

Insights into CO Oxidation in Cu/CeO₂ Catalysts: O₂ Activation at the Dual-Interfacial Sites

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Cu clusters supported on CeO₂ have been reported as a promising and active catalyst for CO oxidation. However, the identification of interfacial interactions and active sites is still a great challenge. In this work, we demonstrated that interfacial chemistry can be understood and predicted by using a simple descriptor of adsorbate-surface interactions that uncovers structure-activity relationships. The catalytic activity of CeO₂ supported Cu clusters for CO oxidation was studied by density functional theory. The Cu–Ce dual site mechanism enables the Cu/CeO₂ catalyst to have a much lower reaction energy barrier than the Mars-van Krevelen (M-vK) mechanism and the Cu-only

mechanism. The reaction energy barriers of Cu/CeO_{2-x} with an oxygen vacancy on the CeO₂ surface were 0.10, 0.37 and 0.77 eV, respectively. The excellent performance of Cu/CeO₂ catalysts is related to the interfacial interaction between Cu and CeO₂ and their synergistic redox behaviors, and oxygen vacancies facilitate the generation and stabilization of active Cu⁺ species through the interaction with Cu clusters. And we have identified the binding energy of O₂^{*} can describe the CO oxidation activity of Cu/CeO₂. Our study provides insight into the nature of active sites for Cu/CeO₂ catalysts and guidance for high-performance.

Introduction

CO oxidation catalytic processes have been extensively studied in the context of automotive emission control and hydrogen fuel cell applications.^[1] Metal clusters supported oxides are typical catalysts for the low temperature CO oxidation.^[2] The interfacial interaction between metal clusters and oxide surfaces is essential to the overall reaction. CeO₂ is widely employed as a support due to its highly surface active and reversible redox cycle Ce⁴⁺/Ce³⁺, as well as its unique ability to release and store oxygen.^[3] In addition, small CeO₂ nanoparticles can oxidize CO directly, which could be another reason for the improved activity of ceria catalysts.^[4] The noble metals such as Au, Pt and Pd supported on CeO₂ have attracted widespread attention^[2a,5] and the significance of interactions between noble metals and CeO₂ has been emphasized, in which the shape and size of ceria maintains the metal clusters via strong metal-support chemical bonding.^[6] However, due to the scarcity and high cost, noble-metal catalysts are not suitable for large-scale applications. The searching of alternatives for base metal catalysts, especially Cu/CeO₂ systems, is one of the optimal strategies in CO oxidation.^[7] The Cu/CeO₂ catalysts exhibit better catalytic performance than Pt/CeO₂ catalysts after the calcination in air at 800 °C for low-temperature CO oxidation.^[8] It was found that the oxide support can improve the catalytic reaction rate by confining the molecule O₂ within the Au-oxide interface region, and then

carry out co-assisted O₂ dissociation.^[9] The active sites proposed in these studies are mainly associated with metal-oxide support interfaces. Cai et al. compared the different properties of supported Pt and Au catalysts in CO oxidation. They found that O₂ can only be adsorbed at the interface of Au clusters and TiO₂(110) support, while it can be adsorbed at both the interface of supported Pt catalyst and the metal Pt sites.^[10] However, detailed information on the chemical properties of the metal-support interface in Cu/CeO₂ system during CO oxidation reactions is scarce. Cluster-support interactions affect the composition, size, and shape of the metal clusters, which further influence the catalytic performance.

Moreover, the underlying mechanism of CO oxidation are still under intense debate. Evidence of the Mars-van Krevelen (M-vK) mechanism for CO oxidation was found by observing a significant amount of CO conversion, in experiments of the absence of gas phase oxygen.^[11] Meanwhile, other mechanism of CO oxidation involving bound oxygen species such as peroxide species activated on Cu⁺ was proposed by the Time-Resolved X-ray Absorption Spectroscopy.^[12] Due to the coexistence of multiple oxidation states of cerium and copper in the catalyst including Cu²⁺/Cu⁺,^[12–13] Ce⁴⁺/Ce³⁺,^[14] Cu⁺/Cu⁰,^[7a] and Cu³⁺/Cu²⁺^[15] redox couples, the mechanism of CO oxidation at the atomic scale remains uncertain, depending on the reaction conditions, copper loading, and pretreatment history. Density functional theory (DFT) has become a powerful tool for discussing reaction mechanisms and predicting the rate of basic reaction steps.^[16] Since it is not realistic to generate a sufficient number of potential configurations manually, the selection of a reasonable and stable structure for supported clusters is an urgent issue in modelling. Therefore, more systematic conformational sampling algorithms such as particle swarm optimization algorithm or evolutionary algorithm are required.^[16b,17]

Liu et al.^[18] reported that Cu clusters supported on CeO₂ nanorods exposed dominantly (111) surfaces exhibited the

