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# Stabilizing platinum atoms on CeO<sub>2</sub> oxygen vacancies by metal-support

## T interaction induced interface distortion: Mechanism and application <sup>Ch</sup><sub>up</sub>

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### ABSTRACT

Exploring thermally robust single atom catalysts (SACs) is of great significance. Here, we develop a universal strategy for stabilizing Pt atoms on the mono-oxygen vacancies of CeO<sub>2</sub> with diverse exposed facets. The stabilization mechanism was proposed that the formed Pt-O-Ce interface will be taken into distortion spontaneously to keep thermodynamics stable through strong metal-support interactions. The highest degree of Pt-O-Ce distortion is achieved over Pt1-CeO<sub>2</sub>{100} material, which exhibits exceptional efficiency and thermal stability for oxygenated hydrocarbon removal. The enhanced adsorption capacity of O<sub>2</sub> and methanol confirmed in the distortion interface is seen as another crucial reason for improving the stability of SACs. Methanol oxidation on Pt1-CeO<sub>2</sub>{100} obeys the L-H mechanism under relatively low temperature and then goes through to the MVK mechanism with temperature increasing. We believe that these results would bring new opportunities in the fabrication of SACs and applications of them in thermal reactions.

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### 1. Introduction

The dispersion of isolated metal atoms on support surfaces provides a foundation for maximizing the atomic efficiency of precious metals in catalytic reactions [1,2]. For this reason, single atom catalysts (SACs) often possess unprecedented catalytic performance, a trait which in recent years has been capitalized upon and evidenced in several important reactions driven by thermal, electric, and light-energy [3–5]. In light of growing concerns associated with the emission of volatile organic compounds (VOCs) [6–9], several recent publications have demonstrated the potential of using SACs for the low-temperature destruction of VOCs [10,11]. We too, recently demonstrated that a Pt<sub>1</sub>-Co<sub>3</sub>O<sub>4</sub> SAC was exceptionally active for the destruction of oxygenated VOCs [12]. Despite the progress made, a great challenge remains; to develop thermally and chemically stable SACs, which required to be

used in large scale traditional thermal reactions, such as catalytic combustion of hydrocarbons, water-gas shift and methane mineralization [13,14]. The development of thermally robust SACs that can sustain reductive/oxidative processes under high temperature attracts huge interest and challenge for its application [15].

Several strategies have been invoked by researchers to synthesize materials that possess these desirable properties, consisting of (i) reducing the loading quantity of active metal components; (ii) adding the protective species; (iii) exploiting defect vacancies or voids in supporting materials [16–18]. These strategies aim to enhance metal-support interactions and/or prevent the aggregating tendency of isolated atoms. However, as discussed by Xiao and co-workers, the stabilizing mechanism of classical strong metal-support interaction remains elusive in the above mentioned methods [19]. As such, we consider it to be of high importance that a logical approach is implemented, to govern the

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appropriate selection of metal(s) and support(s) used for the synthesis of SACs, for specific applications [20,21]. Several notable studies have investigated how support-metal strong interactions (SMSIs) influence such catalysts, using both experimental and computational techniques [22]. Li and co-workers recently investigated how on-site Coulomb interactions influence the catalytic performance of Au catalysts supported on several tetravalent-metal dioxides of  $\text{MO}_2$  ( $M = \text{Ti, Zr, Ce, Hf, and Th}$ ) [23]. The study confirmed that the radial contraction and low orbital energies of the 3d and 4f orbitals in these  $\text{MO}_2$  oxides are caused by fundamental quantum primogenic effects, which is of great significance for the determination of valence state as well as charge distribution of gold atoms [23]. An additional study by O'Connor et al., predicted the interaction strengths between metal atoms and oxide supports according to the smallest absolute contraction figures and selection operator regression [24]. The investigation concluded a correlation between binding of interfaces and readily available physical properties of supports; such as oxophilicity measured by oxide formation energy, which can be measured by the oxygen vacancy formation energy. These properties can be used to screen interaction strengths between metal-support pairs, which will undoubtedly aid the design of stable SACs moving forward [25]. Varieties of approaches are available for stabilization of isolated metal atoms;  $\text{CeO}_2$  for instance as most extensively investigated supports for the SMSI, possesses exclusive redox properties, which have their origin in the effect of quantum primogenic, making it an ideal candidate to support and stabilize single atom sites [26]. In addition, it possesses a diverse electronic structure, which can lead to exposed facets [27].

Regrettably, much of the previous work in this area has predominantly focused on dissecting information on the function of the active sites; nevertheless, the properties of heterogeneous catalysts frequently depends on the synergy between supported phases and support, the extent of which, is often magnified by means of an interface limiting effect [28]. An example of this was recently presented by Bao and co-workers [29], who constructed a series of metal-oxide interfaces, which are considered to be the active sites for  $\text{CO}_2$  activation and CO reduction, where a synergistic effect between Au and  $\text{CeO}_x$  promotes the stability of key carboxyl intermediate (\*COOH) and thus facilitates  $\text{CO}_2$  electroreduction. This has been further evidenced by Murray and co-workers [30], who proposed an evident enhancement for the CO oxidation rate in ceria-based catalysts at the ceria-metal interface, for a range of group VIII metal catalysts, revealing the significance from the support. Shen and co-workers exposed the prospect of stabilizing Au nanoparticles utilizing an interfacial anchoring pattern of gold-oxide [31], which confirmed that the structuring of Au-ceria interfaces facilitates the regeneration of adsorbed molecular CO and energetic oxygen species on ceria. As such, we consider that it is crucial to design a stable mono-dispersed active interface for thermo-catalytic reactions, over which the single atom sites are anchored to the defected sites through SMSIs. Despite several single atom materials having been developed and utilized for the destruction of VOCs, the intrinsic mechanism for the oxidation of VOCs and the relationship between catalytic performance and electronic structure have been somewhat overlooked [6–9].

The work herein, focuses on the construction of a Pt-O-Ce active interface, in which platinum atoms are stabilized on  $\text{CeO}_2$  oxygen vacancies. According to our experimental and theoretical investigations, this interface was confirmed to distort; a phenomenon which is facilitated by SMSIs. We propose that this SMSI is compounded by chemical bonding and relevant charge transfer at active interfacial regions. The distortion degree at the Pt-O-Ce interfaces was enhanced attributing to the different electron structures of  $\text{CeO}_2$  support with diverse exposed facets. Compared with  $\text{Pt}_1\text{-CeO}_2\{110\}$  and  $\text{Pt}_1\text{-CeO}_2\{111\}$  samples, the Pt-O-Ce active interface over  $\text{Pt}_1\text{-CeO}_2\{100\}$  exhibits the highest intensity of distortion degree and thus catalyst possesses the exceptional catalytic efficiency and thermal stability for oxygenated hydrocarbon removal. Furthermore, the intrinsic methanol oxidation

mechanism over  $\text{Pt}_1\text{-CeO}_2\{100\}$  material was revealed, which further assists with the identification of active sites in these materials during oxidation reactions. We hope the present study can provide fundamental assistance in the design of novel SACs with SMSIs; to expand the application of these catalysts in this important area of research.

## 2. Experimental section

### 2.1. Preparation of single atom catalysts

The procedures for preparation of  $\text{CeO}_2$  supports followed the previous reported [32], and the details of which were displayed in Supplementary Material. Immediately, the abundant surface oxygen vacancies over  $\text{CeO}_2$  supports were constructed by reducing in the hydrogen atmosphere at  $250^\circ\text{C}$  for 2.5 h. The obtained defective supports were mixed with 50 mL of deionized water and stirred for 20 min. After stirring for another 30 min, a urea solution (1 M) was added when the mixture was heated up to  $60^\circ\text{C}$ , which allows the slow decomposition of urea to reach the final pH of 8.5. Then, the amount of desired chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , 1.5  $\text{mg Pt mL}^{-1}$ ) was added to the above solution dropwise. The mixture was aged at  $60^\circ\text{C}$  for another 1.5 h under vigorous stirring. The powder samples were collected after rotary evaporation and thorough washing with deionized water. The dried sample was obtained after keeping it in vacuum overnight at  $70^\circ\text{C}$ . The single atom  $\text{Pt}_1\text{-CeO}_2$  materials were obtained by annealing in Ar at  $250^\circ\text{C}$  for 2 h and in 5%  $\text{H}_2/\text{Ar}$  at  $200^\circ\text{C}$  for 2 h successively.

### 2.2. Catalyst characterizations

$\text{N}_2$  sorption isotherms were measured at 77 K on a Builder SSA-6000 apparatus. XRD measurements were performed using a powder diffractometer (Bruker D8 Advance) with  $\text{Cu-K}\alpha$  radiation. High resolution transmission electron microscopy images were recorded on a JEOL JEM-F200 (Japan) microscope. The resolution HAADF-STEM images of aberration-corrected scanning transmission electron microscopy were recorded on the ARM200F (Japan) microscope. The X-ray absorption fine structure spectra were collected in the Beijing Synchrotron Radiation Facility (BSRF). X-ray photoelectron spectroscopy experiments were carried out on a Thermo Fisher ESCALAB Xi<sup>+</sup> (America) instrument with  $\text{Al-K}\alpha$  radiation. The electron paramagnetic resonance spectra were measured using a A300–9.5/12 (Switzerland) X-band EPR spectrometer. Positron annihilation spectrum was performed with a Trap based slow positron beam (RGM-1/APBS-2, America).  $^1\text{H}$  magic angle spinning nuclear magnetic resonance was recorded on the AVANCE III 400WB (Bruck, Germany). Laser Raman spectra were obtained on a LabRAM HR Evolutions spectrometer (Horiba, Japan) by employing an excitation wavelength of 532 nm line of Ar ion laser. Ultraviolet-visible spectroscopy absorption spectra were recorded using a PE Lambda 950 (Perkin Elmer, America). Temperature-programmed reduction/desorption and titration experiments were recorded on a PCA-1200 (Builder, China) equipped with a TCD. operando FT-IR spectra for  $\text{CO}/\text{NH}_3$  adsorption were performed on the Bruker Tensor 37 (Bruck, Germany) equipped with an MCT detector. The experimental details for these characterizations can be found in Supplementary Material. Besides, the catalytic performance evaluation processes and operando DRIFTS investigations were given in Supplementary Material.

### 2.3. Density functional theory studies

All the density functional theory (DFT) calculations were performed with the Vienna ab initio simulation package (VASP) code [33]. The exchange and correlation energy functional was expressed in the GGA-PBE [34]. The projector-augmented wave (PAW) method was used to describe the interactions between ions and electrons [35]. The valence electrons were solved in the plane-wave basis with a cutoff energy of 400 eV. To accurately describe the localization of Ce 4f electrons, we



**Table 1**  
Positron lifetimes and relative intensities of prepared Pt<sub>1</sub>-CeO<sub>2</sub> catalysts.

Sample	$\tau_1$ (ps)	$\tau_2$ (ps)	$I_1$ (%)	$I_2$ (%)	$I_2/I_1$	$\tau_{av}$ (ps) <sup>a</sup>
CeO <sub>2</sub> {111}	207 ± 6	412 ± 19	79.6 ± 2.7	20.4 ± 2.7	0.26	248.82
CeO <sub>2</sub> {110}	240 ± 11	427 ± 10	67.2 ± 3.1	32.8 ± 3.1	0.49	301.34
CeO <sub>2</sub> {100}	275 ± 7	406 ± 21	60.7 ± 5.8	39.3 ± 5.8	0.65	326.48
Pt <sub>1</sub> -CeO <sub>2</sub> {111}	205 ± 3	450 ± 19	81.1 ± 2.1	18.9 ± 2.1	0.23	251.31
Pt <sub>1</sub> -CeO <sub>2</sub> {110}	234 ± 6	450 ± 21	69.9 ± 4.0	30.1 ± 4.0	0.43	299.02
Pt <sub>1</sub> -CeO <sub>2</sub> {100}	268 ± 10	453 ± 25	64.2 ± 7.3	35.8 ± 7.3	0.56	334.23

Note: <sup>a</sup> $\tau_{av} = \tau_1 \times I_1 + \tau_2 \times I_2$ .

conducted the DFT + U calculations with a value of  $U_{eff} = 4.5$  eV. The setting of Hubbard-like term ( $U_{eff}$ ) follows the approach explored by Cococcioni and De Gironcoli [36]. The convergence criteria for the energy calculation and structure optimization were set to  $1.0 \times 10^{-4}$  eV and a force tolerance of 0.05 eV/Å, respectively [37]. The Brillouin-zone integration was performed using a  $1 \times 1 \times 1$   $\Gamma$ -centered k-point mesh with Gaussian smearing set to 0.05 eV.

