Catalytic Reaction Mechanism of NO–CO on the ZrO\textsubscript{2} (110) and (111) Surfaces

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Abstract: Due to the large population of vehicles, significant amounts of carbon monoxide (CO), nitrogen oxides (NO\textsubscript{x}), and unburned hydrocarbons (HC) are emitted into the atmosphere, causing serious pollution to the environment. The use of catalysis prevents the exhaust from entering the atmosphere. To better understand the catalytic mechanism, it is necessary to establish a detailed chemical reaction mechanism. In this study, the adsorption behaviors of CO and NO, the reaction of NO reduction with CO on the ZrO\textsubscript{2} (110) and (111) surfaces was performed through periodic density functional theory (DFT) calculations. The detailed mechanism for CO\textsubscript{2} and N\textsubscript{2} formation mainly involved two intermediates N\textsubscript{2}O complexes and NCO species. Moreover, the existence of oxygen vacancies was crucial for NO reduction reactions. From the calculated energy, it was found that the pathway involving NCO intermediate interaction occurring on the ZrO\textsubscript{2} (110) surface was most favorable. Gas phase N\textsubscript{2}O formation and dissociation were also considered in this study. The results indicated the role of reaction intermediates NCO and N\textsubscript{2}O in catalytic reactions, which could solve the key scientific problems and disputes existing in the current experiments.

Keywords: Nitric oxide; Carbon monoxide; Zirconium dioxide; Density functional theory; Reaction mechanism

1. Introduction

Heterogeneous catalysis always be used to decrease the emission of automobile exhausts (CO, NO\textsubscript{x}, and HC), such as the Rhodium catalytic system to convert toxic gas NO to inactive product N\textsubscript{2} \cite{1,2}. However, the rare and expensive characteristics of noble metal Rh limit its widespread use. Thus, quantities of investigations have been conducted to develop effective and economical catalyst systems.

As zirconium dioxide (ZrO\textsubscript{2}) has high thermal stability, excellent redox properties and an acid–basic site on its surface, it is a good catalyst and support material for various reactions, such as CO\textsubscript{2} methanation \cite{3,4}, water–gas shift \cite{5,6}, NH\textsubscript{3} selective catalytic reduction \cite{7,8}, and hydrodeoxygenation \cite{9,10}. Especially, the transition metal oxide dispersed onto the surface of ZrO\textsubscript{2} exhibits powerful activity for NO reduction. Okamoto et al. \cite{11} found that Cu/ZrO\textsubscript{2} catalysts showed high NO conversion to N\textsubscript{2} at low temperature through a nitrous oxide (N\textsubscript{2}O) intermediate for a NO–CO reaction. As the supporter, ZrO\textsubscript{2} has better performance than CeO\textsubscript{2} in reducing the energy barrier of NO dissociation \cite{12}. Besides, ZrO\textsubscript{2} also provides abundant NO\textsubscript{x} adsorption sites \cite{13–15}, which is beneficial for NO reduction. Koga et al. discovered that c-ZrO\textsubscript{2} (110) ultrathin film covering a Cu surface exhibited high NO\textsubscript{x} reduction activity \cite{16}.

NO reduction by CO may simultaneously eliminate two kinds of pollutants and convert them into harmless CO\textsubscript{2} and inactive N\textsubscript{2}, via the stoichiometric reaction 2CO + 2NO → 2CO\textsubscript{2} + N\textsubscript{2}. Dramatically,
isocyanate (NCO) species and gas phase N₂O were detected via experimental equipment during the reaction of NO with CO [17,18]. NO–CO reaction mechanisms involving NCO and N₂O as intermediate complex have been considered on Co₃O₄ (110)-B [19], Pd/γ-Al₂O₃ (110) [20], and Cu-doped SrTiO₃ (100) [21] catalyst surfaces. It is widely believed that CO abstracts lattice oxygen of catalyst to produce CO₂ and oxygen vacancy through the Mars–van Krevelen mechanism [22], and then NO reduction occur on the defective catalyst surface via NCO or N₂O intermediate species to form N₂. Although previous studies have provided significant insight on NO–CO catalytic reaction mechanism, the catalytic cycle paths of NO reduction by CO on ZrO₂ surfaces remain elusive.

