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DFT + U study of the CO + NO_x reaction on a CeO₂(110)-supported Au nanoparticle

Jie Zhang, Xueqing Gong*, Guanzhong Lu #

Key Laboratory for Advanced Materials, Centre for Computational Chemistry and Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, China

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ABSTRACT

The adsorption and reactions of CO and NO_x on a Au₆ nanoparticle supported on the CeO₂(110) surface have been studied using density functional theory calculations corrected by on-site Coulomb interactions (DFT + U). The results show that CO can strongly adsorb on the top site of the Au nanoparticle with an adsorption energy of ~1.2 eV, while the adsorption of NO on both the Au nanoparticle and the interface between the nanoparticle and the CeO₂ support is generally much weaker. However, at the interface, formation of the N₂O₂ dimer followed by cleavage of the terminal N–O bond is an effective way to decompose NO_x. For the complete process, the first step of the CO + N₂O₂ reaction can readily occur in Langmuir-Hinshelwood mode with an activation energy of only ~0.4 eV, leading to the formation of N₂O and CO₂ via an intermediate ONNOCO species. In contrast, the second step to eliminate N₂O requires a rather high energy barrier of ~1.8 eV through a Eley-Rideal type collision reaction. Further analyses show that the unique electronic properties of Ce can induce the electron transfer and localization from supported Au to surface Ce cations, which then promotes the formation of negatively charged N₂O₂. Moreover, the structural flexibility of the Au nanoparticle also facilitates the adsorbed CO to approach and react with N₂O₂ at the interface.

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1. Introduction

CeO₂-based rare earth materials are widely used as the main component in three-way catalysts for automobile exhausts emission control by converting hazardous hydrocarbons (HCs), CO, and nitrogen oxides (NO_x) to H₂O, CO₂, and N₂, which are much less harmful to the environment [1–4]. It is generally believed that the excellent catalytic performance of CeO₂ is related to the unique 4f orbital of Ce, which has strong localization characteristics [5]. Owing to such special electronic properties, CeO₂ is considered to be an electron storage component

with high oxygen storage capacity (OSC) that can also help release/store oxygen by forming/filling oxygen vacancies under reducing/oxidizing conditions [6,7]. Accordingly, a large number of studies have been conducted to investigate the activity of surface- and bulk-oxygen in various reactions [8–12]. Different experimental strategies have been used to make CeO₂ surfaces more active, such as metal-ion doping and preparation of CeO₂ with various nanoscale morphologies [13–17]. Moreover, it has been shown that the addition of Zr to CeO₂ can greatly increase its OSC, that the best ratio of Zr/Ce is 1:1 and that the Ce_{0.5}Zr_{0.5}O₂ solid solution in the specific κ -phase can give the

* Corresponding author. Tel: +86-21-64251101; Fax: +86-21-64252923; E-mail: xgong@ecust.edu.cn# Corresponding author. Tel: +86-21-64252827; Fax: +86-21-64252923; E-mail: gzhlu@ecust.edu.cn

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highest OSC [7,18].

The three common crystal facets exposed on nanocrystalline CeO₂ are (100), (110), and (111), and the shape of the CeO₂ nanoparticles, which can determine the type and relative amount of exposed facets, will then influence their reactivities in applications [11,13,19]. Single-crystal CeO₂ nanorods with well-defined crystal planes have been designed and prepared, and are predominantly covered with (110) facets. These nanorod materials exhibit higher activity for CO oxidation than CeO₂ particles, which mainly contain (111) facets [13,20]. These results suggest that the (110) surface, which is the second most stable surface among the low-index ceria surfaces, may exhibit higher chemical activities than the other surfaces. In several recent studies it has been reported that once oxygen vacancies formed on the CeO₂(110) surface, the surface would be more active and able to interact with reductive species such as NO and NO₂, which would fill the O vacancies of the surface with their O atoms. On the other hand, oxidative species such as CO can be oxidized by surface O atoms to generate CO₂ and surface O vacancies. Such a surface redox cycle suggests that CeO₂ not only acts as supporting material for catalytic reactions, but is also involved in surface reactions [21–24].

Au catalysis has been a hot topic in heterogeneous catalysis over the last few decades, and highly dispersed Au particles supported on different metal oxides have been shown to be extremely active for CO oxidation [25–28], the water-gas-shift reaction (WGS) [29–31], hydrocarbon oxidation [32], and NO reduction at low temperatures [33,34]. Among the metal oxide supports tested for Au nanoparticles, CeO₂ has been found to be one of the most active in many catalytic applications [35,36]. Liu et al. [37] carefully investigated the activity of a single Au atom supported on the CeO₂(111) surface in the WGS reaction. From their density functional theory (DFT) calculations, electron transfer to the localized nonbonding 4*f* orbital of CeO₂(111) was found to induce the oxidation of Au, and the positively charged Au^{δ+} species was determined to be the site for strong adsorption of CO and subsequent reactions. In the case of CO oxidation, Wang et al. [26] suggested that gold with a wire-like or several other specific configurations could efficiently adsorb CO and O₂ and promote CO oxidation in both supported and unsupported Au systems. In other studies, the interfaces between Au nanoparticles and oxide supports, as well as the structural flexibility, have been suggested to be important for low-temperature CO oxidation [27,38,39].

In recent years, Au-based catalysts have also attracted great interest in the field of NO_x decomposition. Wang et al. [40] studied N₂O formation on the Au(111) surface and found that the coupling of two NO molecules to form N₂O₂ was preferred and its subsequent dissociation was more likely to occur than single NO molecule dissociation. In addition, Zhang et al. [41] concluded that NO could react with pre-covered oxygen on the Au(111) surface to form NO₂ under different O coverages, and, because of the very weak adsorption of atomic oxygen on the surface, such NO oxidation by pre-covered oxygen proceeds via the Eley-Rideal mechanism.

Rare-earth oxides and Au nanoparticles have extensive applications, and have attracted very wide research interest. In

particular, supported Au/CeO₂ catalysts have been shown to be able to simultaneously remove CO and NO_x, which are both important air pollutants, in vehicle emission control applications [42–44]. Compared with the most common process of CO oxidation through reaction with O₂, the CO + NO_x reaction may simultaneously eliminate both the pollutants, which could bring more environmental benefits than the CO + O₂ reaction. In this study, we investigated the related chemical processes and reactions catalyzed by a six-atom Au nanocluster (Au₆) supported on the CeO₂(110) surface with DFT calculations, with the aim of elucidating the possible reaction pathways between CO and NO_x in the corresponding systems. Detailed steps of the reactions, including adsorption and all the possible surface pathways of reactants, were considered. In addition, the role of the unique electronic structures of the CeO₂ supports in the various catalytic reaction steps were carefully studied and are discussed.

2. Calculation details

The DFT calculations were performed with a Hubbard-U term (DFT + U) to correct for the description of the electronic properties of ceria [45,46], where U = 5 eV was applied to the Ce 4*f* states [47–49]. The Vienna Ab initio Simulation Package was used. The valence electronic states of Ce (4*f*, 5*s*, 5*p*, 6*d*, 6*s*), Au (5*d*, 6*s*, 6*p*), O (2*s*, 2*p*), C (2*s*, 2*p*), and N (2*s*, 2*p*) were described by plane-wave basis sets with a cut-off energy of 350 eV, and core-valence interactions were treated with the projector augmented wave method [50,51]. The PW91 electron exchange-correlation functional of the generalized gradient approximation was used [52,53]. The transition states (TSs) in the reactions were determined by the constrained minimization method [54,55] and electron charge analyses were performed by Bader decomposition of the charge density [56].

