DFT study of CO oxidation on Cu$_2$O–Au interfaces at Au–Cu alloy surfaces

D. Liu,$^{ab}$ Y. F. Zhu$^a$b and Q. Jiang$^a$b

Although Au–Cu alloy nanoparticles on inert substrates show high activity for catalyzing CO oxidation, the corresponding catalytic mechanism is not clear. To clarify the mechanism of this alloy catalysis method, CO oxidation reactions on Au–Cu alloy surfaces with different surface oxidation states are studied via density functional theory simulations. The simulation results indicate that on AuCu$_{111}$ and Cu$_2$O/Au$_3$Cu$_{111}$, CO and O$_2$ cannot move together for reactions since they are adsorbed on separate Cu sites. On Cu$_2$O–Au/Au$_3$Cu$_{111}$, O$_2$ prefers to be located at the Cu hollow sites near Cu$_2$O–Au interfaces. When CO diffuses to its neighboring Au sites, they can easily combine to generate CO$_2$, for which the reaction barriers are no more than 0.42 eV. The Au and Cu synergetic effect for catalyzing CO oxidation can be realized on Cu$_2$O–Au interfaces at Au–Cu nanoparticle surfaces.

Introduction

Gold was regarded as an inert metal until Haruta et al. found that Au nanoparticles dispersed on oxide substrates, such as TiO$_2$ and Fe$_2$O$_3$, show high catalytic activity for low temperature CO oxidation. On bulk gold surfaces, O$_2$ adsorption is weak and corresponding oxygen dissociation barriers are higher than 1 eV, which makes further CO oxidation impossible. When CO and O$_2$ react on Au/TiO$_2$ catalysts, O$_2$ molecules are strongly adsorbed on the Au nanoparticle–TiO$_2$ substrate circumferential interfaces. Via this interfacial adsorption mode, activated O$_2$ molecules can easily react with the CO molecules adsorbed on neighboring Au sites. However, this synergetic effect is of little help in catalysis relies on the type of substrates. The catalytic activity for CO oxidation of the Au/SiO$_2$ catalyst is significantly reduced because inert SiO$_2$ substrates cannot offer the strong adsorption for O$_2$ molecules.

Alloying with a second metal is an effective way to obtain active Au-based binary nanoparticles on inert supports. Recently, Au, Cu and Au–Cu binary nanoparticles (dimensional sizes of 2–5 nm) on inert SBA-15 mesoporous silica substrates have been synthesized for catalyzing CO oxidation. Cu/SBA-15 is inactive below 100 °C and Au/SBA-15 only possesses moderate activity at room temperature. However, CO conversion remains at 100% from room temperature (RT) to 300 °C on Au–Cu/SBA-15. In addition, the turnover frequencies of CO oxidation on Au–Cu/SBA-15 are three times larger than those on Au/MCM-41 mesoporous silica. When a large amount of H$_2$ is introduced, the CO conversion rates on Au–Cu/SBA-15 reach 60–80% at RT. As the reaction temperature increases to 80 °C (operational temperature for H$_2$ fuel cells), the CO conversion rates are still 50–70%, whereas the corresponding values only are 20% and 0% for Au/SBA-15 and Cu/SBA-15.

Structural changes in Au–Cu nanoparticles (Au/Cu atomic ratio 1/1) during the catalytic process of CO oxidation are observed via in situ XRD measurements. The Au–Cu binary particles obtained by calcination have a gold core and a CuO shell. To obtain active Au–Cu particles, a subsequent reduction treatment is carried out in H$_2$ at 550 °C. After this reduction treatment, Cu cations are reduced to alloy with the interior Au atoms and the structure of particles reverts to the Au$_3$Cu intermetallic phase. When the reduced Au–Cu nanoparticles are used to catalyze CO oxidation in the temperature range of RT to 300 °C, their Au$_3$Cu structure hardly changes. In situ XANES results indicate that some Cu atoms are oxidized from Cu$^0$ to Cu$^{+}$ and Cu$^{2+}$, whereas Cu$_2$O and CuO structures are absent in XRD measurements.

These Cu cations may come from surface oxidation during the catalytic process. The reaction temperature for CO oxidation is much lower than that for nanoparticle calcination. At this moderate temperature range (RT to 300 °C), Au–Cu nanoparticles are not totally covered by Cu$_2$O oxide layers and there are still Au sites on their surfaces. Infrared spectroscopy measurements indicate that after O$_2$ introduction, CO adsorption on Au sites of Au–Cu nanoparticles is decreased dramatically, whereas CO adsorption on Cu sites of these particles remains unchanged. However, the presence of gold improves the oxidation resistance of copper. Extended X-ray absorption fine structure (EXAFS) measurements show that there are one and a half oxygen neighbors for each Cu cation on average on the surface of the Au–Cu nanoparticles, which proves that...
Cu$_2$O constitutes the majority of the surface oxides. Cu$_2$O is an incomplete oxide, on which O$_2$ can be adsorbed.

