Supporting Information

Mechanisms of Enhanced Sulfur Tolerance on Samarium (Sm)-doped Cerium Oxide (CeO$_2$) from First Principles

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1. H$_2$S decomposition and SO$_2$ formation pathways

The activation energies for H$_2$S decomposition and SO$_2$ formation were determined along the examined pathways as shown in Figure S1 (note that H atoms were not taken into account in the activation energy calculations of SO$_2$ formation reaction).

**Figure S1.** Schematic diagrams of H$_2$S decomposition and SO$_2$ formation on stoichiometric CeO$_2$ and Sm-doped CeO$_2$.

An overall reaction pathway from H$_2$S adsorption to SO$_2$ desorption was examined by calculating total energy change ($\Delta E$) between two adsorbed intermediates; for example, $\Delta E_{\text{H}_2\text{S}*\text{HS}^*} = E_{\text{HS}^*} + E_{\text{H}^*} - E_{\text{H}_2\text{S}*} - E^*$, where $\Delta E_{\text{H}_2\text{S}*\text{HS}^*}$ is $\Delta E$ between H$_2$S* and HS*, $E$ is the total energy of a surface with adsorbed species, subscripts are adsorbed species, and $E^*$ is the total energy of a clean surface.

**Figure S2.** The overall reaction pathways of H$_2$S decomposition and SO$_2$ formation on stoichiometric CeO$_2$ (dashed lines) and Sm-doped CeO$_2$ (solid lines). * and S* (SO*) indicate a clean surface and adsorbed sulfur on lattice oxygen, respectively.
2. Adsorption configurations of $S^* + H^+ + H^+$ on stoichiometric CeO$_2$

![Figure S3](image)

*Figure S3.* Adsorption configurations of $S^* + H^+ + H^+$ at hollow sties of stoichiometric CeO$_2$. (a) and (b) energies indicate relative energies of each configuration compared to the total energy of $S^* + H^+ + H^+$ on CeO$_2$ where sulfur is located at the top site of Ce as shown in Figure 2 Case(I) of the main paper.

3. Adsorption of H$_2$S, HS, and S species

**Table S1.** Adsorption energies ($E_{ad}$) of H$_2$S, HS, and S species on the stoichiometric CeO$_2$ and Sm-doped CeO$_2$ surfaces depending on adsorption sites. H$_2$S adsorption calculations are performed only at the Ce top sites since the top site has been known the most stable adsorption site for H$_2$S.$^1$ Sulfur on the top of dopants is restrained in x and y directions. Figure (a) and (b) show adsorbed $S^*$ on the Ce top of CeO$_2$ and the Sm–O bridge of Sm-doped CeO$_2$, respectively. $^{(c)}$Adsorbates strongly interact with the lattice oxygen of the Ce–O bridge site. $^{(d)}$None means that no stable configuration is found.

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<th>CeO$_2$</th>
<th>Sm-doped CeO$_2$</th>
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<tbody>
<tr>
<td></td>
<td>Ce top</td>
<td>Ce–O bridge$^{(c)}$</td>
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<tr>
<td>H$_2$S*</td>
<td>−0.21</td>
<td>−</td>
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<tr>
<td>HS*</td>
<td>−0.67</td>
<td>−1.61</td>
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<tr>
<td>S*</td>
<td>−0.70$^{(a)}$</td>
<td>−2.58</td>
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4. Total and projected density of state

Figure S4. (A) TDOS of Pr-, Pm-, and Eu-doped CeO$_2$ (dashed lines) and Sm-doped CeO$_2$ (solid lines). (B) PDOS of surface O 2$p$ states (four O atoms) of Pr-, Pm-, and Eu-doped CeO$_2$ (dashed lines), O$_{Pr}$, O$_{Pm}$, and O$_{Eu}$, respectively, and surface O 2$p$ state (four O atoms) of Sm-doped CeO$_2$ (solid lines), O$_{Sm}$. Spin-up and -down are indicated by positive and negative values. The Fermi energy is referenced at 0 eV.

5. Diffusion of subsurface oxygen onto the surface

Subsurface oxygen atoms tend to diffuse onto the surfaces of stoichiometric CeO$_2$ and Sm-doped CeO$_2$ when two surface oxygen atoms are removed during the SO$_2$ formation and desorption. Sm doping enhances the stabilization of oxygen vacant Sm-doped CeO$_2$ by allowing a subsurface oxygen atom near Sm to diffuse onto the surface. In Figure S5, the diffusion distances of the first subsurface oxygen atoms marked by an arrow in stoichiometric CeO$_2$, Sm-doped CeO$_2$ (A), and Sm-doped CeO$_2$ (B) are 0.35, 0.44, and 1.07 Å, respectively. Without the surface oxygen vacancies, for example, SO$_2$* formed surfaces, the diffusion distances of the first
subsurface oxygen atoms on the three surface models are smaller and similar one another (0.24, 0.27, and 0.26 Å for stoichiometric CeO₂, Sm-doped CeO₂ (A), and Sm-doped CeO₂ (B), respectively).

Figure S5. Location of subsurface oxygen atom in two surface oxygen vacant models of stoichiometric CeO₂ (a) and Sm-doped CeO₂ (b and c). (b) and (c) represent Sm-doped CeO₂ (A) and (B) in the main paper Figure 6, respectively.

References