Three common CeO<sub>2</sub> surface terminations of (111), (110) and (100) were chosen for the calculations. The CeO<sub>2</sub>(111) surface consisted of p (3 × 3) nine-atomic-layer supercells with the bottom three layers fixed, the CeO<sub>2</sub>(110) surface was modeled by p(2 × 3) five-atomic-layer supercells with the bottom two layers fixed, and the CeO<sub>2</sub>(100) surface was modeled by an O-terminated p(3 × 3) seven-atomic-layer super-cells with the bottom two layers fixed [38]. To maintain the stoichiometry of the CeO<sub>2</sub>(100) surface and avoid the dipole moment normal to the surface, a half oxygen monolayer was transferred from the surface to the bottom of the slab [39]. The vacuum space that perpendicular to these surfaces was set to 15 Å to minimize the interaction between distinct slab surfaces.

The adsorption energies were defined by the equation,  $E_{ads} = E(\text{adsorbate/surface}) - E(\text{adsorbate}) - E(\text{surface})$ , where  $E(\text{adsorbate/surface})$  is the total energy of a surface interacting with adsorbate, and  $E(\text{adsorbate})$  and  $E(\text{surface})$  are the energies of the isolated adsorbate and clean surface, respectively. Therefore, a negative value means exothermic adsorption. The more negative the adsorption energy, the stronger the adsorption. Reaction transition states (TS) were calculated with the climbing image nudged elastic band (CI-NEB) method [40]. Frequency analysis was carried out to ensure that there was only a single imaginary frequency for the transition state. The energy barrier ( $E_{TS}$ ) was defined as the total energy difference between the transition state and the initial structure. The charge density differences were evaluated using the formula  $\Delta\rho = \rho_{A+B} - \rho_A - \rho_B$ , where  $\rho_X$  is the electron density of X.

### 3. Results and discussion

#### 3.1. Distortion of Pt-O-Ce interface facilitated by strong metal-support interactions

A series of CeO<sub>2</sub> materials were synthesized, each of which consisted predominantly of a specific exposed facet; confirmed by HR-TEM (Fig. S1). Accordingly, CeO<sub>2</sub>{100} (nanocube), CeO<sub>2</sub>{111} (nanopolyhedra) and CeO<sub>2</sub>{110} (nanorod) display clear lattice fringes, with inter-planar spacing equal to 0.27, 0.31 and 0.19 nm, respectively. The FFT (fast Fourier transformation) of exposed facet compares well with the standard CeO<sub>2</sub> crystal planes [26,27,32]. From XRD patterns (Fig. S2), all samples exhibit a fluorite cubic structure with an Fm-3m space group. The peaks centered at 28.5°, 33.8°, 47.4°, 56.3°, 59.1°, and 69.4° are attributed to the (111), (200), (220), (311), (222), and (400) diffractions, respectively [32,41,42]. Following, according to the comparison of the relative intensity of characteristic peaks, the dominating exposed facets over each sample can be concluded. The peaks assigned to (111) and (222) are intense in the CeO<sub>2</sub>{111} samples. The peaks of (200) and (400) are intense in the CeO<sub>2</sub>{100} samples. The peak linked to

(220) is intense in the CeO<sub>2</sub>{110} samples. The analysis of XRD patterns and HR-TEM images clearly demonstrates the main exposed facets of CeO<sub>2</sub> supports.

The abundant oxygen vacancies over CeO<sub>2</sub> were constructed through a reduction process, and then the precursor of Pt species was captured by oxygen vacancies under alkali condition. The optimized structures of these CeO<sub>2</sub> materials were subsequently revealed by the theoretical calculation (Fig. S3) and the formation energies of oxygen vacancy in CeO<sub>2</sub>(111), (110) and (100) surfaces were confirmed to be 2.22, 1.43 and 1.69 eV, respectively (Fig. S4). However, the formation energies of oxygen vacancies in CeO<sub>2</sub>(111), (110) and (100) sub-surfaces were determined to be 2.30, 2.72, and 3.36 eV, much higher than that of surface oxygen vacancies (Fig. S4). It is these low oxygen vacancy formation energies and adsorption energies that allow the Pt atoms are inclined to be stabilized by surface oxygen vacancies. The function of different oxygen vacancies has a significant effect on the performance of single atom materials. Herein, in-depth discussions about the nature of oxygen vacancies and its regeneration processes have been conducted. Cerium oxide can accommodate a high oxygen deficiency by the substitution of lower valent elements on the cation sub-lattice [42,43]. The various kinds of oxygen vacancies not only provided sufficient sites to support active metals, but contributed to oxygen species transport on the surface of materials when involving in the catalytic reactions.

Subsequently, positron annihilation spectroscopy (PAS) was adopted to illustrate that which vacancy plays a key role in trapping Pt atoms. Table 1 provides a list of positron lifespan components ( $\tau_1$ ,  $\tau_2$ ) and corresponding relative strength ( $I_1$ ,  $I_2$ ) for the CeO<sub>2</sub> supports and Pt<sub>1</sub>-CeO<sub>2</sub> SACs. The shortest-lived component ( $\tau_1$ ) is related to small neutral Ce<sup>3+</sup>-oxygen vacancy associates and mono-vacancies. The in-termediate component  $\tau_2$  comes from oxygen vacancy clusters with large size (i.e., dimmers, trimmers, or larger), as a consequence of the interaction among the small neutral Ce<sup>3+</sup>-oxygen vacancy associates [32,41,43]. In comparison, the  $\tau_1$  positron lifespan components slightly decrease upon the loading process from CeO<sub>2</sub> supports to Pt<sub>1</sub>-CeO<sub>2</sub> single atom materials, indicating that the neutral oxygen vacancies especially mono-vacancies are consumed during Pt stabilization. Besides, as illustrated, the reduction of  $I_2/I_1$  ratio reveals the exposure of large size defects is enhanced, which accelerates the diffusive process of oxygen anions, and a consecutive supply of oxygen from the bulk to the surface would ensure a promoted reducibility [32]. Based on previous studies, re-adsorption of oxygen on the point defects was much slower than that on the multiple defects, indicating that multiple defects are liable to be occupied with oxygen clusters in rich oxygen conditions

[32]. Therefore, the mono-vacancies are preferred to combine with oxydryl under alkali conditions, which are decisive to capture the precursor of Pt species (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O).

According to the sequential analyses of these substances by HR-TEM (Figs. S5–S7), the Pt nanoparticles cannot be founded in these HR-TEM and HAADF images. It is hard to distinguish the Pt atoms under the TEM experimental conditions. Therefore, the aberration-corrected scanning transmission electron microscopy (ac-STEM) was subsequently utilized to probe the Pt<sub>1</sub>-CeO<sub>2</sub> catalysts (Fig. 1a–c), and individual Pt atoms could be observable as uniformly dispersed. The

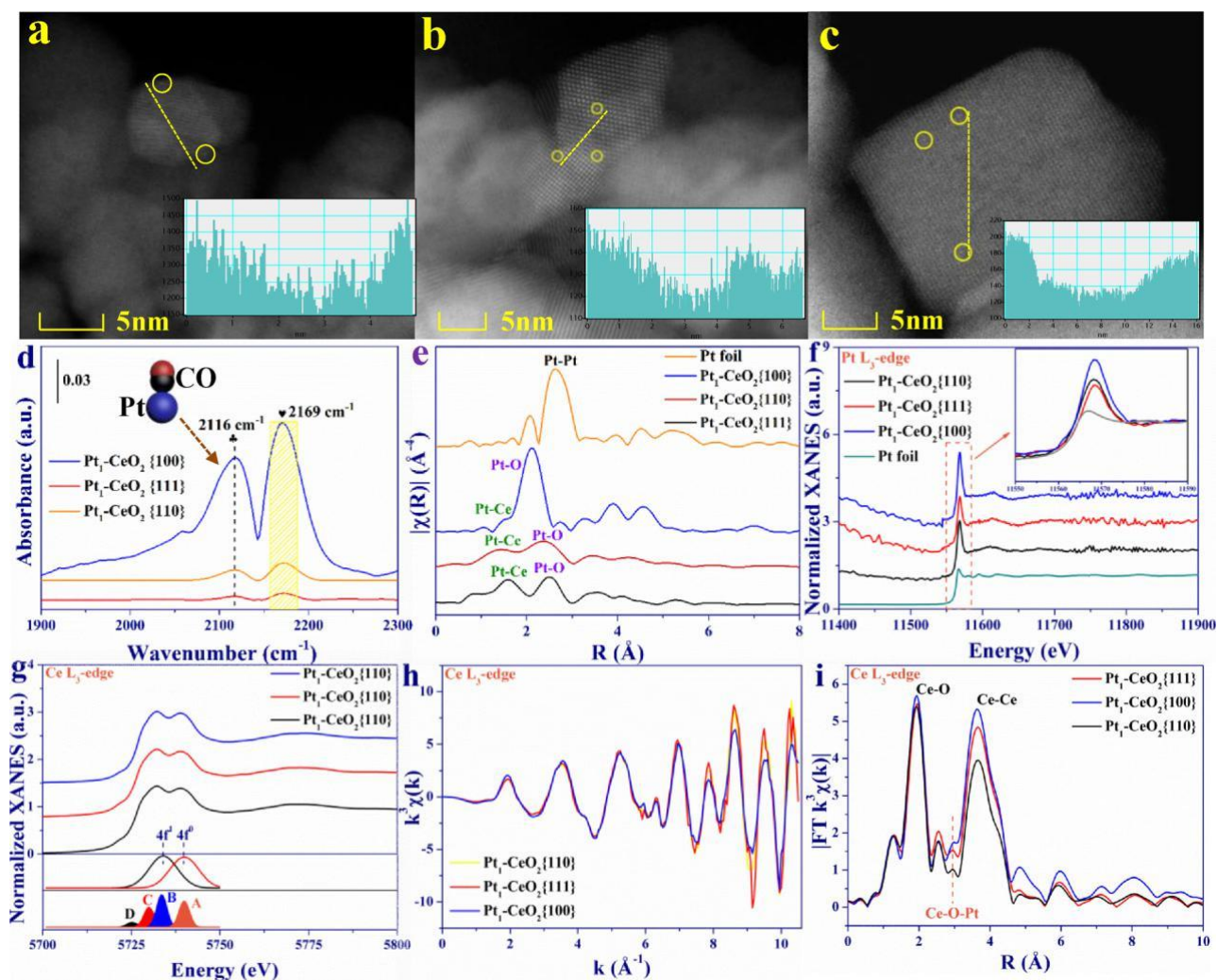


Fig. 1. (a-c) Aberration corrected HAADF-STEM images of Pt<sub>1</sub>-CeO<sub>2</sub> materials (the pixel intensity profile was supplied in the insert images); (d) In situ FTIR spectra of CO adsorption over prepared materials; (e) R-space spectra from Pt L<sub>3</sub>-edge EXAFS data; (f) Pt L<sub>3</sub>-edge XANES spectra; (g) Ce L<sub>3</sub>-edge XANES spectra; (h) Corresponding EXAFS fitting curves at the k space; (i) k<sup>3</sup>-weighted Fourier transform EXAFS spectra at the R space.

Table 2

Structural parameters of Pt<sub>1</sub>-CeO<sub>2</sub> materials extracted from the EXAFS fitting results.