It has been reported that Cu$_2$O layers can grow epitaxially on the surface of Au–Cu particles with small lattice mismatch.\textsuperscript{11} In addition, Cu$_2$O–Au in-plane coherent interfaces can also be formed along the close-packed crystal directions.\textsuperscript{11,12} After the surface oxidation of Au–Cu nanoparticles, coherent linear interfaces are generated between the Cu$_2$O and Au surface layers. The CO oxidation reactions may just occur on these Cu$_2$O–Au interfaces.\textsuperscript{11,14}

In this work, CO + O$_2$ reactions on Cu$_2$O–Au interfaces at surfaces of the Au$_3$Cu alloy are simulated by the density functional theory (DFT) method. In addition, the bond length, charge transfer (CT) and partial density of states (PDOS) of some adsorption and reaction states during the catalytic process are also analyzed for understanding the essence of these chemical reactions. For comparison, the adsorption status and further possible reaction of CO + O$_2$ on AuCu and Cu$_2$O/Au$_3$Cu alloy surfaces are investigated to explain why unoxidized and totally oxidized Au–Cu nanoparticles are inert for CO oxidation.

Simulation details

In the first-principles DFT\textsuperscript{15,26} simulations, the DMol3 module\textsuperscript{17,18} was used for the geometric optimization, reaction process imitation and analysis of CT and PDOS. We employed the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof functional (PBE)\textsuperscript{19} to describe exchange and correlation effects. During the geometric optimization process, the energy convergence, maximum force and maximum distance were $5.0 \times 10^{-4}$ eV, 0.1 eV Å$^{-1}$ and $5.0 \times 10^{-3}$ Å, respectively. In the electronic settings, to reduce the computational cost, the DFT semi-core pseudo-potentials (DSPP) method\textsuperscript{20} was used to replace core electrons by a single effective potential and introduce some degree of relativistic correction into the core. The self-consistent field (SCF) tolerance value was $3.0 \times 10^{-4}$ eV and the double numerical plus d-functions (DND) were chosen as the basis set.\textsuperscript{21} To speed up convergence, a thermal smearing of 0.1 eV was applied to the orbital occupation. The calculations were spin unrestricted.

In the simulation of searching for transition states (TS), the calculation initially performed a linear synchronous transit (LST)\textsuperscript{21} maximum, which was followed by energy minimization in directions conjugated to the reaction pathway. TS approximation obtained via LST/optimization was then used to perform a quadratic synchronous transit (QST) maximization to determine the transitional states more accurately. The convergence tolerance of the root mean square (RMS) force was 0.15 eV Å$^{-1}$ and the maximum number for a QST step was set as 5. For the CT properties, atom charges would be calculated via the Hirshfeld population analysis.\textsuperscript{22} For PDOS calculations, the empty bands were chosen as 12.

The Au–Cu nanoparticles with dimensional sizes of 2–5 nm usually have polyhedral constructions, such as cuboctahedrons, icosahedrons and decahedrons.\textsuperscript{23,24} For these small particles, close-packed facets still occupy the majority of surfaces.\textsuperscript{25,26} The atom arrangement of these facets is the same as that of bulk (111) surfaces. Therefore, four layers of (111) slabs with periodicity of $(4 \times 6)$ were built for representing the surfaces of nanoparticles [the in-plane lattice directions are (110)]. When the slabs were used for the geometric optimization and modeling reaction processes, the underneath two atomic layers were fixed to simulate the interior of Au–Cu alloys. A vacuum of 18 Å was added along the normal directions of the slabs. K-points were chosen as $3 \times 2 \times 1$, for which the actual spacing is 0.03, 0.03 and 0.04 Å$^{-1}$ in the three lattice directions. First, two extreme cases are considered. When Au–Cu nanoparticles (Au/Cu atomic ratio 1/1) undergo no Cu oxidation and Au surface enrichment, the atom packing of their surface facets should be similar to AuCu(111), which is shown in Fig. 1(a). However, when all Cu atoms in Au–Cu nanoparticles are oxidized and enriched at surfaces via calcination at high temperature, the atom packing of their surface facets should be similar to CuO(111) and Cu$_2$O(111). In contrast to inert CuO surfaces, Cu$_2$O surfaces possess active sites for adsorbing reactants.\textsuperscript{27} The geometric structure of Cu$_2$O(111) is shown in Fig. 1(b). Differentiating the oxidation states, there are two Cu cation sites at Cu$_2$O(111) surfaces: the oxygen coordinatively saturated (Cu$_{CSA}$) and unsaturated (Cu$_{CUS}$) surfaces.\textsuperscript{28} Under the Cu surface atom layer, there are two oxygen atom sub-surface layers; one layer binds with Cu$_{CSA}$ sites and the other binds with Cu$_{CUS}$ sites.

As mentioned above, AuCu nanoparticles maintain the Au$_x$Cu$_{1-x}$ structure when they are only partially oxidized. In this case, part of their surface is a single layer of Cu$_2$O oxide growing on the Au$_3$Cu core. Cu$_2$O/Au$_3$Cu(111) represents this epitaxial system, which is shown in Fig. 1(c). In Cu$_2$O/Au$_3$Cu(111), the oxygen atom sub-surface layer connecting with Cu$_{CUS}$ sites is absent since Au–O bonding is forbidden.\textsuperscript{9,10} However, the oxygen atom sub-surface layer connected with Cu$_{CSA}$ sites can be thermodynamically stabilized via binding with Cu atoms in the Au$_3$Cu alloy. Because of this oxygen deficiency on Cu$_2$O/Au$_3$Cu surfaces, the surface Cu$_{CUS}$ sites would change to oxygen uncoordinated ones, which are defined as Cu$_{UNC}$. This surface oxide structure is similar to the construction of an Ag$_2$O oxide layer on Ag surfaces.\textsuperscript{29} Although the geometric structures of surface oxides are similar to those of corresponding bulk oxides, their electronic properties may be quite different because the surface oxides seem like periodic on-surface and sub-surface oxygen adsorption on metal surfaces. The oxygen adsorption and Cu$_2$O surface oxide formation on Cu(111) and their electronic properties have been studied in detail via DFT-GGA simulations.\textsuperscript{28,31} Therefore, it is appropriate to investigate the Cu$_2$O surface oxide on Au$_3$Cu(111) by the same method.