The CeO₂(110) surface was modeled as a periodic slab with seven CeO₂ layers, with the bottom two layers fixed, while the other layers were allowed to relax during all the calculations. The force threshold of all the relaxed atoms was set to 0.05 eV/Å. Spin polarization was considered in all the calculations. The vacuum height between slabs was ~10 Å to eliminate the interaction between neighboring slabs. The CeO₂(110) surface was built by a 2 × 3 supercell, and we removed a whole CeO₂ row along the $[\bar{1}10]$ direction to model the characteristic structure of reconstructed CeO₂(110) determined by experimental measurement [57] (Fig. 1(a)). The supported Au nanoparticle was constructed using a six-atom cluster, which was placed and optimized only on one side of the slab (Figs. 1(b) and (c)). The Brillouin zone was sampled with a *k*-point meshes of 1 × 1 × 1 because of the large size of the surface cell (~11 × 11 Å²).

To determine the chemisorption energies (*E*_{ad}) of adsorbed molecules to the supported catalyst, we used the following equation:

$$E_{\text{ad}} = -(E_{\text{molecule} + \text{Au}_6/\text{CeO}_2} - E_{\text{Au}_6/\text{CeO}_2} - E_{\text{molecule}})$$

in which *E*_{molecule + Au₆/CeO₂} mol is the total energy of the system involving the supported Au₆/CeO₂(110) catalyst with the adsorbed molecule, *E*_{Au₆/CeO₂} is the total energy of the supported

catalyst, and E_{molecule} is the total energy of the molecule in the gas phase.

3. Results and discussion

Automobile exhaust contains mainly CO, NO_x, and HCs. Much attention has been paid to the disposal of CO through low-temperature catalytic oxidation. As another important process in emission control, NO_x decomposition is still challenging and its by-products, such as nitrite and nitrate, usually exist in the processes and may reduce the overall activity of the catalysts. It is widely expected that the direct reaction between CO and NO_x would be highly beneficial because it can simultaneously remove both compounds. Therefore, the current work aims to study the possible reaction pathways of the reaction of NO with CO on Au₆/CeO₂(110) by DFT+U calculations.

3.1. Au₆ cluster on the CeO₂(110) surface

Scanning tunneling microscopy (STM) of the CeO₂(110) surface structures has been conducted by Nörenberg and co-workers [57]. They found that rows of CeO₂ in the STM images were separated by ~ 11 Å, which indicates a 2×1 surface reconstruction. In Fig. 1(a), we show the structures of the CeO₂(110) surface with such a missing-row reconstruction mode. It exposes three-fold coordinated O (O_{3c}) and six-fold coordinated Ce (Ce_{6c}) atoms on the top surface layer as well as Ce_{7c} and O_{3c} atoms in the missing-row area, which can be actually taken as (111) micro-facets.

In our previous work, we investigated the trimeric Au nanocluster (Au₃) on the unreconstructed CeO₂(110) surface [58]. In that work, we showed that the supported Au₃ cluster could reduce the surface, and the electron donated by Au₃ could localize on one surface cation (Ce³⁺) and further promoted O₂ adsorption and activation by forming negatively charged O₂[−]. These results clearly suggest the possible catalytic activities of

such CeO₂ supported systems. In this work, we simulated the Au₆ cluster supported on the reconstructed CeO₂(110) surface. From the calculated structure (Fig. 1(b)), the supported Au₆ cluster exhibits a 2 + 4 double layer configuration, with the bottom 4 atoms binding to the missing-row site O_{3c} at different heights and the top two atoms sitting on top of the 4-atom bottom layer not directly interacting with the CeO₂ surface. The adsorption energy of the Au₆ cluster was calculated to be 4.24 eV with respect to the same 6-atom Au cluster optimized in the gas phase, which is rather high for supported Au clusters. With respect to adsorbed Au₆, the average bond distance between the bottom Au atoms of the cluster and surface O_{3c} atoms that they directly interact with was measured to be ~ 2.17 Å, and the adsorption has very small effect on the structural parameters of the CeO₂ support.

From the calculations, we determined that Au₆ adsorption induced partial reduction of the supporting CeO₂(110) surface. As shown in Fig. 1(c), there are two localized 4f electrons on two neighboring Ce_{6c} atoms of the top of the CeO₂ row directly bonding with the Au₆ cluster, which is consistent with our early study [58] and the work reported by several other groups regarding transition metal clusters supported on CeO₂ surfaces [59,60].

3.2. CO and NO adsorption on Au₆/CeO₂(110)

On this supported Au₆ cluster, there are three main types of adsorption sites (Fig. 1(c)): (1) the top site on a single Au atom that is not interacting with the CeO₂ support (T); (2) the bridge site between the two top Au atoms (B₁) and between one top and one bottom Au atom (B₂); and (3) the hollow site surrounded by one top Au and two bottom Au atoms (H). In this work, the adsorption energies of CO and NO were calculated for adsorption to the above Au sites as well as to interfacial Ce cations.

The adsorption of CO and NO on transition metals (including

Fig. 1. Calculated structures of (a) the CeO₂(110)- 2×1 reconstructed surface (side view) and (b) the side view and (c) top view of a Au₆ cluster supported on the reconstructed CeO₂(110)- 2×1 surface. The four different adsorption sites of Au₆ are labeled in (c). Side views (from [110]) of the adsorption of (d) CO and (e) NO on the Au top site, and (f) two CO and (g) (from [001]) two NO molecules on two Au top sites. Key: O, red; Ce, ivory; Au, gold; C, gray; and N, blue. The isosurfaces of spin unpaired electrons are plotted in white in (c).

Table 1

Calculated adsorption energies (E_{ad}) of CO, NO, two CO, and two NO molecules on the different adsorption sites of Au_6/CeO_2 .

Molecule	Adsorption site	E_{ad}/eV	Figure
CO	T	1.20	1(d)
	B ₁	0.96	—
	B ₂	0.38	—
	H	0.89	—
	Ce ³⁺	0.24	—
NO	T	1.03	1(e)
	B ₁	0.68	—
	B ₂	0.64	—
	H	0.41	—
	Ce ³⁺	0.44	—
2CO	T	2.06	1(f)
2NO	T	1.56	1(g)

Au) has been extensively investigated in many experimental and theoretical studies [61,62]. In our recent study of the structures and activities of Au nanoclusters on TiO_2 supports [28], we found that CO preferred to adsorb on the top site of Au. In the current work, we again found that the top site (T) was the most favorable adsorption site for both CO and NO on $\text{CeO}_2(110)$ -supported Au_6 . In Table 1, we list the calculated adsorption energies (E_{ad}) of these two molecules on the various adsorption sites. Adsorption of CO (Fig. 1(d)) and NO (Fig. 1(e)) on the top site of Au_6 was much stronger than on the other Au sites or Ce^{3+} at the interface. Moreover, the calculated E_{ad} of CO (1.20 eV) was significantly higher than that of NO (1.03 eV), which suggests that there is competitive adsorption between CO and NO on supported Au_6 , and that adsorption of CO is more energetically favorable than NO.

