

CO Oxidation Mechanism on CeO₂-Supported Au Nanoparticles

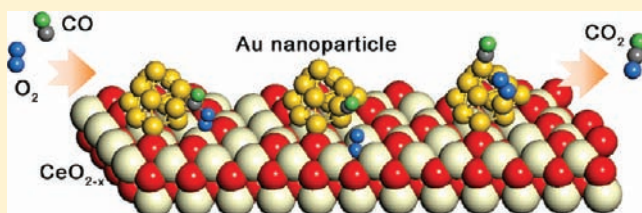
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S Supporting Information

ABSTRACT: Density functional theory was used to study the CO oxidation catalytic activity of CeO₂-supported Au nanoparticles (NPs). Experimental observations on CeO₂ show that the surface of CeO₂ is enriched with oxygen vacancies. We compare CO oxidation by a Au₁₃ NP supported on stoichiometric CeO₂ (Au₁₃@CeO₂-STO) and partially reduced CeO₂ with three vacancies (Au₁₃@CeO₂-3VAC). The structure of the Au₁₃ NP was chosen to minimize structural rearrangement during CO oxidation. We suggest three CO oxidation mechanisms by Au₁₃@CeO₂: CO oxidation by coadsorbed O₂, CO oxidation by a lattice oxygen in CeO₂, and CO oxidation by O₂ bound to a Au–Ce³⁺ anchoring site. Oxygen vacancies are shown to open a new CO oxidation pathway by O₂ bound to a Au–Ce³⁺ anchoring site. Our results provide a design strategy for CO oxidation on supported Au catalysts. We suggest lowering the vacancy formation energy of the supporting oxide, and using an easily reducible oxide to increase the concentration of reduced metal ions, which act as anchoring sites for O₂ molecules.



INTRODUCTION

More than two decades have passed since Haruta's pioneering finding that supported small Au nanoparticles (NPs) catalyze CO oxidation at or below room temperature.¹ Experimental and theoretical studies on the catalytic properties of oxide-supported Au NPs have suggested thus far that the size of Au NPs,^{2–5} their structural fluxionality,^{6–8} their electronic interaction with supporting materials,^{3,8–10} and the presence of a Au NP–support interface^{7,11,12} are factors that activate supported Au NPs. Because of high computational costs and the limited resolution of experimental methods, current understanding of catalytic activity on oxide-supported Au NPs is based on highly model systems, for example, gas-phase crystalline Au NPs,^{2,4} tiny Au clusters supported on oxide surfaces,^{6,7,13,14} or Au NPs on clean oxide surfaces.¹⁵

Among the various oxides, CeO₂ has been recognized as the best supporting material for catalysis at Au NPs¹⁵ due to its high oxygen storage and release capacity, facile oxygen vacancy formation, and the presence of a narrow Ce f-band.¹⁵ Experimental studies have shown that the surface of CeO₂ can easily be enriched with oxygen vacancies^{15–17} and that Au NPs bind strongly to these vacancies.¹⁸ Lawrence et al. recently demonstrated that catalytic activity is a function of the concentration of oxygen vacancies for the CO oxidation activity of CeO₂ nanorods, NPs, and the bulk surface.¹⁷ Oxygen vacancy formation on the CeO₂ surface accompanies the reduction of adjacent Ce⁴⁺ ions to Ce³⁺, and the concentration of Ce³⁺ ions is proportional to that of oxygen vacancies.¹⁷ Localized electrons on the occupied 4f-orbital of Ce³⁺ ions contribute to the electronic interaction between reduced CeO₂ and supported Au NPs.^{15,19}

CeO₂-supported Au is regarded as a promising catalytic system, because it combines highly active components, Au NPs

and CeO₂. To design a catalyst, a detailed analysis of catalytic activity of CeO₂-supported Au NPs is required. Several reactive species, such as lattice oxygen,¹³ under-coordinated Au atoms in Au NPs,² and a Au ion substituting a lattice Ce ion,²⁰ have been independently reported as reactive species for CO oxidation by CeO₂-supported Au NPs. The local electronic state of the reactive Au species likely also plays a role.^{13,21,22} The CO oxidation process by CeO₂-supported Au NPs has not, however, been systematically studied as a single system. Previous studies, which considered tiny Au clusters or Au ions, were not able to investigate the role of the atomic coordination or the morphology of Au NPs that become important as the size of the NPs increase. Even the most extensive study on the role of the under-coordinated Au atoms of Au NP was performed on Au crystallites,² so the effect of the CeO₂ support was missing.

Furthermore, from an industrial perspective, model systems of Au NPs supported on a well-ordered and clean CeO₂ surface may not be relevant. The surface of industrial-grade oxide supporting material is likely to be highly defected, have broken metal–oxygen bonds, oxygen or metal ion vacancies, grain boundaries, and steps under realistic conditions. Furthermore, the concentration of defects would increase with reduction of the size of the oxide support to the nanoscale. Defects can alter the local stoichiometry of the oxide support and significantly affect the catalytic properties of supported Au NPs. The strong binding between vacancies and Au NPs means that their interactions are inevitable,¹⁸ so the effect of defects on the catalytic properties of the Au NPs must be considered as well.

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In this work, we used density functional theory (DFT) to study and compare CO oxidation catalyzed by Au₁₃ NPs supported on stoichiometric and partially reduced CeO₂ surfaces. We optimized the structure of gas-phase Au₁₃ NPs and subsequently supported them on CeO₂ surfaces. We find that three different reaction pathways, two of them are dependent upon the nature of the supporting oxide, contribute to the overall rate of CO oxidation. On the basis of the reaction mechanisms, we suggest a strategy for the design of CeO₂-supported Au catalyst for CO oxidation.

METHODS

Choice of Au Nanoparticle: Size and Structure. Current computational resources are insufficient to study supported Au NP catalysis on experimental time and length scales. Hence, choosing the most appropriate size and shape of Au NPs is critical for studies involving model systems. In a recent report, Zhang et al. investigated fcc or hcp-like crystalline two-layer closed-packed CeO₂-supported Au NPs.¹⁹ These clusters were generated by depositing Au atoms onto the CeO₂ surface with a single oxygen vacancy,¹⁹ a process that is relevant to physical deposition in high-vacuum conditions. Their conclusion was that a hcp-like Au₁₁ NP was likely to be present on the surface and to be catalytically active. In this work, we considered Au₉ and Au₁₀ clusters of structure similar to the Au₁₁ cluster, except with the topmost capping Au atom removed¹⁹ to avoid this atom's unrealistically low coordination number (see Figure 1 of ref 19). We examined the stability of these structures on CeO₂ with a single vacancy (CeO₂-1VAC) and three triangular surface vacancies (CeO₂-3VAC). We also tested the stability of these clusters with adsorbed CO and O₂ molecules (see Figure S1).

We found that, as Zhang et al. reported,¹⁹ fcc-like Au₉ and hcp-like Au₁₀ NPs were stable on CeO₂-1VAC. However, the Au–Au atomic bonds of Au₁₀@CeO₂-3VAC, which has a hexagonal bottom layer structure, are unfavorably stretched (Figure S1(c,d)). Au₉, which has a triangular bottom layer configuration, remained stable on CeO₂-3VAC but deformed upon O₂ and CO adsorption (Figure S1(b,e,f)). Although fcc or hcp-like small Au NPs were found to be the most stable structures on CeO₂-1VAC, they became unstable when the number of vacancies in CeO₂ increased. Likely, the strong interaction between Au atoms and oxygen vacancies induces structural deformation of Au₉ and Au₁₀ NPs.

