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Article

Structures and reactivities of the CeO₂/Pt(111) reverse catalyst: A DFT+U study

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ARTICLE INFO

Article history:

Received 9 January 2020

Accepted 23 February 2020

Published 5 September 2020

Keywords:

CeO₂/Pt reverse catalyst

Interface structure

Oxygen vacancy

CO oxidation

Density functional theory

ABSTRACT

For heterogeneous catalysts, the build-up of interface contacts can influence markedly their activities. Being different from the conventional supported metal/oxide catalysts, the reverse type of oxide/metal structures, e.g. the ceria/Pt composite, have emerged as novel catalytic materials in many fields. However, it remains challenging to determine the optimal interface structure and/or the metal-oxide synergistic effect that can boost catalytic activities. In this work, we conducted density functional theory calculations with on-site Coulomb interaction correction to determine the optimal structures and investigate the physical as well as catalytic properties of various CeO₂/Pt(111) composites containing CeO₂(111) monolayer, bilayer, and trilayer at Pt(111). We found that the interaction strength between CeO₂(111) and Pt(111) substrate first reduces as the ceria slab grows from monolayer to bilayer, and then largely gets converged when the trilayer occurs. Such trend was well rationalized by analyzing the number and distances of O–Pt bonds at the interface. Calculated Bader charges uncovered the significant charge redistribution occurring around the interface, whereas the net electron transfer across the interface is non-significant and decreases as ceria thickness increases. Moreover, comparative calculations on oxygen vacancy formation energies clarified that oxygen removal can be promoted on the CeO₂/Pt(111) composites, especially at the interface. We finally employed CO oxidation as a model reaction to probe the surface reactivity, and determined an intrinsic activity order of monolayer CeO₂(111) > monolayer CeO₂(111)/Pt(111) > regular CeO₂(111). More importantly, we emphasized the significant role of the moderate ceria-Pt interaction at the interface that endows the CeO₂/Pt reverse catalyst both good thermostability and high catalytic activity. The monolayer CeO₂(111)/Pt(111) composite was theoretically predicted highly efficient for catalyzing CO oxidation.

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1. Introduction

Ceria-based materials have found wide applications in many

catalytic processes [1], such as vehicle emission purification [2], water-gas shift reactions [3], CO oxidation [4] etc. Their excellent performance primarily stems from the unique Ce 4f

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This work was supported by National Key R&D Program of China (2018YFA0208602), National Natural Science Foundation of China (21825301, 21573067, 21421004, 21903025) and Program of Shanghai Academic Research Leader (17XD1401400). The authors also thank the National Super Computing Center in Jinan for the computing time.

DOI: 10.1016/S1872-2067(20)63564-1 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 9, September 2020

orbital with strong electron localization characteristics, typically exhibiting the dynamic $\text{Ce}^{4+}/\text{Ce}^{3+}$ transition [5–8]. Accordingly, the process of oxygen vacancy (O_v) formation has aroused great interest, anticipating that the geometric/electronic structure and/or thermostability of O_v may directly affect the performance of CeO_2 catalysts [9,10]. For example, Li *et al.* [11] found that the subsurface O_v is 0.18 eV more stable than the surface one at $\text{CeO}_2(111)$, and they also proposed a preferable two-step O_v diffusion mechanism in contrast to the conventional surface hopping mechanism. Nolan *et al.* [12] and Fabris *et al.* [13] investigated O_v formation on the three low index CeO_2 surfaces and found that the formation energies follow the order of $(111) > (110) > (100)$. Nevertheless, most of previous theoretical studies employed pure ceria models for simulating physical and/or chemical properties, while the significant role of the interface structure in composite catalysts remains largely elusive.

Being different from the conventional metal/oxide catalysts, the reverse type of ‘oxide supported on metal (i.e. oxide/metal)’ composites have recently emerged as novel catalytic materials with distinct activities [14–16]. In particular, thin ceria films deposited on metal substrates, such as $\text{Pt}(111)$ [17], $\text{Rh}(111)$ [18,19], $\text{Cu}(111)$ [20], and $\text{Au}(111)$ [21], were successfully synthesized and characterized in experiments. Using the low-energy electron diffraction (LEED) technique, Hardacre *et al.* [22] observed a (4×4) geometry pattern at ceria/Pt composites, which corresponds to a 3:4 lattice matching between $\text{CeO}_2(111)$ and $\text{Pt}(111)$. Chan *et al.* [19] carefully characterized the structure of ceria films on the $\text{Rh}(111)$ surface using the LEED, scanning tunneling microscopy (STM), and X-ray photoemission spectroscopy (XPS). They found that the ceria/Rh composites are composed of several atomic layers of $\text{CeO}_2(111)$ on the $\text{Rh}(111)$ substrate, and the deposited CeO_2 shows a O:Ce ratio of 1.96:1 with slightly contracted lattice parameter relative to the bulk ceria. There are also STM measurements showing that ultrathin ceria films at metal substrate often yield small islands with a thickness about one or two O-Ce-O layers [23,24]. Theoretically, Spiel *et al.* [17] constructed three types of ceria/Pt composites composed of monolayer $\text{CeO}_2(111)$ on the $\text{Pt}(111)$ substrate, and found that aligning surface oxygens of $\text{CeO}_2(111)$ right on the top sites of interface Pt atoms could enhance the stability of $\text{CeO}_2(111)/\text{Pt}(111)$ composites. Chan and coworkers [15] investigated the thermostabilities of defective $\text{CeO}_2/\text{Rh}(111)$ composites, and found that O_v prefers to form at the interface rather than on the ceria surface. Nevertheless, fine structural resolution of the reverse oxide/metal catalysts at the atomic level is still very rare, hindering the progress in the clarification and regulation of the structure-property relationship.