In addition to the adsorption of a single NO and CO molecule, we also considered their adsorption at higher coverages. As shown in Table 1, the co-adsorption of two CO molecules on the two top Au sites had a total adsorption energy of 2.06 eV (Fig. 1(f)). Interestingly, for the co-adsorption of two NO on the top of the Au_6 cluster, the calculations showed that they could actually form a N_2O_2 dimer (Fig. 1(g)), and the adsorption energy estimated with respect to two gas-phase NO molecules

was 1.56 eV. From the above results, we can therefore conclude that adsorption of CO is much more energetically favorable than NO on supported Au_6 at both low and high coverages.

3.3 Adsorption of N_2O_2 at the Au_6/CeO_2 interface

Rodriguez et al. [63] found that Au supported on metal oxides can act as bi-functional catalysts for the WGS reaction, i.e., the adsorption and dissociation of water take place on the metal oxides while CO adsorbs to Au, and the subsequent reactions occur at Au/metal oxide interfaces. In this work, we also tested if there were other favorable adsorption configurations for NO when the supported Au_6 was covered with CO.

Our calculated results reported in Section 3.2 have already shown that a single NO molecule only weakly adsorbs to interfacial Ce^{3+} sites (0.44 eV, Table 1). In contrast, when two NO molecules adsorbed to two neighboring Ce^{3+} atoms, they were found to be able to readily couple to form the N_2O_2 dimer with almost no energy barrier. Four possible adsorption structures of the N_2O_2 dimer were determined at the interface, which are shown in Fig. 2. Moreover, the E_{ad} calculated with respect to the energies of the gas-phase dimer and the surface with the CO pre-covered Au_6 cluster are listed in Table 2.

From the calculated adsorption structures and energies, the N_2O_2 dimer only binds to the interfacial Ce^{3+} atom, and it prefers an O/O-down configuration, in which the two O atoms of the dimer bind with two Ce^{3+} atoms (Fig. 2(b)). The adsorption energy was calculated to be 1.24 eV, which is significantly higher than that of the dimer in N/N-down (0.73 eV, Fig. 2(a)) or N/O-down (0.92 eV, Fig. 2(c)) configurations. Interestingly, we also located the adsorption state in which the dimer sits

Table 2

Calculated E_{ad} of N_2O_2 at the Au_6/CeO_2 interface.

Adsorption site	Adsorption configuration	E_{ad}/eV	Figure
Ce^{3+}	N/N-down	0.73	2(a)
	O/O-down	1.24	2(b)
	N/O-down	0.92	2(c)
$\text{Au}-\text{CeO}_2$	N/O-down	0.98	2(d)

Fig. 2. Calculated adsorption structures of N_2O_2 on $\text{Au}_6/\text{CeO}_2(110)$ with pre-covered CO: (a) N/N down at Ce, (b) O/O down at Ce, (c) N/O down at Ce, and (d) N/O down at the $\text{Au}-\text{CeO}_2$ interface. Upper row: top view, and bottom row: side view from the direction of the dashed arrow.

across the interface with one O atom bound to a Ce^{3+} atom and one N atom bound to an interfacial Au atom, and the corresponding E_{ad} was calculated to be 0.98 eV (Fig. 2(d)).

3.4. Reaction between CO and NO on Au_6/CeO_2

Au nanoparticles exhibit catalytic activities in low-temperature CO oxidation by O_2 , and the detailed mechanisms have been extensively studied both experimentally and theoretically [64,65]. However, the study of CO oxidation by NO is still limited. In this work, we systematically calculated the reaction pathways for the reaction of CO and NO on the Au_6/CeO_2 supported catalytic system.

According to our calculations regarding the adsorption of CO and NO in this system, NO is unable to compete with CO for the adsorption sites on the supported Au_6 cluster under low and high coverages. In contrast, in the system with the Au cluster already covered with CO, two NO molecules can still form a strongly adsorbed N_2O_2 dimer at the interface. Accordingly, we studied the redox reaction between CO and N_2O_2 taking the co-adsorbed system with one CO on top of a Au atom and N_2O_2 in the bridging configuration at the $\text{Au}_6/\text{CeO}_2(110)$ interface with the terminal O atom pointing toward CO as the initial state (IS1, Fig. 3, Fig. 2(d)). As shown in the calculated energy profiles of the reaction (Fig. 3), the co-adsorption energy of CO and N_2O_2 in IS1 was calculated to be 2.18 eV. When the reaction occurs, CO moves toward N_2O_2 to combine with the terminal O atom for CO_2 formation. In the corresponding transition state (TS1, Fig. 3) located through the calculations, the distance of OC–ONNO was determined to be 1.785 Å, the C–O bond in CO increased to 1.340 Å, and the distance of the terminal O–N bond in N_2O_2 increased to 1.341 Å.

By comparing the structures of TS1 and IS1, the Au atom occupied by the CO molecule actually moves with the CO molecule in the reaction, which may facilitate its approach toward the N_2O_2 molecule. Accordingly, from their calculated energies, the reaction barrier of this process was determined to be only 0.39 eV, suggesting that this combination would easily occur under mild conditions. This result is consistent with the work of Wang et al. [40], who found that formation of N_2O from the N_2O_2 dimer could easily occur on the Au(111) surface.

Fig. 3. Calculated energy profile and structures of important states for the CO reaction with N_2O_2 on Au_6/CeO_2 . The clean surface with N_2O_2 and CO in the gas phase was set to zero for the total energies.

After TS1, a relatively stable intermediate complex OCONNO (IM1, Fig. 3) was determined to occur at the interface. The bond between the C atom and the terminal O atom of N_2O_2 decreased to 1.417 Å, while the terminal O–N bond of N_2O_2 further increased to 1.437 Å. Compared with TS1, this intermediate state was calculated to be 0.19 eV more stable. From Fig. 3, it then needs to go through another transition state (TS2) to fully break the terminal N–O bond to form CO_2 . The energy barrier corresponding to this second TS (TS2) was 0.80 eV, and the distances between the terminal O atom and OC and NNO were determined to be 1.318 and 1.858 Å, respectively. After TS2, N_2O and CO_2 form and naturally desorb because of their very weak adsorption to the surface (~ 0.2 eV for N_2O and ~ 0.1 eV for CO_2). Nevertheless, the final state (FS1) with gas-phase N_2O and CO_2 is still remarkably stable, and, as shown in Fig. 3, the overall process for CO oxidation by adsorbed N_2O_2 is highly exothermic on the Au_6/CeO_2 catalyst.

3.5. Decomposition of N_2O

As another important hazardous nitrogen oxide species, N_2O and its decomposition has been the topic of many studies [66–68]. In particular, it has been found that transition metal catalysts can promote the activation and dissociation of N_2O [69–71].