Surface formation energies of three low-index c-ZrO₂ (100), (110) and (111) were computed, as shown in Table S1. In this study, we adopted the most stable surface (111) and a relatively reactive surface (110) as the exposed surfaces. The adsorption behaviors of CO and NO on ZrO₂ (110) and (111) surfaces and possible reaction pathways for CO₂ and N₂ formation with corresponding energy evolution were carefully discussed based on DFT calculations. Through in-depth analysis and research, the role of reaction intermediates NCO and N₂O in catalytic reactions will be clarified, which can solve the key scientific problems and disputes existing in the current experiments.

2. Results and Discussion

2.1. CO and NO Adsorption on ZrO₂ (110) Surface

The structure models of ZrO₂ (110) surface, as shown in Figure 1a, exposes threefold coordinated O (O₃c) and sixfold coordinated Zr (Zr₆c) atoms. In the surface, the Zr–Zr bond distance is 3.710 Å and the Zr–O bond distance is 2.247 Å. The lattice constant of ZrO₂ bulk is 5.115 Å, which is in good agreement with experimental result of 5.090 Å [23].

Three adsorption sites were considered (Figure 1b): (1) the top site of Zr (Zr₋), (2) the top site of O (Oₗ), and (3) the bridge site between two O atoms (Oᵦ). We have systematically calculated the adsorption energies of CO (C-end and O-end) and NO (N-end and O-end) gas molecules on ZrO₂ (110) surface, and the Table 1 lists all the value of E_ads.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Structure models of (a) the side view and (b) corresponding top view of ZrO₂ (110)-2 × 2 surface. (b) Three possible adsorption sites for CO and NO gas molecules are labeled. Optimized adsorption structures of (c) CO C-end, (d) CO O-end, (e) NO N-end, and (f) NO O-end on Zr₋ site. Red, cyan, gray, and blue spheres represent the O, Zr, C, and N atoms, respectively.
Table 1. Adsorption energies ($E_{\text{ads}}$) of CO and NO gas molecules on the different adsorption sites of ZrO$_2$ (110) surface.

| Gas Molecule | Adsorption Site | $E_{\text{ads}}$ (eV) | Figure |
|--------------|-----------------|------------------------|--------|
| CO           | C-end           | Zr$_T$ −0.676          | 1(c)   |
|              |                 | O$_T$ −0.675           | -      |
|              |                 | O$_b$ −0.227           | -      |
|              | O-end           | Zr$_T$ −0.359          | 1(d)   |
|              |                 | O$_T$ −0.257           | -      |
|              |                 | O$_b$ −0.231           | -      |
| NO           | N-end           | Zr$_T$ −0.788          | 1(e)   |
|              |                 | O$_T$ −0.776           | -      |
|              |                 | O$_b$ −0.253           | -      |
|              | O-end           | Zr$_T$ −0.575          | 1(f)   |
|              |                 | O$_T$ −0.290           | -      |
|              |                 | O$_b$ −0.047           | -      |

As shown in Figure 1, after fully structural optimization, CO (C-end and O-end) and NO (N-end and O-end) gas molecules preferred to adsorb on Zr$_T$ site of ZrO$_2$ (110) surface. As for CO molecule adsorption, $E_{\text{ads}}$ of CO (C-end and O-end) adsorbed on Zr$_T$ site was $−0.676$ eV and $−0.360$ eV, respectively, indicating the C-end adsorption was more energetically favorable than O-end. In the same way NO N-end adsorption was more stable than NO O-end adsorption on ZrO$_2$ (110) surfaces. Coordinates for all the optimized structures were presented in Table S3.

