activity, *Angew. Chem., Int. Ed.*, 2020, **59**, 20691–20696.
- 13 L. Nie, D. Mei, H. Xiong, B. Peng, Z. Ren, X. I. P. Hernandez, A. DeLaRiva, M. Wang, M. H. Engelhard, L. Kovarik, A. K. Datye and Y. Wang, Activation of surface lattice oxygen in single-atom Pt/CeO₂ for low-temperature CO oxidation, *Science*, 2017, **358**, 1419–1423.
- 14 X. Li, X. I. Pereira-Hernandez, Y. Chen, J. Xu, J. Zhao, C. W. Pao, C. Y. Fang, J. Zeng, Y. Wang, B. C. Gates and J. Liu, Functional CeO_x nanoglues for robust atomically dispersed catalysts, *Nature*, 2022, **611**, 284–288.
- 15 W. Wan, J. Geiger, N. Berdunov, M. Lopez Luna, S. W. Chee, N. Daelman, N. Lopez, S. Shaikhutdinov and B. Roldan Cuenya, Highly Stable and Reactive Platinum Single Atoms on Oxygen Plasma-Functionalized CeO₂ Surfaces: Nanostructuring and Peroxo Effects, *Angew. Chem., Int. Ed.*, 2022, **61**, e202112640.
- 16 L. Zhang, Q. Bao, B. Zhang, Y. Zhang, S. Wan, S. Wang, J. Lin, H. Xiong, D. Mei and Y. Wang, Distinct Role of Surface Hydroxyls in Single-Atom Pt₁/CeO₂ Catalyst for Room-Temperature Formaldehyde Oxidation: Acid-Base *Versus* Redox, *JACS Au*, 2022, **2**, 1651–1660.
- 17 D. Wu, S. Zhou, C. Du, J. Li, J. Huang, H.-X. Shen, A. K. Datye, S. Jiang, J. T. Miller, S. Lin and H. Xiong, The



- proximity between hydroxyl and single atom determines the catalytic reactivity of Rh₁/CeO₂ single-atom catalysts, *Nano Res.*, 2024, **17**, 397–406.
- 18 L. Zhang, B. Zhang, P. Xue, J. Li, Z. Zhang, Y. Yang, S. Wang, J. Lin, H. Liao, Y. Wang, Y. Yao, S. Wan and H. Xiong, The Effect of Pretreatment on the Reactivity of Pd/Al₂O₃ in Room Temperature Formaldehyde Oxidation, *ChemCatChem*, 2021, **13**, 4133–4141.
 - 19 P. Bera, K. R. Priolkar, A. Gayen, P. R. Sarode, M. S. Hegde, S. Emura, R. Kumashiro, V. Jayaram and G. N. Subbanna, Ionic Dispersion of Pt over CeO₂ by the Combustion Method: Structural Investigation by XRD, TEM, XPS, and EXAFS, *Chem. Mater.*, 2003, **15**, 2049–2060.
 - 20 H.-H. Liu, Y. Wang, A.-P. Jia, S.-Y. Wang, M.-F. Luo and J.-Q. Lu, Oxygen vacancy promoted CO oxidation over Pt/CeO₂ catalysts: A reaction at Pt–CeO₂ interface, *Appl. Surf. Sci.*, 2014, **314**, 725–734.
 - 21 H. A. Aleksandrov, K. M. Neyman, K. I. Hadjiivanov and G. N. Vayssilov, Can the state of platinum species be unambiguously determined by the stretching frequency of an adsorbed CO probe molecule?, *Phys. Chem. Chem. Phys.*, 2016, **18**, 22108–22121.
 - 22 X. I. Pereira-Hernandez, A. DeLaRiva, V. Muravev, D. Kunwar, H. Xiong, B. Sudduth, M. Engelhard, L. Kovarik, E. J. M. Hensen, Y. Wang and A. K. Datye, Tuning Pt–CeO₂ interactions by high-temperature vapor-phase synthesis for improved reducibility of lattice oxygen, *Nat. Commun.*, 2019, **10**, 1358.
 - 23 D. Kunwar, S. Zhou, A. DeLaRiva, E. J. Peterson, H. Xiong, X. I. Pereira-Hernández, S. C. Purdy, R. ter Veen, H. H. Brongersma, J. T. Miller, H. Hashiguchi, L. Kovarik, S. Lin, H. Guo, Y. Wang and A. K. Datye, Stabilizing High Metal Loadings of Thermally Stable Platinum Single Atoms on an Industrial Catalyst Support, *ACS Catal.*, 2019, **9**, 3978–3990.
