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Article

A DFT+U study of the structures and reactivities of polar CeO₂(100) surfaces

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ABSTRACT

Density functional theory calculations corrected by on-site Coulomb interactions were carried out to study the structures of polar CeO₂(100) surfaces as well as activities during catalytic CO oxidation. The stabilities of various CeO₂(100) termination structures are discussed, and calculated energetics are presented. The most stable CeO₂(100) surface was obtained by removing half the outermost full layer of oxygen and the surface stability was found to decrease as the exposed oxygen concentration was increased. Assessing the reaction pathways leading to different final products during CO oxidation over the most stable CeO₂(100) surface, we determined that the formation of carbonate species competed with CO₂ desorption. However, during CO oxidation on the less stable CeO₂(100) surfaces having more exposed oxygen, the CO is evidently able to react with surface oxygen, leading to CO₂ formation and desorption. The calculation results and electronic analyses reported herein also indicate that the characteristic Ce 4f orbitals are directly involved in determining the surface stabilities and reactivities.

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1. Introduction

Cerium dioxide (CeO₂) is widely used in many important catalytic processes, such as vehicle emission control, the water-gas-shift reaction and petroleum cracking [1–4]. This material is especially useful in many catalytic oxidation reactions, including the oxidation of CO [5–7]. The unique catalytic performance of CeO₂ in these applications is related to its remarkable ability to store and release oxygen [8]. Accordingly, it is important to understand the formation of oxygen vacancies in ceria and the related structural, energetic and electronic properties, as these may directly affect the activity of CeO₂ in various applications [8]. Many experimental and theoretical studies

have revealed some important characteristics of oxygen vacancies on low-index ceria surfaces [9–19], among which CeO₂(111) has been determined to be the most stable, followed by CeO₂(110) and (100) [20–24].

CeO₂(100) is unstable due to the presence of surface dipoles, as it is a Tasker Type 3 oxide surface with an A–B–A–B layered structure, where A is the oxygen anion and B is the cerium cation [25]. In several theoretical studies employing a slab model, CeO₂(100) has been constructed by removing half the O on both the top and bottom layers. In this manner, the entire slab maintains a stoichiometric composition and is also non-polar, both of which allow periodic *ab initio* calculations [26]. Nevertheless, there have been few detailed studies of the

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surface structures and compositions of CeO₂(100), and its surface activities during catalytic reactions are not yet clearly understood.

Several experimental studies have already shown that the CeO₂(110) and/or (100) facets are more active than the more common CeO₂(111) facets for catalytic reactions such as CO oxidation [27,28]. In particular, Zhou *et al.* [27] used high-resolution transmission electron microscopy to examine CeO₂ nanorods and nanoparticles and found that the exposed (100) and (110) planes on the CeO₂ nanorods were unusually reactive.

In the present work, we employed calculations based on density functional theory corrected by on-site Coulomb interactions (DFT+U) to obtain a better understanding of the atomic compositions, structures and stabilities of CeO₂(100) surfaces. This theoretical approach has previously been successfully applied to the study of the surface and bulk distributions of oxygen vacancies, metal doping and adsorption/reaction of probe molecules on ceria catalysts [29–37]. We also modeled CO oxidation on these same surfaces to further examine the reactivity of CeO₂(100).

2. Experimental

The spin-polarized DFT+U calculations were conducted using the Vienna *ab initio* Simulation Package (VASP) [38,39]. The projector-augmented wave (PAW) method [40,41] was employed to describe the interactions between the atomic core and valence electrons. The cerium 5s, 5p, 5d, 4f and 6s electrons and the carbon and oxygen 2s and 2p electrons were included as the valence electrons and a kinetic energy cutoff of 400 eV was applied in conjunction with the plane wave basis set expansion. We selected a U value of 5.0 eV for the Ce 4f states based on previous theoretical studies [42–44]. Slabs were employed to model the CeO₂ surfaces with a vacuum gap of > 0.15 nm. While studying surface compositions, the CeO₂(100) surface was modeled using a slab with 12 atomic CeO₂ double layers in which all the atoms were allowed to relax. In contrast, surface adsorption and reaction analyses employed a slab with 7 CeO₂ double layers, with the bottom two layers being fixed during calculations. A 2 × 2 expansion of the surface unit cell was applied and Brillouin-zone integration was performed with a 2 × 2 × 1 Monkhorst-Pack grid [45].

