NO Adsorption and Oxidation on Mn-doped CeO$_2$ (111) Surfaces: A DFT+U Study

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ABSTRACT

The adsorption of NO molecules on Mn-doped CeO$_2$ (111) surfaces for NO oxidation has been studied by employing the periodic density functional theory plus $U$ (DFT+$U$) method. Through our calculations, it is demonstrated how Mn-doped CeO$_2$ with superior NO oxidation activity benefits from the high mobility of the oxygen near the Mn cations. On unreduced Mn-doped CeO$_2$ (111) surfaces, the NO molecule preferentially interacted with the first neighboring O of the Mn cation, with the N also bonding to an Mn cation ($E_{\text{ads}} = -3.30$ eV) or Ce cation ($E_{\text{ads}} = -2.90$ eV). When NO adsorbs on the surface of defective Mn-doped CeO$_2$ with O$_2$ adsorbed in advance, an ONOO$^*$ four atoms species is formed on the surface ($E_{\text{ads}} = -2.51$ eV and $-2.02$ eV), which is an intermediate and can decompose into NO$_2$, NO$_2^*$ and O$_2^*$. The adsorption structure with higher adsorption energy has a closer geometry to NO$_2$, indicating a deeper oxidation of NO. The calculation results indicate that the presence of Mn only has a strong effect on the nearby oxygen atoms and that the Mn-doped CeO$_2$ surface has similar properties to a noble metal in NO oxidation catalysis. In DOS plots, the spin of the electron state of the adsorption structures involving the oxidation of NO is symmetric, indicating that electron transfer occurs from the slab to NO and strong covalent bonds are formed between N and O on the slab, which can also be confirmed by the charge density difference plots.

Keywords: Adsorption; Ceria; Manganese; NO; Density functional theory.

INTRODUCTION

Nitrogen oxides (NO$_x$) emitted from automobile and coal-fired power plant cause a variety of environmental problems, such as acid rain, photochemical smog, secondary organic aerosols and ozone depletion (Chen et al., 2017; Huang et al., 2017). To reduce air pollution resulted from NO$_x$, advances in NO$_x$ removal technology have drawn much attention and been quite rapid. NO oxidation plays an increasingly significant role in NO$_x$ removal technologies (Bray and Schneider, 2015; Xie et al., 2017), including NO$_x$ storage and reduction (Lin et al., 2013; Zhang et al., 2016), selective catalytic reduction (Zahaf et al., 2015; Chen et al., 2016; Guo et al., 2017), dry sorbent injection (Rezaei et al., 2015) and absorption in wet flue gas desulfurization (Liu et al., 2014; Guo et al., 2015b). Cerium oxide has been widely utilized in catalysts pleased in these mobile source and stationary source applications, due to its outstanding oxygen storage capacity (OSC) (Atribak et al., 2008; Zhang et al., 2011; Hong et al., 2016). Using ceria alone is still insufficient for high catalytic activities required in industrial catalysts. More researchers focus on the modification of CeO$_2$ with transition metals to increase the activity and thermal stability (Kehoe et al., 2011; Vanpoucke et al., 2014; Yu et al., 2016). Because transition metal oxides exhibit several oxidation states and better redox properties (Tan et al., 2012), they can take full advantage of the OSC of ceria. Besides, the valence of dopant cations is usually lower than the valence of Ce$^{4+}$, therefore oxygen atoms in doped CeO$_2$ are affected, making them more reactive and easier to be removed (Zhang et al., 2012; McFarland and Metiu, 2013). Among the doped catalysts, Mn-doped CeO$_2$ solid solution have shown excellent catalytic performance in NO oxidation, attaining an efficiency of 75%–85% at 250–325°C (Li et al., 2012; McFarland and Metiu, 2013). The substitution of Ce$^{4+}$ by Mn$^{3+}$ and Mn$^{2+}$ favors the creation of structural defects, induces more surface active oxygen species which further promote the oxidation activity (Lin et al., 2013; Liu et al., 2017a).