 - 24 P. Xie, T. Pu, A. Nie, S. Hwang, S. C. Purdy, W. Yu, D. Su, J. T. Miller and C. Wang, Nanoceria-supported single-atom platinum catalysts for direct methane conversion, *ACS Catal.*, 2018, **8**, 4044–4048.
 - 25 A. Ankudinov, J. Rehr, J. J. Low and S. R. Bare, Sensitivity of Pt X-ray absorption near edge structure to the morphology of small Pt clusters, *J. Chem. Phys.*, 2002, **116**, 1911–1919.
 - 26 J. Resasco, L. DeRita, S. Dai, J. P. Chada, M. Xu, X. Yan, J. Finzel, S. Hanukovich, A. S. Hoffman and G. W. Graham, Uniformity is key in defining structure–function relationships for atomically dispersed metal catalysts: the case of Pt/CeO₂, *J. Am. Chem. Soc.*, 2019, **142**, 169–184.
 - 27 H. A. Aleksandrov, K. M. Neyman and G. N. Vayssilov, The structure and stability of reduced and oxidized mononuclear platinum species on nanostructured ceria from density functional modeling, *Phys. Chem. Chem. Phys.*, 2015, **17**, 14551–14560.
 - 28 Y. Lu, S. Zhou, C.-T. Kuo, D. Kunwar, C. Thompson, A. S. Hoffman, A. Boubnov, S. Lin, A. K. Datye, H. Guo and A. M. Karim, Unraveling the Intermediate Reaction Complexes and Critical Role of Support-Derived Oxygen Atoms in CO Oxidation on Single-Atom Pt/CeO₂, *ACS Catal.*, 2021, **11**, 8701–8715.
 - 29 H. N. Pham, A. DeLaRiva, E. J. Peterson, R. Alcala, K. Khivantsev, J. Szanyi, X. S. Li, D. Jiang, W. Huang, Y. Sun, P. Tran, Q. Do, C. L. DiMaggio, Y. Wang and A. K. Datye, Designing Ceria/Alumina for Efficient Trapping of Platinum Single Atoms, *ACS Sustainable Chem. Eng.*, 2022, **10**, 7603–7612.
 - 30 D. Donadio, L. M. Ghiringhelli and L. Delle Site, Autocatalytic and cooperatively stabilized dissociation of water on a stepped platinum surface, *J. Am. Chem. Soc.*, 2012, **134**, 19217–19222.
 - 31 Y. Lee, G. He, A. J. Akey, R. Si, M. Flytzani-Stephanopoulos and I. P. Herman, Raman analysis of mode softening in nanoparticle CeO_{2-δ} and Au–CeO_{2-δ} during CO oxidation, *J. Am. Chem. Soc.*, 2011, **133**, 12952–12955.
 - 32 D.-Y. Wei, M.-F. Yue, S.-N. Qin, S. Zhang, Y.-F. Wu, G.-Y. Xu, H. Zhang, Z.-Q. Tian and J.-F. Li, *In situ* Raman observation of oxygen activation and reaction at platinum–ceria interfaces during CO oxidation, *J. Am. Chem. Soc.*, 2021, **143**, 15635–15643.
 - 33 X. Sun, J. Lin, H. Guan, L. Li, L. Sun, Y. Wang, S. Miao, Y. Su and X. Wang, Complete oxidation of formaldehyde over TiO₂ supported subnanometer Rh catalyst at ambient temperature, *Appl. Catal., B*, 2018, **226**, 575–584.
 - 34 X. Chen, G. He, Y. Li, M. Chen, X. Qin, C. Zhang and H. He, Identification of a Facile Pathway for Dioxymethylene Conversion to Formate Catalyzed by Surface Hydroxyl on TiO₂-Based Catalyst, *ACS Catal.*, 2020, **10**, 9706–9715.
 - 35 Y. Huo, X. Wang, Z. Rui, X. Yang and H. Ji, Identification of the Nearby Hydroxyls' Role in Promoting HCHO Oxidation over a Pt Catalyst, *Ind. Eng. Chem. Res.*, 2018, **57**, 8183–8189.

