Mechanical properties of M-Zr (M=Cr, Al, Mn) co-doped ceria: A first-principles study

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Abstract. Zr-doped ceria has been extensively been used in three-way catalyst industry due to the excellent physical and chemical properties. Co-doping technology is always employed to improve the stability of the materials by hindering the phase segregation into CeO\textsubscript{2} and ZrO\textsubscript{2} individual phases. In this paper, we have intensively studied the stability of M-Zr co-doping systems (M=Cr, Al and Mn) under different growth conditions and under the applied stress. The results show that the O-rich growth condition is very beneficial to the formation of these compounds. Compared with Cr and Mn atoms, Al atoms produce a different type of lattice distortions, which all can improve the stability of the whole system. Among these candidates, Al-Zr co-doping can be most easily formed. Furthermore, our researches demonstrate that under a small strain range, co-doping might increase the mechanical properties of the systems by the solid solution strengthening.

1. Introduction

With the development of automobile industry, exhaust emission has become an important part of air pollution in China since 2009. As the core of the automobile exhaust converter, three-way catalyst has been widely used in the automobile industry. Ceria has excellent physical and chemical properties such as good mechanical polishing performance and high oxygen storage capability (OSC), which plays an important role in the automobile exhaust purification [1].

To improve the catalyst performance of cerium dioxide, researchers always optimize the ion-transport properties by adding extrinsic dopants, including alkaline earth metals, transition metals and rare earth metals, et al. [2-14]. Among these candidates, Zr doping into CeO\textsubscript{2} is a commonly used method to enhance the OSC and catalytic efficiency of the materials in experiments [15-18]. They found Zr could reduce the high formation energy of oxygen vacancies in ceria, which is beneficial to the transport of the charged oxygen vacancies. However, the addition of zirconium might cause some stability problems during the operation [17]. Experimenters has found that Zr atoms tend to segregate together and make the solid solution separate into CeO\textsubscript{2} and ZrO\textsubscript{2} individual phases. The instability could largely weaken the catalytic performance.

A co-doping technology can be an effective methodology to mitigate the Zr segregation in
Zr-doped CeO$_2$ materials. Experimentally, they have observed that Al-Zr and Pd-Zr co-doping can help increase the oxygen vacancy and make their properties superior than before [19-20]. In our previous paper, we have theoretically studied 12 kinds of M-Zr co-doping systems by employing first-principles methods [21]. The structures, the formation energy and the oxygen vacancy formation in the systems are addressed. Our calculated results demonstrate that M (M= Cr, Al, Mn, Co, Pd, Tc, Rh and Cd) can retard Zn diffusion and segregation and then ensure the OSC property of Zr-doped CeO$_2$ materials. However, the stability also depends on the different growth conditions and the co-doping effects on the mechanical properties of the materials are still unclear. A further investigation could help us deeply understand the design of CeO$_2$ materials.

First-principles computational tensile tests (FPCTT) can be used to study the mechanical properties and even the changes in chemical bonding as a response to the applied stress [22-23]. Through the tests, the effects of the dopants on the stability of the materials can be fully evaluated. In this paper, we will choose M= Cr, Al and Mn as representatives, which has larger association energies with Zr [21] to make a further investigation on the stability of co-doped ceria. Thus, we will organize the remainder of the paper as follows. In section II, computational methods and details are described. Section III presents the calculated results for the stability under different growth conditions and the mechanical properties of ceria by using the FPCTT. Finally, a short summary is given in section IV.

2. Computational methods and details

The code we have used is the Vienna ab initio simulation package (VASP) [24]. The electron-ion interaction was described using the projector augmented wave (PAW) method [25] and the electron exchange and correlation were treated within the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form [26]. For all calculated systems, the energy cutoff for the plane wave basis set was 500 eV and spin-polarization was permitted. In order to account for the strong on-site Coulomb repulsion among the Ce 4f electrons, a Hubbard parameter U is also included and U was set as 5 eV [27]. In all the calculations, we employed a 2×2×2 supercell containing 96 atom sites and a 4×4×4 k-mesh in Monkhorst-Pack Scheme for the integration over Brillouin zone. These parameters assure a total energy convergence of 0.01 meV·atom$^{-1}$. The structures of pure ceria and co-doping systems M-Zr-CeO$_2$ were shown in Fig. 1. The lattice constant of the bulk fluorite structure CeO$_2$ was calculated to be 5.48 Å, in good agreement with the previous experimental values and ab initio calculations [28-32].

![Figure 1. The supercells of (a) pure ceria and (b) co-doping systems M-Zr-CeO$_2$. The red, yellow, green and blue balls represent O, Ce, Zr and M atoms, respectively.](image)
3. Results and discussions

3.1. The stability of co-doping systems under different growth conditions

We began by calculating the formation energies of the co-doping systems. Two nearest-neighboring Ce atoms were substituted by M and Zr simultaneously, which could form a M-Zr pair in the supercell as shown in Fig. 1(b). The formation energy (ΔE_f) under different growth conditions can be calculated by

\[ \Delta E_f = E^{\text{tot}}(\text{CeO}_2 - M - Zr) - E^{\text{tot}}(\text{CeO}_2) - \mu_{Zr} - \mu_M + 2\mu_{Ce}. \]  