Sample	Pt-Ce		Pt-O		$\sigma^2$ (Å <sup>2</sup> )	E <sub>0</sub> (eV) <sup>b</sup>
	R (Å)	CN <sup>a</sup>	R (Å)	CN <sup>a</sup>		
Pt <sub>1</sub> -CeO <sub>2</sub> {110}	1.896 ± 0.011	2.13 ± 0.05	2.01 ± 0.002	3.05 ± 0.14	0.003 ± 0.002(Pt)	1.13 ± 0.02
Pt <sub>1</sub> -CeO <sub>2</sub> {100}	1.901 ± 0.005	1.78 ± 0.06	1.98 ± 0.003	2.45 ± 0.05	0.002 ± 0.001(Pt)	1.45 ± 0.06
Pt <sub>1</sub> -CeO <sub>2</sub> {111}	1.903 ± 0.006	2.01 ± 0.11	2.03 ± 0.008	2.32 ± 0.18	0.007 ± 0.001(Pt)	1.56 ± 0.03

Note: <sup>a</sup> Integer number constrained. <sup>b</sup> Constrained to be equal for same fit. R is interatomic distance (the bond length between central atoms and surrounding coordination atoms); CN is the coordination number;  $\sigma^2$  is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); E<sub>0</sub> is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model).

abundant representative ac-STEM images were supplied to clearly identified the existence of single atoms over prepared Pt<sub>1</sub>-CeO<sub>2</sub> samples (Fig. S8). Subsequently, further characterization of these materials was conducted by infrared spectroscopy, utilizing CO as the probe molecule. In Fig. 1d, the adsorption bands centered at 2169 cm<sup>-1</sup> at room temperature are attributed to the gaseous carbon monoxide adsorbed over the surface of catalysts. The obtained adsorption peaks at 2116 cm<sup>-1</sup> are the evidence of CO in the presence of atomically dispersed Pt [21,44,45]. Importantly, XAFS as an authoritative method is very relevant to get further proof of the single atom status, as displayed in Fig. 1e and Table 2. The prominent peak centered at around 1.89–1.90

and 1.98–2.03 Å are assigned to the Pt-Ce and Pt-O contribution, respectively. Almost no Pt-Pt contribution is observed [46–48]. The coordinations of Pt atoms with Pt-Ce and Pt-O bonding are included in Table 2. To be specific, the Pt<sub>1</sub>-CeO<sub>2</sub>{100} sample exhibits a Pt-O coordination number of 2.45 ± 0.05 with a radial distance of 1.98 ± 0.003 Å and possesses a Pt-Ce coordination number of 1.78 ± 0.06 with a radial distance of 1.901 ± 0.005 Å.

An in-depth analysis of the electronic metal-support interaction is the fundamental of understanding the stabilization mechanism in this active interface. Herein, a great number of methods were then developed that involved electronic structure analysis of Pt<sub>1</sub>-CeO<sub>2</sub> SACs. The Pt L<sub>3</sub>-edge normalized XANES (Fig. 1f) revealed the electronic states

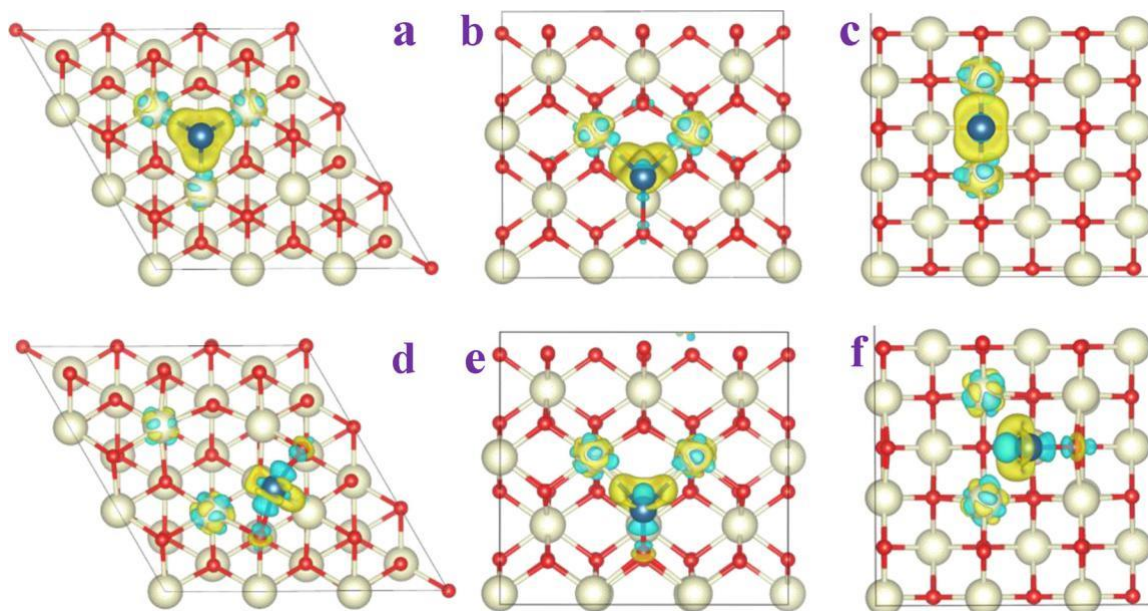


Fig. 2. Calculated charge density differences of (a) Pt<sub>1</sub>-undistorted-CeO<sub>2</sub>{111}, (b) Pt<sub>1</sub>-undistorted-CeO<sub>2</sub>{110}, (c) Pt<sub>1</sub>-undistorted-CeO<sub>2</sub>{100}, (d) Pt<sub>1</sub>-distorted-CeO<sub>2</sub>{111}, (e) Pt<sub>1</sub>-undistorted-CeO<sub>2</sub>{110}, and (f) Pt<sub>1</sub>-undistorted-CeO<sub>2</sub>{100}.

above the Fermi level concentrated on platinum. Since the density of unoccupied 5d electronic states can be probed by the L<sub>3</sub> transition, it is widely accepted to use the white-line (WL) intensity as an indicative index for the oxidation state of Pt [49]. Obviously, the Pt<sub>1</sub>-CeO<sub>2</sub> samples have significantly higher WL intensities than Pt foil, implying more Pt d-band vacancies and consequently a larger amount of Pt with positive charge centering in prepared SACs, which is attributed to the electron transfer through strong metal-support interaction after Pt atoms stabilized [49,50]. The positively charged intensity of Pt over prepared SACs increased in the order of Pt<sub>1</sub>-CeO<sub>2</sub>{111} < Pt<sub>1</sub>-CeO<sub>2</sub>{110} < Pt<sub>1</sub>-CeO<sub>2</sub>{100}, illustrating that the mutual action between Pt atoms and CeO<sub>2</sub> supports is impacted by the exposed facet of CeO<sub>2</sub> due to its diverse electronic structures. In addition, the systematic edge change of the Pt L<sub>3</sub> edge over Pt<sub>1</sub>-CeO<sub>2</sub>{100} towards higher energy, implying that the electron donation extent of Pt to CeO<sub>2</sub> support is the most intense among all SACs [50].

From Ce L<sub>3</sub>-edge normalized XANES spectra (Fig. 1g), all of the major bands presented a double white line characteristic of a mixture of the two cerium ground-state electronic configurations, 4f<sup>0</sup> and 4f<sup>1</sup> [51]. In order to eliminate the influence from the background, all spectra involve subtraction of an arctangent function, and then Gaussian functions are used for fitting. These exhibit two evident peaks often marked as A and B. Peak A is assigned as a Ce<sup>4+</sup> peak with the final state 2p<sup>5</sup>4f<sup>0</sup>5d<sup>1</sup>, indicating an excitation of an electron from the Ce 2p shell to its 5d shell, with an absence of an electron in the 4f shell [51,52]. Peak B is a Ce<sup>4+</sup> peak as well, but with a different final state of 2p<sup>5</sup>4f<sup>1</sup>5d<sup>1</sup>v, indicating another excited electron from the valence band (O 2p shell) to the Ce 4f shell besides a similar one with peak A, and a hole (v) is generated in the valence band. Peak C is occasionally termed as a Ce<sup>3+</sup> peak [51,52]. An extra minor peak (D) exists at pre-edge and possibly is caused by transitions to the bottom of the conduction band [51,52]. Direct details on the fraction of Ce present as Ce<sup>3+</sup> can be found from the ratio region of peak C (related with Ce<sup>3+</sup>) and the total region of peak A, B, and C (A and B are related with Ce<sup>4+</sup>). The enhancement of Ce<sup>3+</sup> ratio for SACs is ascribed to the balancing of Fermi level and charge density between Pt atoms and CeO<sub>2</sub> support through strong metal-support interaction, which was determined by fitting of the Lorentzian peak (Figs. 1h and S9). A peak around 1.8 Å<sup>-1</sup> corresponds to single scattering from first shell oxygen atoms. The peaks detected at 1.8 and 9.4 Å<sup>-1</sup> are attributed to the refinement of first and

higher neighbor correlation [51,52]. The difference intensity of detected peaks probably attributes to the crystal size of CeO<sub>2</sub> particle. In addition, as displayed in Fourier transform magnitudes of Ce L<sub>3</sub>-edge EXAFS (Fig. 1i), the Ce-O and Ce-Ce path are linked with the signal at 1.9 and 3.6 Å, respectively [53]. Importantly, the band detected at 2.9 Å is assigned to the Ce-O-Pt [52]. It is reasonably supposed that the structure is taken into distortion under strong metal-support interaction from curve-fitting analysis of our XAFS results.

The formation of Pt-O-Ce interface after Pt atoms stabilized in defects and the balance of charge density through SMSIs was detailed by the theoretical thermodynamic analysis. The modeling structures of Pt atoms adsorbed at oxygen vacancies over CeO<sub>2</sub> surfaces are shown in Fig. S10. On these surfaces, Pt atoms are connected by surrounding Ce and the adsorption energies of Pt are found to be -4.00, -3.29, and -3.48 eV over the Pt<sub>1</sub>-undistorted-CeO<sub>2</sub>{111}, {110} and {100} surfaces, respectively. Notably, we observed that the Pt-O-Ce interfaces are inclined to distort for thermodynamic stable through the metal-support strong interaction (Fig. S11), where single atom Pt is connected with Ce and surface O atoms. The intense electron transfers in these distorted Pt-O-Ce interfaces are quantified. On the interface of Pt<sub>1</sub>-distorted-CeO<sub>2</sub>{111}, the shift of Pt takes endothermic energy of 0.72 eV. However, the Pt<sub>1</sub>-distorted-CeO<sub>2</sub>{110} and Pt<sub>1</sub>-distorted-CeO<sub>2</sub>{100} surfaces are identified to form more easily with the exothermic energy of -0.64 and -0.74 eV. The results illustrate that the structure distortion process over Pt<sub>1</sub>-CeO<sub>2</sub>{100} sample tends to occur spontaneously. To further investigate the changes of electronic structure and valence state during interface distortion, the charge density difference (CDD) was calculated and given in Fig. 2. Combined with the magnetic moment of Ce, single atom Pt gets the charge and shows the valence of -2 with no Ce<sup>4+</sup> have been reduced on the surface of Pt-undistorted-CeO<sub>2</sub> catalysts. When the interface shifted, the balance of charge density increase and reduction, and the change of magnetic moment of Ce

indicate that Pt shows the valence of 0 with two Ce<sup>4+</sup> have been reduced to Ce<sup>3+</sup>.