In this work, we also calculated the interaction of N_2O with the supported catalyst and its dissociation. We found that N_2O did not have a strong interaction with Au_6 or the interface of $\text{Au}_6/\text{CeO}_2(110)$ ($E_{\text{ad}} = \sim 0.2$ eV). Therefore, direct N_2O dissociation by transfer of the terminal O atom to the supported Au_6 cluster was studied. Fig. 4 shows the calculated structures of the important states during the dissociation and the corresponding energy profile. The initial state of dissociation (IS2) involves weakly bonded N_2O with the O atom pointing toward the Au_6 cluster. In the transition state (TS3), the length of the dissociating O–N bond was determined to be 1.372 Å, and the reaction barrier was 1.78 eV, suggesting that dissociation is kinetically unfavorable, which is in agreement with experi-

Fig. 4. Calculated energy profile and structures of the important states of N_2O decomposition on Au_6/CeO_2 . The clean surface with N_2O in the gas phase was set to zero for the total energies.

mental results that N_2O decomposition on Au-based catalysts require high temperatures of $\sim 500\text{--}600\text{ K}$ [72–74].

After TS3, the terminal O atom of N_2O would adsorb on the bridge site (B_2) of the Au_6 cluster and the N_2 molecule would leave into the gas phase. The above N_2O dissociation process for N_2 formation was exothermic by 0.64 eV (Fig. 4).

Considering that CO may prefer to adsorb to the Au cluster because of its strong adsorption, we also investigated another pathway for N_2O reduction by the direct reaction of N_2O with a pre-adsorbed CO molecule. Fig. 5 shows the calculated structures of the transition state (TS4) of the reaction between gas-phase N_2O and CO adsorbed on the top site of Au_6 together with the energy profile for the complete process. In TS4, the distance between the terminal O atom of N_2O and the C atom of CO was determined to be 1.775 Å, and the O–NN bond distance increased from $\sim 1.200\text{ Å}$ in gas-phase N_2O to 1.509 Å. After the transition state, N_2 and CO_2 form and desorb as the desired products. From the energy profile, this process has an energy barrier of 1.86 eV and is highly exothermic by 2.25 eV, suggesting that it is favorable, although high temperatures are needed.

3.6. Discussion

Au nanoparticles supported on CeO_2 substrates have been extensively studied for WGS and CO oxidation reactions. In our recent work [58], we investigated O_2 adsorption on $\text{CeO}_2(111)$, (110), and (100) surfaces with a supported Au trimer cluster (Au_3). It was found that the Au_3 cluster could reduce the supports by transferring one electron to be localized in the 4f orbital of one surface Ce cation, turning it into Ce^{3+} . Moreover, the O_2 molecule can only adsorb to a Ce cation of the $\text{CeO}_2(110)$ support, which exhibits a flat open morphology without protruding lattice O atoms, by accepting the localized electron into its anti-bonding $2\pi^*$ state. In other words, the O_2 molecule ac-

tually becomes an activated O_2^- species, and the relatively strong electrostatic attraction between O_2^- and the Ce^{4+} cation largely contributes to its favorable adsorption.

In this work, NO adsorption was found to be significantly weaker than CO adsorption on supported Au_6 at both low and high coverages. However, NO adsorption exhibits unique properties at the Au_6/CeO_2 interface. Similar to CO, a single NO molecule has relatively low adsorption energy at the interface. Interestingly, two NO molecules can easily combine to form the N_2O_2 dimer at the interface with a calculated adsorption energy of $\sim 1\text{ eV}$. In addition, such favorable adsorption of N_2O_2 is not affected by the co-adsorption of CO on the Au_6 cluster, suggesting that there is not competitive co-adsorption of the two reactants in these two areas.

By performing electronic analyses, we found that these results regarding the adsorption of N_2O_2 could be explained by the characteristic electronic properties of the CeO_2 support. As shown in Fig. 1(c), the adsorption of Au_6 causes the reduction of $\text{CeO}_2(110)$ by transferring two electrons to the support, which are localized in 4f orbitals of two surface Ce atoms beside the Au_6 cluster. Interestingly, the occurrence of these Ce^{3+} cations is not affected by the adsorption of CO on the Au_6 cluster (Fig. 6(a)). The localized electrons can then be transferred to N_2O_2 to increase its stability (see below) and its electrostatic attraction with the support Ce^{4+} cations. For instance, as shown in Fig. 6(b), N_2O_2 adsorbed at the interface to one Ce atom and one Au atom accepts one localized electron while the other electron is still on the nearby free Ce^{3+} cation. These results clearly show the unique catalytic role of the localized 4f electron of Ce that, as well as directly transferring to molecules like O_2 , can promote the formation of intermediate species, such as negatively charged N_2O_2^- , and strong electrostatic attraction to the surface. It also needs to be emphasized that the formation of negative N_2O_2^- as the result of electron transfer from surface Ce^{3+} can actually strengthen the N–N bond within the dimer [75]. This is particularly desirable for the treatment of NO-based hazardous molecules because it would greatly increase the chance of the occurrence of N_2 .

From our calculations of the detailed processes of N_2O_2 reaction with CO, we have shown the important catalytic properties of Au nanoparticles, especially from a geometric point of view. As we have mentioned, in the $\text{CO} + \text{N}_2\text{O}_2 \rightarrow \text{N}_2\text{O} + \text{CO}_2$ reaction, the high mobility of the Au atom that binds CO greatly facilitates the movement of CO toward N_2O_2 , so that the corre-

Fig. 5. Calculated energy profile and structures of important states in the N_2O reaction with CO on Au_6/CeO_2 . The surface with CO pre-adsorbed on the Au cluster and N_2O in the gas phase was set to zero for the total energies.

Fig. 6. Calculated localized spin electron isosurfaces (top view) in the systems with (a) CO adsorption to Au_6 and (b) N_2O_2 adsorption at the interface of CO pre-adsorbed Au_6/CeO_2 .

sponding barrier of their reaction is only ~ 0.4 eV. Moreover, in the case of the $\text{CeO}_2(110)$ -supported Au_6 cluster, the above results indicate that this unique mobility will not be affected by oxidation of the cluster.

4. Conclusions

We performed DFT + U calculations to investigate $\text{CO} + \text{NO}_x$ redox reactions on a Au_6 cluster supported on the reconstructed $\text{CeO}_2(110)$ surface. The results showed that the Au_6 cluster could reduce the surface through donation of two localized $4f$ electrons to two neighboring surface Ce cations at the anchoring site. CO adsorbs significantly stronger than NO to the supported Au_6 catalyst under different coverages, and it may cover all available sites on the cluster. Interestingly, adsorbed CO has no effect on the electron localization of the supporting $\text{CeO}_2(110)$ surface, and the localized electron can be transferred to NO to facilitate the formation and adsorption of negatively charged N_2O_2 . For the $\text{CO} + \text{N}_2\text{O}_2$ reaction, we found that CO adsorbed on the top site of the Au_6 cluster could react with a N_2O_2 dimer adsorbed at the Au-CeO₂ interface with an overall barrier of ~ 1.0 eV to produce CO_2 and N_2O through a Langmuir-Hinshelwood mode. For the subsequent N_2O decomposition process, we determined that N_2O direct dissociation could occur by an O atom of N_2O transferring to the Au cluster or a CO molecule pre-adsorbed on the Au cluster, which both have an energy barrier of ~ 1.8 eV, through an Eley-Rideal mode because N_2O has a rather weak interaction with Au and CeO_2 . This work shows that the electron transferred from Ce^{3+} to the N_2O_2 dimer can strengthen the N–N bond to facilitate N_2 formation, suggesting that the unique electronic properties of CeO_2 -based rare earth materials may make it useful for the elimination of NO and its derivatives.