The total oxygen vacancy formation energy (E_{vac}) was defined as:

$$E_{\text{vac}} = E_{\text{slab}/\text{vac}} - E_{\text{slab}} + 1/2nE_{\text{O}_2}$$

where E_{slab} is the total energy of the CeO₂(100) slab with both the top and bottom layers terminated by a complete layer of oxygen, $E_{\text{slab}/\text{vac}}$ is the total energy of the CeO₂(100) slab with the oxygen layer partially removed, E_{O_2} is the total energy of a gas phase O₂ molecule and n is the total number of oxygen vacancies (or the number of oxygen atoms removed) in the slab. A negative value of E_{vac} indicates that the formation of oxygen vacancies is an exothermic process. It is important to emphasize that the full-layer-O terminated CeO₂(100) slab considered in the above equation is actually non-stoichiometric and O rich. The vacancy formation energies were calculated only to com-

pare the stabilities of different stoichiometric CeO₂(100) surface slabs built by removing the extra O from this non-stoichiometric slab.

The adsorption energy (E_{ads}) of CO on the CeO₂(100) surface was defined as:

$$E_{\text{ads}} = -(E_{\text{CO/CeO}_2} - E_{\text{CeO}_2} - E_{\text{CO}})$$

where $E_{\text{CO/CeO}_2}$ is the total energy of the interacting CO/CeO₂ system and E_{CeO_2} and E_{CO} are the energies of the clean CeO₂ surface and of an optimized CO molecule, respectively. Accordingly, a positive E_{ads} values indicates that the adsorption process is exothermic.

3. Results and discussion

3.1. Structure of the polar CeO₂(100) surface

The surface structures of various low index CeO₂ surfaces, especially the most stable CeO₂(111) surface, have been previously described in detail, as have the configurations and stabilities of the corresponding surface oxygen vacancies [10,11,13]. However, CeO₂(100) is much less stable than CeO₂(111), primarily because it is a polar surface. In this work, we employed symmetric slab models to perform a precise study of the surface compositions, structures and corresponding stabilities of CeO₂(100) surfaces.

The polar CeO₂(100) surface consists of alternating layers of Ce cations and O ions. As a result of this stoichiometry, the number of O ions in each layer is twice that of Ce ions. Accordingly, one can expect that the O-terminated CeO₂(100) surface would involve a complete layer of exposed O atoms and therefore strong repulsive interatomic O–O interactions that might significantly destabilize the surface. In earlier research, a surface with half the top layer of O removed was typically used to model the CeO₂(100) surface [46]. In the current work, we also used this model as a reference to study the surface compositions and stabilities, employing a slab model with 12 layers of Ce cations, and terminating both the top and bottom surfaces of the slab with O while maintaining just half the original complete O layer. This approach ensured that the entire slab remained symmetric while keeping the CeO₂ stoichiometry (Fig. 1). It should be noted that surface models with added CeO₄ units on the CeO₂(100) surface have also been proposed to explain the surface structures observed in experimental work [47,48], and the resulting theoretical stabilities have been found to be very similar to that of the reference CeO₂(100) surface. Since we were primarily interested in studying surface compositions (that is, the O coverage effect of the O-terminated CeO₂(100) surface) we did not include these additional CeO₄ in the current work.

To study other possible surface compositions, we built symmetric and stoichiometric slabs by leaving more than half the full layer of O on the top and bottom surfaces while creating the corresponding number of O vacancies (O_v) in the bulk to maintain stoichiometry. Specifically, within a 2 × 2 surface cell, each full-layer surface of the slab consisted of 8 O ions, so the reference surface slab had 4 O on the surface of each side (Fig. 1(b) and 4V+0V in Fig. 2). The other surfaces analyzed had 5–8

Fig. 1. Structures of $\text{CeO}_2(100)$ surfaces. (a) Top view of $\text{CeO}_2(100)$ with a full layer of exposed O; (b) Top view of $\text{CeO}_2(100)$ with half the full layer of O removed; (c) Side view of the most stable surface slab considered in this work; (e) and (f) Illustrations showing the $\text{CeO}_2(100)$ in (a) and (b), respectively. The O atoms are in red and Ce in white, and V represents oxygen vacancies.