In the above equation, \( E^{\text{tot}}(\text{CeO}_2 - M - Zr) \) and \( E^{\text{tot}}(\text{CeO}_2) \) represent the total energies of co-doping and pure ceria systems, \( \mu_{Zr}, \mu_M \) and \( \mu_{Ce} \) are the chemical potential Zr, M and Ce respectively. For all the elements, two extreme growth environments have been considered, namely, O-poor and O-rich growth conditions. In the former case, the O-poor means that metals are rich. Hence \( \mu_{Zr}, \mu_M \) and \( \mu_{Ce} \) are equal to the energies of metal atoms in bulk. For the latter one, the chemical potentials of metal element correspond to the ones in oxides, i.e. CeO_2, ZrO_2, Al_2O_3, Cr_2O_3 and MnO. Here, we take CeO_2 as an example. The chemical potential of Ce in the bulk CeO_2 is correlated by

\[ \mu_{Ce} + 2\mu_O = E_{\text{CeO}_2}^{\text{bulk}}, \]

where \( E_{\text{CeO}_2}^{\text{bulk}} \) is the total energy of CeO_2 (per formula unit). \( \mu_O \) is given by the energy of per O atom in gaseous oxygen. Then, we can derive the formation energies of the co-doping systems in different growth conditions.

Figure 2. The formation energies of M-Zr-CeO_2 systems under O-poor and O-rich growth conditions.

As shown in Fig.2, we can see among these systems, Al-Zr co-doping can be easily formed. Its formation energy is in the range of [1.03, 2.62] eV. The formation of Cr-Zr-CeO_2 systems are comparatively difficult with the formation energy of [3.21, 5.84] eV. Obviously, the O-rich growth condition is very beneficial to the fabrication of these compounds. Through the change of growth conditions, the formation of Mn-Zr-CeO_2 systems might be more energetically favorable than Al-Zr-CeO_2 systems.

In order to deeply understand the interactions between different atoms in the co-doping systems, we now resort to the analyses of the electronic structures. The calculated charge density difference in the M-Zr co-doping systems (M= Cr, Al and Mn) is plotted in Fig. 3. The yellow denotes the electron increase zone, and the green is the depletion zone. It clearly shows that oxygen can obtain electrons...
from M and Zr atoms. With more diverse valence states, Cr and Mn atoms can connected with the Zr atom by the middle O. The distances between M-Zr (M=Cr and Mn) become a little shorter after the structure relaxation. For Al, it stays slightly away from the Zr atom after the structure relaxation due to a very small atom radius. The interaction between Al and the middle O is weakened and the Al atom favors to bind strongly with another O. Compared with Cr and Mn atoms, Al atoms produce a totally different type of lattice distortions. As we mentioned before [21], the intense lattice distortion induced by co-doping is responsible for the stability of the systems. This is the underlying reason why the addition of M can have a good effect on the reinforcement of solid solution.

![Figure 3. The calculated charge density difference in the M-Zr co-doping systems (M= Al, Cr and Mn). The colored zones represent the charge density isosurfaces of ±0.005 e/a.u.³. Namely, the yellow and green isosurfaces indicate gain and loss of electrons, respectively.](image)

### 3.2. The stability of co-doping systems under the applied stress

To embark on the research of the mechanical properties of M-Zr co-doping systems, we employed the FPCTT. For the systems with and without co-doping, we fully relaxed the configuration in each strain by uniformly elongating 2% along Y- and Z-axis, respectively. The calculated total free energies as a function of strain are clearly shown in Fig. 4. With the increase of the strain, the energies of all the systems have gone up evidently. It demonstrates that the applied stress makes these systems unstable. However, compared with the pure and doped CeO$_2$ systems, the responses to the strain is indeed different. In Fig.4, we can clearly note that the curves of pure CeO$_2$ intersect with these of doped CeO$_2$ when loading along both Y- and Z directions. For each doped systems, there is no intersection between their curves.

The corresponding stress-strain curves can be obtained by the first derivatives from energy-strain relationship or directly read from the output of the VASP programs. The results along different axes are shown in Fig 5. It is seen clearly that the stress-strain curves and figures of the all the co-doping systems have very similar values and structures when stretching. Along the Y-direction, their curves reach the theoretical ultimate tensile stress (UTS), about 10 GPa with a strain as large as 8%; For the curves along the Z-direction, their values of the UTS are around 12 GPa, and the corresponding strain is in the region 10~12%. As a comparison, the maximum points could not appear in the whole stretching process for pure CeO$_2$. The main reason is that the pure system has high symmetry along the stress direction. In such a case, the structure might deform uniformly and maintain a metastable state when loading. Once the doped atoms are introduced, the stress could be concentrated around these atoms, and the bond breaking is likely to happen. Thus, the doped atoms can be recognized as a breaking point in the rupture process.
4. Conclusion

In summary, we have systematically investigated the stability of M-Zr co-doping systems (M= Cr, Al and Mn) under different growth conditions and the corresponding mechanical properties by using first-principles calculations have been also reported. It was found that the O-rich growth condition is very beneficial to the formation of these compounds. Compared with Cr and Mn atoms, Al atoms produce a different type of lattice distortions, which all can improve the stability of the whole system.
Among these candidates, Al-Zr co-doping can be easily formed. Moreover, the FPCTT testified that in a small strain range, co-doping might increase the mechanical properties of the systems though it could be a breaking point in the rupture process. M-Zr-CeO$_2$ (M= Cr, Al and Mn) could be promising candidates when applied in three-way catalyst industry.

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