There are four types of coherent interfaces between Cu$_2$O and Au on Au$_3$Cu(111), which differentiate the boundary Cu and O sites (Fig. 2). For all of them, the in-plane linear interfaces are designed to lie along the close-packed (110) direction according to experimental results.\textsuperscript{11,12} Cu$_{CSA}$ sites can always connect with Au sites on interfaces because they occupy three quarters of the whole Cu surface atom layer. There are no Au–O bonds at Cu$_2$O–Au interfaces, which means that interfacial Cu$_{CSA}$ sites lose one coordinated oxygen atom and are converted to new...
oxygen coordinatively unsaturated sites (Cu\textsubscript{NCUS}). In Fig. 2(a and b), Cu\textsubscript{UNC} and Cu\textsubscript{NCUS} sites are both on Cu\textsubscript{2}O–Au interfaces. The difference between them is that the sub-surface oxygen is located near interfaces for the former and the on-surface oxygen is located near interfaces for the latter. In Fig. 2(c and d), only Cu\textsubscript{NCUS} sites are on the Cu\textsubscript{2}O–Au interfaces and the difference between them is as the same as that in Fig. 2(a and b). The total cohesive energy difference between these slabs and that of Cu\textsubscript{2}O/Au\textsubscript{3}Cu(111) and Au/Au\textsubscript{3}Cu(111), $\Delta E\textsubscript{slab}$, derives from the generation of Cu\textsubscript{2}O–Au interfaces. It is impossible to describe the interfacial energy of linear Cu\textsubscript{2}O–Au interfaces in units of Joules per square meter. Therefore, the interfacial energy, $\gamma_{\text{in}}$, is calculated in electron volts per atom, and is calculated via the formula $\gamma_{\text{in}} = \frac{\Delta E\textsubscript{slab}}{N_{\text{in}}}$, where $N_{\text{in}}$ is the total number of atoms at the interface.
the Cu2O–Au interfaces in a slab. \( \gamma_{\text{in}} \approx 0.65 \text{ eV per atom} \) for Cu2O–Au interfaces in Fig. 2(a and b) and \( \gamma_{\text{in}} \approx 0.70 \text{ eV per atom} \) for Cu2O–Au interfaces in Fig. 2(c and d). The \( \gamma_{\text{in}} \) values are similar to the surface energy values of Au(111). The high \( \gamma_{\text{in}} \) values of Cu2O–Au interfaces may be due to the lattice oxygen deficiency of the CuUnc sites. Nevertheless, if the Cu2O–Au interfaces do not form, the edges of Au and Cu2O are exposed to surfaces where the surface energy values are extremely large. To catalyze CO oxidation at Cu2O–Au interfaces, active CuUnc sites are necessary. Because of the higher \( \gamma_{\text{in}} \) values and absence of CuUnc sites, the Cu2O–Au interfaces in Fig. 2(c and d) are excluded. In Fig. 2(b), on-surface oxygen atoms are adjacent to interfaces, which may hinder the adsorption of reactants. Therefore, the Cu2O–Au/Au3Cu(111) slab with both CuUnc and CuNCUS sites on Cu2O–Au interfaces and sub-surface oxygen atoms adjacent to Cu2O–Au interfaces [Fig. 2(a)] are chosen as the catalytic substrate for the CO oxidation reaction, which is also shown in Fig. 1(d).

Results and discussion

The adsorption status and reaction of CO oxidation on AuCu and Cu2O/Au3Cu(111)

The stable and meta-stable adsorption positions of reactants CO, O2 and O on AuCu and Cu2O/Au3Cu(111) are shown in Fig. 3 and the corresponding adsorption energy values, \( E_{\text{ad}} \), are listed in Table 1. In general, CO is vertically adsorbed on the top sites of metal surface atoms, whereas O is adsorbed in the hollow sites of metal surfaces. O2 is adsorbed on metal surfaces in three states: top-bridge-top (tbt), top-hollow-bridge (thob), and bridge-hollow-bridge (hhb). For fcc and hcp hollows, the thob state can be sub-divided into the top-fcc-bridge (tfb) and top-hcp-bridge (thb) states. Similarly, the hhb state can be sub-divided into the bridge-fcc-bridge (ffb) and bridge-hcp-bridge (hhb) states. In addition, the Au and Cu sites should be distinguished for Au–Cu alloy surfaces.