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Graphical Abstract

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DFT + U study of the CO + NO_x reaction on a CeO₂(110)-supported Au nanoparticle

Jie Zhang, Xueqing Gong*, Guanzhong Lu*
East China University of Science and Technology

CeO₂(110)-supported Au₆ clusters strongly favor adsorption of CO on the Au top site and N₂O₂ at reduced interfacial Ce³⁺ cations, and exhibit unique catalytic activity toward subsequent CO + NO_x redox reactions for CO₂ and N₂ formation.

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CeO₂(110)负载Au纳米颗粒催化CO + NO_x反应的DFT + U研究

张洁, 龚学庆*, 卢冠忠[#]

华东理工大学结构可控先进功能材料及其制备教育部重点实验室, 计算化学中心, 工业催化研究所, 上海200237

摘要: 通过在位库伦校正的密度泛函理论(DFT+U)方法计算, 我们研究了CO和NO_x分子在Au负载CeO₂(110)表面的吸附. 结果表明, CO在Au纳米颗粒的顶位有很强的吸附能, 大约为1.2 eV, 而NO在Au纳米颗粒上或者Au与CeO₂载体界面处都是弱吸附. 然而, 当NO_x在界面处形成N₂O₂二聚体之后, 通过断裂末端的N–O键能够有效地被降解. 纵观整个反应过程, 第一步CO + N₂O₂的反应遵循了Langmuir-Hinshelwood机理, 活化能只有0.4 eV, 通过形成ONNOCO的中间物种最终产生N₂O和CO₂. 不同的是, 第二步消除N₂O反应遵循了Eley-Rideal碰撞机理, 需要相当高的能垒, 约为1.8 eV. 通过进一步分析表明, 稀土Ce元素独特的电子特性能够使电子从Au上转移并且局域到载体表面的Ce阳离子上, 并且有助于形成带负电的N₂O₂分子. 而且Au纳米颗粒有很强的结构流动性, 能够促进吸附的CO分子靠近界面处的N₂O₂并与之反应.

关键词: 密度泛函理论; 三效催化剂; 二氧化铈; 金纳米颗粒; 一氧化碳; 氮氧化物; 氧化还原反应; 电子局域

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*通讯联系人. 电话: (021)64251101; 传真: (021)64252923; 电子信箱: xgong@ecust.edu.cn

[#]通讯联系人: 电话: (021)64252827; 传真: (021)64252923; 电子信箱: gzhlu@ecust.edu.cn

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1. 前言

稀土材料CeO₂作为三效催化剂(TWC)的主要成分被广泛地用于汽车尾气排放控制. 其目的是将有毒有害的碳氢化合物(HCs), CO和氮氧化物(NO_x)转化成对环境无害的H₂O, CO₂和N₂^[1–4]. 通常认为, CeO₂出色的催化性能与其独特的Ce原子4f轨道强局域特征有关^[5]. 正是由于这种特殊的电子结构, CeO₂能够作为电子存储器在还原/氧化的条件下形成/填补氧空穴从而释放/储存O₂, 因此CeO₂具有很高的储放氧性能(OSC)^[6,7]. 因此, 大量研究探讨了CeO₂在不同反应中表面氧和体相氧的活性^[8–12]. 例如, 利用金属离子掺杂的方法或者制备出不同纳米尺寸形貌的CeO₂都有助于提高催化活性^[13–17]. 通过将Zr元素添加入CeO₂材料中能明显提高其OSC性能, 最佳的Zr/Ce比例为1:1, 而且以 κ 相结构的Ce_{0.5}Zr_{0.5}O₂固溶体表现出了最优的储放氧性能^[7,18].

CeO₂纳米晶体中最常见的三个晶面是(100), (110)和(111)面, 而其形貌决定了暴露晶面的类型和数量, 影响着它在反应中的活性^[11,13,19]. 通过设计和制备出的单晶纳米棒状的CeO₂可以暴露出大量(110)晶面, CO催化氧化反应表明, 这种纳米棒状材料比纳米颗粒形貌的CeO₂表现出了更高的催化活性, 而后者主要是由稳定性较高的(111)晶面构成的^[13,20]. 这表明在低指数晶面中, 第二稳定的CeO₂(110)面表现出更高的活性. 最近的研究发现, CeO₂(110)一旦形成氧空穴之后, 表面将更加活泼并与可还原性的气体NO, NO₂相互作用, 这些气体分子中的O原子能填补CeO₂表面的氧空穴. 相反地, 可氧化性物质CO能够被CeO₂表面的晶格氧氧化成CO₂而再次产生表面的氧空穴. 因此, 表面氧化还原意味着CeO₂不仅作为催化反应中的载体材料, 而且自身能够参与到表面反应当中^[21–24].

与此同时, Au催化剂在过去数十年间在多相催化领域中成为一个研究的热点. 氧化物载体负载的高分散Au颗粒在CO氧化^[25–28], 水汽变化(WGS)^[29–31], 烃类氧化^[32]和NO还原^[33,34]等反应中都表现出极高的催化活性. 在Au纳米颗粒负载的氧化物载体中, CeO₂是最具化学活性的载体之一^[35,36]. Liu等^[37]详细研究了单个Au原子负载CeO₂(111)的WGS反应. DFT计算结果表明, Au原子上的部分电子能够转移到CeO₂(111)中高度局域的非键Ce-4f轨道从而引起Au颗粒氧化, 带正电荷的Au^{δ+}物

种提供了CO分子的强吸附位并促进了后续的反应. 在CO氧化的研究中, Wang等^[26]提出, 线性结构和其他一些特殊构型的Au纳米簇能有效地吸附CO和O₂分子, 提高CO氧化的能力. 研究还发现, Au与氧化物载体的界面以及Au团簇的结构流动性同样对CO低温氧化起到非常重要的作用^[27,38,39].

在最近几年, Au基催化剂在NO_x降解的应用领域也引起了研究者的广泛兴趣. Wang等^[40]研究了Au(111)表面N₂O的形成机理. 他们发现, 相比单个NO分子的解离, 两个NO分子聚集成N₂O₂之后更容易解离产生N₂O. 除此之外, Zhang等^[41]认为, 在Au(111)表面的不同O原子覆盖度的情况下, NO将与O反应生成NO₂. 这是因为O原子在表面的吸附作用很弱, 与NO的氧化反应是通过Eley-Rideal机理发生的.