2.2. Reaction Mechanism of NO Reduction with CO on ZrO$_2$ (110) Surface

2.2.1. Path 1

The Mars–van Krevelen (MvK) mechanism is a universal reaction step for CO oxidation [24] and NO–CO reaction [19] on metal oxide surfaces. As shown in Figure 2, the NO–CO catalytic cycle reaction started when the first CO gas molecule adsorbed on Zr$_T$ site (state $ii$) with an adsorption energy of $−0.676$ eV, and with the change of lattice O–C distance to 3.098 Å. After adsorption, CO extracted surface oxygen atom to form CO$_2$ and a surface oxygen vacancy (state $iii$) through the MvK mechanism. In the corresponding transition state (TS1), the lattice O-CO bond decreased to 1.568 Å and the lattice O–C–O angle changed to $116.105^\circ$. Moreover, the energy barrier for this process was 1.948 eV, the result clearly shows that CO oxidation reaction can happen smoothly on ZrO$_2$ (110) surface by using exhaust temperature. We calculated two cycle reaction mechanisms (path 1 and path 2) and N$_2$O formation mechanism all share common steps to form oxygen vacancies on ZrO$_2$ (110) surface.

In the next step, CO$_2$ desorption into the gas phase (state $iv$) costs energy of 0.283 eV, then O$_V$ was occupied by the first NO gas molecule forming a O$_V$-NO complex structure (state $v$), and the energy of 2.310 eV is released. Subsequently, the next CO weakly adsorbed to adjacent O atom of the NO (state $vi$) with an adsorption energy of $−0.510$ eV. In TS2, the N-O bond broke and O atom moved toward CO to form OC-O bond by overcoming an energy barrier of 2.263 eV, and the OC-O bond length was changed from 2.683 Å at state $vi$ to 1.637 Å. After TS2, the second CO$_2$ molecule formation occurs (state $vii$). The reaction was exothermic by 1.246 eV. The similar reaction steps have been explored for Pd/$\gamma$-Al$_2$O$_3$ (110), the second CO abstracted lattice O atom from N-loaded Pd/$\gamma$-Al$_2$O$_3$ (110) surface with an energy barrier of 1.88 eV [20].
Then, the second CO₂ desorbed into the gas phase leaving a N-doped surface (state vii), in which N atom embedded at surface oxygen vacancy site. The desorption energy of CO₂ is approximately 0.3 eV, the interaction of ZrO₂ surface with CO₂ was much weaker than that with NO (E_ads = 0.7 eV), which have been reported by Luo et al. [13]. After the second CO₂ desorption, the second NO gas molecule located at N-doped ZrO₂ (110) surface (state ix) with the binding energy of −0.068 eV. Once NO interacted with the embedded N atom, formation of a relatively stable intermediate complex bent N₂O (state x) was very easy. As we can see from the energy profile (Figure 2), the process could facilely occur without energy barrier and release 3.286 eV energy. The energy barrier for N₂O dissociation was extremely low only 0.002 eV. After TS3, N-O bond and N-Zr bond dissociated to produce N₂ (state xi), then N₂ desorption into gas phase cost 0.458 eV, O atom successively diffused to oxygen vacancy site via an obvious barrierless process with releasing energy of 0.510 eV, the integrated ZrO₂ (110) surface was recovered eventually.

Accordingly, from calculated energy profile (Figure 2), the overall catalytic cycle is strongly exothermic. However, the second CO oxidation has greater activation energy of 2.263 eV, determining the rate of catalytic cycle. We proposed the other catalytic cycle path to produce CO₂ and N₂ via NCO species.

