First-principles study of NO reduction by CO on transition metal atoms-doped CeO$_2$(111)

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ABSTRACT

We present here a density functional theory plus $U$ study of NO reduction with CO, catalyzed by a single transition metal atom (TM = Zr$_1$, Tc$_1$, Ru$_1$, Rh$_1$, Pd$_1$, Pt$_1$)-doped CeO$_2$(111). The catalytic center was identified as the TM dopant in combination with lattice oxygen. The investigation into $N_2$ selectivity focused on three key elementary steps: gaseous $N_2O$ formation, subsequent re-adsorption, and N–O bond scission to produce $N_2$. In these steps, Rh$_1$, Pd$_1$, and Pt$_1$/CeO$_2$(111) exhibit a higher selectivity, whereas the other systems (Zr$_1$, Tc$_1$, Ru$_1$) TM$_1$/CeO$_2$ show a lower selectivity. The higher selectivity displayed by Pt$_1$, Pd$_1$, and Rh$_1$ dopants arises from the availability of valence d electrons, which permit the formation of strong chemical bonds with the reactants and intermediates. Calculated results agree well with experimental findings, and the insights gained can be used to guide the rational design of the doped oxides for catalysis.

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Keywords: Nitrogen oxide reduction, Single atom, Single transition metal atom/ceria, Cleavage, Density functional theory plus $U$

1. Introduction

There is increasing evidence that smaller metal particles dispersed on metal oxides can have superior catalytic activity or selectivity [1–4]. As the metal particle size decreases from nanometers to sub-nanometers, the presence of single metal atoms becomes highly likely. Recent advances in material synthesis methods, surface science, and atomic resolution microscopes [5] provide convincing evidence for the presence of single metal atoms and their role in catalysis [6]. For example, single Pt atoms embedded in the surface of γ-Al$_2$O$_3$ [7] and iron oxides [6] were proposed to be responsible for the observed low-temperature oxidation of CO. Moreover, single Pt atoms stabilized by allali metal ion clusters could catalyze the low-temperature water gas shift reaction (WGS) [8]. It was also recently found to have a remarkably high WGS activity when it was atomically dispersed on iron oxides [9]. The atomically dispersed Ir accounted for ~70% of the total catalytic activity, with the remaining activity stemming from sub-nanosized clusters and nanoparticles.

Density functional theory (DFT) has been used to describe catalytic reactions at surfaces in great detail and accuracy and has the great advantage of being able to treat single atom-doped metal oxides in two respects. First, single atom catalysis greatly decreases the complexity of the catalyst structure, which makes it possible to accurately perform simulations using DFT, reducing the well-known material gap between experimental and theoretical studies. Second, the simpler catalyst structure will result in a largely reduced computational cost. There are already some computational reports that suggest that transition metals (such as Mn [10], Ru [11], Pd [12], and Pt [13]) doped into metal oxides (CeO$_2$ [14], TiO$_2$ [15], and ZnO [16,17]) could possess additional adsorption sites and a higher oxidation activity for H$_2$O, CO, CH$_4$, etc., compared with...
the undoped metal oxides. Moreover, dopants exhibiting a lower valence state may activate lattice oxygen and lead to lower reaction barriers [18].

NO reduction becomes increasingly important against the background of rapid economic growth. In combustion engines, there are two common technologies for removal of NO under different air-to-fuel ratios: NO storage-reduction (NSR) [19–21] in lean-burn engines and selective catalytic reaction (SCR) [22–24] in rich-burn engines. NO reduction by CO, leading to the formation CO2 and N2, is a reaction common to both technologies and has the advantage of simultaneously removing two pollutants. To catalyze the reaction, three-way precious metal catalysts including Rh, Pd, or Pt are widely used [22,25,26]. The high cost of these precious metals, however, requires a continuous improvement in atomic efficiency and stability. Recently, atomically dispersed Pd1, Rh1, and Pt1 ions in CeO2 [26–30] were synthesized in the absence of mixed phases using a solution combustion method [31,32]. These catalysts showed an excellent catalytic activity, selectivity, and stability for the (NO + CO) reaction at low temperature. However, when the dopant is a left-hand transition metals (TM), such as in the CeZrO2 mixed oxide system, a low reduction activity for NO is found, while the catalytic activity for oxidation reactions (CO) is high [33]. Furthermore, Ce0.5Zr0.50O2 was also reported to show a much lower oxygen-storage capacity than Ce0.90Ru0.10O1.94 [34].