Several studies provide a theoretical and electronic insight into the catalytic redox processes of Mn-doped CeO$_2$ oxides by density functional theory (DFT) computation (Cen et al., 2012b; Zhang et al., 2012; Pintos et al., 2013), which may reveal the enhanced catalytic performances. Pintos et al. (2013) reported Mn-dopant promotes surface...
active oxygen atoms release, the creation of surface oxygen vacancies and bulk anionic mobility. The oxidation state of Ce remained unaltered as \( \text{Ce}^{4+} \) when an O atom was removed from the topmost anionic layer of the surface system and Mn cation exhibits in a (3+) oxidation state. On reduced Mn substitutionally doped CeO\(_2\) (111) surfaces, the adsorbed O\(_2\) could be effectively activated to form superoxo (O\(_2^-\)) and/or peroxo species (O\(_2\)\(^2-\)) (Cen et al., 2012b). The Mn doping induce the Mn 3d-0 2p gap state instead of Ce 4f acting as an electrons acceptor and donor during the first oxygen vacancy formation and O\(_2\) replenishing. The formation energy of the first and second oxygen vacancies are \(-0.46\) eV and 1.40 eV, respectively. In contrast, the formation energy of a single oxygen vacancy on CeO\(_2\) (111) was 2.08 eV.

More specifically, the NO oxidation mechanism on Mn-doped CeO\(_2\) surfaces remains unresolved. Experimental analysis on NO adsorption on MnCeO\(_x\) surface evidenced that the monodentate nitrate, bridging nitrate and bidentate nitrate could be observed after NO + O\(_2\) adsorption (Guan et al., 2011; Liu et al., 2013). It is found that the activity of monodentate nitrate and bridging nitrate over the catalysts is much higher than that of bidentate nitrate (Guan et al., 2011). However, NO adsorption or oxidation on Mn-doped CeO\(_2\) surface has not been studied by DFT computation, although relevant research, such as NO and NO\(_2\) adsorption on CeO\(_2\) and NO\(_2\) adsorption on Mn-Ce composite oxides, has been reported in recent years (Nolan et al., 2006; Yang et al., 2006; Lu and Chen, 2014). Yang et al. (2006) found NO adsorption on CeO\(_2\) (110) and (111) surfaces has weak molecule-surface interaction, with adsorption energy of approximately \(-0.04\) to \(-0.18\) eV. The adsorption of NO and NO\(_2\) on the reduced surfaces is much stronger and N\(_2\) and NO tend to be formed, because the O-end of the adsorbed NO and NO\(_2\) molecules fill the oxygen vacancies (Nolan et al., 2006; Yang et al., 2006). Lu and Chen (2014) studied the NO\(_2\) reduction on ceria and Mn-doped CeO\(_2\) (111) surfaces. NO\(_2\) adsorbs more strongly on the Mn-doped CeO\(_2\) surfaces. NO\(_2\) adsorbs more strongly on the Mn-doped CeO\(_2\) surfaces. NO\(_2\) adsorbs more strongly on the Mn-doped CeO\(_2\) surfaces.

In this work, we attempt to address the NO adsorption and oxidation catalyzed by Mn-doped CeO\(_2\) (111) surfaces at theoretical level, applying the DFT+U approach. The adsorption properties (geometry, energies and electronic properties) and the influence of oxygen vacancy are addressed. The possible mechanisms for NO oxidation on Mn-doped CeO\(_2\) surfaces are also discussed.

THEORETICAL APPROACH

Plane-wave density functional theory (DFT) calculations were performed in the Vienna ab initio simulation package (VASP) version 5.2 (Kresse and Furthmuller, 1996a, b). The electron exchange-correlation functional was treated with GGA-PW91 (Perdew et al., 1992; Perdew and Wang, 1992) with the projector-augmented wave method (PAW) (Blochl, 1994; Kresse and Joubert, 1999). The calculations were carried out using the Brillouin zone sampled with \( 3 \times 3 \times 3 \) Monkhorst-Pack mesh k-points grid with a cutoff energy of 500 eV and a Gaussian smearing of 0.1 eV. The 2s\(^2\)2p\(^2\), 2s\(^2\)2p\(^4\), 3d\(^4\)S\(^1\), and 5s\(^5\)p\(^6\)6s\(^5\)d\(^4\)f\(^2\) electrons were included explicitly as the valence for the N, O, Mn and Ce atoms, respectively, and the remaining electrons were kept fixed as core states. The DFT with the Hubbard \( U \) term (DFT+U) method (Dudarev et al., 1998) was applied to accurately correct the strong on-site Coulomb interactions of Mn 3d and Ce 4f states. According to previous study, the U value is chosen as 4.5 eV for Ce 4f and 5 eV for Mn 3d (Cen et al., 2012b; Cockayne et al., 2013).