O ions maintained on each surface, while the corresponding 1–4 O vacancies were left in the bulk area of each half of the slab. We initially constructed a $\text{CeO}_2(100)$ surface with 5 surface O ions and 1 O_v in the bulk of each half of the slab (3V+1V in Fig. 2), and Table 1 summarizes the oxygen vacancy formation energies calculated with respect to the slab having a complete layer of O on both sides. In the case of the reference $\text{CeO}_2(100)$ surface with half the full layer of O removed, the calculated total O vacancy formation energy was -12.97 eV. The overall oxygen vacancy formation energies for the surfaces with 5 O ions were determined to be -7.4 to -1.0 eV, indicating

that these surface structures were less stable than the reference surface. In addition, by comparing the relative stabilities of slabs with 5 surface O ions and one bulk O_v at different positions, it was clear that the bulk O_v prefers to remain close to the surface within the subsurface area, and that the slab becomes less stable as the O_v moves deeper into the bulk.

We also built and studied $\text{CeO}_2(100)$ slabs with 6 and 7 O ions on each surface. Correspondingly, 2 and 3 O_v were distributed in the bulk of each side of the slabs (see 2V+2V and 1V+3V). Again, we considered different locations of these vacancies in the bulk. The data in Table 1 clearly show that, as the number of O ions on the surface increases, the overall stability is reduced. It is also once more evident that the bulk oxygen vacancies are preferentially situated close to the surface.

As an extreme case, we also studied a surface with a complete O layer. Accordingly, a total of 4 oxygen vacancies were distributed in the bulk area of each half of the slab (0V+4V). Again, we considered variations in the O_v distribution. The calculated vacancy formation energies in Table 1 demonstrate that a uniform distribution of the vacancies among the different

Fig. 2. Diagrams of the different $\text{CeO}_2(100)$ surfaces considered in this work.

Table 1

Total oxygen vacancy formation energies calculated for different $\text{CeO}_2(100)$ surfaces. The surface structures here correspond to those illustrated in Fig. 2, with the O_v distributed in 1–4 layers below the top surface layer (Fig. 1(c)).

Structure	E_{vac} (eV)				
4V+0V	-12.97				
3V+1V	1	2	3	4	
	-7.40	-6.71	-3.47	-1.04	
2V+2V	1,2	1,3	1,4	2,3	2,4
	1.70	7.56	5.33	5.42	6.66
				7.51	
1V+3V	1,2,3	1,2,4	1,3,4	2,3,4	
	9.26	9.02	10.24	12.50	
0V+4V	1	2	3	4	uniform distribution
	9.87	18.75	23.35	24.71	23.63

bulk layers resulted in much lower stability compared with the scenario in which all the vacancies are in the same layer close to the surface. In general, the calculated results show that the surface configuration with half the complete O layer removed is the most energetically stable among all the stoichiometric $\text{CeO}_2(100)$ surfaces considered in this work.

3.2. CO oxidation over $\text{CeO}_2(100)$

CeO_2 -based materials are currently used as active component in three-way catalysts for vehicle emission control. Therefore, in this work, we also examined CO oxidation over $\text{CeO}_2(100)$ to illustrate the potential catalytic activity of this material. We initially selected the most stable $\text{CeO}_2(100)$ surface, terminated with a half layer of O. The adsorption of CO was modeled at two different sites; at a surface lattice O with two-fold coordination (O_{2c}) and at a surface O vacancy (Fig. 3(a) and (b)). The calculated adsorption energies and structural parameters at these two sites are provided in Table 2, from which one can see that the CO adsorption at both sites is relatively weak, although adsorption at an O_v site is slightly more favorable. This result is largely consistent with the data reported for experimental assessments of CO adsorption on CeO_2 by Wu *et al.* [49].

We subsequently predicted the results for a reaction between CO and a single surface O_{2c} on $\text{CeO}_2(100)$, using the CO adsorption state on an O_v as the initial state (ISA, Fig. 4) of the reaction.

According to the results of our calculations, a bent CO_2 species (IMA, Fig. 4) is adsorbed on the surface following the direct reaction between CO and a surface lattice O_{2c} , with a O–C–O bond angle of 128° . The barrier for the formation of this bent CO_2 at the surface was determined to be 0.67 eV, and the OC– O_{2c} distance in the transition state (TSA1, Fig. 4) was found to be 0.1673 nm. From the energy profile in Fig. 4, one can also see that the CO_2 adsorption is an exothermic process with an energy change of approximately 0.5 eV. The bent CO_2 adsorbed on the $\text{CeO}_2(100)$ surface may move into the gas phase (FSA-1),

Fig. 3. Calculated CO adsorption structures on $\text{CeO}_2(100)$ on top of a surface O_{2c} (a) and an oxygen vacancy (b).