综上所述, 稀土氧化物和Au纳米颗粒都有着广泛的应用和研究价值. 尤其是负载型Au/CeO₂催化剂在汽车尾气排放控制这一领域的应用. 这类催化剂能够同时消除CO和NO_x这两类主要空气污染物^[42–44]. 相比最为主流的采用O₂氧化来消除CO, CO + NO_x的相互反应能够同时消除这两种污染物, 显然更具环保效益. 然而, 该类型反应的研究却是比较有限的. 为了阐明CO与NO_x之间相互作用的可能的反应路径, 本文通过建立CeO₂(110)负载的6个Au原子簇(Au₆)模型, 用Hubbard-U校正的密度泛函理论(DFT + U)研究了相关的表面化学过程和催化反应. 详细考察了各种反应步骤, 包括吸附和所有可能的表面反应路径. 此外, 我们还仔细探讨了CeO₂在不同催化反应步骤中, 其独特的电子结构所体现的作用.

2. 计算方法和模型

本文采用了DFT + U计算方法以准确描述Ce元素的电子结构^[45,46], 其中U = 5 eV作用到Ce的4f轨道^[47–49]. 采用的是Vienna Ab-initio Simulation Package程序包, Ce (4f, 5s, 5p, 6d, 6s), Au (5d, 6s, 6p), O (2s, 2p), C (2s, 2p)和N (2s, 2p)作为价电子组态, 用投影缀加平面波的方法描述核-价电子的相互作用, 平面波基组展开的截断能取350 eV^[50,51]. 同时, 采用广义梯度近似框架下的PW91作为交换相关泛函^[52,53]. 计算的反应过渡态(TS)采用了约束最小化方法^[54,55], 并用Bader电荷密度分解来分析反应中的电子结构变化^[56].

我们构建了7层的CeO₂(110)板层模型,最底部的两层原子被固定而其他原子做结构弛豫。弛豫原子力的收敛标准设定为0.05 eV/Å。在计算中同时考虑了自旋极化效应。在两个板层模型之间的真空层高度选取了~10 Å以消除相邻板层之间的相互作用。CeO₂(110)表面由2 × 3的超晶胞模型构建,并根据实验^[57]沿着[110]方向去除一条CeO₂来模拟出重构(110)表面的特征结构(见图1(a))。构建了6个Au原子模型来模拟Au纳米团簇,将其负载于CeO₂一侧的板层模型上(见图1(b)和(c))。鉴于整个超晶胞表面大小为~11 × 11 Å²,因此布里渊区的k点取值为1 × 1 × 1。

吸附分子在催化剂表面的化学吸附能的计算公式为:

$$E_{\text{ad}} = -(E_{\text{molecule}} + E_{\text{Au}_6/\text{CeO}_2} - E_{\text{Au}_6/\text{CeO}_2} - E_{\text{molecule}})$$

其中, $E_{\text{molecule}} + E_{\text{Au}_6/\text{CeO}_2}$ 为Au₆/CeO₂(110)与吸附分子相互作用的体系总能量, $E_{\text{Au}_6/\text{CeO}_2}$ 为负载型催化剂的体系总能量, E_{molecule} 为气相分子的能量。

3. 结果与讨论

汽车尾气中主要含有CO, NO_x和HCs三种主要成分,人们多关注于CO低温催化氧化的处理上。作为汽车尾气控制另外一个非常重要的过程,NO_x的降解处理仍然是一个挑战。另外,反应的副产物诸如硝酸盐和亚硝酸盐也会降低整个催化剂的活性。与此同时,通过CO与NO_x的直接反应能同时消除这两类空气污染物,所以这类方法是非常高效的。因此本文通过DFT + U计算研究了NO与CO在Au₆/CeO₂(110)表面上反应的可行路径。

3.1. Au₆团簇负载CeO₂(110)表面

Nörenberg等^[57]通过扫描隧道显微镜(STM)观察了CeO₂(110)的表面结构。结果发现,每条CeO₂晶列之间的间隔为~11 Å,表明该表面经历了2 × 1扩展的重构过程。CeO₂(110)表面失去一条CeO₂结构的重构模型如图1(a)所示。最表层的CeO₂暴露了3配位的O原子(O_{3c})和6配位的Ce原子(Ce_{6c}),而在缺失一排CeO₂的局部表面处,暴露了7配位的Ce原子(Ce_{7c})和3配位的O原子(O_{3c}),此处也能看作为(111)晶面的微观结构。

在前期工作中,我们计算了3个Au原子组成的团簇(Au₃)在CeO₂(110)单晶表面的吸附^[58]。结果发现,Au₃纳米团簇能够还原CeO₂表面,并且Au₃上的电子可以转移并局域到表面邻近的Ce⁴⁺上,将其还原到Ce³⁺,同时进一步促进O₂的吸附并将O₂活化成带负电荷的O₂⁻。这充分说明了CeO₂负载型催化剂的催化活性。本文模拟了Au₆

纳米团簇负载于重构CeO₂(110)表面结构。优化后的结构如图1(b)所示,负载的Au₆纳米团簇呈现了2 + 4的双层原子构型。底层的4个Au原子与失去一排CeO₂晶列处的不饱和O_{3c}成键,其高度位置略有差异。而顶端的2个Au原子位于底层4个Au原子的上方,其配位数较少,与CeO₂表面没有任何直接的相互作用。经计算得到Au₆团簇的吸附能高达4.24 eV(参考气相中该Au₆原子团簇优化后的能量),与CeO₂载体有相互作用的底层4个Au原子与表面直接相连的O_{3c}原子的平均距离只有2.17 Å。因此,对于负载的金属来说,Au₆与载体有很强的相互作用。从结构上来看,Au₆纳米颗粒的负载对于CeO₂(110)载体的结构形变影响也很小。

通过计算,我们再次确定了Au₆纳米团簇的吸附引起了CeO₂(110)载体表面部分还原。正如图1(c)所示,在与Au₆团簇成键的那条表面CeO₂晶列上,两个邻近的表层Ce_{6c}上出现了两个4f局域电子,与本课题组之前的计算结果^[58]和其他课题组计算的过渡金属团簇负载于CeO₂表面的结果高度一致^[59,60]。

3.2. CO和NO在Au₆/CeO₂(110)表面吸附

在负载的Au₆团簇颗粒上,主要存在着3种可吸附位点(见图1(c)),分别是(1)与CeO₂载体无任何相互作用的独立Au原子的顶位吸附位点(T);(2)处于两个顶层Au原子之间的桥位吸附位点(B₁)和处于一个顶层Au原子和一个底层Au原子之间的桥位吸附位点(B₂);(3)处于两个底层Au原子和一个顶层Au原子之间的三重空位吸附位点(H)。本文计算了CO和NO分子在上述Au团簇吸附位以及界面Ce阳离子上的吸附能。

事实上,许多实验和理论计算都研究了CO, NO分子在过渡金属包括Au催化剂上的吸附情况^[61,62]。本课题组近期研究了Au纳米颗粒负载于TiO₂载体的结构和催化活性^[28],我们发现CO的最佳吸附位点是在Au纳米颗粒的顶位。本文再次发现,CO和NO分子在Au₆/CeO₂催化剂上最佳吸附位置依然在Au的顶位处(T)。表1列出了CO和NO分子在Au₆/CeO₂催化剂上不同吸附位上的吸附能(E_{ad})。通过比较,CO(图1(d))和NO(图1(e))分子在Au团簇顶位处的吸附都明显强于各自在Au团簇其他的吸附位或是载体Ce³⁺上的吸附位。而且CO的吸附能($E_{\text{ad}} = 1.2$ eV)明显高于NO($E_{\text{ad}} = 1.03$ eV),说明CO和NO在负载的Au₆纳米团簇上还存在竞争吸附的关系,而前者与Au原子的相互作用更强,更有利于CO在Au₆上的吸附。

除了单个CO和NO分子在Au₆/CeO₂(110)表面上吸

附, 我们同样考虑了两者在高覆盖度下的吸附情况. 如表1所示, 2个CO分子在2个Au顶位处的共吸附能为2.06 eV (图1(f)). 有趣的是, 当2个NO分子共吸附在2个Au原子顶位处的时候, NO能自发地结合成N₂O₂二聚体的结构(图1(g)), 算得其吸附能为1.56 eV (参考2个NO气相分子的能量). 由此可见, 无论是在低覆盖或者高覆盖度的情况下, CO都比NO更容易占据Au₆团簇上的吸附位.