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Supporting information for this article is available on the WWW under
<https://doi.org/10.1002/ejic.202200656>

highest activity compared with those exposed mostly (100) and (110) facets. Chen et al.^[7a] observed that Cu clusters dominantly located on $\text{CeO}_2(111)$ by a bilayer configuration, with an average width of ~ 1.0 nm using a combination of STEM and EELS. As a model, we chose a Cu_8 cluster supported on $\text{CeO}_2(111)$ surface. This cluster was chosen because it represents sub-nanometer sized Cu clusters and was optimized with a bilayer structure, which has been often observed in loaded metal particles.^[5a,7a, 16b, 19] It was experimentally demonstrated that the noble metal ~ 1.0 nm Pt clusters are also anchored to the $\text{CeO}_2(111)$ surface, so the size matched as well as tractable Pt_8 clusters were selected for DFT calculations.^[19] Hensen et al. calculated the kinetic barriers of CO oxidation at the Pd- CeO_2 interface using a model of a Pd_8 cluster on $\text{CeO}_2(111)$, and they pointed out that Pd_8 clusters resemble the structure of Pd nanoparticles and are small enough to facilitate calculations.^[16b] In addition, experiments have indicated that Pd_8 and Au_8 clusters can be synthesized on Al_2O_3 and MgO , respectively.^[20]

In this study, we used the particle swarm optimization (PSO) algorithm combined with density functional theory calculations (DFT) to determine the minimum energy structure of the Cu_8 cluster on stoichiometric and defective $\text{CeO}_2(111)$ surfaces, which is the most stable surface termination of cerium, and to further explore the mechanisms of CO oxidation. We have investigated the mechanism of efficiently enhancing CO oxidation activity by Cu–Ce double sites with reference to lattice oxygen sites and single Cu sites. And we further pointed out that the oxygen vacancies on the CeO_2 surface play a key role in CO oxidation catalysis. The Cu–Ce dual site enables the Cu/ CeO_2 catalyst to have a much lower reaction energy barrier than the others. The excellent performance of Cu/ CeO_2 catalysts is related to the interfacial interaction between Cu and CeO_2 and their synergistic redox behaviors. And oxygen vacancies facilitate the generation and stabilization of active Cu^+ species through the interaction with Cu clusters. These results not only shed light on understanding metal-support interactions and the nature of active sites at the atomic level, but also provide a novel strategy for rational design of ceria-supported metal catalysts.

Results and Discussion

Cu_8/CeO_2 Structure Optimization

To identify the most sufficiently stable structure of a Cu_8 cluster supported on the $\text{CeO}_2(111)$, we performed a systematic structure search via CALYPSO method. The simulation process of Cu_8/CeO_2 is schematized in Figure 1a. The energy evolution diagrams are shown in Figure S1. The five most stable isomers of a free Cu_8 cluster and Cu_8 supported on the $\text{CeO}_2(111)$ are presented in Figure S2. For comparison, We showed that the most stable structure of the free Cu_8 cluster in Figure 1b adopts a bicapped octahedral geometry with four Cu atoms in both the upper and lower layers, which is consistent with previous predictions.^[21] The same methodology was employed to obtain the most stable structures of Cu_8/CeO_2 (Figure 1c and 1d) and

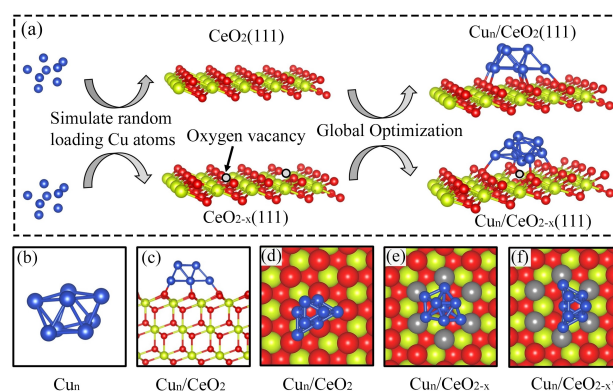


Figure 1. (a) Schematic illustration of the formation process of supported Cu_8 cluster on CeO_2 (b) Optimized structure of free Cu_8 cluster. (c, d) Side and top views of the most stable structures of Cu_8 on the stoichiometric $\text{CeO}_2(111)$ surface. (e, f) The most stable and metastable structures of Cu_8 on the defective $\text{CeO}_{2-x}(111)$ surface. Blue, red, and yellow spheres represent Cu, O and Ce atoms, respectively. Gray spheres represent O atoms adjacent to oxygen vacancies (V_O) on the surface of CeO_{2-x} .

$\text{Cu}_8/\text{CeO}_{2-x}$ (Figure 1e). Compared with the free Cu_8 clusters, the interactions between Cu_8 cluster and CeO_2 support led to a different Cu_8 cluster geometry. The Cu cluster shows a bilayer structure with three Cu atoms on the top layer and five Cu atoms in the bottom layer interaction with lattice O atoms on the $\text{CeO}_2(111)$ surface. In addition, we also investigate the effect of oxygen vacancy on Cu_8 cluster supported $\text{CeO}_2(111)$ surface due to its unique store and release capacity. The Cu_8 cluster preferentially binds to this oxygen vacancy and the most stable structure is slightly different compared with stoichiometric ceria. The metastable structure $\text{Cu}_8/\text{CeO}_{2-x}$ (Figure 1f) has the same configuration as the most stable structure Cu_8/CeO_2 (Figure 1d). Energetically, the metastable structure is thermodynamically less stable than the most on $\text{CeO}_{2-x}(111)$ by 0.16 eV. For other metastable structures, the energy is all more 0.5 eV higher than the most stable structure, which is an unstable state in thermodynamics. Besides, according to radial distribution function, Cu clusters on CeO_2 retains the bulk copper FCC structure in the first three coordination shells (Figure S3).