In our previous work [40], we studied NO reduction by CO on the Pd1-doped CeO2(111) surface. The catalytic cycle is summarized in Scheme 1. The reaction center mainly involved the TM dopants associated with lattice oxygen. The main factors that affect the N2 selectivity of the (NO + CO) reaction on TM1/CeO2(111) can be summarized in terms of the TM dopant and the oxygen vacancies. The TM dopants, which possess more d electrons than Ce ions, can provide adsorption sites for NO and CO. Oxygen vacancies that are created by CO may help NO undergo conversion into N2. The major influences on N2 selectivity can be discerned from examining the following elementary steps. First, oxygen vacancy formation is an elementary step. CeO2 is a well-known oxygen-storage capacitor (OSC), but whether this ability is enhanced or reduced after introducing the TM dopant requires discussion. The second factor is the complexity of the release of the product N2O into the gas phase. The formation of gaseous N2O would lower the selectivity to N2.

The third and final aspect is N2 formation from N2O*, where the adsorption configurations of N2O* require study. Experimental work has shown that Pt- and Rh-doped CeO2 in addition to Pd, also exhibit promising N2 selectivities, but the reason for this is unknown. Moreover, whether other TM dopants are active for this catalytic cycle also requires research.

To address the above questions, we performed DFT calculations to study the selectivity to N2 on Zr1, Tc1, Ru1, Rh1, Pd1, and Pt1-doped CeO2(111) surfaces. In Section 3.1, CO oxidation on TM1/CeO2(111) is discussed; in Section 3.2, the transition from N2O* to gaseous N2O on TM1/CeO2(111) is presented; and in Section 3.3, the N2O adsorption configurations on TM1/CeO2(111) surfaces with oxygen vacancies are treated. Finally, in Section 3.4, the second N–O bond scission during the reduction of N2O to N2 is examined.

2. Theoretical approaches and computational details

Spin-polarized total energy calculations were performed based on the all-electron projected augmented wave (PAW) method and DFT+U methodology, within the generalized gradient approximation (GGA-PW91) functional as implemented in the Vienna Ab Initio Simulation Package (VASP) [41–45]. A cutoff of 400 eV was used for the plane wave expansion. U = 5 eV was applied to Ce 4f states in line with previous calculations [12,35,46]. The oxide surface was modeled via a CeO2(111)-p(3×3) supercell with a thickness of three O–Ce–O tri-layers (27 Ce atoms and 54 O atoms in total) separated by a 15 Å vacuum. For the surface Brillouin zone sampling, we employed a Monkhorst-Pack (1×1×1) Γ-centered k-points grid [37,47]. The calculation based on the Monkhorst-Pack of (2×2×1) lowers the total energy by less than 0.02 eV. The top two tri-layers and the adsorbates were relaxed until the residual force on each ion was less than 0.02 eV/Å.

To simulate Zr1, Tc1, Ru1, Rh1, Pd1, and Pt1/CeO2(111) catalysts, one surface Ce cation was substituted by a single Zr1, Tc1, Ru1, Rh1, Pd1, or Pt1 atom (Fig. 1). All adsorptions and reactions were performed on one side of the exposed surface with the transition metal dopant, and a dipole moment correction along the z-direction was applied. The climbing-image nudged elastic

![Scheme 1](image1.png)  
**Scheme 1.** Catalytic cycle for NO reduction by CO on TM1/CeO2(111) surface.

![Fig. 1](image2.png)  
**Fig. 1.** Top (a) and side (b) view of slab models for TM1/CeO2(111). The TM1 dopant is located at a surface Ce site (blue). The gray and red spheres represent a Ce atom and an O atom, respectively.
band (CI-NEB) method [48,49] was used to search the transition states (TSs) for all the elementary reactions studied. The minimum energy pathway for each elementary reaction was discretized by a total of six images between the initial and final states. The TS was denoted by the highest amplitude image along the minimum energy path. The activation energy \( (E_a) \) of each elementary reaction was calculated by the Born-Oppenheimer energy difference between the TS and the initial state (IS) without including zero-point energy contributions.