In Fig. 3(a), CO can be adsorbed on the Au site of AuCu(111) (CO-I) with \( E_{\text{ad}} = -0.32 \text{ eV} \). In comparison, CO binds strongly to the Cu site (CO-I) due to its low adsorption energy of \( E_{\text{ad}} = -0.83 \text{ eV} \). The most stable O2 adsorption position is the Cu2 bridge (O2-I). In this adsorption state, although the two oxygen atoms bind separately with two Cu sites, the O–O bond is not parallel to the Cu2 bridge (the angle of interaction is about 40\(^\circ\)), which differs from the tbt state. Therefore, this new adsorption state is the tilted tbt state. For this stable O2 adsorption position, \( E_{\text{ad}} = -0.39 \text{ eV} \). When O2 is placed on the AuCu3 or AuCu2 hollows, it will spontaneously move to the Cu4 bridge. The only exceptions are O2 adsorption on AuCu3 hollows in the tbt-Au top and thb-Au top states (O2-II and O2-III). For these two meta-stable adsorption states, the \( E_{\text{ad}} \) values are \(-0.19 \) and \(-0.13 \text{ eV} \), respectively. In addition, O2 adsorption on the Au2 bridge is endothermic. The O atom adsorption is much stronger than that of O2 molecules because the atomic oxygen has lost the strong O–O bond. The most stable adsorption position for oxygen atoms is the AuCu2 fcc hollow (O-I) with \( E_{\text{ad}} = -4.40 \text{ eV} \). Other meta-stable O adsorption positions are AuCu4 hcp, AuCu fcc and hcp hollows (O-II, O-III and O-IV), for which \( E_{\text{ad}} \) values are \(-4.27, -3.84 \) and \(-3.73 \text{ eV} \), respectively. In Fig. 3(b), CO can only be adsorbed on the CuUnc site of Cu2O/Au3Cu(111) (CO-I) with \( E_{\text{ad}} = -1.12 \text{ eV} \). The most stable O2 adsorption position is the Cu1 fcc hollow site (O2-I). In the tbt-CuUnc top state, \( E_{\text{ad}} \) reaches \(-0.49 \text{ eV} \). At the same adsorption position, the other two meta-stable adsorption states are tbf-CuUnc top and bbf-CuUnc top (O2-II and O2-III), for which the \( E_{\text{ad}} \) values are \(-0.29 \) and \(-0.24 \text{ eV} \), respectively. Similar to the CO adsorption, O can only be adsorbed on the Cu3 fcc hollow (O-I) with \( E_{\text{ad}} = -4.04 \text{ eV} \).

The possible reaction mechanism of CO oxidation on unoxidized AuCu alloy surfaces is shown in Fig. 4. According to the reactant adsorption results, O2 can be meta-stably adsorbed on the Cu2 bridge of AuCu(111) in the tilt tbt state. Even if O2 molecules are adsorbed at AuCu2 hollows in the tbt-Au top and thb-Au top states, they can easily diffuse to the Cu3 bridge with a small diffusion barrier of \( E_{\text{db}} = 0.15 \text{ eV} \). In Fig. 4(a–c), when the O2 molecule on the Cu2 bridge is dissociated to form two O atoms, it needs to overcome the reaction barrier of \( E_{\text{rb}} = 0.74 \text{ eV} \). The direct O2 dissociation on AuCu(111) is not easy. Considering the direct reaction of O2 with CO, they must be co-adsorbed on the neighboring surface sites. At the ordered AuCu alloy surfaces, the Au and Cu sites are next to each other.
However, CO prefers to bind with the Cu site of AuCu(111). To react with O₂ on the Cu₂ bridge, CO must move to the Au site between them, as shown in Fig. 4(d–f). A reaction barrier of $E_{rb} = 0.81$ eV is calculated for this movement, which means that CO undergoes desorption and re-adsorption during this process. When CO is adsorbed on the Au site with O₂ on its neighboring Cu₂ bridge, their co-adsorption energy increases to $E_{ad} = 0.88$ eV as shown in Fig. 4(f) [$E_{ad} = -1.22$ eV for the initial state (IS)].

Owing to this meta-stable adsorption state, the reaction tends to be reversible and the corresponding $E_{rb}$ is only 0.44 eV. Therefore, on AuCu(111) surfaces, it is difficult for CO on the Cu site to move close to O₂ on the Cu₂ bridge for further reactions. In addition, O₂ molecules can still dissociate into O atoms on AuCu(111) because the corresponding $E_{rb}$ value is similar to that of O₂ dissociation on Pt(111).³³ According to Fig. 4(c), after O₂ dissociation, the two atoms are located at the AuCu₂ and Au₃Cu