Electronic Structures

Systematic analysis of the electronic structure provides insights into the interactions between Cu cluster and CeO_2 surface. For Cu_8/CeO_2 , $\text{Cu}_8/\text{CeO}_{2-x}$ and metastable $\text{Cu}_8/\text{CeO}_{2-x}$, Bader charges indicate that Cu_8 clusters all carry a positive charge, the value of $|+1.44\text{e}|$, $|+0.82\text{e}|$ and $|+1.13\text{e}|$, respectively (Figure S4 and Table S1). The top Cu layer in Cu cluster remains metallic Cu^0 , whereas the bottom Cu layer remains a positive charge. That is, the electron depletion of Cu atoms on the interface alters their chemical states toward Cu^+ . This charge distribution is consistent with the previous work.^[7a] However, the Cu atom above the oxygen vacancy of the CeO_2 surface remains a slightly negative charge (Table S1), suggesting that vacancy affects the geometry and electronic structure of the interface.

Figure 2 shows the electronic analysis of the interactions between Cu_8 clusters and CeO_2 supports. For Cu_8/CeO_2 , the isosurface of excess spin charge density displays that two Ce^{3+} ions are generated (Figure 2a, top panel). For defective CeO_{2-x} , two additional Ce^{4+} are expected to be reduced to Ce^{3+} on the surface due to the presence of an oxygen vacancy. For metastable surfaces, total four Ce^{3+} are indeed observed (Figure 2c, top panel), while for the most stable structures, only three Ce^{3+} are observed and electrons are trapped at the oxygen vacancy (Figure 2b, top panel). The projected density of states reveals localization of excess electrons in Ce 4f orbitals. A comparison of the bottom panel of Figure 2, the electron localization function (ELF) maps further elucidate that an electron was trapped on an oxygen vacancy site in $\text{Cu}_8/\text{CeO}_{2-x}$ configuration. This phenomenon is often observed by ERP in experiment, leading to a higher catalytic performance of various catalytic reactions.^[22] These results indicate that O vacancies have a great influence on the structure of the supported metal clusters and the charge transfer from the cluster to the ceria substrate.

Bonding charge analysis shows charge depletion and accumulation at the copper-ceria interface, as shown in Figure 3. The interfacial plane-integrated bonding charge $\Delta Q(z)$ was calculated based on the self-consistent electron density. The bonding charge distribution indicates the strong chemical bonding at the interface by the charge transfer. The metal-support interfacial charge transfer only involves the bottom Cu atoms and the first O–Ce–O tri-layer of the ceria support.

Comparing Cu cluster supported on stoichiometric and defective CeO_2 surface, there are marked differences in the regions between Cu and surface O atoms. The electron accumulation for $\text{Cu}_8/\text{CeO}_{2-x}$ is significantly greater than that for Cu_8/CeO_2 . More obviously, a notable depletion of electrons can be observed in the region between the O and Ce layers for $\text{Cu}_8/\text{CeO}_{2-x}$ (Figure 3b), which indicates that the charge transfer now occurs from the reduced ceria surface (Ce^{3+} ions) to the oxygen vacancy site, thus leaving just one extra Ce^{3+} ion instead of two. For $\text{Cu}_8/\text{CeO}_{2-x}$, electron depletion is not obvious (Figure 3c), thus leaving two extra Ce^{3+} ions due to the oxygen vacancy.

CO Oxidation on $\text{Cu}_8/\text{CeO}_2(111)$

In order to mimic the catalytic behavior of the optimized structures for the CO oxidation, we explored three reaction mechanisms, including the special Cu–Ce interfacial dual-site mechanism in addition to the widely accepted Mars-van Krevelen (M-vK) and Langmuir–Hinshelwood (L–H) mechanisms.^[23] At first, we explored the M-vK mechanism, in which the lattice O atoms of ceria are involved in the CO oxidation (Figure 4). The CO is adsorbed on the bottom Cu^+ atoms to form the CO-Cu^+ species and reacts with adjacent lattice O atom provided by the ceria support, accompanied by the reduction of Ce^{4+} and formation of an oxygen vacancy. This process is the rate-limiting step of the reaction. As illustrated in