Ce species in these SACs were presented in mixed Ce<sup>3+</sup> and Ce<sup>4+</sup> valence states and the existence of Ce<sup>3+</sup> was primarily ascribed to the balance of charge density during interface distortion. Therefore, the content of Ce<sup>3+</sup> species can be seen as an indicator of the distorted degree over prepared SACs [54,55]. The distortion degree in this study is defined for evaluating the intensity and extent of the surficial



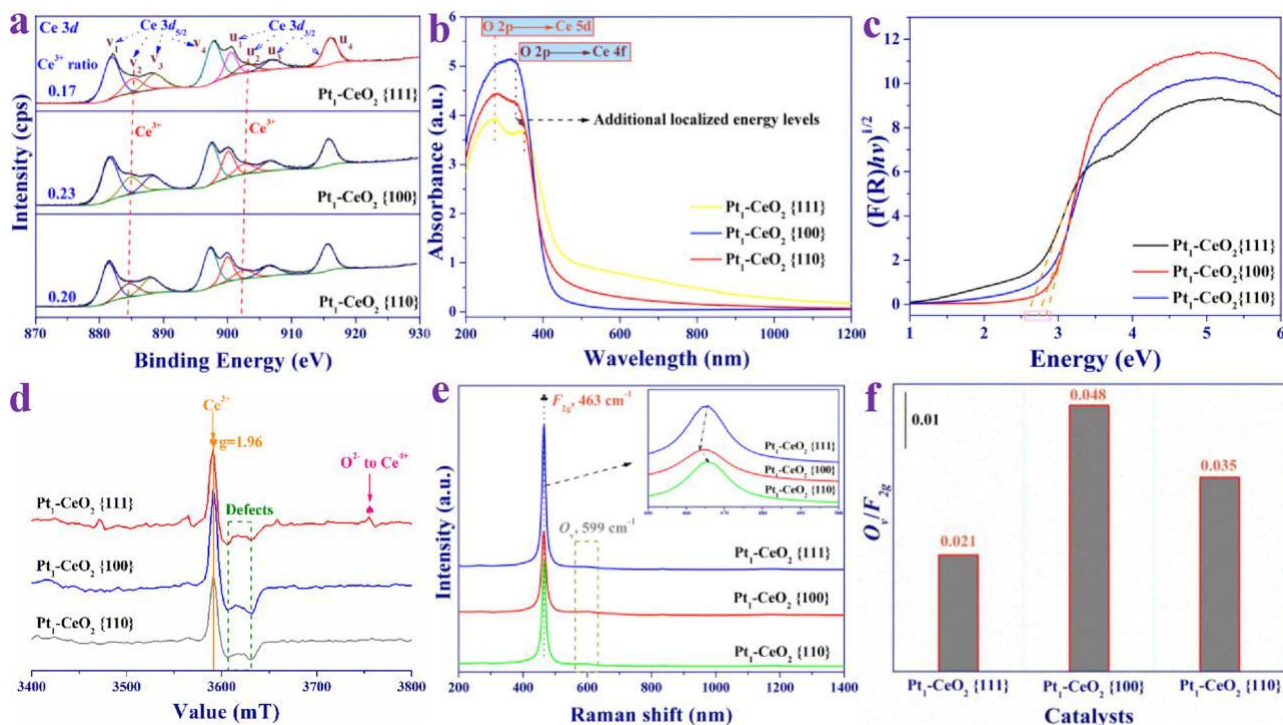


Fig. 3. (a) Ce 3d XPS spectra of Pt<sub>1</sub>-CeO<sub>2</sub> materials; (b) UV-vis absorption spectrum of Pt<sub>1</sub>-CeO<sub>2</sub> catalysts; (c) The optical bandgap of prepared samples evaluated by linear extrapolating; (d) Electron paramagnetic resonance of Pt<sub>1</sub>-CeO<sub>2</sub> samples; (e-f) Laser Raman spectra of Pt<sub>1</sub>-CeO<sub>2</sub> materials.

PtOeCe bonding torsional strength [24,38]. The PtOeCe bonding will transform the original bonding structure and angle as the function of the stabilization process. The higher distortion degree in the single atom Pt<sub>1</sub>-CeO<sub>2</sub> catalysts means that the PtOeCe bonding exhibits the more intense deformation through a strong metal-support interaction process compared with its origin combination methods. XPS data have been reported as another evidence for proving the resulting variation of valence states through SMSIs in these SACs (Figs. 3a, S12–S13). For Ce 3d spectra (Fig. 3a), the deconvoluted peaks of v<sub>1</sub>, v<sub>2</sub>, v<sub>3</sub>, v<sub>4</sub> were a consequence of the Ce 3d<sub>5/2</sub> region, and the labeled peaks of u<sub>1</sub>, u<sub>2</sub>, u<sub>3</sub>, u<sub>4</sub> resulted from the Ce 3d<sub>3/2</sub> region [56]. In detail, the peaks signed as v<sub>2</sub> and u<sub>2</sub> corresponded to the Ce<sup>3+</sup> valence species and the other signed peaks were Ce<sup>4+</sup> valence species [56,57]. The proportion of Ce<sup>3+</sup>/(Ce<sup>3+</sup>+Ce<sup>4+</sup>) in each catalyst was then evaluated quantitatively and the ratios were obtained as 0.23, 0.20, and 0.17 for the Pt<sub>1</sub>-CeO<sub>2</sub>{100}, Pt<sub>1</sub>-CeO<sub>2</sub>{110}, and Pt<sub>1</sub>-CeO<sub>2</sub>{111} catalysts, respectively, which can be listed as an indicator for the sequence of interface distortion intensity. Notably, Pt<sub>1</sub>-CeO<sub>2</sub>{100} exhibited the highest ratio of Ce<sup>3+</sup>, attributing to the most intensity of electron transfer in the distorted interface during SMSIs among these samples, which is generated by balancing Fermi energy level between the Pt species and CeO<sub>2</sub> supports.

The electron transfer process in the distorted interface was further verified by the UV-vis absorption spectra, given in Figs. 3b and S14. Two strong absorption bands centered at about 296 and 335 nm were ascribed to the charge-transfer transition from O 2p to Ce 5d orbital and O 2p to Ce 4f orbital, respectively [58,59]. The optical bandgaps calculated based on the UV-vis absorption spectra of Pt<sub>1</sub>-CeO<sub>2</sub>{100}, Pt<sub>1</sub>-CeO<sub>2</sub>{110}, and Pt<sub>1</sub>-CeO<sub>2</sub>{111} are 2.85, 2.75, and 2.58 eV, respectively (Fig. 3c). The redshift of Pt<sub>1</sub>-CeO<sub>2</sub>{100} is attributable to the extra concentrated energy levels (oxygen vacancies) within the bandgap, absorbing with relatively low energy photons, which was further proved by electron paramagnetic resonance (Fig. 3d). The extra strong resonance line at g = 1.96 is assigned to the responding of Ce<sup>3+</sup> species [60,61]. This increased intensity of Ce<sup>3+</sup> single over Pt<sub>1</sub>-CeO<sub>2</sub>{100} sample is attributed to the decrease of Ce<sup>4+</sup> ions to Ce<sup>3+</sup>

with electrons produced by the structure distortion; moreover, this protruding electron is also inclined to be trapped in oxygen vacancies around the distorted interface, which gives a characteristic peak at about 3610–3630 mT in EPR spectra [60,61]. The abundant oxygen vacancies promoted by the distorted Pt-O-Ce interface were valued by Raman spectra accordingly. As displayed in Fig. 3e, the abrupt strong peak approximately 463 cm<sup>-1</sup> and another weak one at 603 cm<sup>-1</sup> result from the oxygen atoms symmetric stretching (the fluorite structure, F<sub>2g</sub> signal) and Frenkel-type anion defects (O<sub>v</sub>), respectively [56,57,59,60]. The blue shift of F<sub>2g</sub> peak from Pt<sub>1</sub>-CeO<sub>2</sub>{100} to Pt<sub>1</sub>-CeO<sub>2</sub>{110} and Pt<sub>1</sub>-CeO<sub>2</sub>{111} indicates the enhancement of defects content [41,59,60]. In-depth, the concentration of the oxygen vacancy is indexed with the relative ratio between the defect band and the F<sub>2g</sub> signal [57]. As shown in Fig. 3f, the highest O<sub>v</sub>/F<sub>2g</sub> value is confirmed over the Pt<sub>1</sub>-CeO<sub>2</sub>{100} sample, revealing that the enhanced distortion of the interface greatly promoted the generation of defects around it.

The above experimental and theoretical results illustrate that upon Pt atoms are stabilized in surface mono-defects, and the formed Pt-O-Ce interface will be taken into distortion spontaneously to keep thermo-dynamics stable through strong metal-support interactions. This interaction is combined with the balance of charge density, which brings about the variation of valence state and electronic structure of SACs. The ratio of Ce<sup>3+</sup> species is a clear positive correlation with the distortion degree of the interface, which is predictable given the fact that this species is known as a crucial factor for stabilizing single atom sites in thermal reactions.

### 3.2. Oxygenated hydrocarbon oxidation over Pt<sub>1</sub>-CeO<sub>2</sub> single atom catalysts

The catalytic performance of Pt<sub>1</sub>-CeO<sub>2</sub> materials with distorted Pt-O-Ce interfaces was determined for oxygenated hydrocarbons removal (Fig. 4 and Table S1). We claimed that the Pt<sub>1</sub>-CeO<sub>2</sub>{100} material exhibits excellent decomposition efficiency (Fig. 4a), over which 90% of methanol (700 ppm) could be decomposed (T<sub>90</sub>) at just 52 °C, much lower than that of Pt<sub>1</sub>-CeO<sub>2</sub>{110} (T<sub>90</sub> of 68 °C) and Pt<sub>1</sub>-CeO<sub>2</sub>{111} (T<sub>90</sub>

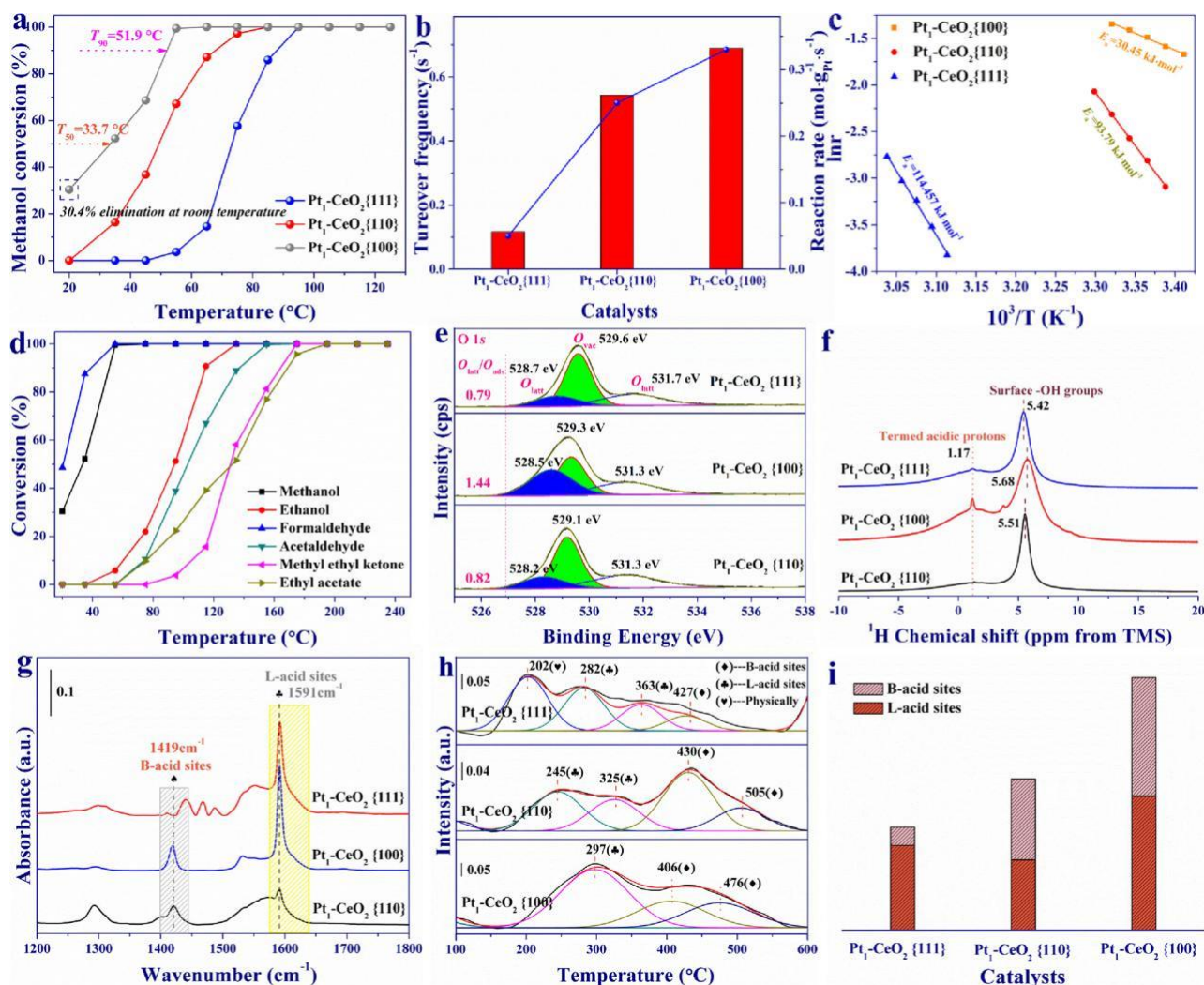


Fig. 4. (a) Catalytic performance of methanol oxidation over prepared Pt<sub>1</sub>-CeO<sub>2</sub> materials; (b) Reaction rate and turnover frequency for methanol oxidation over active catalysts at 50 °C; (c) Arrhenius plots of methanol oxidation over Pt<sub>1</sub>-CeO<sub>2</sub> catalysts; (d) Light-off curves of typical oxygenated hydrocarbons decomposition over Pt<sub>1</sub>-CeO<sub>2</sub>{100} material; (e) O 1s XPS spectra of Pt<sub>1</sub>-CeO<sub>2</sub> catalysts; (f) <sup>1</sup>H solid-state MAS NMR spectra of Pt<sub>1</sub>-CeO<sub>2</sub> materials; (g) NH<sub>3</sub>-IR experiments over Pt<sub>1</sub>-CeO<sub>2</sub> materials; (h,i) Temperature programmed desorption of NH<sub>3</sub> for Pt<sub>1</sub>-CeO<sub>2</sub> material.