Table 2

Calculated adsorption energies and structural parameters for CO adsorption on top of a lattice O_{2c} or an O_v on the $\text{CeO}_2(100)$ surface.

Adsorption site	Adsorption energy (eV)	OC–O distance (nm)
O_{2c}	0.02	0.3063
O_v	0.33	0.2865

Fig. 4. Calculated energy diagram and corresponding structures of key states during the CO reaction with O_{2c} over the most stable $\text{CeO}_2(100)$ structure. The energy changes between different states, as well as their relative stabilities with respect to the ISA, are indicated.

and we also performed a series of constrained calculations to determine whether there is a transition state for this desorption process. No significant energy barrier was identified for this highly exothermic step (energy change of approximately 2.3 eV).

In addition to CO_2 desorption, we also found that bent CO_2 molecules on the surface can react with other surface lattice O_{2c} to form two different types of carbonate species. The reaction between the adsorbed CO_2 and a nearby surface O_{2c} was examined and it was found that an upright carbonate species (FSA-2, Fig. 4) is formed initially with an associated energy barrier of 0.49 eV (TSA-2, Fig. 4). This carbonate formation process is significantly exothermic by 2.15 eV. Subsequently, this upright carbonate can transition to a flat carbonate species on the surface, with a small barrier of 0.20 eV. This flat carbonate is in fact even more stable than the upright species, by 0.84 eV.

3.3. CO oxidation on metastable $\text{CeO}_2(100)$

This study systematically examined the surface structures of $\text{CeO}_2(100)$ and their corresponding stabilities. In addition to the most stable termination state, we also determined several metastable $\text{CeO}_2(100)$ surfaces, having higher coverages of surface O. To obtain a comprehensive understanding of the catalytic activity of $\text{CeO}_2(100)$, we also modeled CO oxidation over a metastable $\text{CeO}_2(100)$ surface having one extra surface lattice O in addition to half a full O layer. The adsorption of CO on four different sites on this surface was considered: at an extra surface lattice O_{2c} (O_d), a standard surface O_{2c} (O_s), an O_v site and a surface Ce atom. The calculated adsorption energies and structural parameters at the four different sites are provided in Table 3. These data show that, similar to the results obtained with the most stable $\text{CeO}_2(100)$ surface, CO adsorptions were very weak at these sites. Thus, it is very likely that the CO can again react with surface O through an MvK mechanism on this metastable $\text{CeO}_2(100)$ surface.

We subsequently adopted the adsorption states of CO at the O_s and O_d sites as the initial states (ISB and ISC, respectively,

Table 3

Calculated adsorption energies and structural parameters for adsorbed CO on metastable CeO₂(100).

Adsorption site	Adsorption energy (eV)	OC–O distance (nm)
O _d	0.04	0.2950
O _s	0.01	0.3255
O _v	0.32	0.2854
Ce	0.18	0.2881

Fig. 5) for its reaction with a typical surface O_s and an additional O_d. It is evident from the calculated energy profiles in Fig. 5 that the barriers were determined to be 0.60 and 0.41 eV, respectively, both of which are lower than the value obtained using the most stable CeO₂(100) surface. These results suggest that the extra surface lattice O is relatively more reactive than the ordinary surface O. Interestingly, we identified no intermediate state involving the adsorbed CO₂ species after the transition states (TSB and TSC) for the CO reaction with these two surface O, and found that a linear CO₂ species forms immediately above the surface.

3.4. Electronic structures

Additional information regarding the reactivities of surface O and reaction intermediates within the CO oxidation process over CeO₂(100) was obtained by electronic structure analyses of the various key reaction states on the most stable and metastable CeO₂(100) surfaces.