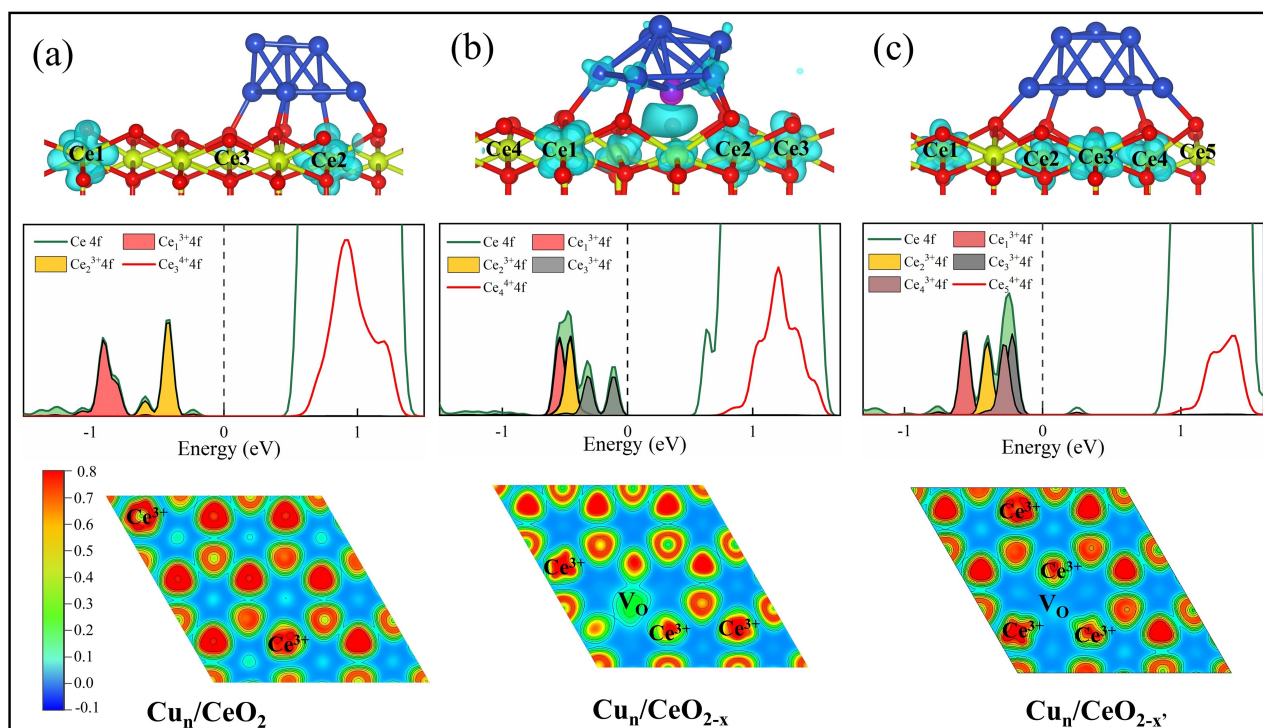


Figure 2. Electronic analysis of the interactions between Cu_8 clusters and CeO_2 supports: (a) the stoichiometric $\text{CeO}_2(111)$ surface, (b) the most stable defective $\text{CeO}_{2-x}(111)$ surface, and (c) metastable defective $\text{CeO}_{2-x}(111)$ surface (top: spin density, cyan stands for spin up and purple for spin down; middle: projected electronic densities of states for Ce 4f orbitals; bottom: electron localization function maps). The spin density isosurfaces indicate the position of the Ce^{3+} ions