3.3. N₂O₂在Au₆/CeO₂(110)界面吸附

针对WGS反应, Rodriguez等^[63]发现Au负载于氧化物载体是一类双功能催化剂, 即CO分子在Au上吸附而H₂O的吸附和解离则发生在氧化物表面, 后续的反应发生在金属-载体的界面. 因此本文也考虑了当Au₆团簇上被CO覆盖之后, NO能否与表面其他吸附位有强的相互作用.

前文的计算结果表明, 单个NO分子与界面Ce³⁺的作用依然非常弱. ($E_{ad} = 0.44$ eV, 表1). 然而, 当2个NO在2个邻近的Ce³⁺离子上共吸附时, 它们能非常容易地结合, 从而形成N₂O₂二聚体的结构, 该过程几乎没有能垒.

于是, 我们又计算了N₂O₂分子在CeO₂载体上4种不同的吸附构型, 见图2. 其吸附能(E_{ad})的计算以气相N₂O₂分子与Au₆预吸附CO的表面为参考, 如表2所示.

由计算得到的结构和吸附能, 我们发现当N₂O₂二聚体分子仅与界面处Ce³⁺相互作用时, 最好的吸附结构是O/O原子端朝下与表面的2个Ce³⁺成键(图2(b)), 该结构的吸附能为1.24 eV, 明显强于N/N原子端朝下吸附的构型(0.73 eV, 图2(a))或者N/O原子端朝下吸附的构型(0.92 eV, 图2(c)). 有趣的是, 我们还计算了一种N₂O₂横跨Au-CeO₂界面的吸附构型, 末端一个O原子与载体表面Ce³⁺成键, 而另一头的N原子与一个处于界面的Au原子成键, 其吸附能的大小为0.98 eV (图2(d)).

3.4. Au₆/CeO₂表面CO + NO的反应

大量的实验和理论计算都表明, Au纳米颗粒在低温CO+O₂氧化反应中具有很好的催化活性, 其相关的反应机理也被深入研究^[64,65]. 然而, CO + NO氧化还原反应的研究则相对较少. 因此, 本文系统地研究了CO和NO在Au₆/CeO₂负载型催化体系中的化学反应过程.

通过上述CO和NO在Au₆/CeO₂上的吸附计算可知, 在低覆盖度和高覆盖度条件下, NO在负载的Au颗粒团簇上的吸附能力都不如CO分子. 有趣的是, 即使CO分子已经吸附在Au团簇的顶位, NO仍然可以在Au-CeO₂界面处形成强吸附的N₂O₂二聚体. 于是, 我们研究了CO和N₂O₂之间的氧化还原反应, 并将斜跨在Au₆/CeO₂(110)

界面处的N₂O₂末端的O原子指向着吸附在Au顶位处的CO分子这样的共吸附结构作为反应的初始态(IS1, 图3和图2(d)). 由图3可见, CO和N₂O₂分子在Au₆/CeO₂(110)表面的共吸附能达到了2.18 eV(IS1). 当CO和N₂O₂开始相互反应时, CO分子逐渐地向N₂O₂中的末端O原子靠拢, 目的是与之结合生成CO₂. 此时达到第一个过渡态TS1, OC-ONNO的距离为1.785 Å, CO分子内的键长被拉长到1.340 Å, 而N₂O₂分子中的末端O-N的键长也增加到了1.341 Å.

通过比较IS1和TS1这两个状态, 我们发现吸附CO的Au原子在反应过程中, 随着CO一起移动, 从而促进CO向N₂O₂分子靠拢并与之反应. 从计算的能量来看, 该步反应的活化能垒只有0.39 eV, 说明在较温和的条件下就能发生. 这与Wang等^[40]的研究结果十分一致. 他们通过计算得出, 在Au(111)表面上, N₂O₂二聚体分子很容易生成N₂O.

经过了TS1过渡态之后, 界面处生成了OCONNO这一中间物种(IM1). C原子同N₂O₂中末端O原子相互结合成键, 缩短到了1.417 Å. 而末端的O-N键则增加到1.437 Å. 与TS1过渡态能量相比, IM1这一中间态能量仅稳定了0.19 eV. 由图3可见, OCONNO分子需要经历第二个过渡态TS2以完全断裂N-O键来生成CO₂, TS2的活化能垒为0.80 eV. 在TS2结构中, ONNO末端O原子同C原子和N原子的距离分别被优化为1.318和1.858 Å. 在越过TS2之后, N₂O和CO₂分子由于同Au₆/CeO₂表面都是弱吸附作用(N₂O约为0.2 eV; CO₂约为0.1 eV), 易于从表面脱离进入气相中. 从图3反应能量曲线上看, 反应末态FS1十分稳定, 在整个CO + N₂O₂反应过程中放出大量热能.

3.5. N₂O分解

作为汽车尾气排放中另一类有毒有害污染物, N₂O的降解也已成为研究热点^[66–68]. 特别是研究发现, 过渡金属催化剂能够有效地活化和解离N₂O分子^[69–71].

本文也详细地计算了N₂O与Au₆/CeO₂(110)催化剂表面的相互作用和相关的解离反应. 结果发现, N₂O物种与负载的Au₆纳米团簇或Au-CeO₂载体界面处并无较强的相互作用($E_{ad} = \sim 0.2$ eV). 因此, 我们研究了N₂O通过断裂分子中的末端N-O键使O原子留在Au纳米团簇上方法来直接解离N₂O分子. 图4给出了N₂O单分子解离的反应能量曲线图以及相关结构. 可以看到, 在解离初态(IS2)时, 与表面作用非常弱的N₂O分子的O端指向了Au₆纳米团簇的B₂吸附位. 在TS3中, O-N键的距离为1.372 Å, N₂O的直接解离能垒为1.78 eV, 说明这步解离

反应还是较难发生的, 与之前的研究结果一致, 即 N_2O 分子在Au基催化剂上的解离通常需要 $\sim 500\text{--}600\text{ K}$ 的高温^[72–74].

经过TS3之后, N_2O 中末端的O原子最终吸附在 Au_6 团簇的 B_2 桥位上, 而 N_2 从表面脱离进入气相. 整个反应过程的能量变化如图4所示, 尽管 N_2O 分子需要一个较高的解离能垒, 但是总体反应仍然放热了 0.64 eV .