In the case of the CeO₂(100) surface with an adsorbed CO₂ complex (IMA, Fig. 4) or with various carbonate species (FSA-2 and FSA-3, Fig. 4), we analyzed the electronic structures by calculating the corresponding density of states (DOS). We also calculated the distribution of localized spin electrons in these

systems. The adsorbed CO₂ complex was determined to have two spin-unpaired electrons (Fig. 6(a) and (b)), in keeping with the two isolated gap states in the DOS plot (Fig. 6(c)). The spin-down gap state corresponds to a single localized electron in the 4*f* orbital of one neighboring Ce, while the localized electron at the surface CO₂ contributes to the spin-up gap state. We also calculated the Bader charges for the surface species in this system, and determined that the surface CO₂ species had approximately 0.88 e, indicating that these species should more properly be considered as CO₂[−]. Since the CO molecule is neutral, and the calculated Bader charge of the original surface lattice O was approximately 1.12 e, these results show that the surface adsorption of CO₂ on CeO₂(100) is a redox process, and that overall this process results in a partial electron transfer to surface Ce cations.

We also calculated the DOS and the spin electron densities for the CeO₂(100) surface with adsorbed carbonate species in the FSA-2 and FSA-3 configurations (Fig. 7), and determined multiple gap states from the DOS plots. In the case of the surface with the carbonate in the FSA-2 configuration, three spin-up gap states were identified, one of which is paired with a spin-down state. In contrast, the system with the FSA-3 configuration showed only spin paired electrons in the gap states. Specifically, for the FSA-2 scenario, two surface Ce exhibit two spin-up states, suggesting that the original Ce⁴⁺ ions have been reduced to Ce³⁺. Moreover, the spin-paired gap state in the FSA-2 configuration results from the 2*p* electrons of the carbonate species. In the case of the FSA-3 configuration, the spin paired gap states are associated with two localized electrons in the 4*f* orbitals of two surface Ce.

We also analyzed the electronic structures of the FSB and FSC states during the CO reaction with O_s and O_d on the metastable CeO₂(100) surface. The resulting DOS diagram demonstrates the existence of two gap states for these two structures,

Fig. 5. Calculated energy diagram and structures of key states during the CO reaction with O_s and O_d on metastable CeO₂(100). The energy changes between different states, as well as their relative stabilities with respect to the ISB, are indicated.

Fig. 6. Calculated isosurfaces of spin electrons in the IMA state ((a): top view, (b): side view), and the corresponding DOS data (c) for CO oxidation on CeO₂(100).

Fig. 7. Calculated isosurfaces of spin electrons in the FSA-2 ((a): top view, (b): side view) and FSA-3 ((c): top view, (d): side view) states during CO oxidation on $\text{CeO}_2(100)$, and the corresponding DOS plots ((e) and (f)).

again as a result of localized Ce^{3+} electrons (Fig. 8). It is evident from the calculated distribution of the localized electrons that the two Ce^{3+} in the FSB system remain in the subsurface area while, for the FSC system, one Ce^{3+} is in the subsurface area and the other is in the third layer (Fig. 9). It is important to note that the Ce^{3+} is located in the surface area following the formation of gas phase CO_2 in conjunction with the FSA-1 state during the reaction on the most stable $\text{CeO}_2(001)$ (Fig. 9).

3.5. Discussion

In this work, the compositions of $\text{CeO}_2(100)$ surfaces were systematically studied using the DFT+U method. From the calculated surface structures and corresponding energetics, we can conclude that the surface having half the full O layer being removed is the most energetically stable. In addition, as the O remaining on the surface increases, the surfaces become less stable. To better understand the electronic origin of the stabi-

ties and reactivities of these surfaces during CO oxidation, we examined the electronic structures of the most stable and metastable surfaces determined in this work.

No gap states or localized spin electrons were identified for the most stable $\text{CeO}_2(100)$ surface (Fig. 1(b)). The calculated spin charge density distributions of the several metastable $\text{CeO}_2(100)$ structures are shown in Fig. 10. Interestingly, it is evident that, even if these surface slabs are overall stoichiometric, spin electrons still occur at various surfaces and bulk atoms, suggesting electron transfer between O and Ce ions. As an example, if the most stable $\text{CeO}_2(100)$ surface is modified by moving one O from the bulk to the surface (Fig. 10(a)), the surface O as well as some surface and bulk Ce cations appear to possess partial spin electrons, indicating charge transfer from the surface O (O^{2-}) to Ce cations (Ce^{4+}), such that these O^{2-} ions are actually oxidized. Moreover, one can also see that, as the oxygen vacancies moves further into the bulk (Fig. 10(b)), oxidized O ions and reduced Ce cations can also occur at the sur-

Fig. 8. Calculated DOS plots for the FSB (a) and FSC (b) states during CO oxidation on metastable $\text{CeO}_2(100)$.

face and around the vacancies in the bulk. These results can possibly be attributed to the increased local coverage of O ions when extra O are present at the surface, promoting the transfer of electrons from these surface O ions to surface or bulk Ce cations to reduce electrostatic repulsion. Moreover, these oxidized O ions (O^-) can also be expected to be highly active for reactions, due to their radical character.