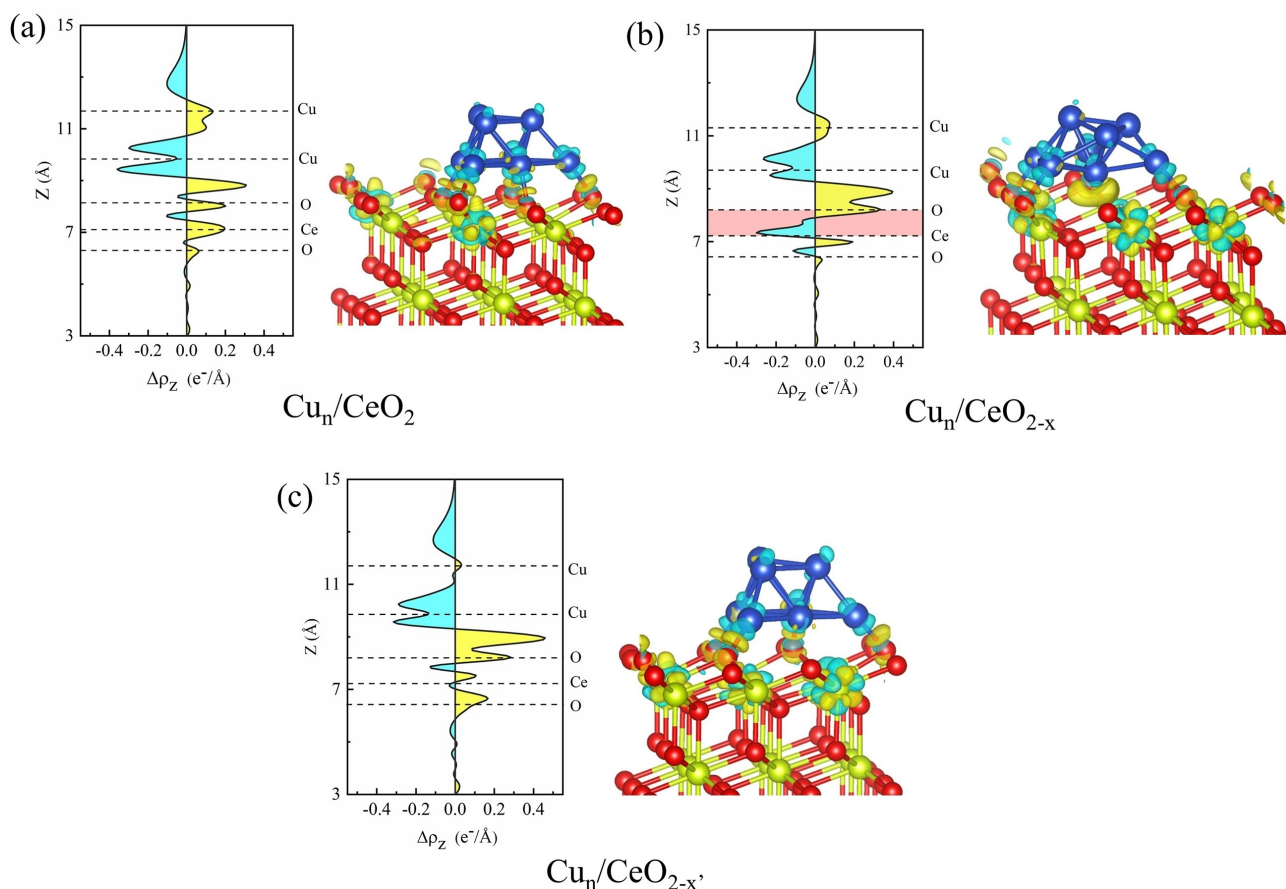


Figure 3. Calculated bonding charge analysis for Cu_8 cluster supported by the stoichiometric $\text{CeO}_2(111)$ surface (a) and defective $\text{CeO}_{2-x}(111)$ surface (b, c). The left panels represent plane-integrated bonding charge $\Delta\rho_z(z)$ plotted as a function of z-coordinate across the copper-ceria interface. The right panels display bonding charge at the value of $0.006 \text{ electrons}/\text{\AA}^3$. Electron depletion and accumulation are represented by cyan and yellow, respectively.

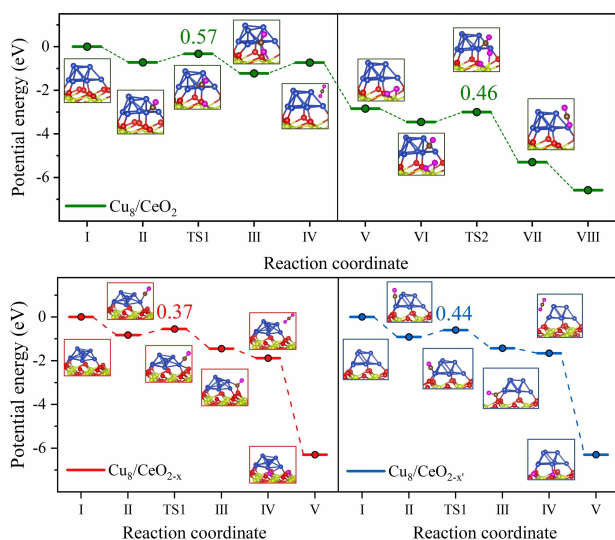


Figure 4. Potential energy diagrams and configurations for CO oxidation via Mars-van Krevelen (M-vK) mechanism on $\text{Cu}_8\text{CeO}_2(111)$, $\text{Cu}_8\text{CeO}_{2-x}$ and $\text{Cu}_8\text{CeO}_{2-x'}$.

Figure 4, the activation barrier of the step is 0.57, 0.37, and 0.44 eV for Cu_8/CeO_2 , $\text{Cu}_8/\text{CeO}_{2-x}$ and $\text{Cu}_8/\text{CeO}_{2-x'}$ respectively. For Cu_8/CeO_2 , the oxygen vacancy is replenished by O_2 molecule and O–O bond is elongated to 1.44 $\text{\AA}$. For $\text{Cu}_8/\text{CeO}_{2-x}$ and $\text{Cu}_8/\text{CeO}_{2-x'}$, upon contact with gaseous O_2 , oxygen vacancies may be directly refilled to regenerate the Cu_8/CeO_2 catalyst as shown in Figure 4. Then, the second CO reacts with the O_2 species and complete the reaction cycle. The enhancement of V_O -promoted $\text{Cu}_8/\text{CeO}_{2-x}$ catalyst arises mainly from facile activation of CO due to strong metal-support interactions. Overall, the surface oxygen vacancies tune the interfacial properties of $\text{Cu}_8/\text{CeO}_{2-x}$.

The chemical state of metal supported on oxides might influence the reaction pathway of CO oxidation.^[24] Due to the interaction between Cu and CeO_2 , the Cu atoms in the bottom layer remain positively charged, while the Cu atoms in the top layer still obtain a metallic state. Therefore, we also explored CO oxidation via the Langmuir-Hinshelwood (LH) mechanism. As shown in Figure 5, O_2 molecule reacts with co-adsorbed CO to form CO_2 and activation barrier of the rate-limiting step is 1.13, 0.77, and 0.94 eV, for Cu_8/CeO_2 , $\text{Cu}_8/\text{CeO}_{2-x}$ and $\text{Cu}_8/\text{CeO}_{2-x'}$ respectively. Simultaneously the remaining adsorbed oxygen atom migrates to the hollow positions of the three Cu atoms

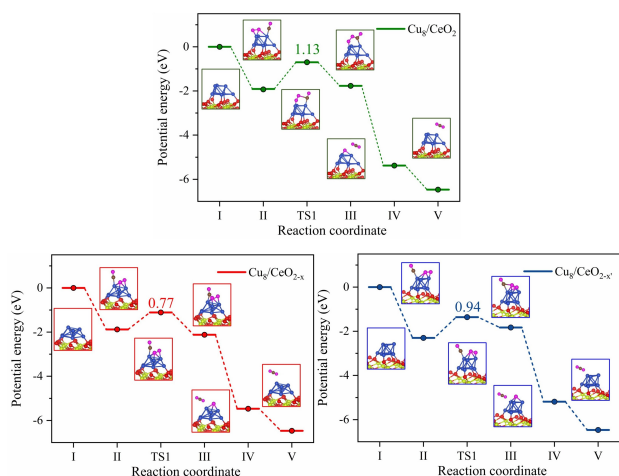


Figure 5. Potential energy diagrams and configurations for CO oxidation via Langmuir-Hinshelwood (LH) mechanism on Cu_8CeO_2 , $\text{Cu}_8\text{CeO}_{2-x}$ and $\text{Cu}_8\text{CeO}_{2-x'}$ (111).