To find other Au NP structures, which could be more stable when supported on CeO₂ at oxygen vacancies under CO oxidation conditions, we modeled particles that are known to be stable when formed with capping-ligands in solution. This chemical synthesis process is the most promising method for the mass production of NPs.²³ Two sizes of ligand-covered small Au NPs can be found in the literature.^{24–26} Häkkinen and co-workers did calculations of a ligand-covered Au₁₁ NP of the size that was studied by Zhang et al. and reported the CO oxidation mechanism.²⁶ The Frenkel and Nuzzo groups reported that monodispersed ligand-capped icosahedral (Ih) Au₁₃ NPs are stable in solution.²⁵ They also successfully supported ligand-capped Au₁₃-Ih NPs on anatase-TiO₂.²⁴ It is this Au₁₃ cluster that we used to generate a stable supported Au nanoparticle. To do this, we initially optimized unsupported Au₁₃ NPs in vacuum conditions and then reoptimized the most stable isomers on a CeO₂ support. The Au₁₃ cluster was found to be stable upon CO or O₂ adsorption, so we used the Au₁₃@CeO₂-STO and Au₁₃@CeO₂-3VAC in our CO oxidation studies. To test the sensitivity of our results with respect to particle size and structure, the most important steps for CO oxidation were repeated on the Au₉ and Au₁₀ clusters and were shown to be consistent with that acquired from Au₁₃.

Computational Details. Initial structures of Au₁₃ NPs were generated from molecular dynamic simulations at 300 K using the quantum Sutton–Chen many-body potential.²⁷ More than 10 three-dimensional initial structures, as well as previously reported planar and cage structures,²⁸ were optimized at the GGA-level with spin-polarized DFT. For structure optimization, we used an all-electron scalar

relativistic basis set²⁹ as implemented in the DMol³ code.³⁰ The exchange-correlation energy was evaluated with the PBE functional,³¹ and the orbital cutoff range was 5.0 Å. We used a Fermi smearing method with a width of 0.007 hartree. The energy, force, and displacement convergence criteria were set to 10⁻⁵ hartree, 0.002 hartree/Å, and 0.005 Å, respectively.

The CeO₂ support was described with a 4 × 4 CeO₂(111) slab with 6 atomic layers and 20 Å of vacuum (Figure 1). The three upper layers

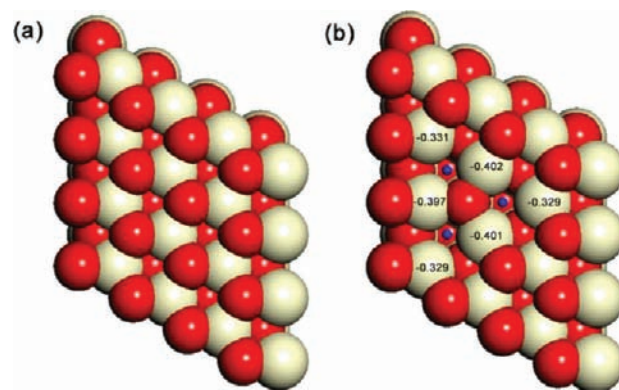


Figure 1. A 4 × 4 CeO₂(111) slab was used to model (a) stoichiometric CeO₂ and (b) partially reduced CeO₂ with three vacancies. A change in Bader charge due to the presence of the vacancies (shown in adjacent Ce ions) confirms that Ce ions are partially reduced from Ce⁴⁺ to Ce³⁺. Blue small spheres show the vacancy sites; ivory and red spheres represent Ce and O atoms.

of the CeO₂ slab were relaxed during geometry optimization. Experiments on vacancy formation in the CeO₂ surface showed that a linear oxygen trivacancy is preferred to a triangular vacancy,¹⁶ whereas DFT calculations predict a triangular structure as the most stable (in our calculation, a triangular trivacancy is more stable by as much as 0.16 eV). Esch et al. reported that diffusion of single oxygen vacancies in the CeO₂ surface and their polymerization requires thermal energy.¹⁶ The morphology and distribution of single and poly oxygen vacancies in the CeO₂ surface and their effect on electron localization are highly complicated.^{32–34} In this study, we are focusing on the effect of the presence of oxygen vacancy and reduced Ce³⁺ ions on CO oxidation by CeO₂-supported Au NPs. Thus, we chose the DFT-predicted triangular trivacancy to maximize the interaction between the vacancies, the partially reduced Ce³⁺ ions, and the supported Au₁₃ NP. While the morphology and the concentration of oxygen vacancies could affect CO oxidation by Au on CeO₂, this consideration is outside the scope of our current work.

We performed spin-polarized DFT calculations in a plane-wave basis with the VASP code³⁵ using the PBE³¹ functional. To treat highly localized Ce 4f-orbital, DFT+U³⁶ with $U_{\text{eff}} = 5$ was applied. The plane wave energy cutoff was 400 eV, and ionic cores were described by the PAW method implemented in VASP.³⁷ The Brillouin zone was sampled at the Γ -point. The convergence criteria for the electronic structure and the geometry were 10⁻⁴ eV and 0.01 eV/Å, respectively. We used the Gaussian smearing method with a finite temperature width of 0.1 eV to improve convergence of states near the Fermi level. The location and energy of transition states (TSs) were calculated with the climbing-image nudged elastic band method.³⁸

RESULTS AND DISCUSSION

Structural Optimization of Au₁₃@CeO₂-STO and Au₁₃@CeO₂-3VAC. Strong relativistic effects in Au lead to its unique electronic structure, which includes a contracted 6s shell and a significant s–d hybridization.^{39–41} The relativistic effects stabilize a planar structure in small Au clusters.^{28,39} The relativistic effect is prominent even in larger Au NPs consisting of more than 60 atoms.⁴² Nørskov and co-workers have

reported that the structure of TiO₂-supported Au NPs is quite flexible during CO oxidation.⁶ Structural evolution of Au NPs is observed in various size ranges.^{42–44}

When the structure of a Au NP evolves upon adsorption, it is difficult to separate the intrinsic affinity of the adsorbate to the Au NP from the additional contribution caused by the structural change. We therefore minimize the structural evolution of Au NPs during the reaction by using highly stable Au₁₃ NP on CeO₂.

To find a sufficiently stable structure of supported Au₁₃, we optimized Au₁₃ NPs in the gas phase and then again on the CeO₂ surface. Figure 2 shows the planar geometry of Au₁₃ that

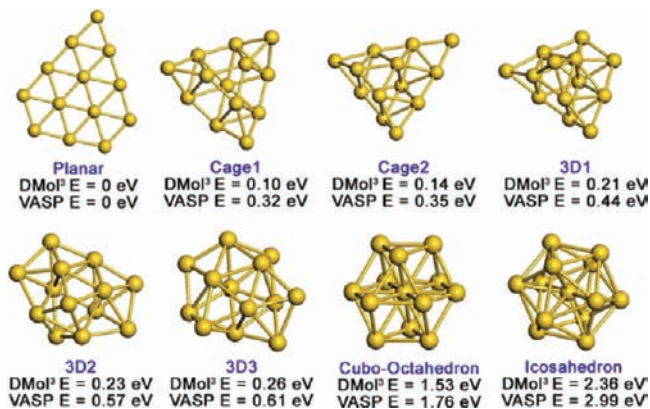


Figure 2. Eight stable structures of the Au₁₃ NP. Cohesive energies are relative to the most stable planar structure calculated with two different DFT codes. All-electron-based DMol³ calculations generally predict a narrower energy gap between isomers as compared to the pseudopotential-based VASP calculations.

is the most stable structure in the gas phase. Regardless of the structure, all Au₁₃ isomers took a doublet spin state ($S = 1/2$). Because the energy differences between isomers were found to be small, we supported each isomer on both the stoichiometric CeO₂-STO and partially reduced CeO₂-3VAC surfaces.