The supercell model was built from the cubic CeO\(_2\) cell with a lattice constant of \( a = 5.488 \) Å. For the surface model, the (111) surface was modeled to characterize the NO-surface interactions. The slab model was a \( 3\times3\times3 \) lateral cell with nine atomic layers thick and a 15 Å vacuum gap in the direction perpendicular to the surface. One Ce atom of the outermost Ce layer (111) slab was replaced by a Mn atom, giving an overall dopant concentration of 3.7%. The bottom three atomic layers were fixed at their bulk-truncated positions, while the top six atomic layers were relaxed. Relaxation of the model was carried out until the maximum Hellmann–Feynman force was less than 0.02 eV Å\(^{-1}\).

The adsorption energies \( (E_{\text{ads}}) \) were defined as:

\[
E_{\text{ads}} = E_{\text{slab+NO}} - E_{\text{slab}} - E_{\text{NO}}
\]

where \( E_{\text{slab+NO}} \) and \( E_{\text{slab}} \) are the total energies of the doped CeO\(_2\) films with and without NO adsorbed, and \( E_{\text{NO}} \) is the total energy of a NO molecule in the gas phase. Charge density difference (CDD, \( \rho \)) plots were used to examine the bonding between the NO and the surface, which was obtained as:

\[
\Delta \rho = \rho_{\text{slab+NO}} - \rho_{\text{slab}} - \rho_{\text{NO}}
\]

In this equation, \( \rho_{\text{slab+NO}} \) represents the charge density for the adsorbed system; while \( \rho_{\text{slab}} \) and \( \rho_{\text{NO}} \) indicate the charge density of the non-adsorbed subsystem and the NO molecule.

The different possible adsorption sites are labeled in Fig. 1, the O atoms bond to Mn at the top and bottom layer are labeled as O\(_t\) and O\(_b\), respectively. After optimization, the six nearest O atoms from Mn atom are pulled closer centripetally to the Mn atom, consistent with the previous works on studying the influence of Mn doping on the geometric structure of CeO\(_2\) (111) (Cen et al., 2012a). The Ce-O bond in unrelaxed model is 2.38 Å, and after optimization, the Mn–O\(_t\) bond length and Mn–O\(_b\) bond length are 2.28 Å and 2.21 Å, respectively.

For comparison, the properties of a free NO and NO\(_2\) molecule were calculated using a unit cell with the same scale as Mn-doped CeO\(_2\) (111). The optimized NO bond length was 1.17 Å; the corresponding experimental values are 1.15 Å. The optimized N-O bond length in NO\(_2\) was
1.21 Å with an O-N-O bond angle of 133.8°, and the corresponding experimental values are 1.20 Å and 133.8°.

RESULTS AND DISCUSSION

Adsorption and Oxidation of NO on Mn-doped CeO$_2$ (111) Surfaces

The adsorption of NO molecules on the Mn-doped CeO$_2$ (111) surfaces was investigated by optimizing the structures from different initial configurations, e.g., Mn top, Ce$_1$ top and Ce$_2$ top. NO is found to form strong chemical bonds with the Mn-doped CeO$_2$ (111) surfaces. The calculated NO adsorption energies are given in Table 1. As can be seen in Fig. 2, the NO molecule preferentially interacts with the nearest neighbor O of the Mn dopant. Consequently, the NO bond stretched up to 1.21 Å. The N atom also bonds to Mn cation (2.13 Å) or Ce cation (2.64 Å). Obviously, NO adsorption on Mn top is stronger than Ce$_1$ top. The adsorption energies at Ce$_1$ top is –2.90 eV with the N-O$_t$ bond length 1.34 Å and O-N-O bond angle 118.1°, while the adsorption energies at Mn top is –3.30 eV, with the N-O$_t$ bond length 1.32 Å and O-N-O bond angle 119.7°, more similar to the O-N-O structure in NO$_2$. In addition, there is also significant relaxation of the O$_t$, moving 0.63 Å out from the surface. As the single oxygen vacancy near Mn cation is stable with a formation energy of –0.46 eV (Cen et al., 2012a), the formation of NO$_2^*$ from O-N-O structure is feasible. In the study of NO adsorption energy on other transition metal oxides, the adsorption energy is relatively lower than that in this paper (Pietrzyk, 2005; Uzunova et al., 2009; Wang et al., 2010; Zhang et al., 2015; Liu et al., 2017b; Nugraha et al., 2017), and the direct formation of analogous NO$_2^*$ structure in the first step of adsorption has not been observed. NO adsorption on Ce$_2$ top is much weaker than at the other two sites, without the formation of O-N-O structure. These results indicate that the presence of Mn only has a strong effect on the nearby oxygen atoms.