of 88 °C) samples, which is a significantly lower temperature than typical active materials reported for methanol oxidation, e.g., 3.5 wt.% Au/Fe<sub>2</sub>O<sub>3</sub> (T<sub>90</sub> of 150 °C), 1.5 wt.% Pd/HY (T<sub>90</sub> of 130 °C) and Pt<sub>1</sub>-Co<sub>3</sub>O<sub>4</sub> (T<sub>90</sub> of 96 °C) catalysts (Table S2). A subsequent estimation for the reaction rate and turnover frequency (TOF) of Pt supported catalysts was provided. A reaction rate of 0.33 mol·g<sub>Pt</sub><sup>-1</sup>·s<sup>-1</sup> at 55 °C was determined for Pt<sub>1</sub>-CeO<sub>2</sub>{100} material, which is higher than that observed over Pt<sub>1</sub>-CeO<sub>2</sub>{110} (0.25 mol·g<sub>Pt</sub><sup>-1</sup>·s<sup>-1</sup>) sample and over 6 times higher than Pt<sub>1</sub>-CeO<sub>2</sub>{111} (0.05 mol·g<sub>Pt</sub><sup>-1</sup>·s<sup>-1</sup>) catalyst (Figs. 4b and S15). The TOFs exhibited were based on the dispersion of Pt in each catalyst (Figs. 4b and S16). The results clearly reveal that the activity of all Pt sites in Pt<sub>1</sub>-CeO<sub>2</sub>{100} catalyst (0.68 s<sup>-1</sup> at 50 °C) was substantially improved, which has a larger value over the other catalysts in previous literature on this reaction until now; particularly, 3.3 and 2.5 times higher than that reported over Pd/CeO<sub>2</sub>-ZrO<sub>2</sub> (0.22 s<sup>-1</sup>) and Pt<sub>1</sub>-Co<sub>3</sub>O<sub>4</sub> (0.29 s<sup>-1</sup>) catalysts (Table S2). Based on this data, Arrhenius plots were extracted and apparent activation energy (E<sub>a</sub>) was determined for methanol oxidation (Fig. 4c). The E<sub>a</sub> of Pt<sub>1</sub>-CeO<sub>2</sub>{100} catalyst (30.45 kJ mol<sup>-1</sup>) is substantially lower than that of Pt<sub>1</sub>-CeO<sub>2</sub>{110} (93.79 kJ mol<sup>-1</sup>) and Pt<sub>1</sub>-CeO<sub>2</sub>{111} (114.46 kJ mol<sup>-1</sup>) catalysts. The Pt<sub>1</sub>-CeO<sub>2</sub>{100} SAC with the highest distortion intensity exhibits the best catalytic efficiency for methanol oxidation; as expected, which was adopted to decompose typical oxygenated

hydrocarbons as proof of its universality, as displayed in Fig. 4d. For each of the substrates investigated, current literature reported catalysts are also displayed for comparison, as summarized Tables S3–S6. As demonstrated, the prepared Pt<sub>1</sub>-CeO<sub>2</sub>{100} catalyst exhibits considerable efficiency for the oxidation of formaldehyde, acetaldehyde, ethanol, methyl ethyl ketone, and ethyl acetate at low temperature (< 200 °C), compared with previously reported works.

According to the observed activity of Pt<sub>1</sub>-CeO<sub>2</sub> SACs, analysis is performed for detailed correlation between catalytic performance and structural properties including: high quantity of lattice oxygen (Fig. 4e), abundant surface acid sites (Fig. 4f–i), sufficient surface-bound hydroxyl species (Fig. 4f), low temperature reducibility (Fig. S17), suitable oxygen/methanol adsorption capacity (Figs. S18 and S19) and an abundance of oxygen vacancies (Fig. 3e, f and Table 1). According to the theoretical studies and experiment data involved in this work, we point out that the evident rise in the amount of lattice oxygen species and surface acid sites over the Pt<sub>1</sub>-CeO<sub>2</sub>{100} catalyst is possibly the utmost factor for improving the catalytic performance [6–8,12]. As shown in Fig. 4e, a fitting for O 1s XPS spectra of all materials reveals three peaks with binding energies of approximately 528.7, 529.6, and 531.7 eV, which can be associated with the lattice oxygen (O<sub>latt</sub>), oxygen vacancy (O<sub>vac</sub>), and surface adsorbed oxygen (O<sub>ads</sub>), respectively [62,63]. The relative content of surface oxygen vacancies over all



three samples was enhanced with the order of Pt<sub>1</sub>-CeO<sub>2</sub>{100} < Pt<sub>1</sub>-CeO<sub>2</sub>{110} < Pt<sub>1</sub>-CeO<sub>2</sub>{111}, which is ascribing to the more surface small neutral oxygen vacancies are occupied by the single atoms Pt sites in Pt<sub>1</sub>-CeO<sub>2</sub>{100} sample. It is widely known that with certain catalysts, lattice oxygen plays an important role in catalytic performance in the oxidation of hydrocarbons [4–6]. The results are quite noteworthy from quantification of the peaks attributed to lattice oxygen and surface adsorbed oxygen. The O<sub>latt</sub>/O<sub>ads</sub> ratio of Pt<sub>1</sub>-CeO<sub>2</sub>{100} material is calculated to be 1.44, which is noticeably higher than that of Pt<sub>1</sub>-CeO<sub>2</sub>{111} (O<sub>latt</sub>/O<sub>ads</sub> = 0.79) and Pt<sub>1</sub>-CeO<sub>2</sub>{110} (O<sub>latt</sub>/O<sub>ads</sub> = 0.82) catalysts.

For evaluating the acid sites of prepared SACs, <sup>1</sup>H solid-state MAS NMR (Fig. 4f) was subsequently incorporated to identify the unit structure of prepared materials. For these materials, the foremost peak observed at a chemical shift of roughly 1.17 ppm is attributable to the termed acidic protons and bands at around 5.42–5.68 ppm could indicate the asymmetric stretching of surface hydroxyl [64,65]. The enhanced intensity of characteristic peaks illustrates that the Pt<sub>1</sub>-CeO<sub>2</sub>{100} material possesses substantial proton-provided acid sites. The corresponding kind of acid species of all the materials was further estimated by NH<sub>3</sub>-IR (Fig. 4g) and NH<sub>3</sub>-TPD (Fig. 4h, i). For NH<sub>3</sub>-IR experiments (Fig. 4g), the bands detected at 1419 and 1591 cm<sup>-1</sup> could be used as an indication for the symmetric vibrations of NH<sub>4</sub><sup>+</sup> species on Brønsted acid sites and Lewis acid sites, respectively. The most intense peaks of NH<sub>3</sub> adsorption over Pt<sub>1</sub>-CeO<sub>2</sub>{100} sample illustrates that the enhanced amount and intensity of acid sites over the materials [6]. Furthermore, a subsequent deconvoluted with the Gauss curve fitting method for the NH<sub>3</sub>-TPD profiles of materials provides several peaks (Fig. 4h) corresponding to the physically-adsorbed NH<sub>3</sub> (< 220 °C), ammonia-adsorbed on Lewis acid sites (240–380 °C) and ammonia-adsorbed on Brønsted acid sites (> 400 °C) [6]. Accordingly, the quantitative assessment of different acid species was evaluated by counting the peak area of NH<sub>3</sub>-TPD experiment, as shown in Fig. 4i. The prepared Pt<sub>1</sub>-CeO<sub>2</sub>{100} SAC exhibits the maximum amount of Brønsted acid sites and Lewis acid sites [6]. The promoted Lewis acid sites correlate to the formation of oxygen vacancies; meanwhile, the abundant Brønsted acid sites promote VOC molecules adsorption and accelerate the regeneration of surface hydroxyl, which is benefit for intermediates decomposition during VOC oxidation.

### 3.3. Stabilizing Pt atoms by Pt-O-Ce interface distortion

The stability (especially; thermal and reaction stability) of a single atom catalyst is crucial for its application in thermal reactions. In this work, the electronic metal-support interaction in Pt-O-Ce interface is responsible for stabilizing Pt atom in Pt<sub>1</sub>-CeO<sub>2</sub> materials (Fig. 5a). In order to explore the reaction stability of SAC materials, an extra study was performed where the catalytic performance was monitored for an extended 800 min at 52 °C in a mixture airflow, as displayed in Fig. 5b. Negligible deactivation can be observed for all catalysts, suggesting

their excellent reaction stability in the total oxidation of methanol. As CO<sub>2</sub> is one of the reaction products, commonly present in industrial exhaust streams, it is of significance to clarify its influence on the long-term oxidation behavior of the SACs. As illustrated in Fig. 5c, CO<sub>2</sub> exhibited a detrimental effect on methanol oxidation ascribed to the strong adsorption of CO<sub>2</sub>, methanol, and O<sub>2</sub> molecules on the catalyst surface. When 3 vol.% CO<sub>2</sub> was introduced into the stream, the reduction of methanol conversion of ca. 4.6 %, 10.7 %, and 5.8 % can be observed over Pt<sub>1</sub>-CeO<sub>2</sub>{100}, Pt<sub>1</sub>-CeO<sub>2</sub>{110} and Pt<sub>1</sub>-CeO<sub>2</sub>{111} samples, respectively. Importantly, the original activity was restored after only 40–50 min of cutting off CO<sub>2</sub> in the feed, indicating that the decreases in activity are used as evidence for permanent changes to the SACs.

In order to determine whether these catalysts undergo thermal deactivation, the prepared SACs were annealed at different temperatures (300, 400, 600, and 800 °C) in air and the catalytic performance of resulting materials are shown in Fig. 6a–c. Obviously, the Pt<sub>1</sub>-CeO<sub>2</sub>{100} material possesses the highest thermal stability among these SACs, which displays the similar catalytic efficiency after calcinated at 300 or 400 °C and maintains 70 % catalytic efficiency (at 125 °C) after annealed at 800 °C. However, the activity of both Pt<sub>1</sub>-CeO<sub>2</sub>{110} and Pt<sub>1</sub>-CeO<sub>2</sub>{111} catalysts decreased greatly after annealed at 600 or 800 °C. For instance, the methanol oxidation efficiency (at 125 °C) de-creased to 29 % and 17 % after annealed at 800 °C for Pt<sub>1</sub>-CeO<sub>2</sub>{110} and Pt<sub>1</sub>-CeO<sub>2</sub>{111} samples, respectively. In order to illustrate the changes of single atom sites and CeO<sub>2</sub> supports after the annealed process at 800 °C, the HR-TEM and HAADF images were supplied (Figs. S20 and S21). The microstructure and lattice parameters remain unchanged during the thermal treatment at 800 °C in air condition. Nevertheless, the apparent agglomeration of Pt species was revealed by ac-STEM after this re-calcination process. Additionally, the variation of Pt sites over the re-calcined SACs was examined by the CO-IR experiment (Fig. 6d, f). The Pt atoms over Pt<sub>1</sub>-CeO<sub>2</sub>{110} and Pt<sub>1</sub>-CeO<sub>2</sub>{111} catalysts are totally converted into nanoparticles after annealed at 600 °C; in comparison, the characteristic peak of CO adsorption over Pt atoms can still be detected for Pt<sub>1</sub>-CeO<sub>2</sub>{100} sample calcined at 800 °C. The agglomeration of Pt single atoms is the dominant reason for catalyst deactivation under thermal conditions. The Pt atoms stabilized in CeO<sub>2</sub>{100} facet can prevent its agglomeration to some extent.