### 3. Results and discussion

#### 3.1. CO oxidation

The calculated lattice parameter of bulk CeO$_2$ was 5.49 Å, which agrees well with previous calculations [50]. In this study we use the CeO$_2$(111) surface as the support because it is the most abundant surface facet exposed on pristine CeO$_2$ [51]. Each surface Ce atom coordinates with seven oxygen atoms, and the optimized Ce-O bond length is 2.37 Å. The calculated formation energy of an isolated TM$_1$ atom occupying a pre-existing Ce vacancy is highly exothermic with a value of –20.73 eV (Zr$_1$), –15.23 eV (Tc$_1$), –12.75 eV (Ru$_1$), –10.09 eV (Rh$_1$), –7.34 eV (Pd$_1$), and –9.65 eV (Pt$_1$). This suggests that the substituted TM$_1$ atom is stable and would be resistant to segregation and agglomeration toward larger metal particles. The high coordination number of a substituted TM$_1$ atom with lattice oxygen $O_1$ is decisive for its stability and cationic charge state.

The complete phase diagram of Pd-CeO$_2$(111) under relevant conditions was studied thoroughly by Janik et al. [39] using ab initio thermodynamics. In that work, a number of configurations including Pd$_1$ adatoms on CeO$_2$(111), Pd$_1$ substituted at the surface Ce sites, the subsurface sites, and Pd$_1$ clusters were studied, and their relative stabilities with respect to Pd bulk metal and oxides were compared. They found that Pd could form single adatoms on the surface or substitute with the surface Ce sites under a wide range of oxygen chemical potentials. Accordingly, the TM$_1$ atom substituted at the surface Ce sites is used in the present work unless stated otherwise.

As shown in Scheme 1, the catalytic center for NO reduction by CO involves a cycle between the single transition metal (TM$_1$) and the TM$_1$ with an adjacent oxygen vacancy (TM$_1$-OV$_1$). Oxygen vacancy (OV$_1$) formation has a crucial impact on the integrity and sustainability of the reaction. The computed OV$_1$ formation energies \( (E_v) \) and the reaction energies \( (E_r) \) are listed in Table 1.

The calculated energy of formation \( (E_v) \) of OV$_1$ on the CeO$_2$(111) surface with respect to gas phase O$_2$ is 2.10 eV (endothermic), which is in good agreement with previous reports [52,53]. This indicates the higher activity of the lattice oxygen $O_1$ and the higher reducibility of CeO$_2$(111). The calculated OV$_1$ formation energies on each TM$_1$/CeO$_2$(111) system considered are 1.48 eV (Zr$_1$), 1.20 eV (Tc$_1$), 1.00 eV (Ru$_1$), 1.15 eV (Rh$_1$), 0.65 eV (Pd$_1$), and 1.43 eV (Pt$_1$). All the OV$_1$ formation energies for TM$_1$/CeO$_2$(111) exhibit a considerably reduced value compared with CeO$_2$(111) (2.10 eV), which indicates that the lattice oxygen becomes more active after TM$_1$ dopant introduction.

Our previous work [40] reported that the barrier for CO reacting with O$_1$ on Pd$_1$-doped CeO$_2$(111) (0.11 eV) was lower than that on CeO$_2$(111) (0.42 eV) through the Eley-Rideal (E-R) type of reaction mechanism. Moreover, the reaction energies reveal that this step is highly exothermic, taking values of –1.80 eV (Zr$_1$), –2.09 eV (Tc$_1$), –2.29 eV (Ru$_1$), –2.14 eV (Rh$_1$), –2.63 eV (Pd$_1$), and –1.86 eV (Pt$_1$). The minimum $E_r$ (–1.80 eV on Zr$_1$) is more exothermic than that on CeO$_2$(111) (–1.14 eV). We can infer that the barrier for CO oxidation on the TM$_1$/CeO$_2$(111) surface is lower than that found for CeO$_2$(111) (0.42 eV).

The formation energies of oxygen vacancies on the TM$_1$/CeO$_2$(111) systems studied here are all lower than that of CeO$_2$(111), and the reaction energies are all higher than that of CeO$_2$(111). We can infer that CO oxidation with O$_1$ to create an O$_1$ on Zr$_1$, Tc$_1$, Ru$_1$, Rh$_1$, Pd$_1$, and Pt$_1$/CeO$_2$(111) is a facile step, and oxygen vacancies are available during the whole reaction, an important requisite in our mechanism.