The strong chemical interaction between NO and (111) surface is confirmed by the electronic structure with the appearance of new states correlated to the NO adsorption. In Fig. 3, we compare the projected density of states (PDOS) of NO adsorption on the Mn-doped CeO$_2$ (111) surfaces at Mn top site with that of free NO molecule and clean surface. After NO adsorption, the PDOS of the atomic orbitals of N and ONO change significantly compared with that in free NO molecule, as is clearly seen by the shift to higher energies and the formation of new peaks at a range of from 0 eV to –4 eV. The orbitals of N and ONO are similar to that of O$_t$. By comparing the PDOS of the NO$_2$ molecule (Fig. S1) and O$_{t1}$ (Fig. S2) with that of N, ONO and O$_t$ in Fig. 3(b), it can be concluded that, for N atom, the peaks around 0.8 eV result from the interaction of O 2p and N 2p orbital with the Mn 3d orbital; for ONO and O$_t$, the peaks around –0.8, –1.7 and –2.8 eV mainly result from the electrons in O 2p orbital that are not bonded with N. After adsorption, the spin of electron state of N and ONO are symmetric, indicating the participation of extra electron and the formation of strong covalent bonds between N and O atom that is pulled out from the surface.

The nature of the interaction between the adsorbed NO and the surface has also been characterized by CDD plots calculated from the electron localization function (Becke and Edgecombe, 1990; Silvi and Savin, 1994). Fig. 4 shows the isosurface of CDD plots for the adsorption mode of NO on the Mn-doped CeO$_2$ (111) surfaces at Mn top site. As it can

<table>
<thead>
<tr>
<th>$E_{\text{ads}}$ (eV)</th>
<th>$d$(N-O$_{NO}$) (Å)</th>
<th>$d$(N-O$_t$) (Å)</th>
<th>$d$(N-Mn/Ce) (Å)</th>
<th>O-N-O (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn top</td>
<td>–3.30</td>
<td>1.21</td>
<td>1.32</td>
<td>2.13</td>
</tr>
<tr>
<td>Ce$_1$ top</td>
<td>–2.90</td>
<td>1.21</td>
<td>1.34</td>
<td>2.64</td>
</tr>
<tr>
<td>Ce$_2$ top</td>
<td>–0.95</td>
<td>1.14</td>
<td>—</td>
<td>2.51</td>
</tr>
</tbody>
</table>
Fig. 2. Side view of the lowest energy configuration for NO adsorption on the Mn top, Ce1 top and Ce2 top sites of the Mn-doped CeO2 (111) surfaces; Ce in light yellow, Mn in purple, O in red and N in blue.

Fig. 3. PDOS plot for (a) a free NO molecule and the clean Mn-Doped CeO2 (111) surfaces, and (b) NO adsorbed on the Mn-doped CeO2 (111) surfaces at Mn top site.

be seen, there is a significant increase of electron density between N atom and surface Mn cations, and between N atom and surface O that interact with NO, with significant depletion of the electron density at the region perpendicular to the O-N-O surface around the ONO, Ot1 and N atom.

As experimental and calculation evidence suggests that oxygen vacancies can be easily formed on Mn-doped CeO2 surface, the adsorption of NO at adsorption sites around the surface oxygen vacancy has also been examined. Although NO is found to form chemical bonds with the defected (111) surface, the bond energy is much weaker than on unreduced surface, as shown in Table 2. The highest bond energy is –0.81 eV, at Mn top site and NO no longer form a strong bond with the first neighbor O of the Mn dopant, as shown in Fig. 5. The N-O bond length is almost unchanged with respect to the calculated value for free NO molecule, 1.17 Å. The N atom lies at 2.21 Å above the surface Mn atom so that the resulting distance between the N and the nearest surface O atoms is 2.56 Å. Further indication of weaker chemical interaction between NO and defected surface is inferred by the analysis of the electronic density of states displayed in Fig. 6. From the PDOS of the Mn, O and N atoms for adsorption on the defected Mn-doped CeO2, it can be seen that the atomic orbitals of N and O have only weak overlap with that of Mn, indicating that weaker covalent bonds are formed between NO and the surface.

