Rare earth doping effect on the thermal stability of Ce$_{0.35}$Zr$_{0.60}$M$_{0.05}$O$_2$: insights from experiment and simulation

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Abstract—Ce$_x$Zr$_{1-x}$O$_2$ (CZ) plays an important role in many environment catalytic fields such as automobile three-way catalysts (TWCs), but improving their thermal stability is still a great challenge. In this work, a strategy was proposed to enhance the thermal stability of CZ by combining experiment with ab-initio molecular dynamics (AIMD) method. It is found that the thermal stability of Ce$_{0.35}$Zr$_{0.60}$M$_{0.05}$O$_2$ (M represent La, Y, and Nd elements) could be adjusted by doping the suitable rare earth (RE) elements in the surface of CZ. With this strategy, the thermal stability of Ce$_{0.35}$Zr$_{0.60}$M$_{0.05}$O$_2$ (CZ-Y) with surface doping of Y is highest among these Ce$_{0.35}$Zr$_{0.60}$M$_{0.05}$O$_2$ samples. In comparison with the CZ sample without doping (specific surface area SSA=20.16 m$^2$g$^{-1}$), CZ-Y exhibit superior thermal stability (SSA=26.83 m$^2$g$^{-1}$) after thermal treatment (1100 °C/10 h). To give a deep insight into the RE doping effects, the thermal displacement rate (TDR) of Ce$_{0.35}$Zr$_{0.60}$M$_{0.05}$O$_2$ are further calculated by AIMD. It is found that CZ-Y has the lowest TDR values, which is beneficial for suppressing the thermal displacement of atoms and improving the thermal stability of CZ. This study provides a deep insight into the origin of rare earth (RE) doping effect on Ce$_x$Zr$_{1-x}$O$_2$ (CZ), which is of fundamental interest for the development of high performance CZ in practical applications.

1. Introduction

Ce$_x$Zr$_{1-x}$O$_2$ (CZ) have attracted much interests because of their excellent performance in environment and energy applications such as automobile TWCs$^{[1]}$ and solid oxides fuel cells$^{[2]}$. However, in the practical TWCs applications of CZ materials, the working temperature can reach 900 °C or higher$^{[3]}$. CZ is easy to sinter after a period of time at this temperature, resulting in the loss of SSA, which further reduces the catalysis efficiency and service life of TWC. Therefore, the development of high thermal stability CZ materials is very important for its practical applications.

One of the way to enhance thermal stability of CZ is to dope other elements such as base metals$^{[4]}$ and transition metals$^{[5]}$. In addition, rare earth (RE) elements are also used in CZ to improve the thermal stability of CZ$^{[6]}$. However, deeply understanding the structure-activity relationship between the thermal stability and surface doping structure of CZ at atom level is still lacking, which represents

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a necessary preliminary step to find higher thermal stability CZ materials. Therefore, it is an
significant and challenging task to propose a more precise strategy which can be used to improve the
thermal stability of CZ materials. Combining experiment and AIMD simulation method can help in
this respect[7].

In this work, we investigate the structure-activity relationship between the rare earths (La, Y, and
Nd) surface doping and thermal stability of CZ by combining experiment with AIMD simulation
method. Our investigation focuses on systems of Ce<sub>0.35</sub>Zr<sub>0.60</sub>M<sub>0.05</sub>O<sub>2</sub> due to its widely application in
TWC[8]. The experiment and calculation details are given in section two. The result and discussion are
given in section three, in which the structure properties, thermal stability, and mechanism of RE-doped
Ce<sub>0.35</sub>Zr<sub>0.60</sub>M<sub>0.05</sub>O<sub>2</sub> are discussed. A conclusion is presented in section four.

2. Experimental and Computational details

2.1 Experiment preparation details

The chemical deposition method was used to synthesize the Ce<sub>0.35</sub>Zr<sub>0.60</sub>M<sub>0.05</sub>O<sub>2</sub> samples[9]. The CeCl<sub>3</sub>
and ZrOCl<sub>2</sub> precursor were precipitated with NaOH to form Ce(OH)<sub>3</sub>-ZrO(OH)<sub>2</sub>. Afterwards, La, Y
and Nd ions are further deposited on the surface of the Ce(OH)<sub>3</sub>-ZrO(OH)<sub>2</sub> base. The precipitation
slurry was directly filtered and washed with deionized water. The final wet cake was dried overnight
at 100°C. In the rest of this article, the undoped ceria-zirconia mixed oxide is labeled as CZ. Moreover,
CZ-La, CZ-Y, and CZ-Nd correspond to the La, Y and Nd surface doped Ce<sub>0.35</sub>Zr<sub>0.60</sub>M<sub>0.05</sub>O<sub>2</sub>. The dried
sample was directly put into the muffle furnace and calcined at 830 °C/3 h, which were named as CZ-f
(f represent fresh sample). Afterwards, the above fresh sample was further calcined at 1100°C/10h to
obtain age samples, and which were marked as CZ-La-a, CZ-Y-a, CZ-Nd-a and CZ-a.