From the catalytic perspective, CO oxidation was widely considered as a model reaction to probe the reactivity of CeO_2 -based catalysts [25–27]. As both the geometric and electronic structures of ceria thin films are certainly affected by the metal support, it was anticipated that the reverse ceria/metal catalysts might show distinct catalytic properties compared with the pure ceria materials [26–29]. Recently, by growing well-defined monolayer ceria islands on the $\text{Pt}(111)$ surface

and monitoring Ce oxidation state, Suchorski *et al.* [27] observed enhanced CO oxidation activity on the ceria/ $\text{Pt}(111)$ composites with respect to the free-standing $\text{Pt}(111)$ or $\text{CeO}_2(111)$, and they attributed such enhancement to the optimized electronic structures and accelerated oxygen supply brought by ceria deposition. Besides the ceria/Pt composites, Palomino *et al.* [30] and Mullins *et al.* [31] prepared a series of oxide/ $\text{Au}(111)$ reverse catalysts (e.g. MgO , CeO_2 , TiO_2 , Fe_2O_3), among which they consistently found enhanced oxide-metal interactions and CO oxidation activities relative to the conventional metal/oxide structures. Obviously, the unique catalytic performance of reverse catalysts has been evidenced in many experiments [32,33], though the fundamental understandings on the origins of the promotion effect and catalytic activities are currently very limited, largely owing to the difficulty in determining reliable interface structures.

In this work, we conducted density functional theory (DFT) calculations corrected by on-site Coulomb interaction (for Ce) to systematically examine the structures and stabilities of various $\text{CeO}_2(111)/\text{Pt}(111)$ reverse catalysts. We first focused on the identification of the optimal structure of monolayer $\text{CeO}_2(111)$ on the $\text{Pt}(111)$ support, and then moved to investigate the changes of the thermodynamic, geometric, and electronic properties at the interface as the ceria thickness increases. It was found that the significant impact of metal substrate on ceria slabs, particularly for interface oxygens, can be directly captured by a simple parameter of the O_v formation energy. After clarifying the physical properties of the $\text{CeO}_2/\text{Pt}(111)$ composites, we used the model reaction of CO oxidation to probe the unique catalytic features of the reverse catalysts, through comparative studies of the monolayer $\text{CeO}_2(111)$ with and without the $\text{Pt}(111)$ support as well as the regular $\text{CeO}_2(111)$ surface. Our results underline the significant role of the moderate ceria-Pt interaction at the interface that endows the CeO_2/Pt reverse catalysts both good thermostability and high catalytic activity.

2. Computational methods

Spin-polarized density functional theory calculations were performed by using the Vienna *Ab-initio* Simulation Package (VASP) [34,35]. The exchange-correlation interaction was treated by the Perdew-Wang 1991 (PW91) functional on the basis of the generalized gradient approximation (GGA) [36]. The Kohn-Sham wavefunctions were expanded in a plane wave basis with an energy cutoff of 400 eV, utilizing the projector augmented wave (PAW) method [37,38]. The Pt 5*p*, 5*d*, and 6*s*, the Ce 4*f*, 5*s*, 5*p*, 5*d*, 6*s*, and the 2*s*, 2*p* orbitals of carbon and oxygen atoms were treated as valence states. Throughout the DFT calculations [39], we applied an on-site Coulomb interaction correction, i.e. the DFT + U method, with a U value of 5 eV for the Ce 4*f* orbital, consistent with the previous reports [40–42]. The transition states (TSs) of reactions were located using a constrained optimization scheme [43], and all the calculations for structural optimization and TS search were converged until the forces on each ion were less than 0.05 eV/Å. For the STM simulation, we adopted the Tersoff-Hamann ap-

proximation, using a constant-current mode with bias voltage between -2 V and $+2$ V, to simulate the tunneling current proportional to the local density of states [44]. In addition, we checked the influence of the Van der Waals [45] interaction on both surface reactions and the O_v formation (Table S1), and the negligible energy difference indicates that DFT + U is competent to capture the catalytic trends in CO oxidation on ceria/Pt composites.