2.2.2. Path 2

As presented in Figure 3, the reaction mechanism of Oᵥ surface formation is shared with path 1. Subsequently, NO adsorbed on Oᵥ site, the value of NO O-end adsorption was −1.605 eV, which bound weaker than that of NO N-end. Then, the second CO directly combined with N atom to generate the NCO intermediate (−1.614 eV, state vi). The second NO adsorbed on Zr₁ site adjacent to NCO complex (−0.208 eV, state vii). In the co-adsorption configuration, NCO and NO moved toward each other via TS2 to form a NNCO₂ four-membered ring intermediate (state viii) with an energy barrier of 0.355 eV. The subsequent step was NNCO₂ intermediate dissociation to produce N₂ and CO₂ (state ix) with a

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Figure 2. Energy profile and structure models of reactants, transition states and products for path 1 (NO N-end embed in oxygen vacancy site on ZrO₂ (110) surface). The energy profile is placed in the center, and structure models are placed around.
barrier of only 0.141 eV. With N₂ and CO₂ desorption by costing 0.563 eV energy, the catalytic surface was recovered.

![Figure 3. Energy profile and structure models of reactants, transition states and products for path 2 (NO O-end embed in oxygen vacancy site on ZrO₂ (110) surface). The energy profile is placed in the center, and structure models are placed around.](image)

As we can see from the energy profile (Figure 3), the rate-determining step is the CO oxidation by the lattice oxygen, indicting ZrO₂ (110) surface exhibits weakly catalytic activity for low-temperature oxidation of CO. Liang et al. observed that c-ZrO₂ ultrafine powder showed relatively high activity for CO oxidation with light-off temperature at ~280 °C (50% conversion) and ~550 °C (100% conversion) [25,26]. As reported in the literature, metal doping was particularly effective for the formation of oxygen vacancy [21,27]. As for NO reduction reaction, the formation of oxygen vacancy is crucial for NO adsorption and reduction reaction [28–30]. On defective ZrO₂ (110) surface, NO decomposition and N₂ formation are occur easily as a result of a very small barrier of 0.355 eV via path 2. Although for the defective Co₃O₄ (110)-B surface [19], the most favorable NO reduction processes are energetically less competitive with a higher barrier of 1.48 eV, i.e., the ZrO₂ (110) surface is remarkable for NO reduction.

2.2.3. N₂O formation.

Beginning with the oxygen vacancy surface (state iv, Figure 4) the first gas NO molecule located at O₂ site (state v, Figure 4) by releasing 1.605 eV energy, the second incoming NO molecule N-end bound with surface N atom (state vi, Figure 4) with strong exothermicity of 2.872 eV. Subsequently, the ONN-O bond broke into N₂O via TS2 (Figure 4). After TS2, the gas-phase N₂O (state vii, Figure 4) formation, the barrier for the process was 0.987 eV, the reaction was exothermic by 1.345 eV. Eventually, N₂O desorption into the gas phase (state viii, Figure 4) cost 0.456 eV and ZrO₂ (110) surface recovered.
In cold start engines or lean-burn conditions N$_2$O is the main by-product of NO reduction [31], and the formation of N$_2$O on ZrO$_2$ surface has been observed through NO temperature-programmed desorption experiment [13]. N$_2$O is one of the six greenhouse gases specified in the Kyoto Protocol, the greenhouse activity is 310 times of CO$_2$ [32]. Catalytic systems for N$_2$O decomposition should be employed in catalytic converters.

Three reaction pathways have been calculated on the ZrO$_2$ (110) surface: the gas phase N$_2$O was observed via experimental equipment and in [18] it was also formed by theoretical calculation; our work provides the mechanism of N$_2$O formation. Path 1 involving bent NCO intermediate was proposed to produce harmless CO$_2$ and inactive N$_2$, this cycle had a relatively high barrier than path 2 involving surface NCO intermediate, indicting CO$_2$ and N$_2$ formation mainly through path 2. Besides, the activation barriers for N$_2$O and N$_2$ formation on O$_7$-ZrO$_2$ (110) surface were 0.987 eV and 0.355 eV, respectively. The results imply that NO is selectively converted to N$_2$ versus N$_2$O under mild conditions.