### Table 1  $E_{ad}$ values of reactants CO, O₂ and O on AuCu(111), Cu₂O/Au₃Cu(111) and Cu₂O–Au/Au₃Cu(111)

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Positions</th>
<th>States</th>
<th>$E_{ad}$ (eV)</th>
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<tbody>
<tr>
<td>CO-I</td>
<td>Cu</td>
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<td>-0.83</td>
</tr>
<tr>
<td>CO-II</td>
<td>Au</td>
<td>Top</td>
<td>-0.32</td>
</tr>
<tr>
<td>O₂-I</td>
<td>Cu₂</td>
<td>Tilted tbt</td>
<td>-0.39</td>
</tr>
<tr>
<td>O₂-II</td>
<td>AuCu₂</td>
<td>tbt-Au top</td>
<td>-0.19</td>
</tr>
<tr>
<td>O₂-III</td>
<td>AuCu₂</td>
<td>thb-Au top</td>
<td>-0.13</td>
</tr>
<tr>
<td>O-I</td>
<td>AuCu₂</td>
<td>fcc hollow</td>
<td>-4.40</td>
</tr>
<tr>
<td>O-II</td>
<td>AuCu₂</td>
<td>hep hollow</td>
<td>-4.27</td>
</tr>
<tr>
<td>O-III</td>
<td>Au₂Cu</td>
<td>fcc hollow</td>
<td>-3.84</td>
</tr>
<tr>
<td>O-IV</td>
<td>Au₂Cu</td>
<td>hep hollow</td>
<td>-3.73</td>
</tr>
<tr>
<td>Cu₂O/Au₃Cu(111)</td>
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<td>-1.12</td>
</tr>
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<td>O-I</td>
<td>Cu₂</td>
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### Fig. 4  Illustration of (a)–(c) O₂ dissociation reaction, (d)–(f) CO + O₂ reaction and (g)–(i) CO + O reaction on AuCu(111) surfaces.
hollows. The AuCu$_2$ fcc hollow is the most stable position for O adsorption. O atoms adsorbed on the other three sites can easily diffuse to the AuCu$_2$ fcc hollow with small $E_{\text{dd}}$ values of 0.02–0.25 eV. In Fig. 4(g–i), to react with the O atom on the AuCu$_2$ fcc hollow, CO on the Cu site must move to the Au site between them. The $E_{\text{ad}}$ for this reaction is as high as 0.81 eV, whereas $E_{\text{dd}}$ of the reverse reaction is only 0.35 eV. Therefore, even if O$_2$ is dissociated to O atoms on AuCu(111), they still hardly react with CO molecules.

Because the surface energy of Au is smaller than that of Cu, the gold atoms are usually enriched at the unoxidized Au–Cu alloy surfaces. The Au surface enrichment has been neglected in this AuCu(111) slab. If the Au enrichment is considered, some local parts of the AuCu alloy surface may show an ordered Au$_2$Cu atom arrangement, for which the neighbors of Cu sites are only Au sites. On this Au$_2$Cu surface layer, Cu$_2$ bridges and AuCu$_2$ hollows are absent. O$_2$ adsorption on the Au$_2$Cu hollows and AuCu$_2$ bridges is very weak because the corresponding $E_{\text{ad}}$ values are higher than −0.10 eV. The gold surface enrichment leads to weaker O$_2$ adsorption, which cannot change the fact that CO oxidation is impossible on unoxidized Au–Cu alloy surfaces. In addition, the simulation of CO oxidation on Cu/Au(100) surfaces has been performed by the DFT-GGA method. The $E_{\text{dd}}$ of the CO + O reaction on Cu/Au(100) reaches 0.6 eV, which is a relatively high value. Therefore, the catalysis of CO oxidation using Au–Cu alloys is still difficult even if Cu is totally segregated to their unoxidized surfaces.

The possible reaction mechanism of CO oxidation on the Cu$_2$O surface oxide of Au–Cu alloys is shown in Fig. 5. One of the most common CO oxidation reaction mechanisms on reducible oxides or metal-support interfaces is that the oxides provide their lattice oxygen to react with CO. Based on this consideration, the possibility of the CO reaction with the on-surface oxygen of Cu$_2$O/Au$_2$Cu(111) is investigated first. In Fig. 5(a–c), the transitional state of this CO + O$_2$ on-surface reaction was not observed via our simulations. The difficulty for CO reactions with lattice oxygen may be due to the strong bonding between the on-surface oxygen anions and the Cu cations underneath. If an on-surface oxygen anion is removed from Cu$_2$O/Au$_2$Cu(111), there is an energy cost of 5.71 eV. For comparison, oxygen atom adsorption on Cu(111) has been also calculated, for which $E_{\text{ad}} = −4.91$ eV. The lattice Cu–O bonds in Cu$_2$O surfaces are stronger than the adsorption bonds of oxygen atoms on Cu surfaces. Although oxygen adsorption bonds are weaker, the $E_{\text{ad}}$ value of the CO + O reaction on Cu(111) is calculated to be as high as 0.80 eV. Based on this result, the $E_{\text{ad}}$ value of the CO + O$_2$ on-surface reaction on Cu$_2$O/Au$_2$Cu(111) should be higher than 0.80 eV. In addition, considering the Eley–Rideal mechanism, the possibility of the gas phase CO molecule reaction with the on-surface oxygen of Cu$_2$O/Au$_2$Cu(111) is studied. Similarly, no transitional state is observed. Therefore, the direct reaction of CO with the lattice oxygen of the Cu$_2$O surface oxide is impossible.