This work also investigated CO oxidation over $\text{CeO}_2(100)$ under various surface conditions. From the calculation results,

Fig. 9. Calculated isosurfaces of spin electrons in the FSA-1 ((a): top view, (b): side view), FSC ((c): top view, (d): side view) and FSB states ((e): top view, (f): side view) during CO oxidation on metastable $\text{CeO}_2(100)$.

we determined that the direct interaction between CO and the $\text{CeO}_2(100)$ surfaces is rather weak, similar to the case of CO adsorptions on $\text{CeO}_2(110)$ and (111) surfaces [50,51]. These results therefore indicate that CO oxidation by lattice O at CeO_2 catalysts may follow the MvK mechanism in general.

From the calculated results illustrated in Fig. 4, one can see that, on the most stable $\text{CeO}_2(100)$, the direct reaction between CO and one surface O_{2c} leads to the formation of a negatively charged, bent CO_2 species adsorbed at the surface. The desorption of this species as molecular CO_2 can subsequently occur, as well as its further reaction with another surface O_{2c} , to give rise to various carbonate species on the surface. The latter is much more likely to occur than the generation of gas phase CO_2 . As a result, although the CO_2 desorption has no energy barrier, carbonate formation is still highly competitive from the thermodynamic point of view.

We also examined CO oxidation on metastable $\text{CeO}_2(100)$ to obtain a comprehensive understanding of the behavior of this surface under practical conditions. Surprisingly, it was determined that, during the reaction of CO with an extra O_{2c} and the nearby original half layer O_{2c} , a gas phase CO_2 molecule is directly generated without the formation of negatively charged CO_2 on the surface. This is clearly due to the relatively high activities of these surface O as well as the fact that the presence of too many surface O ions in close proximity to the reaction site inhibits the formation of negatively charged CO_2 . This result is similar to the case of CO oxidation on a 2×1 reconstructed $\text{CeO}_2(110)$ surface. In this scenario, a reconstructed area containing numerous negatively charged surface O ions favors the direct formation of neutral CO_2 without producing

Fig. 10. Calculated isosurfaces of spin electrons in metastable $\text{CeO}_2(100)$ surface slabs (side view, 2×2 supercell).

any negative intermediates [52]. Our results therefore indicate that the distribution pattern of the surface lattice O on CeO₂ catalysts may greatly affect the reactivity of the material.

The reactivities (or stabilities) of CeO₂(100) surfaces can also be identified based on the results of electronic analyses. Fig. 10 demonstrates that the charge distribution in bulk metastable CeO₂(100) is significantly different from that in the most stable variant. As we have explained, the obvious electrostatic repulsion between overly close surface lattice O tends to destabilize these species, meaning that these surface O then lose some electron density so as to become less negatively charged. The resulting less negatively charged surface O can be more reactive in surface reactions compared with the original O²⁻ ions. Most importantly, the Ce⁴⁺ cations in the slab can readily accept these electrons as a result of their unique, empty localized 4f orbitals, which facilitate the charge transfer. Thus, as noted above, surface O with locally high coverages, which may occur when the surface oxygen vacancies are healed by the dissociative adsorption of O₂ molecules, can exhibit relatively high activity during CO oxidation, especially in the case of direct CO₂ formation.