Ce⁴⁺ ions in CeO₂ have an empty 4f-orbital that will partially fill as Ce⁴⁺ ions are reduced to Ce³⁺ (see Figure 1b).⁴⁵ Figure 3

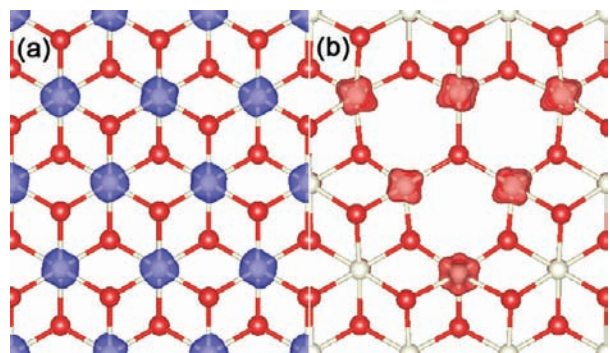


Figure 3. The geometry of the frontier orbital in CeO₂ surface is shown: (a) an empty 4f orbital is the LUMO and localized to Ce⁴⁺ ions of CeO₂-STO, and (b) a partially filled 4f orbital is the HOMO and localized to Ce³⁺ ions of CeO₂-3VAC.

shows the LUMO of CeO₂-STO and HOMO of CeO₂-3VAC. The LUMO of CeO₂-STO is a 4f-orbital localized on the Ce⁴⁺ ions, and the three oxygen vacancies reduce the six nearest Ce⁴⁺ ions to Ce³⁺ with a ferromagnetic spin ordering,

such that $s = 6/2$. The energy difference between the ferromagnetic and antiferromagnetic, $s = 0$, spin states is less than 0.05 eV, which is in agreement with a previous report.³⁴

Ganduglia-Pirovano et al.³⁴ and Li et al.³³ independently found that reducing the nearest neighbor Ce⁴⁺ ions of a single oxygen vacancy is not energetically favorable. The vacancy prefers to be bound to Ce⁴⁺ ions; therefore, two Ce³⁺ would be created away from the oxygen vacancy.³⁴ In our triangularly ordered trivacancy model, the six neighboring Ce⁴⁺ ions were reduced to Ce³⁺. The difference is that the previous studies evaluated the effect of only a single oxygen vacancy. Possible reasons for the observed stability of the well-ordered distribution of Ce³⁺ ions in our calculations include a lack of subsurface oxygen vacancies and polymerization of single oxygen vacancies.

Consistent with experimental observations,¹⁸ Au₁₃ preferentially binds to the oxygen vacancy, and the binding energy of Au₁₃ increases with the number of the oxygen vacancies (Table S1). Planar Au₁₃ is found to be unstable when supported on CeO₂-STO and CeO₂-3VAC (see Figure 4); a three-dimensional structure was favored in both cases.

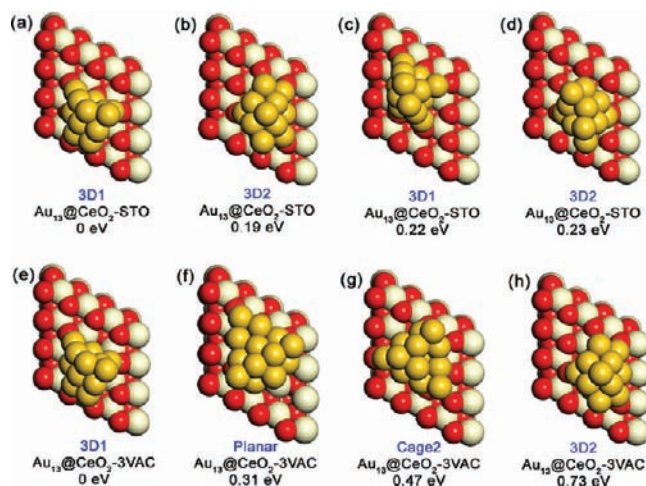


Figure 4. The four most stable geometries of Au₁₃ supported on CeO₂-STO (a–d) and CeO₂-3VAC (e–h). The blue name indicates the original structure of the gas-phase Au₁₃ NP (shown in Figure 2). Energy values are with respect to the most stable structure.

To compare CO oxidation by Au₁₃ supported on CeO₂-STO and CeO₂-3VAC, we used a single structure of the Au₁₃ cluster that was sufficiently stable on both supports. As presented in Figure 4, the (a,e) and (b,h) pairs satisfy this requirement. Even though the (a,e) pair (hereafter, A) is the most stable structure energetically, we instead decided to use the second-most stable structure, the (b,h) pair (hereafter, B), for the following reason.

The exceptional stability of the structures in A (also refer to xyz coordinates in the Supporting Information) is likely due to the Au(111) microfacet composed of 8 atoms on the side of Au₁₃. This is natural because they were generated from the cage 1 structure shown in Figure 2, which has a banded Au(111) microfacet. As a result, Au atoms that do not belong to the microfacet have more distorted and loosely packed structure when supported, and therefore the average coordination number (CN) of the second and third layer Au atoms of A is low, 5.43. This is lower than the average CN of B, 5.71. Moreover, Figure 4 also shows that the lowest-coordinated top

Au atom of A has only three neighboring Au atoms. Such low atomic coordination is an unrealistic model for larger Au NPs; it is rather a special case of small NPs. In the case of B, there is no asymmetric distortion, which can influence the O oxidation calculation. We have therefore selected the B model for further catalysis studies even though the B was less stable than the A. We found that the B model structure remained stable during CO oxidation.

Electronic Interaction between CeO₂ and Au NP. A Bader charge^{46,47} and frontier orbital analysis of the electron interaction between Au₁₃ and CeO₂-STO and CeO₂-3VAC shows that the empty 4f-orbital localized on Ce⁴⁺ ions of CeO₂-STO, the LUMO of CeO₂-STO, draws electrons from supported Au₁₃. Similarly, Au₁₃ attracts electrons from the HOMO of CeO₂-3VAC, the 4f-orbital of Ce³⁺ ions (Figures 3, 5, and 6). One of

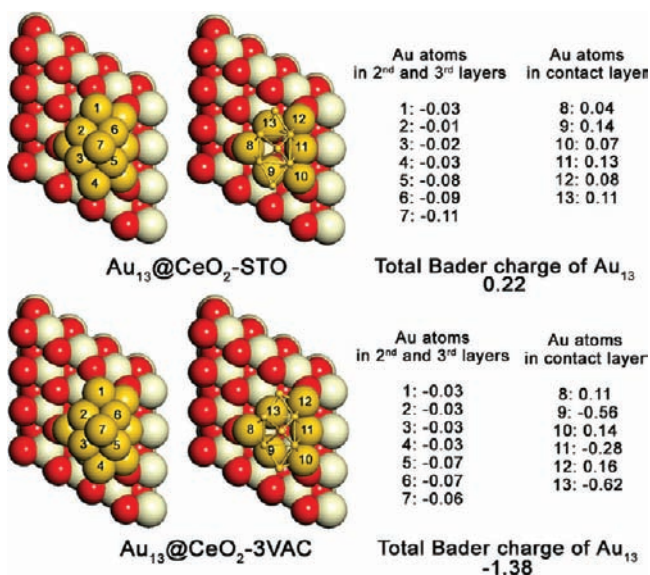


Figure 5. The HOMO of a CeO₂-supported Au₁₃ NP is shown. The HOMO of Au₁₃@CeO₂-STO is plotted in (a)–(c). The HOMO of Au₁₃@CeO₂-3VAC is plotted in (d)–(f). To show electrons localized in the 4f orbital of Ce atoms, the Au₁₃ NP was cut in (c) and (f). An empty 4f orbital of CeO₂-STO draws electrons from supported Au₁₃ NP and becomes the HOMO, whereas the Au₁₃ NP attracts electrons from some of the partially filled Ce³⁺ ions of CeO₂-3VAC.