2.3. CO and NO Adsorption on ZrO$_2$ (111) Surface

ZrO$_2$ (111) surface consists of 3-fold-coordinated oxygen atoms (O$_{3c}$) and 7-fold-coordinated zirconium atoms (Zr$_{7c}$), as shown in Figure 5a.

In Figure 5b three possible adsorption sites are labeled: (1) the top site of Zr (Zr$_T$); (2) the top site of O (O$_T$); (3) the 3-fold O-hollow site (O$_H$). The value of adsorption energies is listed in Table 2.
the adsorption behavior of CO (C-end and O-end) and NO (N-end and O-end) on ZrO$_2$ (111) surface, we again researched that the Zr$_T$ site was the most favorable adsorption site; the CO C-end adsorbed on Zr$_T$ site had maximum adsorption energy $-0.788$ eV, which suggested that CO C-end adsorption was slightly preferred on ZrO$_2$ (111) surface. Moreover, NO O-end adsorption was thermodynamically impossible, because of the positive $E_{ads}$.

2.4. Reaction Mechanism of NO Reduction with CO on ZrO$_2$ (111) Surface

2.4.1. Path 1’

Based on the lowest energy structures of CO and NO on ZrO$_2$ (111) surface, the first step was gas-phase CO interaction with surface Zr atom ($-0.410$ eV, state ii), as shown in Figure 6, CO may incorporate lattice O via TS1 where the distance between CO molecule and O atoms was decreased from 2.787 Å to 1.246 Å. After TS1, a gas phase CO$_2$ molecule (state iii) formed. The energy barrier was equivalent to 2.949 eV. Next, CO$_2$ overcame 0.130 eV binding energy desorption into

**Figure 5.** Structure models of (a) the side view and (b) corresponding top view of ZrO$_2$ (111)-2 × 2 surface. (b) Three possible adsorption sites for CO and NO gas molecules are labeled. Optimized adsorption structures of (c) CO C-end, (d) CO O-end, (e) NO N-end, and (f) NO O-end on Zr$_T$ site.

**Table 2.** Adsorption energies ($E_{ads}$) of CO and NO gas molecules on the different adsorption sites of ZrO$_2$ (111) surface.

| Gas Molecule | Adsorption site | $E_{ads}$ (eV) | Figure |
|--------------|----------------|---------------|--------|
| CO           | C-end          | Zr$_T$        | -0.410 | 5(c) |
|              |                | O$_T$         | -0.129 | -    |
|              |                | O$_H$         | -0.160 | -    |
|              |                | Zr$_T$        | -0.162 | 5(d) |
|              | O-end          | O$_T$         | -0.133 | -    |
|              |                | O$_H$         | -0.154 | -    |
|              |                | Zr$_T$        | -0.041 | 5(e) |
| NO           | N-end          | O$_T$         | 0.078  | -    |
|              |                | O$_H$         | 0.046  | -    |
|              |                | Zr$_T$        | 0.054  | 5(f) |
|              | O-end          | O$_T$         | 0.076  | -    |
|              |                | O$_H$         | 0.055  | -    |
gas-phase. Specifically, the following path 1’ and N₂O formation mechanisms share as common steps as discussed above.

![Figure 6. Energy profile and structure models of reactants, transition states and products for path 1’ (NO N-end embed in oxygen vacancy site on ZrO₂ (111) surface). The energy profile is placed in the center, and structure models are placed around.](image)

Note that the energy barrier corresponding to TS1 (2.949 eV, Figure 6) is evidently high and oxygen vacancy formation on ZrO₂ (111) surface is difficult at low-temperature. Once oxygen vacancy formation on ZrO₂ (111) surface, NO adsorption and reduction are facile.