As discussed above, the prepared SACs exhibit the stability order of Pt<sub>1</sub>-CeO<sub>2</sub>{100} > Pt<sub>1</sub>-CeO<sub>2</sub>{110} > Pt<sub>1</sub>-CeO<sub>2</sub>{111}, consistent with the distortion degree of each active interface. Accordingly, in this work, the designed Pt atoms were stabilized in the exposed oxygen vacancies over CeO<sub>2</sub> support, and then the formed Pt-O-Ce interface will be taken into distortion to keep the thermodynamic stable state, which is the result of strong metal-support interactions and combining with the balance of charge density. Based on the electronic structure analysis of prepared SACs (Fig. 3), the most intense of charge transfer was revealed between Pt atoms and CeO<sub>2</sub>{100} facets, which confirmed the outstanding stability under thermal and reaction conditions in this Pt-O-Ce interface.

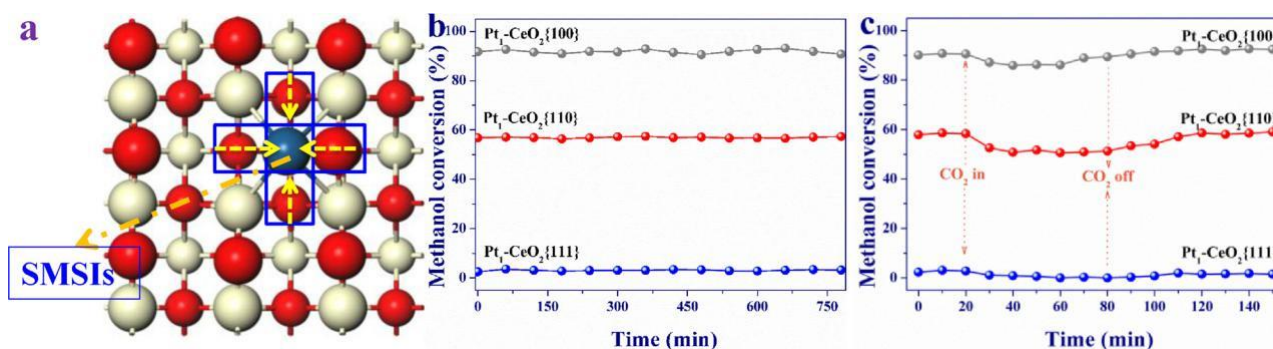


Fig. 5. (a) Optimistic structure of distorted Pt-O-Ce interface over Pt<sub>1</sub>-CeO<sub>2</sub>{100} catalyst; (b) Reaction stability and (c) CO<sub>2</sub>-resistance tests of prepared Pt<sub>1</sub>-CeO<sub>2</sub> materials for methanol oxidation at 52 °C.

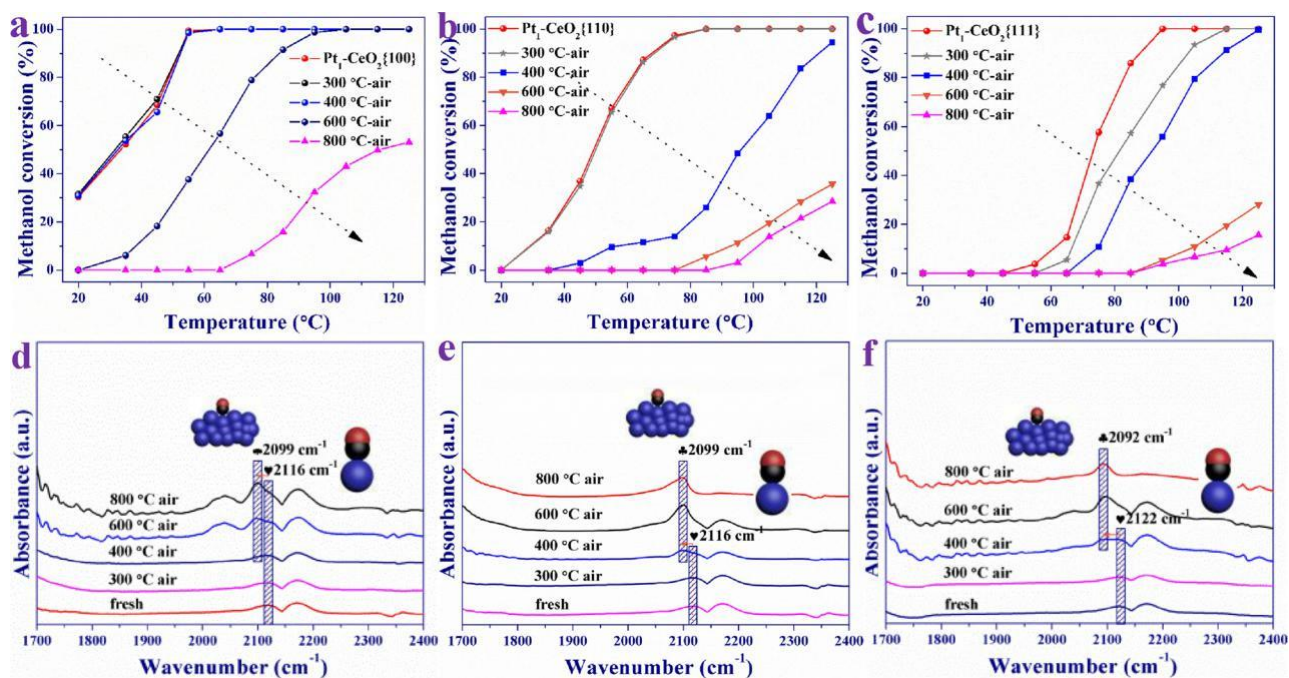


Fig. 6. (a-c) The catalytic performance for methanol oxidation over prepared Pt<sub>1</sub>-CeO<sub>2</sub> materials after annealing at different temperatures; (d-f) CO-IR experiments of prepared Pt<sub>1</sub>-CeO<sub>2</sub> materials after annealing at different temperatures.

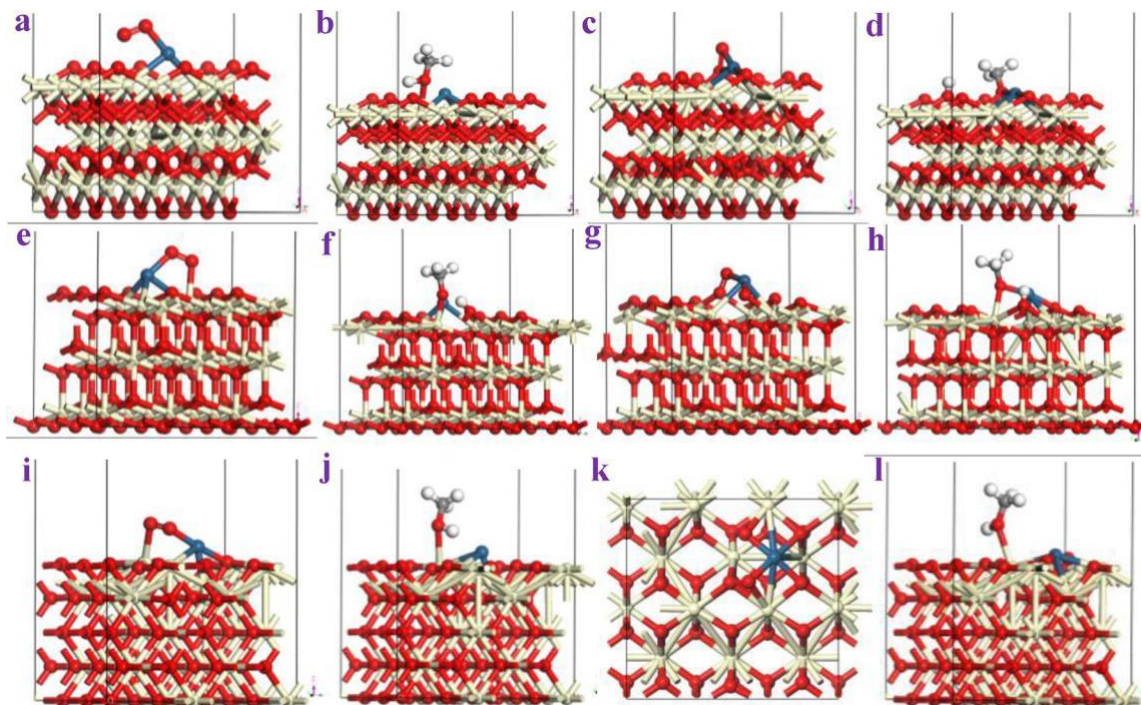


Fig. 7. The optimistic structure of O<sub>2</sub> adsorption over (a) Pt<sub>1</sub>-undistorted-CeO<sub>2</sub>(100), (c) Pt<sub>1</sub>-distorted-CeO<sub>2</sub>(100), (e) Pt<sub>1</sub>-undistorted-CeO<sub>2</sub>(111), (g) Pt<sub>1</sub>-distorted-CeO<sub>2</sub>(111), (i) Pt<sub>1</sub>-undistorted-CeO<sub>2</sub>(110), and (k) Pt<sub>1</sub>-distorted-CeO<sub>2</sub>(110) materials; The optimistic structure of methanol adsorption over (b) Pt<sub>1</sub>-undistorted-CeO<sub>2</sub>(100), (d) Pt<sub>1</sub>-distorted-CeO<sub>2</sub>(100), (f) Pt<sub>1</sub>-undistorted-CeO<sub>2</sub>(111), (h) Pt<sub>1</sub>-distorted-CeO<sub>2</sub>(111), (j) Pt<sub>1</sub>-undistorted-CeO<sub>2</sub>(110), and (l) Pt<sub>1</sub>-distorted-CeO<sub>2</sub>(110) materials (red, gray, white, faint yellow, and indigo spheres represents the O, C, H, Ce, and Pt atoms, respectively) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

The distortion of the active interface significantly promotes the capacity of methanol and O<sub>2</sub> adsorption, which is regarded as another crucial reason for improving the stability of SACs. The adsorption energies and configurations of CH<sub>3</sub>OH and O<sub>2</sub> on the Pt<sub>1</sub>-CeO<sub>2</sub> surfaces were shown in Figs. 7, S22–S23, and Table 3. On the surfaces of Pt<sub>1</sub>-undistorted-CeO<sub>2</sub> catalysts, CH<sub>3</sub>OH and O<sub>2</sub> molecules adsorb on them

with low adsorption energies (> -1.0 eV). Two exceptions of O<sub>2</sub> adsorption on Pt<sub>1</sub>-undistorted-CeO<sub>2</sub>(110) and CH<sub>3</sub>OH adsorption on Pt<sub>1</sub>-undistorted-CeO<sub>2</sub>(100) are due to the occurrence of Pt atom shift and structural distortion after O<sub>2</sub> and CH<sub>3</sub>OH adsorption. It can be found in Table 3 that the adsorption energies of CH<sub>3</sub>OH and O<sub>2</sub> on Pt<sub>1</sub>-distorted-CeO<sub>2</sub> catalysts are higher than Pt<sub>1</sub>-undistorted-CeO<sub>2</sub> catalysts.