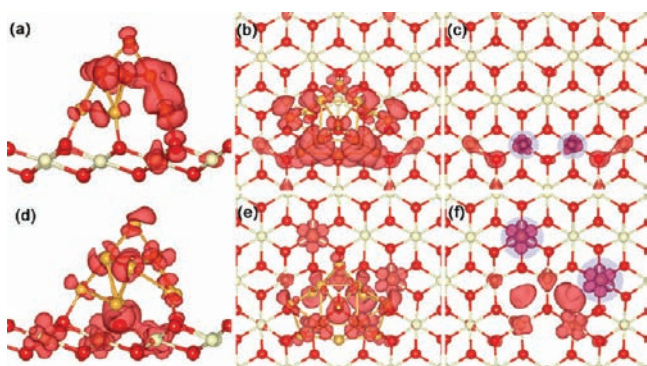


Figure 6. Bader charge analysis on Au₁₃@CeO₂-STO and Au₁₃@CeO₂-3VAC is shown. Electronic interaction between Au₁₃ NP and CeO₂ is localized to contacting layer Au atoms.

the Ce³⁺ ions in Au₁₃@CeO₂-3VAC is, thus, the second nearest neighbor from the oxygen vacancy, as predicted by Li et al.³³ and

Ganduglia-Pirovano et al.³⁴ (see Figure 5f). Electron transfer between Au₁₃ and CeO₂-STO positively charges Au₁₃, whereas electron transfer between Au₁₃ and CeO₂-3VAC negatively charges Au₁₃. We find that the relative stability of isolated Au₁₃ isomers is sensitive to their charge state (Table S2), so the destabilization of a planar Au₁₃ on the CeO₂ surface could be related to electron transfer. Charge transfer would change the valence electron configuration of Au and affect the strength of highly directional s–d hybridization. We postulate that a broken balance of s–d hybridization due to electron transfer from or to the Au₁₃ supplies a driving force for structural evolution. Our results show that the structure of oxide-supported small Au NPs would be quite different from the stable structure of isolated Au NPs. This distinction is important, because small crystalline Au NPs, such as Au₁₂² and Au₁₃ cuboctahedron,²¹ have been used so far as a representative of supported small Au NPs for computational studies.

Bader charge analysis^{46,47} shows that, although the total charge state of Au₁₃ on CeO₂-STO and CeO₂-3VAC is quite different (Figure 5), the electronic interaction is localized in the layer of Au atoms that are in direct contact the substrate. Au atoms in noncontacting layers, the second and third layers in the Au cluster, are less affected by the electronic interaction. The energy of adsorption of CO and O₂ is highly sensitive to the electronic state of the adsorption site.^{21,48–50} We find, however, that CO and O₂ prefer to bind to the under-coordinated Au atoms in noncontacting layers as opposed to negatively or positively charged Au ions.

CO Oxidation by Coadsorbed CO and O₂ on Au₁₃ of Au₁₃@CeO₂. CO and O₂ adsorption were tested on Au₁₃@CeO₂-STO and Au₁₃@CeO₂-3VAC (see Figure S2 for details). The most favorable CO–O₂ coadsorption geometry with the highest coadsorption energy was selected for further CO oxidation studies. Complete CO oxidation by coadsorbed CO and O₂ on Au in Au₁₃@CeO₂-STO is shown in Figure 7a. The energies of adsorption show that Au₁₃ strongly binds CO (–1.05 eV) but binds O₂ relatively weakly (–0.56 eV). Coadsorbed CO and O₂ can react to form a gas-phase CO₂ and a residual Au–O* on Au₁₃ in a –1.64 eV exothermic process with a 0.14 eV activation barrier. We found that the residual Au–O* can directly react with an additional gas-phase CO molecule. Another possible CO oxidation pathway following the formation of Au–O* is the association of Au–O* and Au–CO* to produce CO₂, as shown in Figure S3a. Both CO oxidation pathways from the Au–O* intermediate proceed spontaneously, so the life-span of the Au–O* should be very short.

Figure 7b shows that the presence of oxygen vacancies on the surface of CeO₂ does not affect the mechanism of CO oxidation. Oxygen vacancies strengthen O₂ binding to Au₁₃@CeO₂-3VAC from –0.56 to –0.76 eV. The formation of a gas-phase CO₂ from coadsorbed Au–CO* and Au–O₂*, with a 0.33 eV activation barrier, is the rate-determining step of the reaction.

A microkinetic analysis on the CO oxidation by CeO₂-supported Au₁₃ NPs shows that CO binds more strongly to Au₁₃@CeO₂-STO than does O₂ leading to a low O₂ coverage (see Table 1). The stronger O₂ binding to Au₁₃@CeO₂-3VAC leads to a 10 times higher adsorbed O₂ concentration. However, Table 1 shows that the higher energy barrier for CO oxidation in Au₁₃@CeO₂-3VAC, due to the increased stability of the adsorbed state (stage 1 in Figure 7b), lowers the CO oxidation rate.