(Figure 5 IV). Nevertheless, during the subsequent reaction, DFT calculation indicated that the CO adsorption probability is negligible on Cu atom and CO gas reacts with the adsorbed O^* directly following the Eley-Rideal (E-R) mechanism. The energy barrier of this process is larger than that for the CO oxidation by lattice oxygen, suggesting that this reaction pathway is less favorable dynamically. The results indicated that the Cu^+ species at the interface were considered to be highly active sites for CO oxidation.^[13,25]

In addition to O_2 adsorption at the Cu sites as considered above, O_2 may also be adsorbed on the CeO_2 support surface or at the Cu/CeO_2 interface (Figure 6). Whereas DFT results show that O_2 does not be adsorbed on the stoichiometric CeO_2 (111)

since the adsorption energy is negligible, consistent with previously reported results.^[26] According to our calculations, O_2 can absorb the interface at the Ce–Cu dual sites with adsorption energies of $-0.78 \sim -1.23$ eV (Table S2). CO on Cu_8 and O_2 at a Cu–Ce interfacial site directly dissociated into CO_2 and Cu-O^* . The calculated potential energy diagrams as well as corresponding intermediates and transition state configurations are presented in Figure 6 and Figure S5–S6. The reaction between CO at Cu site and O_2 at the interface has a very small barrier is 0.22, 0.10 and 0.17 eV for Cu_8/CeO_2 , $\text{Cu}_8/\text{CeO}_{2-x}$ and $\text{Cu}_8/\text{CeO}_{2-x'}$ respectively, which exhibits the opposite trend as O_2 adsorption energy. The low reaction energy barriers indicate the step occurs almost spontaneously. The subsequent desorption of CO_2 from the surface to the gas phase. In the next step, a second CO molecule is adsorbed onto the Cu_8 cluster and reacts with the remaining adsorbed O atom to form the second CO_2 .

To further clarify the origin of dual site activity for CO oxidation, we investigated the reaction process of the catalysts for interfacial atomic arrangement, geometries, and electronic structures. Compared with the stoichiometric Cu_8/CeO_2 surface, the oxygen vacancies at defective CeO_2 surface promote the activation of O_2 adsorbed at the interface. And the binding energy of O_2^* can be used as a descriptor to describe the CO oxidation activity of Cu/CeO_2 . The reaction energy barrier is negatively correlated with the adsorption energy of O_2 , which indicates that the strong adsorption of O_2 at the Cu–Ce dual sites is the key to enhance the CO reaction performance. After O_2 adsorption, the CO adsorption energies show an opposite trend (Figure 6d): Cu_8/CeO_2 (-1.57 eV) $>$ $\text{Cu}_8/\text{CeO}_{2-x}$ (-1.32 eV) $>$ $\text{Cu}_8/\text{CeO}_{2-x'}$ (-1.08 eV). The strong adsorption of CO is not conducive to its reaction with activated O_2 , which will result in high reaction barriers and low catalytic performance. The structures of O_2 adsorption at the Cu–Ce dual site are depicted