According to the reactant adsorption results, O$_2$ can be adsorbed meta-stably on the Cu$_3$ fcc hollow of Cu$_2$O/Au$_2$Cu(111) in the tbf-Cu$_{\text{UNC}}$ top state. Even if O$_2$ molecules are meta-stably adsorbed on the Cu$_3$ fcc hollow in the tbf-Cu$_{\text{CSA}}$ top state and the Cu$_3$ hcp hollow in the bbh-Cu$_{\text{UNC}}$ top state, they can easily change to the most stable adsorption state with small diffusion barriers of $E_{\text{dd}} = 0.18$ and 0.03 eV, respectively. In Fig. 5(c–e), when O$_2$ on the Cu$_3$ fcc hollow is dissociated to form two O atoms, it needs to overcome the reaction barrier $E_{\text{dd}} = 0.90$ eV. The direct dissociation of O$_2$ on Cu$_2$O/Au$_2$Cu(111) is not possible. When CO and O$_2$ are co-adsorbed on the Cu$_2$O oxide, they cannot be neighbors, as shown in Fig. 5(f). To react with O$_2$ on the Cu$_3$ fcc hollow, CO on the Cu$_{\text{UNC}}$ site must move to the Cu$_{\text{CSA}}$ site between them. However, when CO is placed on the inert Cu$_{\text{CSA}}$ site, it spontaneously leaves Cu$_2$O/Au$_2$Cu(111). In addition, the movement of O$_2$ to the neighboring sites of CO is impossible because O$_2$ cannot undergo exothermic adsorption once it has left the Cu$_{\text{UNC}}$ site. CO and O$_2$ have no opportunity to meet directly and react on Cu$_2$O/Au$_2$Cu(111). As mentioned above, Cu$_2$O/Au(111) represents the surfaces of the calcined Au–Cu particles. Moreover, the surface structures of Cu$_2$O/Au(111) and Cu$_2$O/Au$_2$Cu(111) should be similar because Au and Au$_2$Cu have the same crystal structure and similar lattice constants. These simulation results can explain why the calcined Au–Cu nanoparticles are inert for CO oxidation.

Moreover, the O$_2$ dissociation and CO oxidation on Cu$_2$O/Au(111) have also been studied using the same DFT-GGA method. The results show that reaction barriers for the direct O$_2$ dissociation, the CO reaction with the lattice oxygen, and the direct CO reaction with O$_2$, are all higher than 1 eV. Therefore, CO oxidation reactions cannot be carried out on both the surface Cu$_2$O oxides of Au–Cu alloys and bulk Cu$_2$O oxides.

Adsorption status and reactions of CO oxidation on Cu$_2$O–Au/Au$_2$Cu(111)

The stable and meta-stable adsorption positions of reactants on Cu$_2$O–Au/Au$_2$Cu(111) are shown in Fig. 6 and the corresponding adsorption $E_{\text{ad}}$ values are listed in Table 1. In Fig. 6(a), the possible O$_2$ adsorption positions near or on Cu$_2$O–Au interfaces are given. As mentioned above, the most stable O$_2$ adsorption position on Cu$_2$O/Au$_2$Cu(111) is the Cu$_3$ fcc hollow site, at which $E_{\text{ad}} = −0.49$ eV in tbf-Cu$_{\text{UNC}}$ top state [O$_2$-I in Fig. 3(h)]. On Cu$_2$O/Au$_2$Cu(111), O$_2$ also prefers to be located at the Cu$_3$ fcc hollow site near Cu$_2$O–Au interfaces. When O$_2$ is adsorbed in the tbf-Cu$_{\text{UNC}}$ top state (O$_2$-I), its $E_{\text{ad}}$ value is only −0.44 eV. However, in the tbf-Cu$_{\text{CSA}}$ top state (O$_2$-II), $E_{\text{ad}}$ for O$_2$ adsorption can reach −0.73 eV. On Cu$_2$O/Au$_2$Cu(111), Cu$_{\text{UNC}}$ is the only active Cu site, which offers strong adsorption for O$_2$. On Cu$_2$O–Au/Au$_2$Cu(111), Cu$_{\text{UNC}}$ and Cu$_{\text{CSA}}$ are both active Cu sites. When O$_2$ is located at the Cu$_3$ fcc hollow site near Cu$_2$O–Au interfaces in the tbf-Cu$_{\text{CSA}}$ top state, Cu$_{\text{UNC}}$ and Cu$_{\text{CSA}}$ may simultaneously offer strong adsorption for O$_2$, which induces a significant decrease in $E_{\text{ad}}$. O$_2$ can also be meta-stably adsorbed on the Cu$_3$ fcc hollow site in the tbf-Cu$_{\text{UNC}}$ top state (O$_2$-III), for which $E_{\text{ad}} = −0.48$ eV. On the Cu$_3$ hcp hollow, O$_2$ is meta-stably adsorbed in the bbh-Cu$_{\text{UNC}}$ top state with $E_{\text{ad}} = −0.40$ eV (O$_2$-IV). In addition, O$_2$ can also be located on only the Cu$_2$O–Au interfaces. On the AuCu$_2$ hcp hollow, O$_2$ is meta-stably adsorbed in the thb-Au$_{\text{UNC}}$ top state (O$_2$-VI), for which $E_{\text{ad}} = −0.21$ eV. On the Au$_2$Cu fcc hollow, where the Cu belongs to the Cu$_{\text{UNC}}$ sites (O$_2$-V), O$_2$ is weakly adsorbed in the tbf-Cu$_{\text{UNC}}$ top state.
state because the corresponding $E_{ad}$ value is only $-0.05$ eV. The adsorption positions of CO and O on Cu$_2$O–Au/Au$_3$Cu(111) are shown in Fig. 6(b). CO can be meta-stably adsorbed on the Au site (CO-I) with $E_{ad} = -0.28$ eV. On the Cu$_{NCUS}$ and Cu$_{UNC}$ sites (CO-II and CO-III), the CO adsorption is stronger due to the low $E_{ad}$ values of $-1.03$ and $-0.75$ eV, respectively. The most stable O adsorption position is the AuCu$_2$ hcp hollow (O-II), on which $E_{ad} = -4.26$ eV is determined. On the Cu$_3$ fcc hollow (O-I), the O adsorption is slightly weaker with $E_{ad} = -4.25$ eV. In addition, O atoms can be adsorbed meta-stably on the Au$_2$Cu fcc hollows at Cu$_{NCUS}$ and Cu$_{UNC}$ sites (O-IV and O-III) and the corresponding $E_{ad}$ values are $-4.00$ and $-3.97$ eV, respectively.