4. Conclusions

We performed DFT+U calculations to study the structures of CeO₂(100) polar surfaces and the reactions between CO molecules and various types of surface O. From the calculated results, we can conclude that, in the case of an O-terminated surface, the full O layer results in significant electrostatic repulsion between the exposed O ions, and the surface is stabilized when the O coverage is reduced. Our symmetric slab model demonstrated that removing half the full layer of O from the top and bottom surfaces produced the most stable stoichiometric surface. Electronic analyses further showed partial electron transfer from the surface O to the Ce⁴⁺ cations (primarily localized in the Ce 4f orbitals) when employing a symmetric, stoichiometric slab with more than half the full O layer maintained on the surface and a corresponding number of O_v in the bulk. This charge transfer process renders the surface O less negative and reduces the electrostatic repulsion among these ions on metastable CeO₂(100) surfaces. CO adsorptions at various CeO₂(100) surfaces are rather weak, and the reaction of CO with surface O follows the MvK mechanism. We further determined that adsorbed bent CO₂ molecules can be formed on the most stable CeO₂(100) surface, and can very readily desorb to the gas phase or react with nearby O_{2c} to generate carbonate species that are more stable than the gas phase CO₂. In contrast, in the case of the metastable CeO₂(100), there is no adsorption of CO₂ species on the surface, and the direct formation of gas phase CO₂ appears to dominate the reaction. High coverage of O, which makes the surface less stable due to the associated electrostatic repulsion, was also found to be the main factor that prevents the occurrence of negatively charged, bent CO₂.

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Graphical Abstract

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A DFT+U study of the structures and reactivities of polar CeO₂(100) surfacesSu-Hong Zhong, Guanzhong Lu, Xue-Qing Gong*
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This work performed calculations to predict the properties of polar CeO₂(100) surfaces, and found that the local coverage of surface O can affect the surface stability. It was determined that Ce 4f orbitals can accept electrons from surface O ions and hence allow changes in the oxidation states of these surface O.

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CeO₂(100)极性面结构与活性的密度泛函理论研究钟素红^{a,b}, 卢冠忠^b, 龚学庆^{a,b,*}^a华东理工大学, 化学与分子工程学院, 计算化学中心, 结构可控先进功能材料及其制备教育部重点实验室, 上海200237^b华东理工大学, 化学与分子工程学院, 工业催化研究所, 结构可控先进功能材料及其制备教育部重点实验室, 上海200237

摘要: CeO₂是一类使用非常广泛的稀土氧化物催化材料, 在许多重要的催化反应过程, 如机动车尾气净化、水汽转换、石油裂解等, 表现出很高的活性。大量研究表明, CeO₂的高活性来源于其表面晶格氧, 正是由于这些晶格氧能够直接参与氧化反应, 同时反应留下的氧空位又能够被气相氧分子吸附填补, 因而体现出很好的储放氧催化性能。目前多数研究采用CO氧化为模型反应, 研究了CeO₂常见的(111)和(110)晶面的晶格氧活性, 但对于其另外一种重要低指数晶面(100)的结构和活性研究却非常有限。需要指出的是, CeO₂(100)是一种极性表面, 这给该表面的模型构建和理论研究带来了困难。为了深入了解这种极性表面的结构稳定性和催化活性, 本文运用在位库仑力校正的密度泛函理论(DFT+U)方法系统研究了CeO₂(100)极性面的可能结构及相关稳定性, 并且深入分析了CO在该表面上的吸附和反应。

本文首先利用板层模型尝试构建稳定的CeO₂(100)极性面结构, 方法是在保证整个板层化学计量配比完整的前提下, 在表层或体相去除氧原子, 同时使得整个板层上下对称不存在极性以利于计算。通过计算发现, 在CeO₂(100)表层分布氧空位的结构比体相中分布氧空位的结构要稳定, 同时, 氧空位的分布越接近表面, CeO₂(100)面的结构稳定性就会越高, 其最稳定的结构是将表层满覆盖氧离子移除一半。

对CeO₂(100)面不同结构的稳定性及相关电子结构分析表明, CeO₂(100)表层满覆盖的氧离子间存在很强的相互排斥作

用, 因此倾向于降低表面氧浓度来提高表面的稳定性. 另外, 这种相互作用会降低相邻氧离子的价态, 并能引起体相铈离子在整体表面维持完整的化学计量比的情况下, 仍能出现局域4f电子而被还原为三价铈.

随后我们研究了CO在CeO₂(100)最稳定和次稳定表面上的氧化反应. 发现CO在不同CeO₂(100)表面的氧空位处吸附较强, 另外, CO在CeO₂(100)最稳定结构上可与表面晶格氧反应形成吸附的CO₂中间物种, 中间物种可直接解离成气相CO₂, 也可以继续与表面晶格氧反应形成碳酸盐. 而在CeO₂(100)次稳定表面上, CO很难与表面晶格氧形成吸附的CO₂中间态, 而直接产生气态CO₂.

关键词: 二氧化铈(100); 在位库伦校正的密度泛函理论; 极性表面; 一氧化碳氧化; 电子局域

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