考虑到CO分子原本就在 Au_6 纳米团簇的顶位上具有很强的吸附能, 本文同样计算了 N_2O 与预吸附CO直接反应来还原. 图5阐明了气相 N_2O 的末端O原子直接与CO中的C原子碰撞的反应过程, 并给出了整个反应的能量曲线图. 在过渡态TS4结构中, N_2O 末端的O原子与CO中C原子的距离计算得为 $1.775\text{ \AA}$, 而O–NN键从气相的 ~ 1.20 增至 $1.509\text{ \AA}$. 经历过渡态之后, 目标反应产物 N_2 和 CO_2 最终从表面脱附. 由整个能量曲线图可见, 该步反应的能垒为 1.86 eV 并最终放热 2.25 eV , 说明尽管该反应路径需要在高温环境下实现, 但最终的热力学状态是非常稳定的.

3.6. 讨论

负载于 CeO_2 的Au纳米颗粒广泛应用于WGS和CO氧化反应. 本课题组曾系统地计算了 O_2 在3个原子尺寸的小颗粒金纳米团簇(Au_3)负载于 $\text{CeO}_2(111)$, (110) , (100) 表面的吸附情况^[58]. 我们发现, Au_3 团簇能够转移一个电子到Ce阳离子的 $4f$ 局域轨道上, 从而使载体表面还原, 将 Ce^{4+} 还原为 Ce^{3+} . 我们发现, 只有 $\text{CeO}_2(110)$ 面具有非常平坦宽广的形貌结构, 不存在任何突出的晶格O原子. 因此, O_2 分子才能在 (110) 表面的 Ce^{3+} 上吸附, 并使 $4f$ 轨道上的局域电子进入其反键 $2\pi^*$ 轨道, 从而被活化成超氧分子. 换句话说, 正是 O_2 分子同表面Ce阳离子之间强静电吸引作用造成了 O_2 分子在 $\text{CeO}_2(110)$ 表面上良好的吸附能力.

本文发现, 在低覆盖度和高覆盖度两种情况下, NO在 Au_6 纳米颗粒上的吸附能总是小于CO. 但是, NO却在 Au_6/CeO_2 界面处表现出了非常独特的性质. 与CO类似, 低覆盖度下NO在界面处的吸附能依然很低. 有趣的是, 当两个NO分子同时在 CeO_2 载体上相互靠近共吸附时, 它们很容易相互结合, 生成 N_2O_2 二聚体的结构, 并且在Au– CeO_2 界面处的吸附能达到 $\sim 1\text{ eV}$. 不仅如此, N_2O_2 的优势吸附构型并不受在Au纳米团簇上CO分子吸附的影响, 这意味着CO和 N_2O_2 这两个反应物在各自吸附的两个区域内(Au团簇和Au– CeO_2 界面)并不存在竞争吸附的问题.

通过进一步的电子结构分析发现, N_2O_2 分子的强吸附依然可以通过载体 CeO_2 特殊的电子结构来解释. 正如图1(c)中的电子局域结构所示, Au_6 纳米颗粒的吸附引起了 $\text{CeO}_2(110)$ 面的还原. Au纳米团簇上的2个电子被转移并局域到2个与Au簇邻近的表面Ce阳离子 $4f$ 轨道上. 有趣的是, 2个 Ce^{3+} 阳离子并不受CO吸附于 Au_6 团簇的影响(见图6(a)). 表面局域电子能进一步地转移到 N_2O_2 中, 增加其与表面的稳定性以及与载体 Ce^{4+} 的静电吸引, 从而促进 N_2O_2 分子吸附. 由图6(b)中可见, 斜跨吸附在Ce原子和Au原子上的 N_2O_2 分子夺走了表面一个 $4f$ 局域电子, 而另一个 $4f$ 局域电子依然保留在表面自由的 Ce^{3+} 阳离子上. 这充分说明Ce元素具有非常独特的催化性能, 其 $4f$ 局域电子不仅能转移到类似 O_2 这样的小分子中, 而且能促进带有负电性的 N_2O_2^- 这一类较大分子的形成, 使其与表面存在着强烈的静电吸引作用, 在反应中成为稳定的中间产物. 需要强调的是, 带负电 N_2O_2 二聚体分子的形成正是 Ce^{3+} 上局域电子灵活转移的结果. Ce^{3+} 上的局域电子能够转移到整个分子中, 并大大增强了N–N键的键能^[75]. 因此, CeO_2 电子转移这类特性将会提高 N_2 的产生机会, 对于处理NO基这类有毒、有害气体是非常可行的.

本文详细计算了CO与 N_2O_2 在 $\text{Au}_6/\text{CeO}_2(110)$ 表面的反应过程, 尤其从Au纳米团簇型貌变化的几何角度揭示了重要的催化特征. 正如前文所述, 在 $\text{CO} + \text{N}_2\text{O}_2 \rightarrow \text{N}_2\text{O} + \text{CO}_2$ 反应中, 具有高度流动性的Au原子有助于CO分子准确地指向并靠近 N_2O_2 进行氧化还原反应, 所以这个过程的能垒只有 $\sim 0.4\text{ eV}$. 而且, 针对Au/ $\text{CeO}_2(110)$ 体系, 上述的计算结果进一步表明, Au原子独特的流动性并不受自身氧化的影响.

4. 结论

采用DFT + U的计算方法, 研究了 Au_6 纳米颗粒负载于 $\text{CeO}_2(110)$ 重构表面用于 $\text{CO} + \text{NO}_x$ 氧化还原反应. 结果表明, Au_6 纳米颗粒通过给出两个 $4f$ 局域电子到邻近的2个表面Ce阳离子上从而引起 $\text{CeO}_2(110)$ 表面部分还原. 对于 Au_6 团簇上的吸附情况, 无论是高覆盖度还是低覆盖度, CO的吸附能都要明显强于NO. 因此, CO能够完全覆盖Au簇上的吸附位点. 有趣的是, CO的吸附并不影响 $\text{CeO}_2(110)$ 载体上局域电子分布的形态; 而且局域电子还可以转移并协助负电性的 N_2O_2 二聚体分子的形成和吸附. 对于 $\text{CO} + \text{N}_2\text{O}_2$ 反应而言, 吸附在Au团簇顶位的CO能够与吸附在Au– CeO_2 界面处的 N_2O_2 二聚体分

子通过Langmuir-Hinsherwood双分子机理相互反应, 生成 CO_2 和 N_2O 产物. 这步反应的总能垒约为1 eV. 在随后的 N_2O 降解反应中, N_2O 分子既可以通过直接解离的方式, 在Au纳米团簇上留下一个O原子, 也可以通过与Au上预吸附的CO分子相互反应来消除. 在这步反应中, 由于 N_2O 分子本身在Au团簇或者 CeO_2 载体上的吸附作用都很弱, 因此反应能垒都会达到~1.8 eV, 并且遵循

Eley-Rideal分子碰撞机理. 通过进一步的电子分析可知, Ce^{3+} 上的局域电子在反应过程中被转移到 N_2O_2 分子中, 从而增强了N–N键能并促成 N_2 的形成. 结果表明, CeO_2 稀土材料这一独特的电子特性对于NO及其衍生物的消除将会起到一定的帮助.

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