In state vi, the NO molecule N-end was located at Oᵥ site with a strong exothermicity of 2.923 eV. Subsequently, the second CO bonded with O atom of the NO to form a NOCO complex (−0.107 eV, state vii). The second CO₂ formation (state viii) arose from NOCO complex with an energy barrier of 0.405 eV (TS2). Desorption of CO₂ cost 0.134 eV. Then, the second NO adsorption on the N-doped surface (−0.629 eV, state ix) via TS3 forms the intermediate N₂O (state x) with a small barrier of 0.350 eV. Followed by a barrierless process of N₂O decomposition to generate N₂ (state xi). With the N₂ desorption, the surface was recovered.

2.4.2. Path 2’

As shown in Figure 7, after the formation of oxygen vacancy, the Oᵥ site was naturally replenished by NO molecule O-end (−3.056 eV, state vi). The second CO approached toward N atom of adsorbed NO (−0.382 eV, state vii) to generate the NCO intermediate (state viii) through TS2 and an energy barrier of 0.385 eV was needed. The next NO could adsorb close to NCO complex (−1.582 eV, state viii) to realize the formation of four-membered ring intermediate NNCO₂ (state ix). The activation barrier for this process was 1.194 eV. Subsequently, the N–C bond and N–O bond cleavage of four-membered
ring NNCO$_2$ led to CO$_2$ and N$_2$ formation (state x), with an almost barrierless processes (0.006 eV). Desorption of CO$_2$ and N$_2$ cost 0.255 eV.

Figure 7. Energy profile and structure models of reactants, transition states and products for path 2’ (NO O-end embed in oxygen vacancy site on ZrO$_2$ (111) surface). The energy profile is placed in the center, and structure models are placed around.

2.4.3. Mechanism involving N$_2$O

The formation process of N$_2$O was same as the case found on ZrO$_2$ (110) surface. The second NO bonded with N atom of first adsorbed NO. With the N-O and N-Zr bond dissociation, N$_2$O formation. The energy profile and corresponding structure models of reactant, transition state and product were illustrated in Figure 8.
Figure 8. Energy profile (a) and structure models (b) of reactants, transition states, and products for N₂O formation on ZrO₂ (111) surface. The energy profile is placed above, and structure models are placed below.

As N₂O is a hazardous by-product, its decomposition processes have been conducted on transition metal surfaces [33,34]. Following with the decomposition mechanism of N₂O on Pd-OV/γ-Al₂O₃ (110) surface proposed by Gao [20]. We calculated N₂O decomposition process on OV-ZrO₂ (111) surface, as shown in Figure 9. The binding energy of N₂O adsorption was equivalent to −0.166 eV, in the corresponding transition state the N–O bond length increased from 1.195 Å to 1.288 Å. By breaking the already activated N–O bond, the desired product N₂ was formed and the dissociated O atom filled the OV. The reaction barrier for N₂O decomposition is 0.288 eV, and the N₂ desorption from the ZrO₂ (111) surface requires 0.128 eV.

From calculated energy barriers, we found that CO oxidation by surface lattice oxygen was the rate-determining step during the process of NO reduction with CO, the reaction barriers were 1.948 eV and 2.949 eV on ZrO₂ (110) and (111) surfaces, respectively. The results indicated that compared with ZrO₂ (111) surface, ZrO₂ (110) surface had more remarkable ability to catalyze NO reduction with CO because of the lower activation barrier. From the calculated adsorption energies, CO and NO all preferred to adsorb on ZrO₂ (110) surface, which is consistent with the results of surface formation energies for (110) surface was relatively reactive than (111) surface. For the reaction mechanism of NO reduction by CO, similar reaction processes were found on ZrO₂ (110) and (111) surfaces. Intermediate complex bent N₂O was produced during path 1, path 1’ and → NCO intermediate was produced during path 2, path 2’, hazardous N₂O gas molecule was formed both on ZrO₂ (110) and (111) surfaces.
3. Materials and Methods

Periodic DFT calculations were executed using DMol³ module of Material Studio software package [35,36]. The exchange-correlation functional was treated by generalized gradient approximation with the Perdew-Wang 91 (GGA-PW91) [37]. The double numerical plus d-functions (DND) basis set was used to optimize all spin unrestricted structures. SCF tolerance was employed to $1.0 \times 10^{-5}$, the convergence tolerance of maximum energy change, maximum force, and maximum displacement were set as $2.0 \times 10^{-5}$ Ha, 0.004 Ha/Å, and 0.005 Å, respectively. The transition states (TS) were calculated with linear synchronous transit (LST) and quadratic synchronous transit (QST) method [38,39] and vibrational analysis was performed to identify TS have only one imaginary frequency.