2.2 AIMD simulation details

Vienna ab initio simulation package (VASP) was used in the AIMD simulation[10] with Perdew-Burke-
Ernzerhof xc functionals. All calculations are performed by Perdew-Burke-Ernzerhof xc functionals[11-
12]. It has been demonstrated in Refs[13] that the spin-polarized DFT+U method should be applied in
order to accurately correct the strong on-site Coulomb repulsion of Ce-4f states. Therefore, in the
current paper, we have used the DFT+U method with U=5.0 eV[13]. Unit-cell parameters and atomic
coordinates were optimized with the convergence condition of 0.02 eV/Å for the configurations. The
calculations were carried out using Monkhorst–Pack mesh k-points with a 450 eV cut-off energy.
Gaussian smearing was used with a width of 0.05 eV to determine the partial occupancies. A vacuum
layer thickness of 15 Å was adopted in this work to calculate TDR. Surface structures was drawn with
a computer program VESTA[14]. In AIMD simulations, a series of temperature conditions starting from
400K to 1600K is considered.

3. Results and Discussions

3.1 Structural properties

To study the phase structure of Ce<sub>0.35</sub>Zr<sub>0.60</sub>M<sub>0.05</sub>O<sub>2</sub> mixed oxides, Figure 1 shows the XRD peaks of
Ce<sub>0.35</sub>Zr<sub>0.60</sub>M<sub>0.05</sub>O<sub>2</sub> samples by different calcined conditions. The XRD peaks of Ce<sub>0.35</sub>Zr<sub>0.60</sub>M<sub>0.05</sub>O<sub>2</sub>
fresh samples were given in Figure 1(a). It is found that each of the diffraction peaks is assigned to the
tetragonal phase structure of the CZ, which indicates that RE doping has little effect on the phase
structure of Ce<sub>0.35</sub>Zr<sub>0.60</sub>M<sub>0.05</sub>O<sub>2</sub>. The XRD peaks of Ce<sub>0.35</sub>Zr<sub>0.60</sub>M<sub>0.05</sub>O<sub>2</sub> aged samples were given as
figure 1(b). More obvious peaks were observed compared with Figure 1(a), suggesting the high
crystallinity happened due to aging process. Based on the Debye-Scherrer equation[15], the grain sizes
of Ce<sub>0.35</sub>Zr<sub>0.60</sub>M<sub>0.05</sub>O<sub>2</sub> samples were calculated and summarized in Table 1. We can observe that the
grain sizes of CZ-Y samples are smaller than that of other CZ samples. It demonstrate that the high
temperature sintering of Ce<sub>0.35</sub>Zr<sub>0.60</sub>M<sub>0.05</sub>O<sub>2</sub> grains can be inhibited by surface doping of Y. This
phenomenon will be further explained by AIMD calculation as follows.
Fig. 1 (a) XRD peaks of Ce0.35Zr0.60M0.05O2 fresh samples; (b) XRD peaks of Ce0.35Zr0.60M0.05O2 aged samples (The XRD data were obtained by Rigaku Smart Lab X-ray diffractometer).

Table 1 The grain sizes of Ce0.35Zr0.60M0.05O2 samples

| Number | Conditions | Grain size (nm) | Number | Conditions | Grain size (nm) | ΔGs |
|--------|------------|----------------|--------|------------|----------------|-----|
| CZ-La-f | Fresh samples (830 °C/3 h) | 7.13 | CZ-La-a | Aged samples (1100 °C/10 h) | 15.3 | 114.6% |
| CZ-Y-f | 6.91 | CZ-Y-a | 14.1 | 104.1% |
| CZ-Nd-f | 7.19 | CZ-Nd-a | 15.7 | 118.4% |
| CZ-f | 7.23 | CZ-a | 15.9 | 119.9% |

*ΔGs:={Gs(aged)-Gs(fresh)}/Gs(fresh) ×100%.