#### 3.2. Formation of N$_2$O$_2^*$ and N$_2$O

Having shown that oxygen vacancies can be available during the whole reaction, we now turn to studying NO reduction on a TM$_1$-OV$_1$ center, as OV$_1$ can act as an oxygen acceptor during N–O bond scission. To test the possibility of direct NO dissociation, the dissociative reaction energy from gas phase NO to N$^*$ and O$^*$ adsorbed at a cation-top was investigated. For stoichiometric CeO$_2$(111) and Pd$_1$/CeO$_2$(111), the calculated reaction energies are highly endothermic (>6 eV). Even for the reduced surfaces where the presence of OV might accommodate the dissociated $O^*$, the reaction energies remain very endothermic at 1.95 eV for O$_1$/CeO$_2$(111) and 3.54 eV for Pd$_1$/O$_1$/CeO$_2$(111). These results indicate that direct NO dissociation into N$^*$ and O$^*$ can hardly contribute to N$_2$ formation, if at all, on either stoichiometric or reduced CeO$_2$(111) and TM$_1$/CeO$_2$(111).

Alternatively, N$_2$ formation might arise from the formation of the N$_2$O$_2^*$ intermediate from two NO$^*$ molecules adsorbed on the surface, followed by the subsequent scission of the N–O bonds. As shown schematically in Fig. 2(a) and (b), N$_2$O$_2^*$ prefers to bind to the TM$_1$-OV$_1$ pairs, one binding via the N atom (N(1)) to a TM$_1$-top site and the other binding via the O atom (O(2)) to an OV$_1$ adjacent to the TM$_1$ atom. The formation energies of N$_2$O$_2^*$ \( (E_n) \) with respect to (NO+NO) in the gas phase (Table 2) on Zr$_1$, Tc$_1$, Ru$_1$, Rh$_1$, Pd$_1$, and Pt$_1$/CeO$_2$(111) are –2.27, –1.87, –2.38, –3.10, –2.88, and –3.55 eV, respectively. The $E_n$ values of TM$_1$/CeO$_2$(111) considered are all much higher than that of trans-N$_2$O$_2$ in the gas phase (–0.71 eV). This reveals that N$_2$O$_2^*$ tends to form on the TM$_1$-OV$_1$ site and the N–N binding energy is only one part of the $E_n$ value on the TM$_1$-OV$_1$/CeO$_2$(111) surface. Moreover, the reaction barriers for the formation of N$_2$O$_2^*$, which were also estimated, are small and sometimes negligible.
The decomposition of $\text{N}_2\text{O}_2^*$ into $\text{N}_2\text{O}$ requires the scission of the TM–N and O–N bond. Sequential or simultaneous scission of these two bonds indicates two potential reaction pathways for this elementary step. We have studied these two pathways on Pd$_1$/CeO$_2$(111) in our previous work [40], and the two effective activation barriers are comparable (1.85 versus 1.96 eV). For simplicity, we investigated the simultaneous dissociation of the TM–N and O–N bonds for the TM$_1$/CeO$_2$(111) system. Calculated activation barriers and reaction energies for the conversion of $\text{N}_2\text{O}_2^*$ to gaseous $\text{N}_2\text{O}$ are summarized in Fig. 3. Calculated barriers for Zr$_1$, Tc$_1$, Ru$_1$, Rh$_1$, Pd$_1$, and Pt$_1$/CeO$_2$(111) are 1.01, 0.07, 0.88, 1.89, 1.96, and 2.05 eV, respectively. The reaction energies for Zr$_1$, Tc$_1$, and Ru$_1$/CeO$_2$(111) are exothermic with values of $-1.08$, $-1.43$, and $-1.06$ eV, respectively. In contrast, the values for Rh$_1$, Pd$_1$, and Pt$_1$/CeO$_2$(111) are endothermic with values of 0.06, 0.34, and 0.22 eV, respectively. As shown in Fig. 3, there is a strong correlation between calculated activation barriers and reaction energies due to the similar TS structures. The desorption of $\text{N}_2\text{O}$ into the gas phase is facile on the left-hand elements in the periodic table, i.e., Zr$_1$, Tc$_1$, and Ru$_1$/CeO$_2$(111). The further to the right the dopants are in the periodic table, the more difficult it is for $\text{N}_2\text{O}$ desorption to occur, e.g., gaseous $\text{N}_2\text{O}$ formation on Rh$_1$, Pd$_1$, and Pt$_1$/CeO$_2$(111) has a higher activation barrier than the other metals studied.