Diffuse reflectance infrared Fourier transform (DRIFT) and FT-IR results indicate that although CO adsorption on Cu sites is stronger than that on Au sites of Au–Cu nanoparticles, the corresponding CO adsorption amount on the former is far less than that on the latter. This may be because surface Cu sites are deficient before the reactions are carried out. Au enrichment on unoxidized Au–Cu alloy surfaces occurs because the surface energy of Au is smaller than that of Cu. Before the introduction of CO and O$_2$, Au sites occupy the majority of the surface of the reduced Au–Cu nanoparticles. Therefore, at the beginning of catalytic reactions, CO can bind more readily with Au sites. In the presence of oxygen, Au–Cu nanoparticles are partially oxidized and Cu$_2$O–Au interfaces are formed between local Cu$_2$O and Au surface layers. According to this model of reactant adsorption, O$_2$ prefers to be located at the Cu hollow sites near the Cu$_2$O–Au interfaces. The diffusion of CO on Au surfaces is very easy. When CO diffuses to the Au sites near the Cu$_2$O–Au interfaces and encounters O$_2$ there, they can combine to generate CO$_2$. 

Fig. 5 Illustration of (a)–(b) CO + O$_{on-surface}$ reaction, (c)–(e) O$_2$ dissociation reaction and (f) CO + O$_2$ reaction on Cu$_2$O/Au$_3$Cu(111) surfaces.

Fig. 6 Illustration of possible adsorption positions of reactants (a) O$_2$ and (b) CO and O on Cu$_2$O–Au/Au$_3$Cu(111) surfaces.
The CO oxidation reaction on Cu$_2$O–Au/Au$_3$Cu(111) can represent this interface catalytic process, which is shown in Fig. 7. First, O$_2$ is stably adsorbed on the Cu$_3$ fcc hollow near the interfaces in the tdb-Cu$_{6}$Cu(111) top state. When O$_2$ molecules are in other meta-stable adsorption states, they can easily change to the most stable state with small di ffusion barriers of 0.03–0.15 eV. Although the O$_2$ adsorption on Cu$_2$O–Au/Au$_3$Cu(111) is strong enough, it still cannot be directly dissociated because the corresponding dissociation barrier is as high as 1.04 eV. When CO diffuses to the Au site next to the Cu$_2$O–Au interfaces, it still has no electronic interaction with O$_2$. This co-adsorption state can be recognized as the IS of CO oxidation reactions, which is shown in Fig. 7(a). Subsequently, CO moves to the neighboring Au site of O$_2$, which only requires a small reaction barrier of $E_{rb} = 0.35$ eV to be overcome. In Fig. 7(c), when CO binds with the Au site near interfaces, it leans towards the O$_2$ molecule. In this meta-stable intermediate state (MS), the co-adsorption energy of CO and O$_2$ reaches $-1.17$ eV, which is lower than that of IS of $E_{ad} = -1.02$ eV. Therefore, there is already weak interaction between CO and O$_2$ in the MS. CO and O$_2$ then move together to form the meta-stable intermediate product O–O–CO, through which the O–O bond can be activated and easily dissociated. The reaction barrier of this combination process is only $E_{rb} = 0.35$ eV. In Fig. 7(e), $E_{ad}$ has reduced to $-1.73$ eV after the formation of O–O–CO, which means that a strong bond is generated between CO and O$_2$. In this intermediate state, the O–O bond has been activated, which is beneficial for further reactions. In Fig. 7(e and f), the transformation of O–O–CO to CO$_2$ and O is easy with $E_{rb} = 0.07$ eV. After the CO$_2$ product molecule desorbs, the remaining O atom is adsorbed on the stable AuCu$_2$ hcp hollow. When another CO molecule diffuses to a neighboring Au site, the molecules can combine to generate CO$_2$ with a moderate reaction barrier of $E_{rb} = 0.42$ eV, as shown in Fig. 7[h–j]. In summary, CO oxidation reactions can be easily carried out on Cu$_2$O–Au interfaces at Au$_3$Cu surfaces.

Cu$_2$O–Au/Au$_3$Cu(111) can only represent Cu$_2$O–Au interfaces located on facets of Au–Cu nanoparticles. In addition to facets, there are still some surface atoms on the edges and vertices of Au–Cu binary particles and Cu$_2$O–Au interfaces may pass through them. It has been demonstrated that these under-coordinated nanoparticle sites can accelerate heterogeneous catalysis. On Au–Cu binary nanoparticles, the CO and O$_2$ molecules adsorbed on edges and vertices should have lower $E_{ad}$ values than those adsorbed on facets. Via this enhanced reactant adsorption, O$_2$ activation and further CO oxidation may become easier. In future work, we intend to consider CO oxidation on Au–Cu clusters with different surface oxidation states, which can represent the surfaces of these binary nanoparticles more realistically.