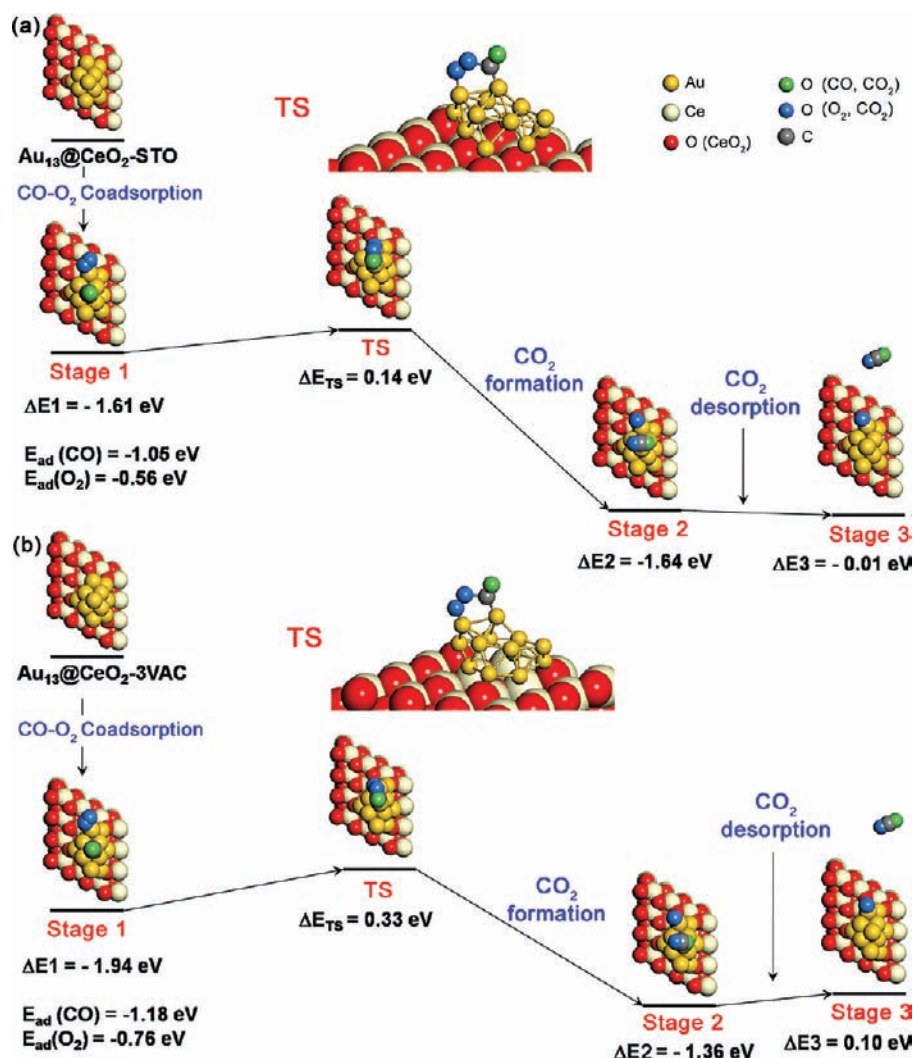


Figure 7. CO oxidation by Au₁₃ of CeO₂-supported Au₁₃ NPs is shown with Au₁₃@CeO₂-STO in (a) and Au₁₃@CeO₂-3VAC in (b). ΔE_x is the energy of the xth stage relative to that of the previous stage; for example, ΔE₃ is the energy difference between stage 3 and stage 2. ΔE_{TS} is the energy of the TS relative to the previous state.

Table 1. Microkinetic Analysis on CO Oxidation by CO and O₂ Coadsorbed on Au₁₃@CeO₂-STO and Au₁₃@CeO₂-3VAC^a

	energy of CO adsorption (eV)	energy of O ₂ adsorption (eV)	barrier (eV)	rate(R3) ^{max} (S ⁻¹)	θ _{O₂}
Au ₁₃ @CeO ₂ -STO	-1.05	-0.56	0.14	7.01 × 10 ⁵	2.63 × 10 ⁻⁷
Au ₁₃ @CeO ₂ -3VAC	-1.18	-0.76	0.33	6.55 × 10 ¹	4.02 × 10 ⁻⁶

^aThe maximum reaction rate on Au₁₃@CeO₂-3VAC can be acquired by increasing the energy of O₂ adsorption from -0.76 to -1.08 eV (4.07 × 10⁶ S⁻¹, θ_{O₂} = 0.51) with fixed CO adsorption energy (-1.18 eV) or decreasing the energy of CO adsorption from -1.18 to -0.86 eV (4.02 × 10⁶ S⁻¹, θ_{O₂} = 0.51). The maximum rate was acquired when the ratio of the energy of O₂ and CO adsorption is approximately 0.9.

Experimental and theoretical studies on CO oxidation by oxide-supported Au NPs report a wide range of barriers for CO oxidation, depending on the cluster size and the supporting oxide.^{51–56} Our calculated barrier for CO oxidation by Au₁₃@CeO₂ is at the lower limit of reported values. Campbell and co-workers reported an experimental barrier of 0.12 ± 0.02 eV for CO oxidation by two-layer Au islands on TiO₂, which is comparable to our case of Au₁₃@CeO₂-STO.⁵² Theoretical studies on CO oxidation by TiO₂- or MgO-supported small Au NPs reported a barrier between 0.1 and 0.5 eV.^{55,56}

The balance of the CO and O₂ adsorption energies, as well as the reaction barrier, accounts for the CO oxidation rate by coadsorbed CO and O₂. Increasing the energy of O₂ adsorption

on Au₁₃@CeO₂-3VAC from -0.76 to -1.08 eV leads to the 1000 times higher CO oxidation rate (4.07 × 10⁶ S⁻¹). The maximum reaction rate of CO oxidation was acquired when the ratio of the energy of O₂ adsorption and CO adsorption (O₂/CO) is 0.90. Because strong adsorption leads to increased energy barriers, lowering the energy of CO adsorption rather than increasing the O₂ adsorption energy is more effective for increasing the CO oxidation rate. Strong CO adsorption on Pt NPs blocks active sites or destabilizes other adsorbates, leading to CO poisoning.⁵⁷ We found that this is the case for small Au NPs as well. As presented by Nilekar et al. in transition metal-Pt shell NPs,⁵⁷ modifying Au NPs with alloying elements would be a promising way for the lower CO adsorption energy and

the lower and higher saturated CO and O₂ concentration, respectively.

The presence of oxygen vacancies and Ce³⁺ ions in the CeO₂ surface does not significantly influence the intrinsic CO oxidation activity of CeO₂-supported Au₁₃. CO oxidation at under-coordinated Au atoms confirms that this process is independent from effects due to the metal–oxide interface and charged Au ions.

Freund and co-workers showed that a corner atom of MgO-supported Au NP reduces its charge state from -0.21 e to $+0.16$ e upon CO adsorption due to Pauli repulsion with the CO-5 σ orbital,⁴⁸ which is consistent with our findings. We found that the Au atom binding CO was positively charged upon CO adsorption ($+0.17$ e and $+0.15$ e in Au₁₃@CeO₂-STO and Au₁₃@CeO₂-3VAC, respectively). A Bader charge analysis,^{46,47} presented in Figure S4, shows that electrons from the Au atom binding CO were redistributed over all of the Au atoms in Au₁₃@CeO₂-3VAC, whereas on Au₁₃@CeO₂-STO the electrons (0.29 e) were largely transferred to the empty 4f-band of Ce atoms, leading to more positively charged Au₁₃ (see Figure S4a). The same amount of charge was transferred to the adsorbed O₂ molecule in both Au₁₃@CeO₂-STO and Au₁₃@CeO₂-3VAC, mostly from the nearest Au atom. Because both CeO₂ supports equally activate the O₂ molecule, and because

the O₂ adsorption is quite localized, we postulate that the increased energy of O₂ adsorption on Au₁₃@CeO₂-3VAC does not originate from the excess electrons in Au atoms of Au₁₃@CeO₂-3VAC. Rather, destabilization of electrophilic Au NP due to charge loss to Ce atoms upon CO–O₂ coadsorption is presumably responsible for the lower coadsorption energy of Au₁₃@CeO₂-STO. Note that the Au NP in Au₁₃@CeO₂-STO lost 0.77 e to O₂ and CeO₂, whereas the Au NP in Au₁₃@CeO₂-3VAC donated 0.37 e, mostly to O₂. Table S3 shows that Au₁₃-3D2 used in this study becomes highly unstable when the NP is positively charged.

Evaluating the reactive regions of Au NPs and their charge state has been a central issue for rational catalyst design. Both positively charged^{13,58} and negatively charged Au ions^{59,60} have been suggested as a reactive center. Other studies instead suggest oxygen vacancies,^{61,62} a metal–oxide interface,^{63,64} or metallic corner atoms⁶⁵ as reactive species. The complete CO oxidation pathway and rate presented in Figure 7 and Table 1 show that charged Au ions play no direct role in CO oxidation, because CO and O₂ preferentially bind to noncontacting Au atoms with low-coordination numbers.