To understand the underlying differences for $\text{N}_2\text{O}$ formation on different TM$_1$/CeO$_2$(111) systems, charge density difference distribution analysis and site-projected density of states (PDOS) calculations were performed on Pd$_1$/CeO$_2$(111) (Fig. 2(a)) and Tc$_1$/CeO$_2$(111) (Fig. 2(b)). The charge density difference distribution shows that $\text{N}_2\text{O}_2^*$ on Pd$_1$/CeO$_2$(111) (Fig. 2(c)) and Tc$_1$/CeO$_2$(111) (Fig. 2(d)) has similar bonding structures, with a pronounced charge accumulation between Pd$_1$/Tc$_1$ and $\text{N}_2\text{O}_2^*$ and a redistribution around Pd$_1$/Tc$_1$ and $\text{N}_2\text{O}_2^*$. However, charge density differences also show that redistribution decreases for Pd more significantly than for Tc.

In addition, PDOS calculations show that there are differences in the electronic structures between N(1)-Pd and N(1)-Tc, (Fig. 2(e) and (f)). For $\text{N}_2\text{O}_2^*$ at Pd$_1$/CeO$_2$(111), Pd 4$d$-electrons dominate the PDOS below the Fermi level. The comprehensive orbital hybridization with the N$_2$:orbital [54], and formation of bonding and antibonding states below and above the Fermi level, are evident. Compared with N(1) and Tc, there is a higher more orbital overlap between the N(1) and Pd, which implies that the Pd–N bond is stronger than the Tc–N bond. For comparison, calculated PDOS results of N(2) and O(2) (Fig. 2(g) and (h)) indicate that the electronic structures of the N–O bond of $\text{N}_2\text{O}_2^*$ on Pd$_1$/CeO$_2$(111) and Tc$_1$/CeO$_2$(111) are very similar. Because both the TM–N and O–N bonds must dissociate for the formation of gaseous $\text{N}_2\text{O}$, the bond energy of TM–N can correspond to the relevant activated reaction barrier.

In summary, $\text{N}_2\text{O}$ is easy to desorb into gas phase on left-hand TM$_1$/CeO$_2$(111) systems, while on the right-hand transition metals Rh$_1$, Pd$_1$, and Pt$_1$/CeO$_2$(111), $\text{N}_2\text{O}$ binds more
strongly and is therefore less likely to desorb. Because the desorption of reactants is unfavorable for the subsequent reduction steps, Rh, Pd, and Pt/CeO$_2$(111) with lower desorption energies may have a higher N$_2$ selectivity than the right TM/TeO$_2$(111).

### 3.3. Re-adsorption of gaseous N$_2$O

As discussed above, N$_2$O is easily formed and can readily desorb into the gas phase on Zr, Tc, and Ru/CeO$_2$(111). Although N$_2$O desorption is difficult on Rh, Pd, and Pt/CeO$_2$(111), there may be some gaseous N$_2$O released during the reaction. As the reduction of N$_2$O to N$_2$ requires the TM$_1$-OV site, the re-adsorption of gaseous N$_2$O is an essential step for N$_2$ formation. In this section, we focus on N$_2$O re-adsorption at the TM$_1$-OV center.

There are two possible N$_2$O adsorption configurations on TM$_1$-OV/CeO$_2$(111) surfaces: a bending mode and a linear form. The calculated adsorption energies of these two configurations for all the TM/TeO$_2$(111) systems studied are shown in Fig. 4. For linearly adsorbed N$_2$O (Fig. 4(b), red frame), the O atom binds with OV and the terminal N atom is oriented to the vacuum. The calculated adsorption energy for the linear configuration is small, typical of physical adsorption, with values in the range from 0.15 to –0.27 eV. The bent adsorbed state (Fig. 4(c), black frame) binds through both N and O at the TM$_1$ site and OV site of TM$_1$-OV/CeO$_2$(111), respectively. The corresponding adsorption energies for Zr$_1$, Tc$_1$, and Ru$_1$ are endothermic with values of 0.13, 0.56, and 0.01 eV, respectively, whereas the values are exothermic at –0.42, –0.56, and –1.12 eV for Rh$_1$, Pd$_1$, and Pt$_1$, respectively.

