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A DFT + U study of V, Cr and Mn doped CeO$_2$(111)

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ABSTRACT

Density functional theory calculations corrected by on-site Coulomb interactions have been performed on CeO$_2$(111) surfaces doped with three different transition metals, namely V-CeO$_2$(111), Cr-CeO$_2$(111) and Mn-CeO$_2$(111). The unique physicochemical properties and catalytic reactivities of these doped surfaces were carefully studied, and specifically, the oxygen formation energies and CO reactions with surface O at different sites were systematically calculated. It has been shown that the dopants can help to form surface oxygen vacancies and increase surface reactivities, and in particular, Mn doped surface gives the best performance in surface reactions.

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1. Introduction

Cerium is among the rare earth elements that have the highest abundance in the earth's crust. Moreover, cerium dioxide (ceria, CeO$_2$) has been widely used as the key component of catalysts in many different fields, such as three-way-catalysis (TWC), water-gas-shift reactions (WGS) and oxidative dehydrogenation [1–6]. A lot of work has been done to illustrate the origin of the catalytic activities of CeO$_2$, and it has been shown that the redox property of Ce cations (Ce^{4+}↔Ce^{3+}) plays an important role in the processes catalysed by CeO$_2$ based catalysts. Presence of oxygen vacancies (O$_v$) and oxygen storage capacity have also been examined to be crucial in catalytic oxidation processes [7,8], and these properties were carefully studied at various low-index CeO$_2$ facets including CeO$_2$(111), (110) and (100), among which CeO$_2$(111) is the most stable one [9–14].

It needs to be mentioned that the catalytic activities of stoichiometric CeO$_2$ surfaces are rather limited, and many studies have been conducted aiming at finding effective approaches to improve the catalytic performances of CeO$_2$ based catalysts. Doping with heteroatoms has been found to be a promising strategy and many different elements have been tried for CeO$_2$ doping. For example, zirconium can be introduced to ceria to form Ce$_{1-x}$Zr$_x$O$_2$ solid solutions, which have been proved to be very active for TWC [15–21], and recently Zr-doped ceria was also found to be highly efficient in

ammonia detection [22]. Mn doped ceria has also been widely studied, which shows that manganese doping can decrease interface energies and increase catalytic activities for hydrocarbon oxidation [23–30]. Modifying ceria catalysts with supported noble metals also attracted intensive interests in recent years, and a great number of studies on ceria-supported single atom or clusters of Pd, Pt and Au showed that such supported catalysts exhibit improved activities for processes like CO oxidation and WGS [21,31–40]. Moreover, CeO$_2$/CuO-Cu catalyst was also found to exhibit rather high activity toward CO oxidation and the catalytic performance is directly determined by dopant [41–44]. Besides numerous experimental findings, some theoretical attempts of understanding transition metal doped ceria are also available [45–51]. Krcha et al. found that the dissociative adsorption energies and activation barriers of methane correlate linearly with formation energies of surface O$_v$, and they also found that dopants can be reduction centres during reactions [52]. As transition metals always have variable valence states, several theoretical studies on divalent, tetravalent and aliovalent elements doped CeO$_2$ have also been conducted [53–56]. However, there are still many challenges in using the density functional theory (DFT) calculations to examine catalysis over metal-doped ceria surfaces as Krcha and Janik mentioned in their review article that the effect of valence changes of doped metals on surface catalytic activities is still unclear and the calculated energies need to be more accurate [57].

In this work, in order to obtain deeper understanding of transition metal doped CeO$_2$, we systematically calculated CeO$_2$(111) surfaces doped with V, Cr and Mn. It shows that the dopants can help to generate surface oxygen vacancies and affect the distri-

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butions of localized extra electrons at the corresponding reduced surfaces. From the calculated energetics, we also found that transition metal doped $CeO_2(111)$ surfaces can exhibit higher activities for CO oxidation.

2. Computational details

The spin-polarized DFT + U calculations were carried out using the GGA-PBE functional implemented in the Vienna ab initio Simulation Package (VASP) [58–60]. We used the project-augmented wave method (PAW) to describe the electron–core interaction, with Ce (5s, 5p, 6s, 5d, 4f), V, Cr, Mn (3d, 4s), C, O (2s, 2p) and H (1s) electrons being treated as valence electrons. To describe the localized 4f states of Ce and the 3d states of V, Cr and Mn properly, the on-site Coulomb interactions correction was used [61]. As suggested by Nolan and co-workers, the U value for Ce 4f was set to 5.0 eV [11,56]. The U values for V, Cr and Mn 3d states were set to 3.0 eV, 3.5 eV and 3.5 eV, respectively, and they were determined by combining our calculation results with those reported in other studies [62–64]. The details are given in the Supplementary Material. The Kohn-Sham orbitals were expanded in plane waves with a kinetic energy cutoff of 400 eV. The calculated lattice parameter of bulk ceria using the DFT + U method (5.436 Å) is in good agreement with the experimental value (5.411 Å).

The clean and doped $CeO_2(111)$ surfaces were all modelled by 9-layer slabs. The bottom 3 layers (one tri-layer) were kept fixed at bulk positions during calculations, while the other layers were allowed to relax. The force threshold was set to 0.05 eV Å^{-1}. The 4×4 expansion of the surface unit cell was applied. The Brillouin-zone integration was approximated by $1 \times 1 \times 1$ grid using the Monkhorst–Pack scheme. The vacuum gap between slabs was set to 15 Å.