**Table 3**  
CH<sub>3</sub>OH and O<sub>2</sub> adsorption on Pt<sub>1</sub>-CeO<sub>2</sub> surfaces.

Eads (eV)	Pt <sub>1</sub> -CeO <sub>2</sub> (111)		Pt <sub>1</sub> -CeO <sub>2</sub> (110)		Pt <sub>1</sub> -CeO <sub>2</sub> (100)	
	undistorted	distorted	undistorted	distorted	undistorted	distorted
CH <sub>3</sub> OH-ads	-0.36	-2.33	-0.66	-1.92	-1.66	-3.45
O <sub>2</sub> -ads	-0.41	-1.91	-3.01	-2.37	-0.17	-2.61

Particularly, for CH<sub>3</sub>OH adsorption on Pt-distorted-CeO<sub>2</sub> catalysts, the O-H of CH<sub>3</sub>OH ruptures spontaneously with O and H connected with Ce/Pt and surface oxygen (O<sub>s</sub>), respectively. Among them, CH<sub>3</sub>OH has the strongest adsorption ability on the surface of Pt<sub>1</sub>-distorted-CeO<sub>2</sub>(100). For O<sub>2</sub> adsorption on Pt<sub>1</sub>-distorted-CeO<sub>2</sub> catalysts, the oxygen molecules fill the exposed oxygen vacancies and connect with neighboring Ce and Pt. The Pt<sub>1</sub>-distorted-CeO<sub>2</sub>(100) surface also possesses the strongest O<sub>2</sub> adsorption. The electronic metal-support interaction in this distorted interface is integrant for stabilizing Pt atom in Pt<sub>1</sub>-CeO<sub>2</sub> materials, which will promote the development and application of stable single atom materials in thermal catalytic reactions.

### 3.4. The intrinsic mechanism for methanol oxidation

The oxidation mechanism and reaction pathways are crucial for the wide application of SACs in hydrocarbon oxidation [6–8,12]. Therefore, the methanol oxidation mechanism over prepared Pt<sub>1</sub>-CeO<sub>2</sub> materials is explored by in situ experiments and DFT studies. In this work, the oxidation of methanol follows a first-order reaction due to the excess of oxygen in the reaction system [12]. As displayed in Fig. 8a–c, the peaks at around 3603–3744 cm<sup>-1</sup> are assigned to the strengthening of surface hydroxyl [6]. The bands between 2780 and 2994 cm<sup>-1</sup> are associated with the C–H bond vibration; thereinto, the frequency centered at 2830 and 2953 cm<sup>-1</sup> are attributed to the δ(C–H) and ζ(C–H) from –CH<sub>2</sub>–CH<sub>3</sub> groups, respectively [66,67]. The confirmation of methoxyl groups (–CH<sub>3</sub>O) was centered at 1021 or 1033 cm<sup>-1</sup>, primarily coming from the OeH bond activation over the active interface [67–69]. The stretching of –CH<sub>2</sub>O groups was formed due to the breakage of C–H bond over methoxyl, which is in line with our previous study [12]. However, the monitored peaks appearing at a relative low temperature around 1060–1090 cm<sup>-1</sup> are indicative of a bridging mode of asymmetrical carbonyl (C = O) groups, which evidently vanishes with temperature increasing [68,69]. This phenomenon strongly indicates that the methanol oxidation processes obey different reaction paths along with temperature ranging. In addition, the detected peaks at 1373 cm<sup>-1</sup> belong to the signal of dioxy-methylene (–CH<sub>2</sub>OO) groups [65,68,69]. The observed sharp peaks at around 1587 or 1588 cm<sup>-1</sup> are associated with carboxyl species (–OCO), which may mainly from the dissociation of dioxy-methylene (DOM) intermediates [66,68,69].

For in-depth analysis of reaction mechanism, we carried out the in situ DRIFTS experiments by switching the reaction conditions at temperatures of T<sub>15</sub> and T<sub>85</sub> during methanol oxidation. As provided in Fig. 8d–f, the methoxyl species are not impacted by changing reaction atmosphere and the peaks of carbonyl groups take the lead at the beginning of reaction in N<sub>2</sub> condition. Obviously, the enhanced intensity peaks at 1373 and 1587/1588 cm<sup>-1</sup> correlate to an increase of DOM and carboxyl species when the air was introduced into the reaction system (the band of carbonyl disappeared in the presence of air). When the N<sub>2</sub> source was re-filled into the reaction cavity, the intermediates are shown to be recovered similarly with the beginning stage. The above results verify that the methanol activation obeys the L-H mechanism under relative low temperatures [7]. In this condition, the surface adsorbed oxygen is adopted as the active oxygen species, which participate in the activation and the DOM (1373 cm<sup>-1</sup>) and carboxyl (1587/1588 cm<sup>-1</sup>) species are produced as the main intermediates.

When the surface oxygen is less, the methanol molecule was decomposed through step broken of the C–H bond in this condition. Interestingly however, differences in the spectra can be seen for the methanol oxidation mechanism over the mono-dispersed Pt-O-Ce interface with the temperature increasing (Fig. 8g–i). Changing the reaction atmosphere at 150 °C did not obviously affect the formation of DOM (1373 cm<sup>-1</sup>) and carboxyl (1587/1588 cm<sup>-1</sup>) species during methanol decomposition, suggesting that these species are mainly generated by the lattice oxygen. It can be concluded that the methanol oxidation at high temperature obeys the MVK mechanism [6,12]. Understandably, the assignments of these vibrational features are ascribed to the distortion of the Pt-O-Ce interface. The Pt atoms are stabilized in the vacancies and the formation of Pt-O-Ce active interface takes into most stability through the distortion process, which is the result of strong metal-support interaction and combining with the intense electron transfer. The compact mutual effect increases the energy barrier for lattice oxygen activation; therefore, the surface adsorbed oxygen is adopted as the active oxygen species and methanol oxidation obeys the L-H mechanism at relative low temperature. With the temperature increasing, the lattice oxygen species from larger oxygen vacancy clusters around Pt atoms sites are activated and promoting the methanol oxidation process tremendously.

Accordingly, the activation mechanism of methanol oxidation over the active Pt-O-Ce interface is proposed and summarized in Fig. 8j. The distortion of the Pt-O-Ce interface enhanced the adsorption of methanol molecules. Consequently, the O assisted OeH bond of methanol is activated, forming adsorbed methoxyl species. It is expected that in this distorted Pt-O-Ce interface, the oxygen species will be supplied at the support/nanoparticle perimeter or on defect sites. Adsorbed methoxyl species undergo β-H transfer with a neighboring O atom and surface hydroxyl group on the surface, forming adsorbed DOM species. The presence of adsorbed DOM molecules is decomposed through a broken process to produce carboxyl intermediates over Pt atoms, which are oxidized into H<sub>2</sub>O and CO<sub>2</sub> evidently. The study of the intrinsic mechanism helps to determine the real active sites during oxidation reactions over SACs and understand the mechanism in a more comprehensive view.

According to the results of decomposition routes and analysis of electronic structure upon, the reaction pathway for CH<sub>3</sub>OH oxidation on Pt<sub>1</sub>-distortion-CeO<sub>2</sub>(100) catalyst revealed by theoretical calculations is shown in Fig. 9, comprised of structures of essential intermediates and transitional state. For a clear illustration, the complete mechanism for reaction consists of several steps: CH<sub>3</sub>OH and O<sub>2</sub> adsorption (states (a)–(c)); two-step C–H cleavage (states (TS1)–(e)); H<sub>2</sub>O desorption (state (f)); C–H cleavage (state (g)); CO<sub>2</sub> and H<sub>2</sub>O desorption (state (h)). After CH<sub>3</sub>OH adsorption (state (b)), OH group of CH<sub>3</sub>OH molecule dissociate spontaneously (CH<sub>3</sub>OH + O<sub>s</sub> → CH<sub>3</sub>O + O<sub>s</sub>H), and O<sub>2</sub> adsorb on the surface with the energy of -0.09 eV and OeO distance of 1.28 Å (state (c)). With the assistance of adsorbed oxygen species, the H of CH<sub>3</sub>O transfers to one oxygen atom with the activation barrier and reaction energy of 0.23 and -1.55 eV, respectively. During this process, the C of CH<sub>2</sub>O combines with the other oxygen atom to form CH<sub>2</sub>O<sub>2</sub>OH group (state (TS1)–(d), CH<sub>3</sub>O + O<sub>2</sub> → CH<sub>2</sub>O<sub>2</sub>OH). Then, a breakdown happens to the C–H bond of CH<sub>2</sub>O<sub>2</sub>OH, along with the transfer of H to neighboring OH to produce H<sub>2</sub>O (state (TS2)–(e), CH<sub>2</sub>O<sub>2</sub>OH → CHO<sub>2</sub> + H<sub>2</sub>O). The barrier for the second C–H bond cleavage is 0.44 eV, with



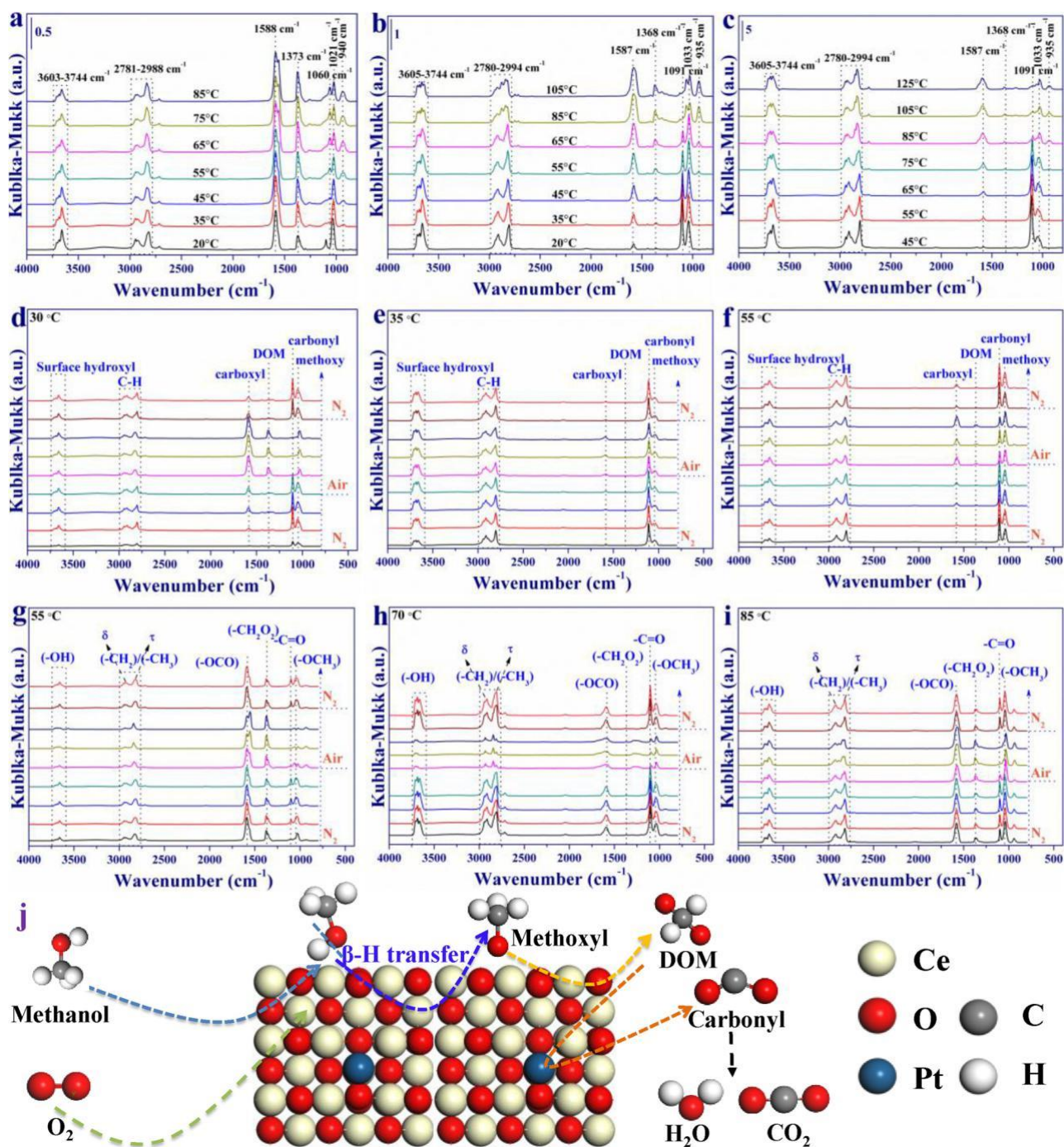


Fig. 8. In situ DRIFTS spectra for methanol oxidation over (a,d,g) Pt<sub>1</sub>-CeO<sub>2</sub>{100}, (b,e,h) Pt<sub>1</sub>-CeO<sub>2</sub>{110} and (c,f,i) Pt<sub>1</sub>-CeO<sub>2</sub>{111} single atom catalysts; (j) The proposed oxidation mechanism for methanol oxidation over Pt<sub>1</sub>-CeO<sub>2</sub>{100} catalyst.

exothermic reaction energy of 2.99 eV. It takes 0.56 eV to make H<sub>2</sub>O desorption (state (f)). Then, the H of CHO<sub>2</sub> transfer to surface O<sub>3</sub>H species accompanied by the generation of CO<sub>2</sub> and H<sub>2</sub>O (state (g)). The step of CHO<sub>2</sub> + O<sub>3</sub>H → CO<sub>2</sub> + H<sub>2</sub>O<sub>s</sub> takes endothermic energy of 1.61 eV. After CO<sub>2</sub> and H<sub>2</sub>O desorption ( $E_{\text{des}} = 1.59$  eV), the surface restores to the Pt<sub>1</sub>-distorted-CeO<sub>2</sub>(100) surface with one oxygen va-vacancy (state (h)).