To elucidate the reasons for the differences between the bent N$_2$O adsorption at the various TM$_1$-OV centers, we separate the bent adsorption energy into two parts: the endothermic deformation energy ($E_d$) (conversion of the linear configuration to a bent configuration) and a binding energy ($E_b$) between the bent configuration and the TM$_1$-OV center, an exothermic process. The calculated adsorption energy of N$_2$O on Pd$_1$-OV/CeO$_2$ ($E_{ad}=–0.56$ eV) is separated into 2.02 eV ($E_d$) and –2.58 eV ($E_b$), while for Zr$_1$-OV/CeO$_2$ ($E_{ad} = 0.13$ eV) the values are 1.99 eV ($E_d$) and –1.86 eV ($E_b$). The deformation energy is comparable for Pd and Zr because of the similar bent configuration of N–N–O: 129.8$^\circ$ (Pd) and 130.3$^\circ$ (Zr). However, the binding strength of Pd is much higher than that of Zr, which is responsible for an endothermic $E_d$ value for Zr and an exothermic value for Pd. Similar results were also found for Pt and Tc, i.e., the deformation energy and the N–N–O angle are comparable (2.88 versus 2.70 eV and 122.2$^\circ$ versus 122.4$^\circ$). The binding strength of Pt (–3.99 eV) is much higher than that of Tc (–2.01 eV). When the binding energy could not compensate for the bending energy, the overall adsorption energy exhibited a positive value.

As discussed in Section 3.2, left-hand TMs have weak bonding with the N, whereas the right-hand TMs bind more strongly. As a result, the stronger binding of Rh$_1$, Pd$_1$, and Pt$_1$/CeO$_2$(111) with N can compensate for the bending energy of N$_2$O, whereas Zr$_1$, Tc$_1$, and Ru$_1$/CeO$_2$(111) do not bind to N with sufficient strength to compensate for the bending energy. Our DFT computations reveal that re-adsorption of gaseous N$_2$O on TM$_1$-OV is weak on the left-hand TM$_1$/CeO$_2$(111), and that linear physiosorption is the preferred mode of adsorption. In contrast, stronger bent chemisorption of N$_2$O is stable for Rh$_1$, Pd$_1$, and Pt$_1$/CeO$_2$(111), which would then exhibit higher N$_2$ selectivities than Zr$_1$, Tc$_1$, and Ru$_1$/CeO$_2$(111).

### 3.4. The formation of N$_2$

In the above section, we examined the elementary steps of gaseous N$_2$O formation and N$_2$O re-adsorption (essential for N$_2$ formation) at TM$_1$-OV centers from the viewpoints of both kinetics and energetics. Having studied the adsorption configurations of N$_2$O on TM$_1$-OV/CeO$_2$(111) surfaces, we addressed the two competing pathways for the reduction and desorption of N$_2$O*. Calculated barriers for N–O bond scission and the desorption energy of N$_2$O* for each TM are presented in Fig. 5(a). It is clear that the barriers for gaseous N$_2$O formation on Zr$_1$, Tc$_1$, and Ru$_1$/CeO$_2$(111) with a linear N$_2$O configuration are larger than the N$_2$O desorption energies (0.23, 0.25, and 0.27 eV for Zr$_1$, Tc$_1$, and Ru$_1$, respectively). This implies that N$_2$O* desorption is easier than its reduction for these systems. In contrast, for Rh$_1$, Pd$_1$, and Pt$_1$/CeO$_2$(111), the desorption energies of N$_2$O with a bent configuration (0.42, 0.56, and 1.12 eV for Rh$_1$, Pd$_1$, and Pt$_1$, respectively) are larger than the reduction barriers (0.04, 0.24, and 0.03 eV for Rh$_1$, Pd$_1$, and Pt$_1$, respectively). This suggests that the reduction process proceeds more easily than desorption.

The reduction barrier from the initial bent state is lower than that from the linear initial state. There are differences in the N–O bond lengths between the linear and bent states, and this influences the reaction barrier. The N$_2$O linear adsorbed state has an N–O bond length of 1.21 Å (Zr), almost equal to that of gaseous N$_2$O (1.14 Å). However, for N$_2$O bent adsorption, the N–O bond length is elongated by 0.14 Å compared with...
the linear adsorbed state, and this leads to the higher activity of the N–O bond in the bent configuration. The smaller angle of N–N–O in the bent configuration (130°) compared with the linear configuration (180°) also helps to preactivate the N–N–O bond.