The morphologies of Ce0.35Zr0.60M0.05O2 aged samples were further observed from the SEM images as shown in Figure 2. It can be found that CZ-Y-a have the sphere-like accumulation morphologies while CZ-La-a, CZ-Nd-a, and CZ-a accumulate together to form irregular morphologies. Moreover, the particles size of CZ-Y-a sample is more uniform and smaller than other samples, indicating CZ-Y-a has better particle accumulation dispersion. According to the high resolution SEM images in Figure 2, it shows that CZ-Y-a sample has richer pores channels and looser surface structure, which indicates that doping of Y improves the total pore volume. Therefore, It can be concluded that CZ-Y has sphere-like accumulation morphology and porous structure, which is in favor of improving the specific surface area[6].

Fig. 2 SEM images of CZYN-L-a, CZLN-Y-a, CZLY-N-a, and CZLYN-a samples (3000k and 8000k represent the magnification times, the SEM figures were observed by using JEOL JSM-7900F)
To ensure the elements surface distribution state of Ce\textsubscript{0.35}Zr\textsubscript{0.60}M\textsubscript{0.05}O\textsubscript{2}, the XPS spectra of Ce\textsubscript{0.35}Zr\textsubscript{0.60}M\textsubscript{0.05}O\textsubscript{2} and Ce\textsubscript{0.35}Zr\textsubscript{0.65}O\textsubscript{2} were further characterized. As shown in Figure 3, the curves of Ce-3d spectra for fresh Ce\textsubscript{0.35}Zr\textsubscript{0.60}M\textsubscript{0.05}O\textsubscript{2} and Ce\textsubscript{0.35}Zr\textsubscript{0.65}O\textsubscript{2} samples were given. It can be noticed that the doping of RE has effect on the Ce elements distribution state in the surface of CZ. As shown in Table 2, the surface composition of Ce, Zr, La, Y, and Nd of fresh and aged Ce\textsubscript{0.35}Zr\textsubscript{0.60}M\textsubscript{0.05}O\textsubscript{2} and Ce\textsubscript{0.35}Zr\textsubscript{0.65}O\textsubscript{2} samples are also calculated by XPS spectra. It can be noticed that both Ce and Zr are homogeneously distributed throughout the Ce\textsubscript{0.35}Zr\textsubscript{0.60}M\textsubscript{0.05}O\textsubscript{2} nanoparticles surface. Moreover, the composition of La, Y, and Nd in the surface region of the CZ particle is higher than that in bulk region of the CZ particle, which demonstrate that La, Y, and Nd atoms mainly distribute on the surface of Ce\textsubscript{0.35}Zr\textsubscript{0.60}M\textsubscript{0.05}O\textsubscript{2}.

Fig. 3. Ce-3d XPS spectra of CZ-La-f, CZ-Y-f, CZ-Nd-f, and CZ-f samples (The XPS spectra was obtained by using Thermo ESCALAB 250XI instrument).

| Number   | Fresh samples Atomic % | Aged samples Atomic % |
|----------|-------------------------|-----------------------|
|          | Ce  | Zr  | La  | Y   | Nd | Ce  | Zr  | La  | Y   | Nd |
| CZ-La    | 0.28 | 0.53 | 0.19 | --  | -- | 0.24 | 0.61 | 0.15 | --  | -- |
| CZ-Y     | 0.30 | 0.56 | --  | 0.14 | -- | 0.26 | 0.56 | --  | 0.18 | -- |
| CZ-Nd    | 0.26 | 0.59 | --  | --  | 0.15 | 0.29 | 0.57 | --  | --  | 0.14 |
| CZ       | 0.34 | 0.66 | --  | --  | -- | 0.31 | 0.69 | --  | --  | -- |