To construct the composite models, we adopted the 3×4 lattice-matching pattern observed in experiments, and built a $p(3 \times 3)$ $\text{CeO}_2(111)$ surface cell on the top of a four-layer $p(4 \times 4)$ $\text{Pt}(111)$ substrate. Considering the lattice parameters of 3.87 Å for ceria and 2.84 Å for Pt, such pattern can cause only small lattice contraction of 2.15% for $\text{CeO}_2(111)$. The Brillouin-zone integration was treated using a $1 \times 1 \times 1$ k-points mesh. During all calculations, the bottom two layers of Pt substrate were kept fixed, while the other Pt and ceria layers were allowed to relax. We altogether considered three types of $\text{CeO}_2/\text{Pt}(111)$ composites with different thickness of ceria. As one can see from Fig. 1(a–c), the monolayer (ML), bilayer (BL), and trilayer (TL) $\text{CeO}_2(111)$ slabs were deposited on the $\text{Pt}(111)$ surface with a large vacuum gap (> 10 Å) separating periodic cells, denoted as the ML, BL, and TL $\text{CeO}_2/\text{Pt}(111)$ models, respectively. For calculations of the regular $\text{CeO}_2(111)$ surface, we used a TL $\text{CeO}_2(111)$ surface model with the bottom two layers being fixed during calculations, as frequently suggested by previous reports [46].

In this work, the oxygen vacancy formation energy (E_{Ov}) was defined as

$$E_{Ov} = E_{vac} + 1/2 E_{O_2} - E_{slab}$$

where $E_{(O_2)}$ is the energy of a gaseous O_2 molecule, and E_{slab} and E_{vac} are energies of the catalyst without and with one oxygen vacancy, respectively.

The adsorption energy of species X ($E_{ad}(X)$) was calculated according to

$$E_{ad}(X) = -(E_{total} - E_{slab} - E_X)$$

where E_{total} represents the energy of the interacting system,

Fig. 1. Calculated structures of (a, d) ML $\text{CeO}_2/\text{Pt}(111)$, (b, e) BL $\text{CeO}_2/\text{Pt}(111)$ and (c, f) TL $\text{CeO}_2/\text{Pt}(111)$ composites from the side and top views, respectively. The cerium, oxygen and platinum atoms are presented as ivory, red and blue balls, respectively. This color notation is used throughout the manuscript.

and E_X is the energy of the adsorbate X species in the gas phase. We can also calculate the adsorption energy of ceria at Pt substrate, $E_{ad}(\text{ceria})$, as follows

$$E_{ad}(\text{ceria}) = -(E_{total} - E_{Pt} - E_{ceria})$$

where E_{Pt} and E_{ceria} are energies of the separated Pt and ceria slabs, respectively.

Moreover, we also calculated the normalized adsorption strength of ceria on the substrate with interface adhesion energies (E_{adh}) according to $E_{adh} = E_{ad}(\text{ceria})/A$, where A is the interface area, and defined the deposition energy of ceria, $E_{depos}(\text{ceria})$, as the adsorption energy of the outmost ceria layer on the underneath CeO_2 slabs in the BL and TL $\text{CeO}_2/\text{Pt}(111)$ composites. Obviously, positive $E_{ad}(X)$, $E_{depos}(\text{ceria})$ or E_{adh} corresponds to the exothermic adsorption/adhesion process, and the more positive the $E_{ad}(X)$, $E_{depos}(\text{ceria})$ or E_{adh} is, the stronger the adsorbate X or ceria slab binds to the surface.

3. Results and discussion

3.1. Structures of $\text{CeO}_2/\text{Pt}(111)$ composites

As the structure of the oxide/metal interface largely determines the thermostability of the corresponding composite catalysts, we first systematically calculated the various adhesion geometries of ML $\text{CeO}_2(111)$ on the $\text{Pt}(111)$ support. In total, 9 types of ML $\text{CeO}_2/\text{Pt}(111)$ structures with different in-plane positions of ceria relative to the Pt substrate are presented in Fig. 2, from which we showed how these structures were constructed by moving the $\text{CeO}_2(111)$ layer along the x and y axes to the different positions. From the calculated energetics, we found that the interaction between ceria and Pt is generally not strong, and the relative shift of the two materials only causes small impact on the $E_{ad}(\text{ceria})$, showing a narrow energy window of 3.20 – 3.50 eV (Table 1). Even for the calculated ML $\text{CeO}_2/\text{Pt}(111)$ structure with the lowest energy (Fig. 2(a)), the calculated E_{adh} of 0.43 J·m $^{-2}$ is just comparable to that of the van der Waals junctions in MoS_2 nanosheets (0.36 – 0.47 J·m $^{-2}$) [47]. A simple reason for the weak ceria-Pt interaction is that Pt is generally not an oxophilic metal (for example, the $E_{ad}(O_2)$ was calculated to be as low as 0.76 eV on the close-packed $\text{Pt}(111)$

Fig. 2. Top views of the calculated structures of ML $\text{CeO}_2/\text{Pt}(111)$ composites (a–i) and their relative positions (in Å) and stabilities with respect to the optimal one with the lowest energy ($x_0, y_0; E_0$) in (a). Two lattice vectors are labelled as x and y , respectively.