For the initial state with the linear configuration, the transition state structure on Zr1/CeO2(111) is shown in Fig. 5(b). The configurations of TSs for Tc1 and Ru1 doped CeO2(111) are similar to that for TM = Zr1. In the TS for linear adsorption, the bond length of N–O is elongated by 0.16 Å, and the O atom almost completely moves into the O vacancy site. For the initial state with the bent configuration, the structure of the transition state for TM = Rh1 or Pt1 is similar to that for Pd1/CeO2(111) (Fig. 5(c)). In the TS for bent adsorption, the bond length of N–O is elongated by 0.38 Å, more than that of the linearly adsorbed state. In general, the bent adsorption configuration possesses a lower reduction barrier than that found with linear adsorption. CeO2(111) doped left-hand TMs can only achieve linear adsorption, while in the case of right-hand TMs, the bent adsorption structure is preferred, and the selectivity of N2 is higher for the right-hand elements on CeO2(111).

In summary, for Zr1, Tc1, and Ru1/CeO2, gaseous N2O is formed easily, and the preferential re-adsorption configuration at TM˪–Ov involves linear physisorption. Moreover, the reduction barrier of N2O* is larger than that of desorption. All three aspects result in a lower N2 selectivity, which agrees well with the experiment work [33], where cerium/zirconium mixed oxides were found to exhibit a small reduction activity for NO. In contrast, for TMs = Rh1, Pd1, or Pt1/CeO2(111), N2O desorbs with difficulty. In addition, the gaseous N2O can easily adsorb on TM˪–Ov with the bent configuration, and the adsorption energies are larger than the reaction barriers to N2 formation. Overall, our results for Rh1, Pd1, and Pt1/CeO2(111) are in good agreement with the experimental studies [26,28,55], where excellent catalytic activity, selectivity, and stability for the NO+CO reaction at low temperature have been demonstrated for Rh+, Pd+, and Pt-doped CeO2.

4. Conclusions

The N2 selectivity of the NO+CO reaction on single transition metal (TM = Zr1, Tc1, Ru1, Rh1, Pd1, and Pt1) atom-doped CeO2(111) surfaces was investigated using density functional theory. The catalytic center was identified as the TM dopant in interaction with lattice oxygen. The study of N2 selectivity focused on three critical elementary steps: gaseous N2O formation, subsequent N2O re-adsorption, and formation of N2. The calculations predict that Rh1, Pd1, and Pt1/CeO2(111) would exhibit a higher N2 selectivity, whereas the left-hand TM˪–CeO2 systems would have a lower N2 selectivity, all consistent with available experimental results. The origin of the high N2 selectivity for Rh1, Pd1, and Pt1/CeO2(111) stems from the availability of d valence electrons because this permits the formation of strong chemical bonds with the reactants and intermediates involved in the reaction.

References

**Graphical Abstract**

First-principles study of NO reduction by CO on transition metal atoms-doped CeO$_2$(111) 

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Right transition metal (TM)-doped CeO$_2$(111) possesses high N$_2$ selectivity because of the right-hand TMs being able to provide more $d$ electrons for stronger binding between the TM and N-containing species. For the left-hand TMs, $d$ electron availability is lower, leading to a weaker binding situation and lower N$_2$ selectivity.

References:


**Abstract**

过渡金属替代的CeO$_2$(111)表面上NO+CO反应机理的理论研究

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摘要：采用DFT+U方法研究了过渡金属替代的CeO$_2$(111)表面上的NO+CO反应机理，探究不同过渡金属对N$_2$选择性的影响。结果表明，在反应过程中，反应活性中心由过渡金属单原子与其最近邻的氧空位组成。NO在过渡金属-氧空位上发生N-O断键，不同过渡金属上该还原步骤的难易程度不同。计算发现，右过渡金属Rh、Pd和Pt替代的CeO$_2$(111)表面可以与吸附物之间形成较强的吸附作用，进而可以达到较高的N$_2$选择性，其主要原因是右过渡金属具有较多的$d$电子，可以与吸附小分子之间形成有效的反馈键。而左过渡金属拥有较少的$d$电子，难以有效抓住吸附物，最终导致较低的N$_2$选择性。

关键词：一氧化氮消除；选择性；单原子；单过渡金属原子/氧化物；密度泛函理论+U

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