The rate of CO oxidation by coadsorbed CO and O₂ at under-coordinated Au atoms would depend on the surface fraction of the under-coordinated Au atoms. Even though Au₁₃

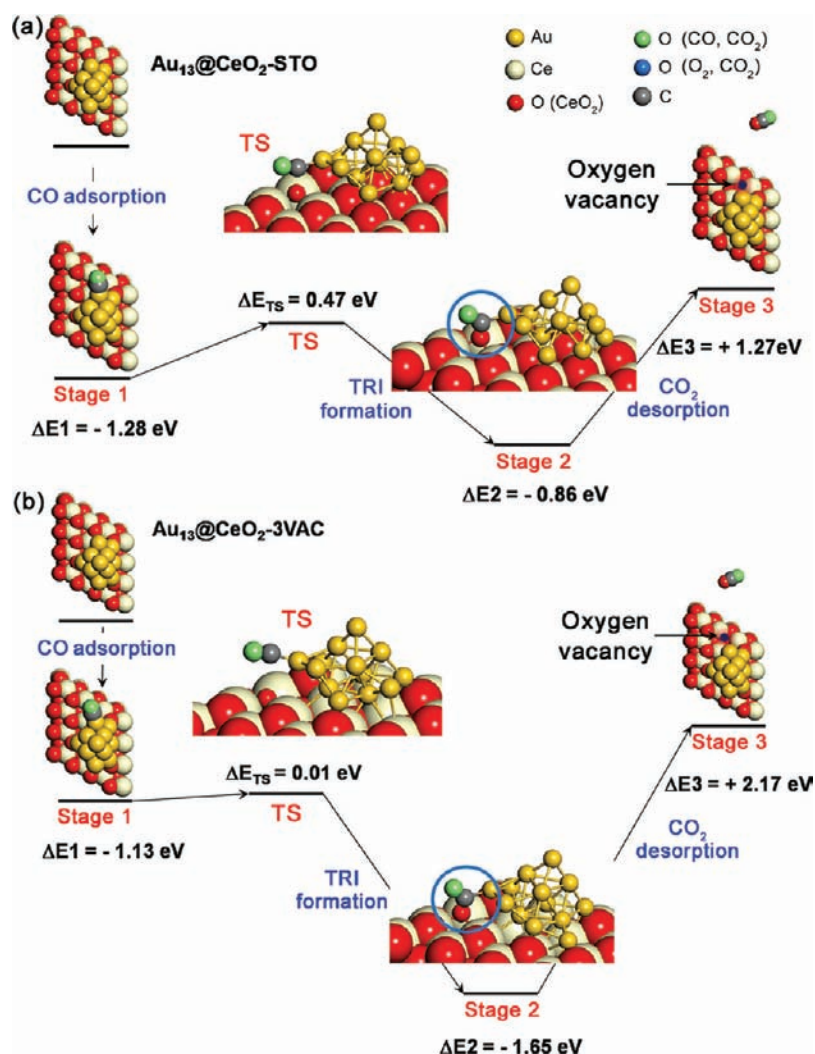


Figure 8. The first half of CO oxidation by M-vK mechanism, oxidation of CO on Au₁₃ by a lattice oxygen atom of CeO₂ support, is shown. Au₁₃@CeO₂-STO is plotted in (a) and Au₁₃@CeO₂-3VAC in (b).

catalyzes CO oxidation by itself, the contribution of this direct CO oxidation by Au NP may decrease as the size of Au NP increases. The role of linear corner atoms rather than individual under-coordinated Au atoms would become important in larger Au NPs, as was recently shown by Shang and Liu.⁶⁶

An increase in the O₂ adsorption energy due to the presence of oxygen vacancies in the surface was also seen for the Au₉@CeO₂-3VAC model (details are described in Figure S1).

CO Oxidation by Lattice Oxygen of CeO₂ and CO on Au₁₃: Mars–van Krevelen Mechanism. Camellone and Fabris reported that a lattice oxygen of CeO₂ oxidizes CO when bound to a Au adatom.¹³ CO oxidation by the Mars–van Krevelen (M–vK) mechanism, in which the oxide directly binds CO, is commonly observed in several modified oxide catalysts, as well.^{20,67} We examined CO oxidation at the Au–CeO₂ interface and found that, contrary to the typical M–vK mechanism, the Au NP binds CO during oxidation.

Figure 8 shows the first half of the CO oxidation process by the M–vK mechanism. Au₁₃ strongly binds a CO molecule by -1.28 eV in Au₁₃@CeO₂-STO and -1.13 eV in Au₁₃@CeO₂-

3VAC. We find that Au–CO* and an adjacent lattice oxygen atom in the CeO₂ support associate to form a triangular reaction intermediate (TRI). Formation of a TRI is highly exothermic with a 0.47 eV energy barrier in Au₁₃@CeO₂-STO and a 0.01 eV energy barrier in Au₁₃@CeO₂-3VAC. Subsequent CO₂ desorption, however, requires 1.27 eV for Au₁₃@CeO₂-STO and 2.17 eV for Au₁₃@CeO₂-3VAC.

This pathway is equivalent to removing a single oxygen atom from CeO₂ and oxidizing a gas-phase CO molecule to CO₂. We find that, because of the high stability of TRI, it is difficult to compensate for the vacancy formation energy with the CO₂ formation energy, and, thus, this leads to a high CO₂ desorption energy. In a low temperature regime, it is probable that the TRI acts as a spectator rather than a reaction intermediate. Entropic contribution to the Gibbs free energy of CO₂ desorption (TS) is -0.66 eV at 298 K (standard entropy of CO₂ is 213.79 J mol⁻¹ K⁻¹ at 1 atm).⁶⁸ Therefore, spontaneous CO₂ desorption would be a rare event at room temperature (or below) and prevent direct participation of lattice oxygen of CeO₂ in CO oxidation. Camellone and Fabris,