Table 2 The atomic composition on CZ surface from XPS analysis

3.2 Thermal stability
To investigate the thermal stability of Ce\textsubscript{0.35}Zr\textsubscript{0.60}M\textsubscript{0.05}O\textsubscript{2} mixed oxides doped with different RE, Figure 4 (a) and (b) give the pore distribution curve of Ce\textsubscript{0.35}Zr\textsubscript{0.60}M\textsubscript{0.05}O\textsubscript{2}. The pore distribution curve of Ce\textsubscript{0.35}Zr\textsubscript{0.60}Y\textsubscript{0.05}O\textsubscript{2} is obviously higher than other samples in the range of 10-20 nm, which indicates that CZ-Y sample has richer pore structure. After aging treatment, the pore distribution curve of CZ-Y is still higher than other samples, meaning that mesoporous structures of CZ-Y is more stable than other samples at high temperature conditions (1100°C/10h). The results in Figure 4 (a) and (b) are in good agreement with the total pore volume (TPV) data seen as Table 3. The SSA of Ce\textsubscript{0.35}Zr\textsubscript{0.60}M\textsubscript{0.05}O\textsubscript{2} samples are shown in Figure 4(c) and (d). The SSA of Ce\textsubscript{0.35}Zr\textsubscript{0.60}La\textsubscript{0.05}O\textsubscript{2}, Ce\textsubscript{0.35}Zr\textsubscript{0.60}Y\textsubscript{0.05}O\textsubscript{2}, Ce\textsubscript{0.35}Zr\textsubscript{0.60}Nd\textsubscript{0.05}O\textsubscript{2}, and Ce\textsubscript{0.40}Zr\textsubscript{0.60}O\textsubscript{2} aged samples were 24.64 m\textsuperscript{2}·g\textsuperscript{-1}, 26.83 m\textsuperscript{2}·g\textsuperscript{-1}, 22.39 m\textsuperscript{2}·g\textsuperscript{-1}, and
20.16 m²·g⁻¹, which also agrees well with the TPV data listed in Table 2. In a word, CZ-Y has higher thermal stability, which further proved that it is beneficial for improving the thermal stability by surface doping of Y.

![Graph of the pore distribution and SSA for Ce₀.35Zr₀.60M₀.05O₂ fresh and aged samples.]

Table 3 The TPV data of Ce₀.35Zr₀.60M₀.05O₂ fresh and aged samples

| Number | Samples | Total pore volume (mL/g) | Number | Samples | Total pore volume (mL/g) |
|--------|---------|--------------------------|--------|---------|--------------------------|
| 1      | CZ-La-f | 0.416                    | 5      | CZ-La-a | 0.098                    |
| 2      | CZ-Y-f  | 0.423                    | 6      | CZ-Y-a  | 0.103                    |
| 3      | CZ-Nd-f | 0.407                    | 7      | CZ-Nd-a | 0.093                    |
| 4      | CZ-f    | 0.387                    | 8      | CZ-a    | 0.090                    |

3.3 Mechanism analysis

To further understand the RE doping effect mechanism for Ce₀.35Zr₀.60M₀.05O₂, the thermal displacement rate (TDR) [16] was further calculated, which are usually used to theoretical describe the stability of materials upon heating. Figure 5 shows the thermal displacement rate of Ce₀.35Zr₀.60M₀.05O₂ surface at 400K-1600K. The TDR of subsurface (layer 2) and bulk layer (layer 3) is larger than surface layer (layer 1), which indicates that surface atoms change their positions more dramatically than atoms in layer 2 and layer 3 with temperature increasing. Figure 5 (e) shows the <110> surface models of Ce₀.35Zr₀.60M₀.05O₂. The TDR of Ce₀.35Zr₀.60M₀.05O₂ at 400K-1600K were further compared as shown in Figure 5 (f). The sequence of TDR was CZ-Y<CZ-La<CZ-Nd<CZ at 1000K-1600K, which agrees
well with the results of SSA in Figure 4. Based on the above theory results, it is beneficial for suppressing the thermal displacement of atoms and improving the thermal stability of CZ by surface doping Y.

Fig. 5 The TDR of CZ-La (a), CZ-Y (b), CZ-Nd (c), and CZ (d) surface at different layers and temperatures; (e) The surface models of Ce_{0.35}Zr_{0.60}M_{0.05}O_{2} (green ball represent Zr, yellow ball represent Ce, red ball represent O, black ball represent doped RE elements). (f) The TDR of Ce_{0.35}Zr_{0.60}M_{0.05}O_{2} at different temperatures (400K-1600K).
4. Conclusion
In summary, to improve the high temperature thermal stability of Ce$_{0.35}$Zr$_{0.60}$M$_{0.05}$O$_2$, a strategy was proposed by combining experiment and AIMD simulation methods. It is found that the thermal stability of CZ could be adjusted by surface doping the suitable RE elements. With this strategy, the thermal stability of CZ-Y with surface doping of Y is highest among these samples. In comparison with the CZ-a sample without doping (SSA=20.16 m$^2$·g$^{-1}$), CZ-Y-a exhibit superior thermal stability (SSA=26.83 m$^2$·g$^{-1}$) at high temperature conditions. The thermal stability mechanism was further analyzed by AIMD simulation. Based on the TDR calculation, it is found that surface doping of Y is beneficial for suppressing the thermal displacement of atoms and improving the thermal stability of CZ. Our results suggest that thermal stability of CZ can be tuned by doping suitable RE elements, which could provide useful insights for the development of high performance CZ in extensive applications.

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