Co-adsorption of NO and O2 on Defective Mn-doped CeO2 (111) Surfaces

Although it is unfavorable to form oxygen vacancies for NO adsorption, the adsorption of O2 will be facilitated by the formation of oxygen vacancies. According to the study of Cen (Cen et al., 2012a) and Huang (Huang and Fabris, 2007), the O2 adsorbed on vacancy sites seems to shift to a
Fig. 4. CDD plot of NO bound on the Mn top 3 site; yellow parts denote electron density excess and light blue parts denote electron density loss; the contours start from 0.01 e/Å³.

Table 2. Calculated adsorption energies and structural parameters for the binding of NO to the defected Mn-doped CeO₂ (111) surface.

<table>
<thead>
<tr>
<th></th>
<th>(E_{\text{ads}}) (eV)</th>
<th>(d(\text{N}-\text{ONO})) (Å)</th>
<th>(d(\text{N-Mn/Ce})) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O, Mn top</td>
<td>-0.81</td>
<td>1.18</td>
<td>2.21</td>
</tr>
<tr>
<td>O, Ce₁ top</td>
<td>-0.68</td>
<td>1.18</td>
<td>2.67</td>
</tr>
<tr>
<td>O, Ce₂ top</td>
<td>-0.50</td>
<td>1.17</td>
<td>2.73</td>
</tr>
</tbody>
</table>

Fig. 5. Side view of the lowest energy configuration for NO adsorption on the Mn top, Ce₁ top, Ce₂ top site of the defected Mn-doped CeO₂ (111) surfaces; Ce in light yellow, Mn in purple, O in red and N in blue.

superoxo species, \(\text{O}_2^-\), which has superior oxidation activity (Wang-Hansen et al., 2013). Consequently, the activity of the catalyst surface is enhanced because active oxygen is formed for oxidation reactions. Therefore, NO adsorption on the surface of defective Mn-doped CeO₂ is studied further with \(\text{O}_2\) adsorbed in advance. The surface with one oxygen vacancy and one \(\text{O}_2\) molecular is denoted as \(\text{O}_2/\text{Ov}\), and NO adsorption at Mn top and \(\text{O}_2\) top sites is investigated. After NO adsorption on \(\text{O}_2/\text{Ov}\) surface, a structure as shown in Fig. 7 is formed. The stable co-adsorption structures are those where a ONOO* four atoms species are formed on surface. At \(\text{O}_2\) top site, \(\text{N}\) binding with one of \(\text{O}\) atoms in adsorbed \(\text{O}_2\) with the elongation of the bond length of NO and \(\text{O}_2\) to 1.18 Å and 1.41 Å, respectively, as shown in Table 3. The bond length of ON-OO is 1.54 Å and the O-N-O bond angle is 113.5°, with an adsorption energy of \(-2.51\) eV. At Mn top site, the four atoms compound [O(1)N(2)O(3)O(4)] adsorbed on the surface with its N(2) binding to Mn and O(4) being closest to the substrate, unlike the structure at \(\text{O}_2\) top site with NO hang in the air. The bond length of NO, \(\text{O}_2\) and ON-OO is 1.18 Å, 1.42 Å and 1.48 Å, respectively. The O-N-O bond angle is 110.9° and the adsorption energy is \(-2.02\) eV. When Fajin et al. (2010); Getman and Schneider (2010) and Fajin et al. (2011) studied the adsorption of NO and \(\text{O}_2\) at Au and Pt surface, they stated that ONOO* structure is the most stable configuration and reaction intermediate. It is suggested that ONOO* can decompose to \(\text{NO}_2^*\) and \(\text{O}^*\), and even direct desorption of \(\text{NO}_2\) could be feasible (Fajin et al., 2011). Therefore, through reaction \(\text{NO} + \text{O}_2^* \rightarrow \text{ONOO}^* \rightarrow \text{NO}_2/\text{NO}_2^* + \text{O}^*\), NO oxidation can be accelerated. These results indicate that Mn-doped CeO₂ surface has a similar property to the noble metal, such as Au and Pt, in NO oxidation catalysis.
Fig. 6. PDOS plot for NO adsorbed on the Mn top site of the defected Mn-doped CeO$_2$ (111) surfaces.

Fig. 7. Side view of bonding geometry for NO bound on O$_2$/Ov site of Mn-doped CeO$_2$ (111) surface; Ce in light yellow, Mn in purple, O in red and N in blue.