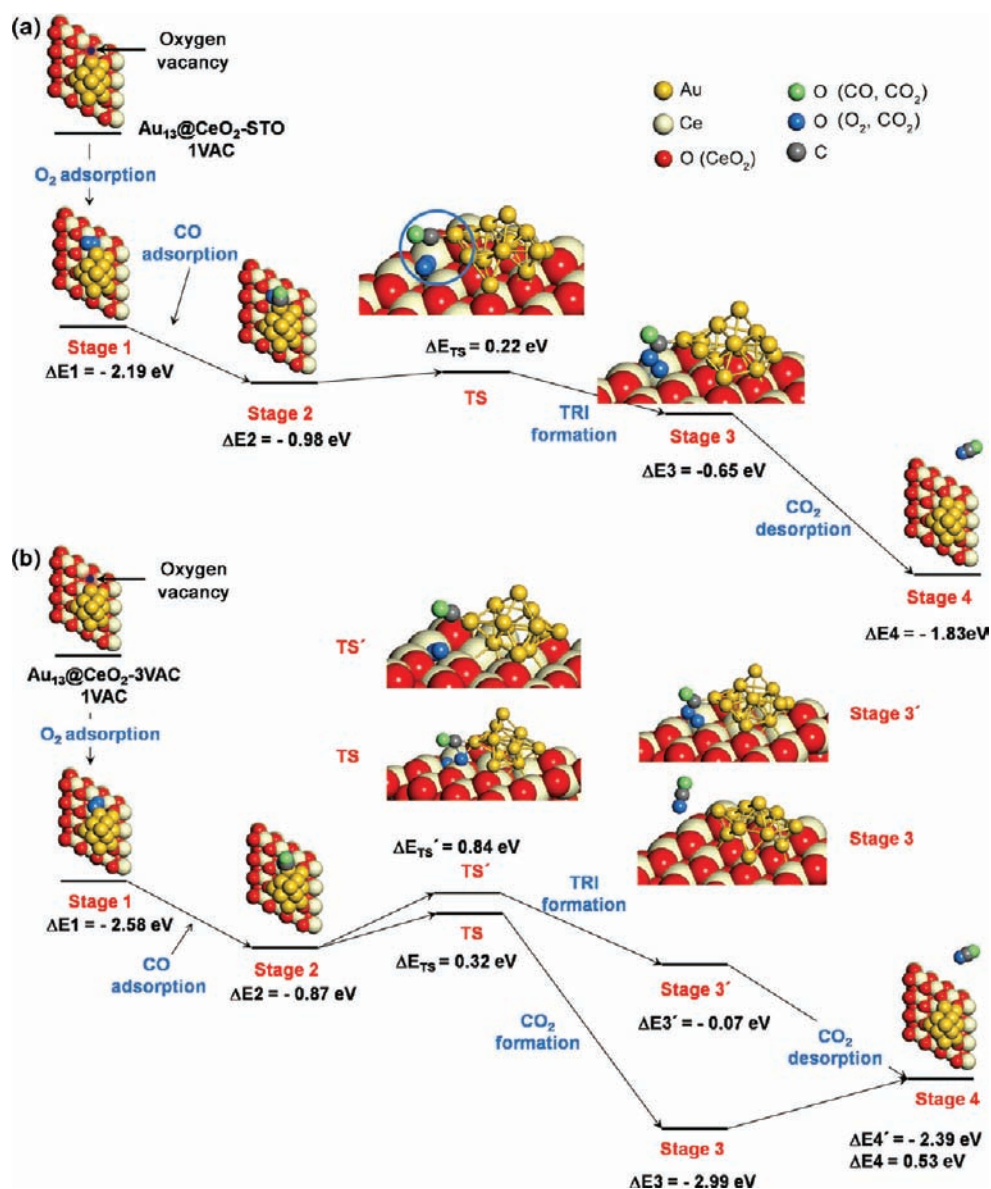


Figure 9. The second half of CO oxidation by the M–vK mechanism is shown for (a) Au₁₃@CeO₂-STO and (b) Au₁₃@CeO₂-3VAC.

in contrast, considered a single, mobile Au adatom, which could bind with an oxygen vacancy and stabilize the system.¹³

Metiu and co-workers have suggested that dopants can lower the vacancy formation energy of the host oxide and, thus, promote the oxidation reaction by the M-vK mechanism.^{20,67,69,70} The vacancy formation energy of Au-doped CeO₂ is negative, which means an oxygen vacancy can form spontaneously in the presence of a Au dopant.^{20,69} The rate-determining step in the reaction, CO₂ desorption from TRI (see Figure 8), is directly related to the vacancy formation in the CeO₂ surface. The enthalpy of CO oxidation is a constant -3.26 eV, so the energy of vacancy formation is the only factor that determines the total reaction energy. From a catalysis design perspective, this relationship indicates that lowering the vacancy formation energy of CeO₂ will lower the CO₂ desorption energy from TRI. Using a doped CeO₂ as a supporting oxide for Au NPs would activate CO oxidation by opening this additional low-temperature reaction pathway.

Figure 9 shows the second half of the CO oxidation process. As a part of the M-vK mechanism of CO oxidation, a surface oxygen vacancy on CeO₂ strongly binds a gas-phase O₂ molecule (V–O₂^{*}) and results in vacancy healing (see stage 1 of Figure 9a and b). The energy of O₂ adsorption is stronger by 0.39 eV in the reduced surface due to the difference in vacancy formation energy on CeO₂-STO and CeO₂-3VAC. This trend is consistent with O₂ adsorption on modified oxides reported by Metiu and co-workers; the oxygen vacancy of easily reducible oxides weakly binds an O₂ molecule.⁶⁷

In the case of Au₁₃@CeO₂-STO, Au–CO^{*} and V–O₂^{*} associate into the TRI with an enthalpy of -0.65 eV and a 0.22 eV energy barrier. CO₂ dissociation from TRI is exothermic by -1.83 eV, so CO₂ is produced spontaneously, and the surface oxygen vacancy is healed. On the other hand, a formation energy of -0.07 eV and a correspondingly high energy barrier of 0.84 eV show that the formation of TRI is a rare event in Au₁₃@CeO₂-3VAC. Rather, Au–CO^{*} and a protruding

O atom of V–O₂^{*} can be directly associated to a gas-phase CO₂ with a lowered energy barrier, 0.32 eV. In this case, CO₂ formation is highly exothermic by -2.99 eV. An energy of 0.53 eV is needed to completely desorb CO₂ from the surface.

When the oxygen vacancy is healed by gas-phase O₂, the Au₁₃@CeO₂-STO releases the excess surface oxygen to form TRI exothermically with an enthalpy of -0.65 eV. In contrast, Au₁₃@CeO₂-3VAC, which is oxygenphilic, has a low TRI formation energy of -0.07 eV. Direct CO₂ formation from V–O₂^{*} and Au–CO^{*} is instead more favorable. The different oxygen affinities of the CeO₂ support significantly alter the available reaction pathways of CO oxidation such that TRI forms in Au₁₃@CeO₂-STO and CO₂ forms directly in Au₁₃@CeO₂-3VAC.

Note that the second cycle of the M-vK mechanism proceeds in the presence of an additional oxygen vacancy, suggesting that the vacancy formation energy affects the CO oxidation reactivity of CeO₂-supported Au NPs. Oxygen vacancies bind gas-phase O₂ molecules and subsequently oxidize Au–CO^{*}.

Au–Ce³⁺ Interface as an Anchoring Site of O₂. Rodriguez et al. recently investigated the role of the Au–CeO₂ interface in the water–gas shift reaction by showing high activity of the inverse catalyst, Au-supported CeO₂ NPs,⁷¹ and suggested a critical role of Ce³⁺ ions.^{64,72} The Au–CeO₂ interface does not accelerate CO oxidation by the M-vK mechanism, so we investigated the Au–CeO₂ interface as an additional binding site of reacting molecules. We find that an oxygen molecule would bind to the Au–Ce³⁺ interface due to the excess electron on the Ce³⁺ and note that O₂ adsorption is dependent on the oxidation state of Ce. Other Au–Ce⁴⁺ bridge sites of Au₁₃@CeO₂-3VAC and Ce⁴⁺ ions of Au₁₃@CeO₂-STO were not able to bind an O₂ molecule as strongly. Therefore, we conclude that the oxygen vacancy, where the Au NP anchors, reduces adjacent Ce⁴⁺ to Ce³⁺ and provides an additional CO oxidation pathway in which CO reacts with O₂ at a Au–Ce³⁺ interface.