Table 1

Calculated adsorption and adhesion energies of ceria slabs as well as the structural parameters of the interface structures (the distance and number of O_i-Pt bonds: $l_{\text{Oi-Pt}}$ and $N_{\text{Oi-Pt}}$) of the ML, BL, and TL CeO₂/Pt(111) composites. For each type of composite, only the results of the most and least stable structures are listed for comparison.

CeO ₂ /Pt(111) composites		$E_{\text{ad}}(\text{ceria})$ /eV	E_{adh} /J·m ⁻²	$E_{\text{depos}}(\text{ceria})$ /eV	$l_{\text{Oi-Pt}}$ /Å	$N_{\text{Oi-Pt}}$
ML	most	3.50	0.43	—	2.13	7
	least	3.20	0.39	—	2.15	7
BL	most	2.77	0.34	8.88	2.17	7
	least	2.46	0.30	8.57	2.17	4
TL	most	3.00	0.37	9.00	2.16	7
	least	2.62	0.33	8.62	2.17	7

surface).

In Fig. 3(a), we present the interface structure of the most stable ML CeO₂/Pt(111) composite from the side view. One can see that the interface oxygens (O_i) located on (or near) the top of substrate Pt atoms can slightly pull the corresponding Pt out of the plane, forming in total 7 O_i-Pt bonds. However, for the less stable structures (Fig. 2(b)–(i)), the mismatched bonding pattern with slightly longer distances of O_i-Pt bonds (Table 1) can be easily recognized. For example, we determined that the average O_i-Pt distance decreases by 0.02 Å for the least stable composite (Fig. 2(i)) compared to the most stable one (Fig. 2(a)), though they involve the same number of O_i-Pt bond.

With the same approach, we also systematically calculated the possible structures of BL and TL CeO₂/Pt(111) composites, and the determined most stable ones are shown in Fig. 1. It needs to mention that Chan *et al.* [19] have conducted STM measurement of the BL CeO₂/Rh(111) composite, which helped them resolve the atomic configurations of the exposed CeO₂(111) surface. In the current work, we also performed STM simulation on the most stable BL CeO₂/Pt(111) structure (Fig. 3(b)). The ordered bright spots representing surface (or near-surface) Ce cations can be easily recognized, and each surface cell is marked by the dashed line in red. It should be note that, Chan *et al.* [19] characterized a 5:7 lattice-matching pattern between CeO₂(111) and Rh(111) from their experiments. In the current work, we adopted the 3:4 pattern observed in experiments for the CeO₂/Pt(111) composites (Fig. 3(b)), and four bright spots along each side of the surface cell can be recognized. Besides, relative lower resolution contrast and absence of one bright spot within each surface cell in the simulated STM image might be largely caused by the rugged

Fig. 3. (a) Enlarged interface structure of the ML CeO₂/Pt(111) and (b) simulated STM image (bias voltage: +1 V) of the BL CeO₂/Pt(111) composite.

surface configuration of the supported CeO₂(111).

To determine the effects of ceria thickness on the interface properties, we compared the interface structures of the ML, BL, and TL CeO₂/Pt(111) composites with the most and least stable structures (see Table 1). It is evidenced that, for each type of CeO₂/Pt(111) composites, the E_{adh} decreases as the $l_{\text{Oi-Pt}}$ increases and/or the $N_{\text{Oi-Pt}}$ decreases (see more samples in Table S2). From their most stable interface structures, we determined the same number of 7 O_i-Pt bonds with the average distances of 2.13, 2.17, 2.16 Å for the ML, BL and TL CeO₂/Pt(111) composites, respectively. On the other hand, their least stable interface structures exhibit either identical $N_{\text{Oi-Pt}}$ but elongated $l_{\text{Oi-Pt}}$ (e.g. ML and TL composites), or identical $l_{\text{Oi-Pt}}$ but fewer $N_{\text{Oi-Pt}}$ (e.g. the BL composite). Most importantly, we determined that the ceria-Pt interaction strength ($E_{\text{ad}}(\text{ceria})$ or E_{adh}) largely decreases as the thickness of the ceria slab increases. Accordingly, the BL and TL CeO₂/Pt(111) structures both give longer $l_{\text{Oi-Pt}}$ distances than the ML CeO₂/Pt(111). Such changes can be attributed to the gradually improved bonding strength within ceria slabs as evidenced by the calculated $E_{\text{depos}}(\text{ceria})$ in Table 1. In general, our results regarding the interaction energies and interface structures show that the physical properties of the reverse CeO₂/Pt(111) composites basically get converged when ≥ 2 ceria layers are deposited on the Pt substrate.