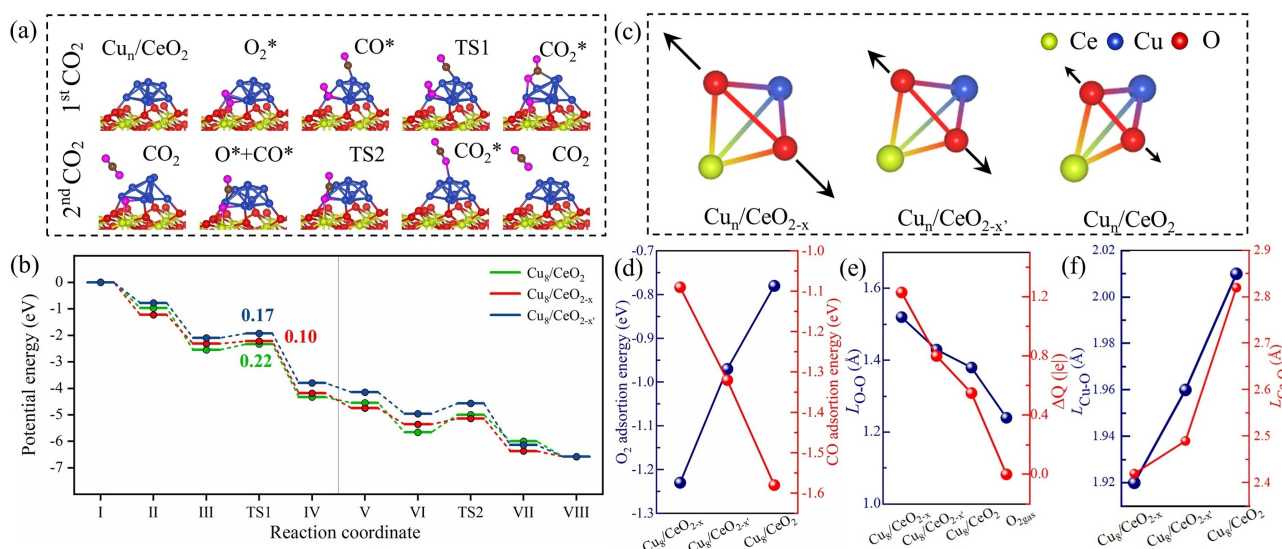


Figure 6. (a) CO oxidation pathway following the dual site mechanism on $\text{Cu}_8\text{CeO}_{2-x}$, $\text{Cu}_8\text{CeO}_{2-x'}$ and Cu_8CeO_2 (111). (b) Potential energy diagrams via dual site mechanism on $\text{Cu}_8\text{CeO}_{2-x}$, $\text{Cu}_8\text{CeO}_{2-x'}$ and Cu_8CeO_2 (111). (c) Schematic diagram of the degree of relaxation of adsorbed O_2^* at the double site. (d) Adsorption energy of O_2^* and CO^* . (e) The relationship between the O–O length and Bader charge. (f) Cu–O and Ce–O bond length.

in the schematic diagram of Figure 6c. The O–O distance is elongated to 1.51, 1.46 and 1.41 Å for $\text{Cu}_8/\text{CeO}_{2-x}$, $\text{Cu}_8/\text{CeO}_{2-x'}$ and Cu_8/CeO_2 , respectively, compared with the calculated equilibrium O_2 gas phase value of 1.24 Å (Figure 6e). Besides, the Cu–O and Ce–O bond lengths show the opposite trends (Figure 6f). These results reveal that the oxygen vacancy can enhance the interaction between O_2 and Cu–Ce dual sites and promote the activation of O_2 . Therefore, this further improves the CO reaction performance.

To deeply understand the activated mechanism of O_2^* at the interface, we further analyzed the electronic structure and the bonding mechanism of O_2 and the Cu–Ce dual site. When O_2 adsorbed on Cu–Ce dual site, a new hybrid state formation due to hybridization between the O 2p and Cu 3d orbitals (Figure 7). Compared to Cu/CeO_2 , the strong hybridization between Cu 3d and O 2p orbitals lead to a more significant discrete of O 2p orbital state in $\text{Cu}/\text{CeO}_{2-x}$ and $\text{Cu}/\text{CeO}_{2-x'}$, indicating that the O_2 molecule is better activated. We also studied the crystal orbital Hamilton population (COHP) and integrated COHP (ICOHP) of O_2^* , Cu–O* and Ce–O* (Figure 7 and Figure S8–S9). The ΔICOHP is defined as the energy of antibonding states below Fermi level (Figure 7). The larger the ΔICOHP value, the more unstable the O–O bond. The ΔICOHP values for Cu/CeO_2 , $\text{Cu}/\text{CeO}_{2-x'}$ and $\text{Cu}/\text{CeO}_{2-x}$ are 1.73, 1.96, and 1.81, respectively, indicating that the O–O covalent bond interaction of $\text{Cu}/\text{CeO}_{2-x}$ was the weakest and most unstable, which also explain that $\text{Cu}/\text{CeO}_{2-x}$ has the better catalytic activity. Besides, the more negative the ICOHP value of Cu–O* and Ce–O*, the stronger the adsorption of O_2 (Figure S7–S8). Based on these results, we found that the Cu–Ce dual site synergy induces electron transfer from this active site to O_2^* , which modulates the interaction between the interface and the

O_2^* intermediate. It also contributes to the modulation of the CO adsorption energy as well as the performance of the CO oxidation reaction. And oxygen vacancies on the CeO_2 surface promote the dual sites synergy.

Conclusion

In summary, we used DFT and CALYPSO approaches to explore the active states of the Cu cluster on $\text{CeO}_2(111)$ catalysts for CO oxidation. Firstly, we determined the minimum energy structure of the Cu_8 cluster on stoichiometric and defective $\text{CeO}_2(111)$ surfaces. Then we explored the proceeding of the CO oxidation via Mars-van Krevelen (M-vK) mechanism, Langmuir-Hinshelwood (LH) mechanism and Dual-site mechanism. The reaction energy barriers of $\text{Cu}/\text{CeO}_{2-x}$ with an oxygen vacancy on the CeO_2 surface were 0.37, 0.77 and 0.10 eV, respectively. The Cu–Ce dual sites mechanism benefits the interface interaction between Cu clusters and CeO_2 surface with respect to M-vK mechanism and Cu-only LH mechanism, tuning a new reaction pathway for CO oxidation by O_2 adsorbed on Cu–Ce bridge sites with much lower energy barriers. The interface effect plays a crucial role and has a strong influence on the catalytic activity. Therefore, the catalytic performance can be further improved by increasing the interface perimeter experimentally.

And we confirmed the critical role of oxygen vacancies on the CeO_2 surface on the catalytic performance. The oxygen vacancy promotes the synergistic interaction of the Cu–Ce dual site, modulates the interaction between the Cu–Ce site and the O_2^* intermediate, and further facilitates the reaction of the adsorbed CO with activated O_2^* . Thus, the dual site mechanism improves the performance of the CO oxidation reaction. Oxygen vacancies not only enhance the Cu/Ce interaction to form more Cu^+ absorption sites, but also trap gas phase oxygen to promote the release of subsurface lattice oxygen and provide more reactive oxygen species. Therefore, increasing the oxygen vacancy content on the surface of Cu/Ce catalyst can also improve the performance of the catalyst. These results provide new insights into the active sites for CO oxidation in Cu/CeO_2 catalysts and offer guidelines for designing the high-performance metal/oxide catalysts.