Surface adsorbed oxygen species can fill in the oxygen vacancy and contributes the surface to restore. The process of surface recovery from one oxygen vacancy surface to the stoichiometric surface on Pt<sub>1</sub>-dis-torted-CeO<sub>2</sub>(100) catalyst is further investigated and shown in Fig. 10. The vacancy site with  $E_{\text{ads}}$  of -2.91 eV (Fig. 10a) creates a large

attractive force for oxygen molecules. As a result, OeO bond has an increased distance of 1.51 Å (1.21 Å in the gas phase), suggesting the existence of peroxide-type O<sub>2</sub><sup>2-</sup> species. Then a dissociation of the OeO bond produces two separate oxygen atoms with one connected with Pt atom and the other occupying the oxygen vacancy. The reaction energy of OeO bond cleavage is -2.38 eV and no activation barrier (Fig. 10b). H atoms from the dissociative chemisorption of water can strongly adsorb on the surface oxygen atoms with the exothermic en-ergy of 3.40 (Fig. 10c) and 3.79 eV (Fig. 10d), respectively. Now, the surface is covered with hydroxyl groups. One H can migrate from lattice oxygen to the OH group bonding with the Pt atom to form H<sub>2</sub>O (Fig. 10e). This is an endothermic process by 1.81 eV. At last, the

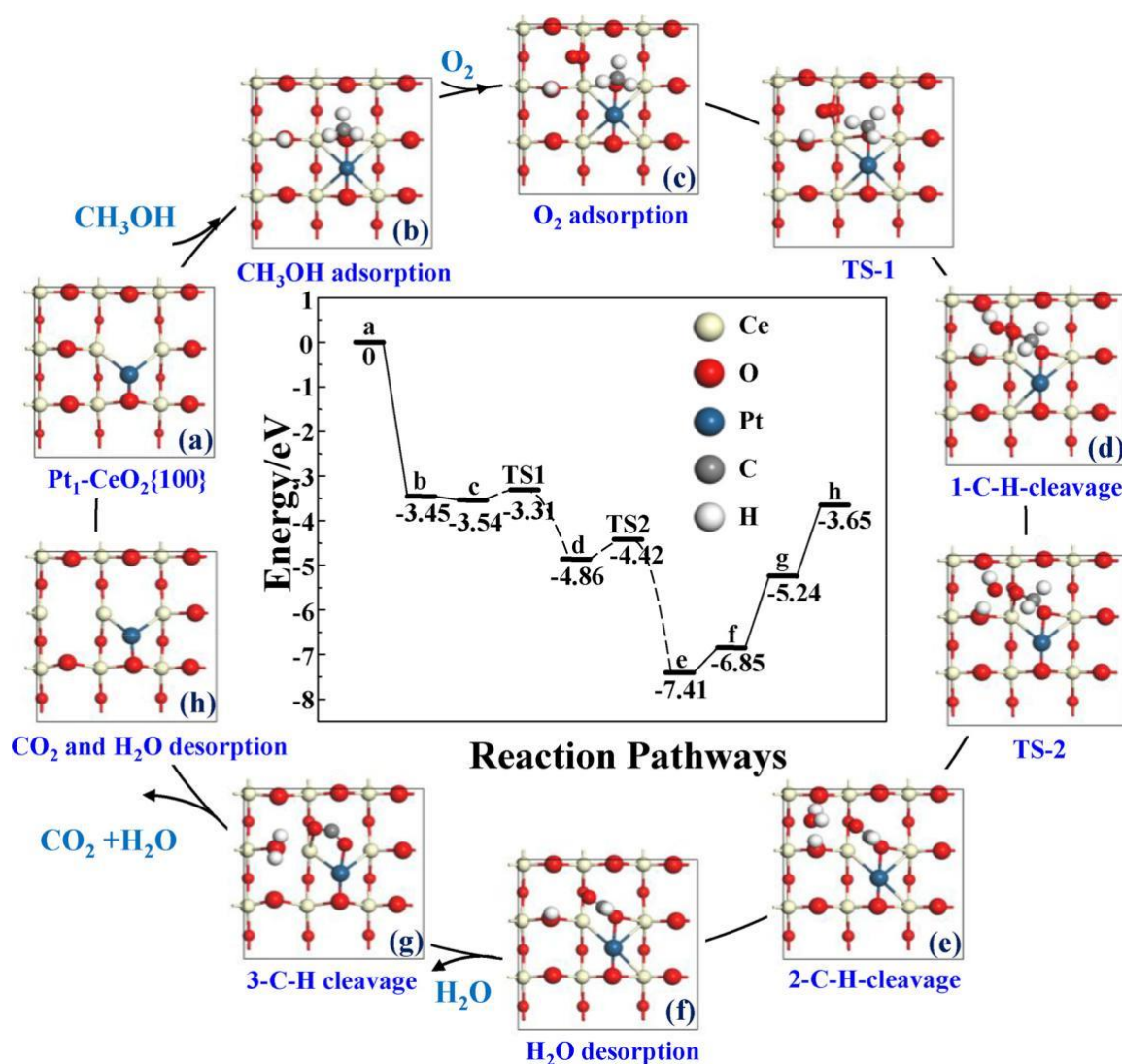


Fig. 9. (a-h) The proposed dynamic mechanism during methanol oxidation over single atom Pt<sub>1</sub>-CeO<sub>2</sub>{100} material.

surface restores to initial Pt<sub>1</sub>-distorted-CeO<sub>2</sub>(100) surface after H<sub>2</sub>O molecule desorption (Fig. 10f) and this step release an energy of 1.50 eV.

#### 4. Conclusions

In summary, we have attempted to develop the stable single atom materials for thermo-catalytic reactions and made clear the stabilizing mechanism induced by classical strong metal-support interaction. Pt-O-Ce interface was constructed by stabilizing Pt atoms on the surface mono-oxygen vacancies of CeO<sub>2</sub> with diverse exposed facets. Combination of advanced characterizations and theoretical calculations, the stabilization mechanism was creatively proposed that the formed Pt-O-Ce interface will be taken into distortion spontaneously to keep thermodynamics stable through strong metal-support interactions. The distortion of Pt-O-Ce interface balances the Fermi energy level and charge density between Pt species and CeO<sub>2</sub> support, which in turn brings about the variation of valence state and electronic structure of materials. The ratio of Ce<sup>3+</sup> species is a clear positive correlation with the distortion degree of the interface, which could be expected on condition that this species is known as a pivotal role for stabilization of single atom sites in thermal reactions. Compared with Pt<sub>1</sub>-CeO<sub>2</sub>{110} and Pt<sub>1</sub>-CeO<sub>2</sub>{111} samples, the Pt-O-Ce active interface over Pt<sub>1</sub>-CeO<sub>2</sub>{100} exhibits the highest intensity of distortion degree and thus

catalyst possesses the exceptional catalytic efficiency and thermal stability for oxygenated hydrocarbon removal. The enhanced adsorption capacity of O<sub>2</sub> and methanol confirmed in the distortion interface is seen as another crucial reason for improving the stability of SACs. Importantly, the intrinsic methanol oxidation mechanism on prepared single atom material was revealed, over which the methanol activation obeys the L-H mechanism under relative low temperature and then goes through to the MVK mechanism under elevated temperatures. These new findings provide valuable guidance for understanding the stabilizing mechanism of SACs through classical strong metal-support interaction and propose a versatile platform for facile accessing stable SACs utilized in various industrial thermal reactions.

#### CRedit authorship contribution statement

Zeyu Jiang: Writing - original draft, Investigation, Formal analysis. Meizan Jing: Writing - original draft, Methodology. Xiangbo Feng: Formal analysis. Jingchao Xiong: Resources. Chi He: Supervision, Project administration, Writing - review & editing, Data curation. Mark Douthwaite: Writing - review & editing. Lirong Zheng: Software, Formal analysis. Weiyu Song: Software, Validation. Jian Liu: Supervision, Software, Validation. Zhiguo Qu: Supervision, Methodology.



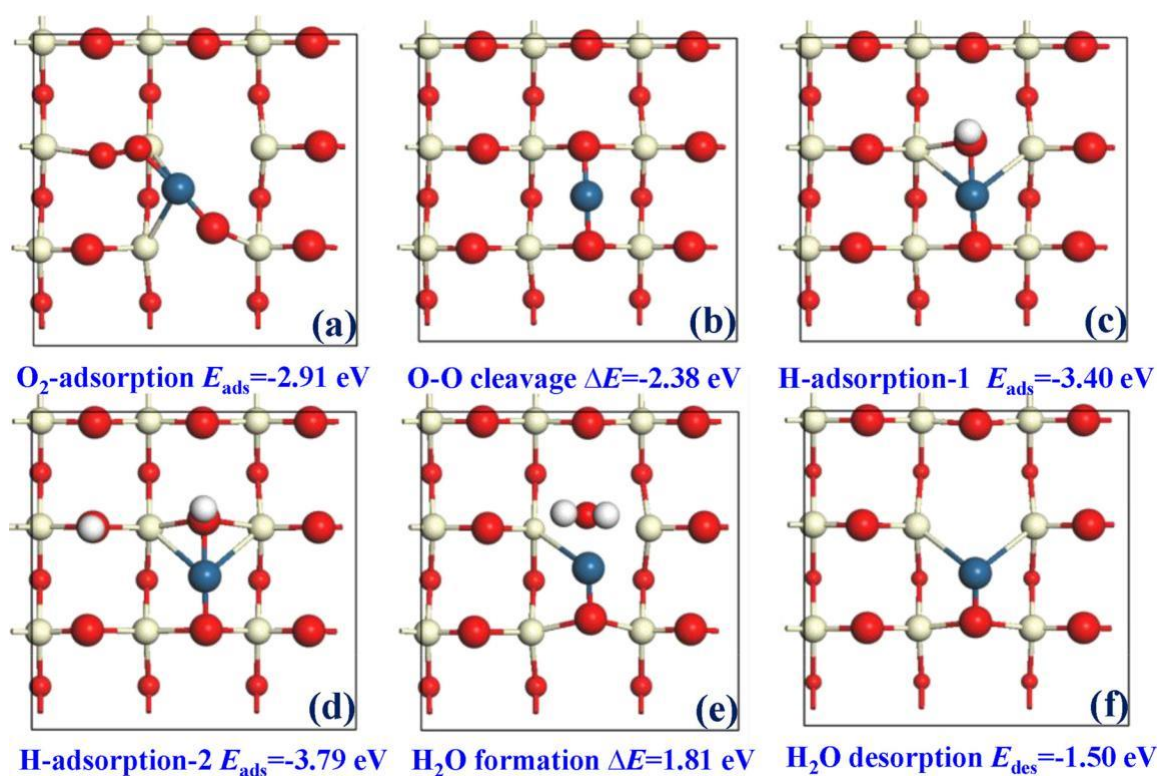


Fig. 10. (a-f) Surface reconstruction process during methanol oxidation over single atom Pt<sub>1</sub>-CeO<sub>2</sub>(100) material.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2020.119304>.

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