3.2. Bader charge analysis

Having obtained the optimal composite structures, we then performed electronic structure and Bader charge analyses to investigate the electronic properties of the ML, BL and TL CeO₂/Pt(111) composites. From the density plots of calculated charge differences (Fig. 4), one can see that drastic charge redistributions occur at the interface regions for all the three types of composites. Specifically, one oxide layer and two metal layers around the interface were found to be significantly affected, in similar manners to the previous results regarding the metal/TiO₂ systems [48]. For the thicker ceria slabs, the top CeO₂ layers gradually become less disturbed as they are located away from the interface (Fig. 4(b), and (c)). Accordingly, calculated Bader charges in Table 2 show that each O_i atom is positively charged by ~ 0.07 |e| and interface Pt is positively charged by ~ 0.04 |e| for the CeO₂/Pt(111) composites with respect to the free-standing ceria slabs and Pt(111) surface;

Fig. 4. Calculated charge differential densities (iso-value of 0.003 |e|/Bohr³) of ML (a), BL (b) and TL (c) CeO₂/Pt(111) composites caused by the ceria deposition, where the yellow and blue densities represent the electron depletion and accumulation, respectively.

Table 2

Calculated Bader charges (amount of charge per atom) of ML, BL and TL CeO₂ slabs before (separated) and after forming contact with the Pt(111) substrate. For the charge transfer results in the last row, positive values indicate that the whole CeO₂ slabs donate certain number of electrons to the Pt substrates and vice versa.

Bader charges	ML CeO ₂ -Pt(111)		BL CeO ₂ -Pt(111)		TL CeO ₂ -Pt(111)	
	separate	composite	separate	composite	separate	composite
O _s / e	-1.185	-1.189	-1.195	-1.191	-1.189	-1.190
O _i / e	-1.185	-1.115	-1.194	-1.125	-1.189	-1.124
Pt (top layer) / e	-0.047	-0.010	-0.047	-0.010	-0.047	-0.007
Charge transfer / e	—	+0.138	—	+0.031	—	-0.003

while the charges of the surface oxygens (O_s) on the top layer of CeO₂/Pt (111) remain basically unchanged (≤ 0.01 |e|). Overall, we determined that the ceria slab only transfers 0.138, 0.031 |e| to the Pt substrate for the ML, BL CeO₂/Pt (111) composites, respectively, whereas Pt donates as low as 0.003 |e| to ceria for the TL composite (last row in Table 2). These results show that the interfacial interactions are mainly contributed by the electrostatic interactions between the top Pt layer and the bottom ceria layer at the interface rather than the covalent hybridization. Such feature was also evidenced by the significant electronic polarization at the interface (Fig. 4) and redistribution within the individual ceria or Pt slabs (Table S3). In addition, considering the accumulation of positive charges at O_i and the negligible electronic changes at O_s, distinct differences in these two types of O can be further expected in catalytic reactions.

3.3. O_v formation

Considering that the excellent oxygen storage/release capacity of ceria is closely related to the O_v formation,[5,6] we then systematically calculated and compared the E_{Ov} at different sites (O_i and O_s) of CeO₂/Pt(111) composites and on the CeO₂(111) surface. Table 3 shows that, for the free-standing CeO₂(111) slabs, the O_v formation energy at surface O_s site (E_{Ov-s}) was computed to be 2.99 and 3.02 eV on the BL and TL surfaces respectively, being ~ 0.8 eV larger than that on the ML slab ($E_{Ov-s} = 2.21$ eV). These results again indicate that the ML CeO₂(111) is quite active and the BL and TL CeO₂(111) are less active and may give reduced adhesion strength with the Pt substrate (Table 1).

In addition, the calculated E_{Ov-s} for all the three types of CeO₂/Pt(111) composites were found to be ~ 0.3 eV lower than those in the corresponding free-standing ceria slabs, and such small energy differences are also consistent with the similar calculated Bader charges on O_s (Table 2). Interestingly, we found that O_v formation turns to be markedly promoted by 1.0–1.5 eV at the O_i site (E_{Ov-i}) at the interface with the Pt substrate, being 0.92, 1.28 and 1.26 eV for the ML, BL, and TL

composites, respectively. The easy removal of the O_i relative to the O_s is probably due to the proper structural accommodation to the as-formed O_{v-i} as provided by the Pt substrate. Besides, these E_{Ov} results again demonstrated the converged physico-chemical properties of the reverse CeO₂/Pt(111) composites when more than two layers of ceria slabs are deposited.

It needs to be particularly noted for the ML CeO₂/Pt(111) composite that both the E_{Ov-i} and E_{Ov-s} are much smaller than that of bulk oxygens in ceria ($E_{Ov} = 3.05$ eV) [49] or other oxides such as TiO₂ ($E_{Ov} = 3.16$ eV) [50]. After carefully examining the composite structures, we found that ceria slabs in the ML CeO₂/Pt(111) is more flexible than that in the BL and TL composite. As illustrated in Fig. 5, the vertical Ce–O_i and Ce–O_s distances (along the *z* direction; Table S4) in the ML CeO₂/Pt(111) can change dynamically to better stabilize the composite, forming different extents of compressed Ce–O_s interactions depending on the absence or presence of O_v at the interface (see vertical distances in Fig. 5(b)–(c) and Ce–O bond length in Table S5). The dynamic distance changes were also observed in the BL and TL CeO₂/Pt(111) composites, but their corresponding extents are relatively suppressed (Tables S4 and S5), owing to the increased structural rigidity in ceria as the slab thickness increases.