Experimental Section

DFT calculations: All spin-polarized density functional theory (DFT) calculations were performed via the Vienna ab initio simulation Package (VASP).^[27] The projector-augmented wave (PAW) method and Perdew–Burke–Erzerhof (PBE) were adopted to describe the core–valence electron interaction and exchange–correlation functional.^[28] The energy cutoff of plane-wave basis set was 500 eV and Brillouin zone integration was sampled with a $3 \times 3 \times 1$ Monkhorst–Pack k-point. The geometric structures were optimized using conjugate gradient algorithm until the forces on all unconstrained atoms were less than 0.01 eV/Å. The DFT + U approach was adopted to take the on-site Coulombic interactions into account, in which U is the Hubbard term. The U value of 5.0 eV was employed to correctly describe the 4f electrons of Ce ions, following our previous study.^[14,29] The climbing image nudged elastic band (CI-

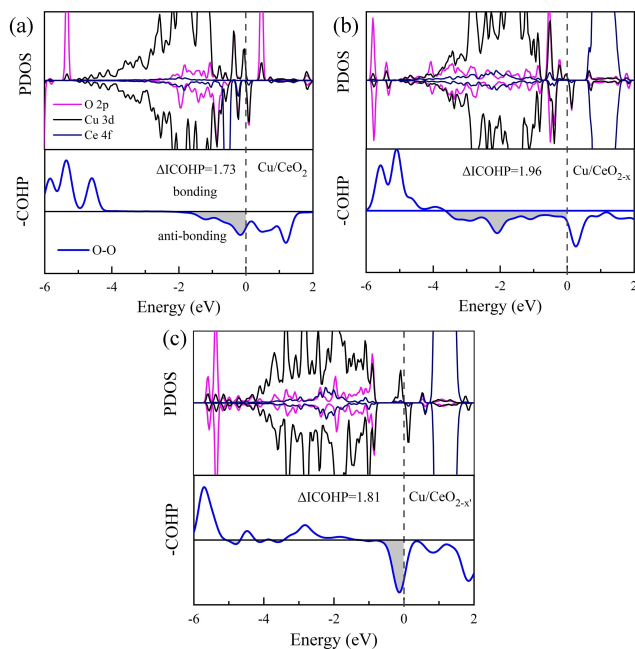


Figure 7. Projected density of states (PDOS) and the COHP of adsorbed O_2 on (a) Cu_8CeO_2 , (b) $\text{Cu}_8\text{CeO}_{2-x'}$ and (c) $\text{Cu}_8\text{CeO}_{2-x}$ (111).

NEB) algorithm was performed to search the transition states for CO oxidation.^[30] Vibrational frequency analysis was used to further confirm the identified transition state. The energy convergence criterion was set to 10^{-6} eV. Bader charges were calculated for electron population analysis.^[31] Crystal Orbital Hamilton Population (COHP) was extracted by LOBSTER package for the analysis of chemical bonding.^[32] COHP and pCOHP (projected COHP) described the strength of atom-pair interactions by dividing the band structure energies into non-bonding, bonding, and anti-bonding contributions.^[33]

CALYPSO

Cu clusters supported on CeO₂ (111) surface were systematically searched via CALYPSO (crystal structure analysis by particle swarm optimization) method,^[34] which has been widely used to predict energetical stable and metastable structures for extended crystals, reconstructed surfaces, low-dimensional materials, clusters and nanoparticles.^[35] CeO₂(111) models composed of nine atomic layers (three O–Ce–O trilayers) in a 3×3 supercell was used. The bottom two trilayers are fixed and the top O–Ce–O trilayer was optimized by particle swarm optimization. For Cu cluster morphology, only the number of atoms in the Cu cluster adsorbed on the surface is required. The particle swarm optimization (PSO) approach consists of four main parts. (1) Twenty initial structures of first generation are randomly generated under the condition of crystal structure symmetry constraints. (2) Once new structure is generated, characterized by the bonding feature matrix to judge the similarity to the previous structures and it is discarded if similar. (3) The geometry optimization of all the structures of each population is carried out by the first principle to drive system to the local minima of potential energy surface. (4) Energy surface minimization is performed by PSO algorithm, which in fact is implemented to create the structures for the next generation. Finally, the whole system converges in multiple cycles, and the search for the structure ends. In all, several hundreds of structures have been optimized to achieve a global minimum. The introduction of random structures (40% of the whole population) in the process of structural evolution can effectively increase the diversity of the population and strengthen the global search ability of CALYPSO method.

Acknowledgements

This work was supported by National Key R&D Program of China (2020YFA0406202), the National Natural Science Foundation of China (22090042, 22008006, and 21731001), and the Fundamental Research Funds for the Central Universities (FRF-IDRY-20-005 and FRF-TP-20-077A1).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: CO oxidation · Density functional calculations · Dual-site mechanisms · Heterogeneous catalysis · Oxygen vacancy

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Manuscript received: October 20, 2022

Revised manuscript received: November 18, 2022

Accepted manuscript online: November 30, 2022