In the study of interaction between CO and the surfaces, the adsorption energies (E_{ads}) were calculated by using the following equation,

$$E_{ads} = -[E(CO/CeO_2) - E(CO) - E(CeO_2)] \quad (1)$$

where $E(CO/CeO_2)$ is the total energy of the interacting system involving CO and the CeO_2 surface, and $E(CO)$ and $E(CeO_2)$ are the total energies of an isolated CO molecule in gas phase and the surface without any adsorbates, respectively.

In this work, the oxygen vacancy formation energy was estimated by using the following equation:

$$E_{vac} = E_{vac-slab} - E(CeO_2) + 1/2E(O_2) \quad (2)$$

where $E_{vac-slab}$ is the total energy of the slab with an oxygen vacancy and $E(O_2)$ is the energy of one gas-phase oxygen molecule.

3. Results and discussion

3.1. Stabilities of different surfaces

In the current work, doped ceria surfaces were constructed by replacing one surface Ce cation with V, Cr and Mn, respectively, and the corresponding optimised surface structures are shown in Fig. 1. For Mn-doped $CeO_2(111)$, we located two different surface structures, which can be called Mn_a-$CeO_2(111)$ (see Fig. 1(a)) and Mn_b-$CeO_2(111)$ (see Fig. 1(b)). The Mn_a-$CeO_2(111)$ gives higher surface energy and it largely keeps the same structure of the stoichiometric $CeO_2(111)$ with the doped Mn moving slightly away from the originally Ce position by only $\sim$0.02 Å. For the more stable Mn_b-$CeO_2(111)$ surface, it appears to be highly distorted and forms completely new local structures at the doped site. The movements of dopants in relaxed structures of V-$CeO_2(111)$ and Cr-$CeO_2(111)$ are also shown in Figs. 1(c) and (d), respectively.

Table 1
Calculated formation energies (in eV) of V, Cr and Mn doped $CeO_2(111)$ surfaces.

Doping Metals	E_{f1}	E_{f2}
V	1.32	4.46
Cr	1.60	5.31
Mn_a	2.36	6.14
Mn_b	1.98	5.76

Table 2
Calculated Bader charges (in e) of different dopant atoms.

Dopants	V	Cr	Mn_a	Mn_b
Charges	2.34	2.13	1.88	2.00

In order to obtain better understanding of the doped $CeO_2(111)$ surfaces involving different transition metal atoms, and in particular, compare the stabilities of different doped $CeO_2(111)$ surfaces, we calculated the formation energies of each surface slab by using the following two equations [53],

$$E_{f1} = E(M\text{-}CeO_2(111)) + E(CeO_2) - E(CeO_2(111)) - E(MO_2) \quad (3)$$

$$E_{f2} = E(M\text{-}CeO_2(111)) + E(Ce) - E(CeO_2(111)) - E(M) \quad (4)$$

where $E(M\text{-}CeO_2(111))$ and $E(CeO_2(111))$ are the calculated total energies of transition metal doped and stoichiometric $CeO_2(111)$ slabs, respectively, while $E(CeO_2)$ and $E(MO_2)$ are the energies of one single CeO_2 and MO_2 unit in corresponding bulk phases, and $E(Ce)$ and $E(M)$ are energies of one single Ce atom and substituent transition metal atom, respectively.

By calculating the formation energies of E_{f1} and E_{f2}, we can actually understand the doping processes and compare their energetics in two different ways. When the two values were calculated to be positive, it can be expected that the doping process is thermodynamically unfavourable with respect to the existence of the separated transition metal species in the form of metal oxide or pure metal. Moreover, the more positive the calculated formation energies are, the more unfavourable the doping processes are, and accordingly, the less stable the doped slabs turn to be. The calculated formation energies of all the doped $CeO_2(111)$ surfaces are listed in Table 1. From these results, we can clearly see that, despite their different absolute values, the calculated E_{f1} and E_{f2} have the same order of E_{f1} (V-$CeO_2(111)$) < E_{f1}(Cr-$CeO_2(111)$) < E_{f1}(Mn_b-$CeO_2(111)$) < E_{f1} (Mn_a-$CeO_2(111)$), and E_{f2}(V-$CeO_2(111)$) < E_{f2} (Cr-$CeO_2(111)$) < E_{f2} (Mn_b-$CeO_2(111)$) < E_{f2} (Mn_a-$CeO_2(111)$)). Due to the fact that these calculated values are all positive, the doping processes are thermodynamically unfavourable, though the V-doped surface turns out to be relatively the most stable one followed by the Cr-doped surface, while Mn doping seems be the most difficult. In addition, for the two types of Mn doped $CeO_2(111)$, the Mn_b-$CeO_2(111)$ is more stable than Mn_a-$CeO_2(111)$, which is largely because that it is more heavily relaxed.

To further understand the stabilities of the doped $CeO_2(111)$ surfaces, we then conducted analyses also from electronic and structural points of view [65,66]. At stoichiometric $CeO_2(111)$ surface, the surface Ce cation is coordinated with 7 O ions and takes the formal charge of +4. When an oxygen vacancy is generated, two extra electrons will be localized at two Ce cations beside the vacancy and reduce them to Ce^{3+} [7]. Accordingly, the calculated Bader charges of the Ce cations at stoichiometric $CeO_2(111)$ and that taking the localized electrons at the surface with the oxygen vacancy are around +2.4 and +2.1 e, respectively. In Table 2, we list the calculated Bader charges of the doped V, Cr and Mn cations at the $CeO_2(111)$, and one can see that the charge of the doped V cation is +2.34 e, indicating that this V cation may also take the formal charge of +4. For the doped Cr, since its calculated Bader