Particularly for the Ce–O_s bond compress induced by the O_{v-i} at the ML CeO₂/Pt (111) composite, we calculated the charge differential density of ML CeO₂/Pt(111) composite without (Fig. S1(a)) and with (Fig. S1(b)) a O_{v-i}. It was found that the presence of O_{v-i} causes slightly stronger electronic interaction as evidenced by the broader differential density, which accordingly induces structural changes such as bond compression or extension. After comparing the calculated bader charges of the two structures (Table S3), we revealed the following features: (i) the interface first oxygen (O_i) layer generally holds similar charge quantity before and after the O_{v-i} formation, whereas the first cerium (Ce₁) layer becomes less positive in the presence of O_{v-i}, which therefore leads to the elon-

Table 3

Calculated E_{Ov} (in eV) at various oxygen sites of free-standing CeO₂(111) and CeO₂/Pt(111) composites containing ML, BL, and TL ceria slabs.

O _v sites		ML	BL	TL
CeO ₂ (111)	O _{v-s} / eV	2.21	2.99	3.02
CeO ₂ /Pt(111)	O _{v-s} / eV	1.92	2.61	2.83
	O _{v-i} / eV	0.92	1.28	1.26

Fig. 5. Illustrations of variations of vertical distances between Ce and O atomic layers (along the *z* direction) in (a) free-standing ML CeO₂ and (b, c) ML CeO₂/Pt(111) composites without and with a O_{v-i} at the interface. Unit of bond distance in Å.

gated O1-Ce1 distance (0.926 Å vs. 0.856 Å; Fig. 5) owing to the reduced electrostatic interaction; (ii) the upper oxygen layer (O2) carries more negative charges (1.222 vs. 1.189 |e|) after O_{v-i} formation, and taking into account the already reduced O1-Ce1 interaction, it is reasonable that the Ce1 would bind the O2 layer stronger with compressed Ce–O distance; (iii) the overall charge transfer between ceria and Pt substrate remains fairly small (0.273 |e|) after O_{v-i} formation, which again signifies the intensive electrostatic interactions rather than the covalent hybridization between the ceria slab (containing O_v at the interface) and Pt substrate.

Overall, these geometric and electronic features regarding the compressed Ce–O_s (or extended Ce–O_i) distances and stronger structural relaxation in the ML CeO₂/Pt(111) could reasonably account for the lower O_v formation energies. Given that O_v formation is widely regarded as an important step in ceria catalysis (e.g. CO oxidation [51]), it is therefore expected that the ML CeO₂/Pt(111) composite might show excellent catalytic activities.

3.4. CO oxidation

Regarding the catalytic performance, we took CO oxidation as a model reaction to study the reactivities of the reverse CeO₂/Pt(111) catalysts. We first calculated CO adsorption at the ML, BL, TL composites and compared to that on the regular CeO₂(111) surface (using a TL model). It was found that ML CeO₂/Pt(111) gives the largest $E_{ad}(CO)$ of 0.20 eV, being twice the value on the CeO₂(111), and the adsorption strength decreases as the ceria slab becomes thicker. These results agree well with experimental observations that the CO adsorption capacity (including both the amount and the strength of CO adsorption) decreases as more ceria are deposited on the metal substrate [26], and also indicate that the ML CeO₂/Pt(111) might be more active than other composites. In addition, considering the weak adsorption of CO, one may also anticipate that CO oxidation via the Langmuir-Hinshelwood (LH) mechanism [52] is not likely to occur on the CeO₂/Pt(111) composites. Therefore, we mainly focused on the Mars-van-Krevelen (MvK) mechanism [53] as widely validated for ceria based catalysts [54,55], and compared the calculated energetics of CO oxidation at ML CeO₂(111) and ML CeO₂/Pt(111) with those on the regular CeO₂(111) surface.