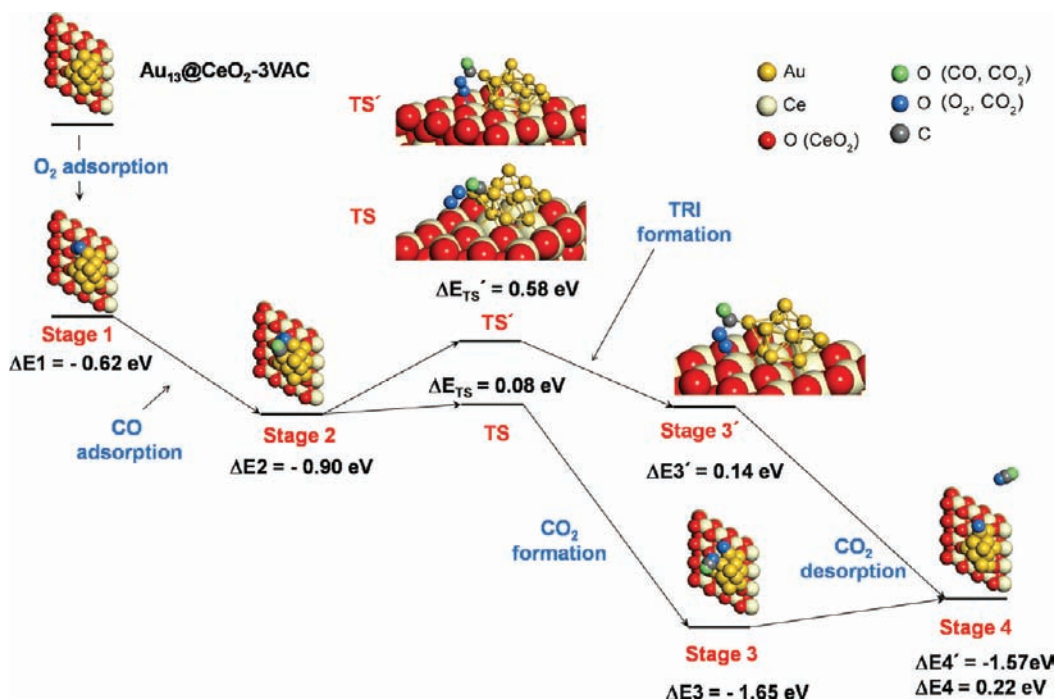


Figure 10. CO oxidation by O₂ adsorbed to Au–Ce³⁺ bridge site is shown. Direct CO₂ production is preferred to CO oxidation through TRI formation.

Figure 10 shows the complete CO oxidation mechanism with O₂ adsorbed on the Au–Ce³⁺ interface and CO on Au₁₃. CO on Au₁₃ and O₂ at an Au–Ce³⁺ interface directly dissociated into CO₂ and Au–O*. Direct CO₂ dissociation is highly exothermic by –1.65 eV with a low energy barrier of 0.08 eV. Another possible pathway can proceed through TRI formation from Au–CO* and O₂ at a Au–Ce³⁺; this pathway is slightly endothermic by 0.14 eV, and the dissociation to CO₂ and Au–O* is highly exothermic by –1.57 eV. An energy barrier of 0.58 eV is required for TRI formation, so CO oxidation through TRI formation would be less favorable than direct CO₂ dissociation. The rest of the reaction proceeds as described in Figure S3(b). Because only 0.22 eV is needed to activate CO oxidation by the Au–Ce³⁺ interface, this process is operational at low temperature. There is a physical bond between the product CO₂ and the Au NP (see stage 3 of Figure 10). Considering the entropic contribution to CO₂ desorption (discussed earlier), we postulate that this process is spontaneous and does not lower the CO₂ production rate. The enthalpy of this step is almost equal to the energy required to activate CO oxidation by under-coordinated Au atoms; however, this pathway's contribution will become more critical as the size of Au NPs increases and thus widens the Au–CeO₂ interface.

Because the Au–Ce³⁺ interface binds an O₂ molecule, CO would readily adsorb on Au₁₃ without competition for the same adsorption site. This process operates only in the presence of reduced Ce³⁺ ions, which are a direct consequence of pre-existing oxygen vacancies. The role of the interface between supported Au NPs and the CeO₂ support is to supply an additional reaction pathway by O₂ adsorbed to Au–Ce³⁺ bridge site and separate O₂ and CO adsorption sites. Oxygen vacancies that reduce adjacent Ce⁴⁺ of CeO₂ to Ce³⁺ ions are essential in activating CO oxidation by the Au–Ce³⁺ interface.

Recently, Green et al. reported the CO oxidation mechanism by the O₂ bound to the Au–Ti bridging site, which is consistent with our finding.⁷³

Nanosize Effect of the CeO₂ Support. We used the CeO₂(111) surface throughout this study; however, as the dimension of CeO₂ support decreases from surface to nanoparticle, the concentration of the Ce³⁺ ions increases due to dangling bonds. It has been shown that the Ce³⁺/Ce⁴⁺ ratio is higher in small CeO₂ clusters^{74,75} and Ce³⁺ ions preferentially occupy under-coordinated sites, edge or corner sites.⁷⁶ High concentration of Ce³⁺ ions in stepped CeO₂ surface was also reported.⁷⁷

Vayssilov et al. recently showed that oxygen transfer from the CeO₂ support to Pt NPs, termed oxygen spillover, occurs due to the low vacancy formation energy of nanostructured CeO₂.⁷⁸ The oxygen spillover was not observed in our case because of high vacancy formation energy of the CeO₂ surface; it has never been reported with Au NPs. Their findings, however, confirm that the size of CeO₂ support has a critical role in catalytic activity of supported NPs.

Carrettin et al. showed that the activity of CO oxidation catalyzed by Au on CeO_{2-x} NPs of ~4 nm diameter is 2 orders of magnitude larger than that of Au on bulk CeO₂.⁷⁹ A low vacancy formation energy of CeO_{2-x} NPs^{78,80} would accelerate CO oxidation by the M–vK mechanism combined with adsorbed O₂ at the Au–Ce³⁺ anchoring site.

CONCLUSION

Herein, we investigate the origin of CO oxidation activity of CeO₂-supported Au NPs by investigating various CO oxidation pathways. On the basis of DFT+U calculations, we suggest the

following CO oxidation pathways by CeO₂-supported Au NPs: CO oxidation by coadsorbed CO and O₂ at Au₁₃ NPs, CO oxidation by lattice oxygen of CeO₂ and Au–CO*, and CO oxidation by O₂ adsorbed to the Au–Ce³⁺ interface.

The underlying properties of the Au NPs, such as under-coordinated Au atoms, create a CO oxidation pathway by coadsorbed CO and O₂. Pre-existing oxygen vacancies in the CeO₂ surface did not alter the reaction pathway for catalysis on the Au NP. Contrary to previous studies, we found that positively or negatively charged Au ions have no direct effect on the pathway and rate of CO oxidation. Oxygen vacancies in the CeO₂ surface strengthen O₂ binding to Au NP and increase the O₂ surface concentration. The high energy barrier, however, due to a stabilized reactant state compensates for the influence of the increased O₂ adsorption energy on CO oxidation activity.

The second process, the M–vK mechanism of CO oxidation by the Au–CeO₂ interface, requires a higher energy and is only active at high temperature. If the vacancy concentration in the CeO₂ surface is high, however, pre-existing vacancies can bind the O₂ molecule and oxidize a Au–CO* by the second half of the M–vK mechanism.

Oxygen vacancies in CeO₂ create Ce³⁺ ions and open a new CO oxidation pathway by O₂ adsorbed on Au–Ce³⁺ bridge site. The contribution of this third process would be higher in easily reducible oxides.

Our findings on the mechanism of CO oxidation catalyzed by Au NPs supported on stoichiometric and partially reduced CeO₂ confirm a critical role of oxygen vacancy in the CeO₂ surface on CO oxidation activity of CeO₂-supported Au NP, providing a theoretical guideline on the design of highly reactive catalysis in the supported NP class.

We suggest that lowering the vacancy formation energy of the supporting oxide using easily reducible oxides or modifying the oxides is promising for higher CO oxidation reactivity by three possible mechanisms: (1) activating the M–vK mechanism of CO oxidation by lowering the energy of CO₂ production, (2) increasing the number of oxygen vacancies in the CeO₂ surface that bind and supply O₂ for the second half of the M–vK mechanism, and (3) increasing the concentration of reduced metal ions, which act as anchoring sites for O₂ molecules.

ASSOCIATED CONTENT

Supporting Information

Details on microkinetic analysis and additional data presented in tables (S1–S3) and figures (S1–S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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