Table 3. Calculated adsorption energies and structural parameters for NO adsorption on O$_2$/Ov site of Mn-doped CeO$_2$ (111) surface.

<table>
<thead>
<tr>
<th>Adsorption sites</th>
<th>$E_{\text{ads}}$ (eV)</th>
<th>$d$(N-O$_{\text{NO}}$) (Å)</th>
<th>$d$(N-O$<em>{\text{O}</em>{2}}$) (Å)</th>
<th>$d$(N-Mn) (Å)</th>
<th>$d$(O-O) (Å)</th>
<th>$\angle$O-N-O (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$/O, O$_2$ top</td>
<td>–2.51</td>
<td>1.18</td>
<td>1.54</td>
<td>—</td>
<td>1.42</td>
<td>113.5</td>
</tr>
<tr>
<td>O$_2$/O, Mn top</td>
<td>–2.02</td>
<td>1.18</td>
<td>1.48</td>
<td>2.21</td>
<td>1.41</td>
<td>110.9</td>
</tr>
</tbody>
</table>

Fig. 8(a) shows the PDOS of the Mn, O and N atoms for NO adsorption on the O$_2$/Ov O$_2$ top site. The peaks of spin up electrons and spin down electrons in ONOO* overlap completely with each other, indicating electrons are in pairs. This result demonstrates the reconfiguration of electrons because of the formation of ONOO* structure. In free ONOO* structure, there should be unpaired electrons, like the peak at –6.5 eV in Fig. 3(a), totally different from the case in Fig. 8(a). Therefore, electron transfer occurs from the slab to ONOO*. For NO adsorption on the O$_2$/Ov Mn top site shown in Fig. 8(b), because of the binding with Mn, there are perturbation of the electronic structure. The CDD plot in Fig. 9 shows that the bond between N and O$_{\text{O}_2}$ in the case of O$_2$/Ov O$_2$ top is stronger than that in the case of O$_2$/Ov Mn top, although the bond length is larger. So the O-N-O bond angle in the case of O$_2$/Ov O$_2$ top is closer to the angle in NO$_2$ and the adsorption energy is higher.

**CONCLUSIONS**

The adsorption geometry, binding energies and electronic structure of NO on Mn-doped CeO$_2$ (111) surfaces were studied by first-principle density functional theory calculations. The results demonstrate how Mn-doped CeO$_2$ with superior NO oxidation activity benefits from the high mobility of the oxygen near the Mn cations.
On unreduced Mn-doped CeO$_2$ (111) surfaces, results of the calculations imply that the NO molecule preferentially interacted with the first O neighbor of the Mn ion, with the N ion also bonding to the Mn cation ($E_{\text{ads}} = -3.3$ eV) or Ce cation ($E_{\text{ads}} = -2.90$ eV). The formation of the O-N-O structure was observed, and this adsorption energy is much higher than on undoped CeO$_2$ surfaces ($E_{\text{ads}} = -0.04$ to $-0.18$ eV). When NO molecules adsorb on a Ce site that is not close to Mn or on a defective Mn-doped CeO$_2$ (111) surface, despite NO forming chemical bonds with the surface, the bond energy is much weaker ($E_{\text{ads}} = -0.50$ to $-0.95$ eV) without the formation of the O-N-O structure. Hence, the presence of Mn only has a strong effect on nearby oxygen atoms. When NO adsorbs on the surface of defective Mn-doped CeO$_2$ with O$_2$ adsorbed in advance, an ONOO$^*$ four atoms species are formed on the surface ($E_{\text{ads}} = -2.51$ eV and $-2.02$ eV), which is an intermediate and can decompose into NO$_2$, NO$_2^*$ and O$^*$. The easily formed oxygen vacancy caused by Mn doping results in the formation of an analogous NO$_2^*$ structure in the first step of adsorption and of ONOO$^*$ in the co-adsorption of NO and O$_2$. More specifically, the adsorption structure with higher adsorption energy has a closer geometry to NO$_2$, indicating a deeper oxidation of NO. These calculation results indicate that the Mn-doped CeO$_2$ surface has similar properties to a noble metal, such as Au or Pt, in NO oxidation catalysis.

In DOS plots, the spin of the electron state of the adsorption structures involving the oxidation of NO is symmetric, indicating that electron transfer occurs from the slab to NO and strong covalent bonds are formed between N and O on the slab. This can be confirmed by the CDD plots.
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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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