The calculated reaction pathways of CO oxidation (toward CO₂ production) via the MvK mechanism on the unsupported ML and regular CeO₂(111) surfaces are shown in Fig. 6. This process starts with a gas-phase CO molecule (IS) which then forms weak interaction with the surface (IM1) and combines with an O_s to form the OC–O_s bond. At the coupling TS, the OC–O_s distance was calculated to be ~1.50 Å while the O–C–O_s angle is ~120°. We determined a coupling barrier of 0.61 eV on the regular CeO₂(111) surface, but a low barrier of 0.33 eV on the ML CeO₂(111). After the coupling, the linear CO₂ (IM2) occurs with an exothermic energy of 0.73 and 1.38 eV on the regular and ML CeO₂(111), respectively. Obviously, the lower barrier and larger energy release on the ML CeO₂(111) relative to the regular surface can be rationalized by their different E_{Ov-s}

Fig. 6. Calculated energy profile and key intermediate structures of CO oxidation via the MvK mechanism on the ML (black) and regular (red) CeO₂(111) surfaces. C atoms are in grey and the top-surface O are in green.

values (2.21 vs. 3.02 eV; Table 3). For the last step of CO₂ desorption, the as-formed CO₂ can leave both surfaces quite easily by overcoming its adsorption energies of ~0.38 eV, leaving an O_v on the surface. Note that previous reports have suggested that the surface O_v at ceria surfaces can be readily recovered [56,57] and consequently the overall reactivity of CO oxidation can be largely determined by the OC–O coupling. Therefore, judging from the above calculated energetics, we expect that the ultrathin ML CeO₂(111) surface can show much higher CO oxidation activity than bulk ceria materials.

For CO oxidation on the ML CeO₂/Pt(111) composite (Fig. 7), the initial reaction steps are very similar to those on CeO₂(111) surfaces, leading to the formation of surface CO₂ (IM2), though lower coupling barrier (0.45 vs. 0.61 eV) and larger energy release (1.69 vs. 0.73 eV) were also determined. These results are again consistent with the vast E_{Ov} difference between the two catalysts (1.92 vs. 3.02 eV; Table 3). In contrast, CO oxidation on the ML composite could form two types of O_v defects at the O_s or O_i site (FS and FS' in Fig. 7) after CO₂ desorption. The former O_{v-s} pathway shows no obvious differ-

Fig. 7. Calculated energy profile and key intermediate structures of CO oxidation via the MvK mechanism on the ML CeO₂/Pt(111) composite. Two possible final states exposing O_v at the O_s and O_i site are labelled as FS and FS', respectively.

ence to that on free-standing ceria surfaces, releasing gaseous CO_2 directly with a small endothermic energy of 0.36 eV; while the latter $\text{O}_{\text{v-i}}$ pathway involves the migration of an interface O_{i} to fill the surface $\text{O}_{\text{v-s}}$ (IM3), which, however, turns to be thermodynamically more preferable by ~ 1.0 eV than IM2.

In addition, though the result of much lower $E_{\text{Ov-i}}$ than $E_{\text{Ov-s}}$ was also evidenced in the BL and TL composites (Table 3), O_{i} migration requires multi-steps of oxygen relay within such thicker ceria slabs, thus being a kinetically much slower process. In this regard, we calculated the energy barrier of O_{v} migration in the ML $\text{CeO}_2/\text{Pt}(111)$ composite using the climbing image nudged elastic band (CI-NEB) method [58]. We determined an energy barrier of 0.92 eV, and the dynamic picture of O_{v} migration was presented in Fig. S2. Therefore, our results indicate that the additional CO oxidation pathway involving $\text{O}_{\text{v-i}}$ formation is a unique feature of the ML $\text{CeO}_2/\text{Pt}(111)$ or perhaps other ML ceria/metal composites. In fact, this speculation was supported by experimental observation of $\text{O}_{\text{v-i}}$ formation in the ML $\text{CeO}_2/\text{Rh}(111)$ catalyst under flowing CO atmosphere [18].

Finally, though an higher OC–O coupling barrier of 0.45 eV was determined on the ML $\text{CeO}_2/\text{Pt}(111)$ than that on the ML $\text{CeO}_2(111)$ film (0.33 eV), the calculated results still indicate that the moderate ceria–Pt interaction at the interface can not only greatly stabilize the composite structure, realizing the synthesize of ultrathin ceria/metal reverse catalysts in experiments [59,60], and it may also largely preserve the superior reactivity of the ML ceria slab. Therefore, the ML ceria/Pt composite reaches a good balance between the thermostability and the reactivity, manifesting itself superior catalysts for catalyzing CO oxidation.

4. Conclusions

In this work, we performed DFT + U calculations to systematically investigate the geometric, electronic, and catalytic properties of the reverse type of $\text{CeO}_2/\text{Pt}(111)$ composites. The following main conclusions can be obtained.

The ceria–Pt interaction strength is closely relevant with the distance and number of O_{i} –Pt bonds formed at the interface, and ML $\text{CeO}_2/\text{Pt}(111)$ shows larger adhesion interaction (0.43

$\text{J}\cdot\text{m}^{-2}$) than the BL or TL composites. Increased thickness of the ceria slab in the $\text{CeO}_2/\text{Pt}(111)$ composites is highly favored for their thermostability, though their physical properties basically get converged when ≥ 2 ceria layers being deposited on the Pt substrate.

The contact between the ceria slab and the Pt substrate can significantly affect the electron distribution of the one ceria layer and two metal layers around the interface, and lowers the O_{v} formation energy by ~ 0.3 eV at the exposed ceria surface whereas as high as 1.3–1.8 eV for the interface O_{i} as compared with the free-standing $\text{CeO}_2(111)$ slabs.