The slab models of ZrO$_2$ (110) and (111) surfaces were built with a 15-20 Å vacuum thickness to avoid interaction between neighboring slabs. The ZrO$_2$ (110) surface consisting of four atomic layers with the lowest two layers being kept fixed in their bulk positions, whereas the others were allowed to relax with adsorbed molecules. The Brillouin zone was sampled with a (1 $\times$ 2 $\times$ 1) Monkhorst–Pack k-point grid [40]. The ZrO$_2$ (111) surface consisting of six atomic layers with the bottom four layers were kept fixed and the top two layers were relaxed. A (2 $\times$ 2 $\times$ 1) Monkost–Pack grid [40] for the ZrO$_2$ (111) surface geometry optimization. In all cases, an orbital cutoff of 5.0 Å was used to improve the computational performance and a 2 $\times$ 2 supercell was applied.

The adsorption energies ($E_{\text{ads}}$) of CO and NO gas molecules on ZrO$_2$ (110) and (111) surfaces were calculated by the following formula,

$$E_{\text{ads}} = E_{\text{(surface + gas molecules)}} - E_{\text{(surface)}} - E_{\text{(gas molecules)}}$$

where $E_{\text{(surface + gas molecules)}}$ is the total energy of the system involving the ZrO$_2$ (110) or (111) catalyst with the adsorbed CO or NO gas molecule, $E_{\text{(surface)}}$ is the total energy of isolated ZrO$_2$ (110) or (111) surface, and $E_{\text{(gas molecules)}}$ is the total energy of a single CO or NO gas molecule.
To validate the methods, we calculated the energy of NO, CO, N\textsubscript{2} and CO\textsubscript{2} molecules in a large unit cell of 10 \AA\times 10 \AA\times 10 \AA, and compared the bond distances with the values calculated at the B3LYP/6-31G(d) level \cite{41}. We listed all the values in Table S2, the calculated bond distances were within 1% of ones.

4. Conclusions

In summary, DFT calculations were performed to investigate NO reduction with CO on ZrO\textsubscript{2} (110) and (111) surfaces. For the ZrO\textsubscript{2} (110) surface, two cycle reaction pathways (paths 1 and 2) for CO\textsubscript{2} and N\textsubscript{2} formation were presented, and the path 2 involving the process of the NCO intermediate interaction with NO was energetically favorable. The similar cycle reaction pathways (paths 1’ and 2’) were found on ZrO\textsubscript{2} (111) surface, but CO oxidation by lattice O had a significantly higher energy barrier of 2.949 eV. The results indicated that compared with ZrO\textsubscript{2} (111) surface, ZrO\textsubscript{2} (110) surface had more remarkable ability to catalyze NO reduction with CO. Our calculations also clearly showed that the existence of oxygen vacancies on ZrO\textsubscript{2} (110) and (111) surfaces were crucial for NO adsorption and reduction reaction. NO healing O\textsubscript{V} was a strongly exothermic process (2.0–3.0 eV) and successive reactions all exhibited lower energy barriers, especially path 2 (0.355 eV) and path 1’ (0.405 eV). The mechanism involving N\textsubscript{2}O also was explored, and the activation barriers for N\textsubscript{2}O formation on O\textsubscript{V}-ZrO\textsubscript{2} (110) and (111) were 0.987 eV and 0.515 eV, respectively. The relatively higher barriers imply that NO is selectively converted to N\textsubscript{2} versus N\textsubscript{2}O under mild conditions.

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