The key step of OC–O coupling in CO oxidation gives the reaction barriers of 0.61, 0.33, and 0.45 eV on the regular and ML $\text{CeO}_2(111)$ surfaces and ML $\text{CeO}_2/\text{Pt}(111)$ composite, respectively, indicating an intrinsic activity trend of ML $\text{CeO}_2(111) > \text{ML CeO}_2/\text{Pt}(111) > \text{regular CeO}_2(111)$. Moderate ceria–Pt interaction at the interface not only greatly stabilizes the composite structure, but also successfully preserves the superior reactivity of the ML ceria slab. Our results demonstrate the ML $\text{CeO}_2/\text{Pt}(111)$ composite as a promising type of catalyst with high activity for CO oxidation.

Conflicts of interest

There are no conflicts of interest to declare.

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Graphical Abstract

Chin. J. Catal., 2020, 41: 1360–1368 doi: 10.1016/S1872-2067(20)63564-1

Structures and reactivities of the $\text{CeO}_2/\text{Pt}(111)$ reverse catalyst: A DFT+U study

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By depositing monolayer ceria on the Pt substrate, the CeO_2/Pt reverse catalyst, comparing to ceria thin film or bulk, shows both good thermostability and excellent catalytic activity towards CO oxidation.

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CeO₂/Pt(111)反向催化剂结构和活性的密度泛函理论研究

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摘要: 铈基材料因其独特的Ce⁴⁺/Ce³⁺转化性质而广泛运用于非均相催化反应中。尽管在实验和理论上对纯净二氧化铈表面的物理和/或化学性质进行了深入研究, 但是与二氧化铈有关的界面结构和反应性能引起了人们的极大兴趣。其中, 已有报道表明, 氧化铈/金属反向催化剂相较于氧化铈、金属或者金属/氧化铈负载材料能明显提高CO催化氧化和水汽转化等反

应活性。然而多数前期研究并没有从理论上给出合理解释,同时也并未说明反向催化剂中氧化铈结构(层数)和性质的关系。可以预见,因受到金属基板的影响,二氧化铈表面的物化性质,如氧空位形成能、电子分布、催化活性等必然会发生变化。本文通过库伦作用校正的密度泛函理论(DFT + U)计算,系统地研究了不同厚度的 $\text{CeO}_2/\text{Pt}(111)$ 反向催化剂几何结构和电子性质,催化CO氧化的性能。本文首先在 $\text{Pt}(111)$ 载体上明确了单层 $\text{CeO}_2(111)$ 的最佳结构,然后研究随着二氧化铈厚度增加,各复合结构界面热力学稳定性、几何结构和电荷性质的变化。

计算结果表明:首先,单层 $\text{CeO}_2/\text{Pt}(111)$ 比双层和三层 $\text{CeO}_2/\text{Pt}(111)$ 复合结构在界面处表现出更强的相互作用,并且其强度与界面结合结构密切相关,如界面O–Pt键的数量及其长度等;其次,氧化铈板层和Pt基板之间的接触会显著影响界面处一个氧化铈层和两个金属层内的电子分布,使氧化铈外暴露表面的氧空位形成能降低 ~ 0.3 eV,而界面氧空位形成能则显著降低1.3–1.8 eV,并且当表面上沉积 ≥ 2 个氧化铈层时,氧化铈/铂复合材料的物理性能会趋向收敛;最后,通过计算单层 $\text{CeO}_2/\text{Pt}(111)$,单层 CeO_2 和模拟体相结构的三层 $\text{CeO}_2(111)$ 表面上的CO氧化过程,结果表明三者均遵循Mvk机理,并且关键步骤 $\text{OC}^{\bullet}\cdots\text{O}_s$ 偶联的反应能垒分别是0.45, 0.33和0.61 eV,表明三者的活性趋势为 $\text{ML CeO}_2 > \text{ML CeO}_2/\text{Pt}(111) > \text{TL CeO}_2(111)$ 。综合考虑到单层 $\text{CeO}_2/\text{Pt}(111)$ 界面处适度的二氧化铈-铂相互作用,一方面可以极大提高复合材料热力学稳定性,另一方面还成功保留了单层二氧化铈的优异催化活性,因此单层 $\text{CeO}_2/\text{Pt}(111)$ 复合材料从理论上认为是一种优异的CO氧化催化剂。

关键词: $\text{CeO}_2/\text{Pt}(111)$ 反向催化剂; 界面结构; 氧空位; CO氧化; 密度泛函理论

收稿日期: 2020-01-09. 接受日期: 2020-02-23. 出版日期: 2020-09-05.

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基金来源: 国家重点研发计划(2018YFA0208602); 国家自然科学基金(21825301, 21573067, 21421004, 21903025); 上海市学术研究负责人计划(17XD1401400).

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