CT of O$_2$ adsorption and PDOS analysis of CO oxidation on Cu$_2$O–Au/Au$_3$Cu(111)

An important premise for CO oxidation on Cu$_2$O/Au$_3$Cu(111) is that O$_2$ prefers to be located at the Cu sites near Cu$_2$O–Au interfaces rather than those inside the Cu$_2$O layers. To explain this preference for reactant adsorption, the CT and bond length of O$_2$ adsorption at the most stable positions of Cu$_2$O/Au$_3$Cu(111) and Cu$_2$O–Au/Au$_3$Cu(111) are analyzed, which is shown in Fig. 8. When adsorption bonds are generated between O$_2$ molecules and the underlying Cu$_2$O surfaces, charges are transferred from the substrates to the reactants and the Coulomb forces between them would determine the bond...
strength. The inter-atomic Coulomb forces are proportional to the absolute value of the product of the positive and negative charges of the atoms and inversely proportional to the bond length. In Fig. 8(a and b), the Cu sites of the Cu2O surfaces are all positively charged without reactant adsorption. At the interior of the Cu2O surfaces, the CT values of the CuUNC and CuCSA sites are 0.06 and 0.18, respectively. For the corresponding interfacial CuUNC and CuCSA sites, the CT values are almost unchanged. The CT value of the CuNCUS sites decreases to 0.09 compared with that of CuCSA sites, which is caused by the coordinate oxygen unsaturation of the CuNCUS sites. In Fig. 8(c and d), after O2 is adsorbed on both Cu2O/Au/Cu(111) and Cu2O–Au/Au3Cu(111), the average CT values of reactants are –0.16 and –0.18, respectively. O2 can obtain more charge from the Cu sites near Cu2O–Au interfaces. Nevertheless, the sum of the charge product of the three Cu–O adsorption bonds is similar for O2 adsorption on Cu2O/Au/Cu(111) and Cu2O–Au/Au3Cu(111). In contrast, the sum of the bond length of the three Cu–O adsorption bonds calculated is 6.24 Å for O2 adsorption on Cu2O/Au/Cu(111) and 6.17 Å for O2 adsorption on Cu2O–Au/Au3Cu(111). The difference comes from the CuNCUS–O bond, which has a bond length of only 1.96 Å. When O2 is adsorbed on the interfacial Cufcc hollow in the tbf-CuUNC and tbf-CuCSA states, the bond lengths of the CuNCUS–O bond are 2.06 and 2.09 Å, respectively. This difference in bond length proves our previous assumption that the interfacial CuUNC sites could offer enhanced adsorption for O2 in the tbf-CuUNC state. Therefore, Cu–O adsorption bonds near the Cu2O–Au interfaces have similar absolute values of the charge product but shorter adsorption bond lengths compared with those at the interior of Cu2O surfaces, which causes their large Coulomb forces and low adsorption energy values.

The increase in charge transfer can only ensure the preference of O2 adsorption near Cu2O–Au interfaces. The O2 activation and eventual dissociation requires the supplementary role of CO. The O–O bond of O2 is generated via extensive orbital hybridization of the 2p electrons. When CO reacts with O2, the orbital hybridization of the O–O bond may decrease and eventually disappear. To clarify the effect of CO assistance on the O2 activation and dissociation, the PDOS changes in the 2p electrons of the reactants during the CO oxidation on Cu2O–Au/Au3Cu(111) are analyzed, which is shown in Fig. 9. First, 2p electrons of C and O, 3d electrons of Cu, and 5d electrons of Au in all slabs have no spin polarization. In Fig. 9(a), the 2p hybridization peak of CO lies at a lower energy level than that of O2 in IS because the C–O bond is stronger than the O–O bond. In the first transitional state (TS1), CO has been desorbed from the Au site, which induces the movement of its hybridization peak to a higher energy level. In Fig. 9(c), the hybridization peak of CO is substantially broadened and weakened in the first meta-stable intermediate state (MS1). At the lower energy end of the valence bands, PDOS of CO and O2 are both slightly increased, which proves the weak interaction of the reactants. Under the influence of CO, the hybridization peak of O2 also decreases. In the second transitional state (TS2), the original hybridization peak of CO almost disappears. However, the simultaneous increase in PDOS of CO and O2 becomes more pronounced. In Fig. 9(e), large hybridization peaks are produced between the 2p electrons of CO and O2 because of the formation of O–O–CO. Before the reaction reaches the meta-stable intermediate state (MS2), the PDOS shapes of the two O atoms belonging to the O2 molecule are similar. In MS2, PDOS of the O atom connecting the Cu2O substrates is significantly reduced at the main hybridization peak (energy level of –6.70 eV).

Fig. 8 CT of Cu sites on (a) Cu2O/Au/Cu(111) surfaces and (b) Cu2O–Au/Au3Cu(111) surfaces. CT of O2 molecules and its connecting Cu sites and bond length of Cu–O adsorption bonds when O2 is stably adsorbed on (c) Cu2O/Au/Cu(111) surfaces and (d) Cu2O–Au/Au3Cu(111) surfaces.
In the meta-stable intermediate product, O–O–CO, the electronic hybridization of this O atom only occurs for the O–O bond. Therefore, the reduced participation of its 2p electrons in hybridization indicates that the O–O bond in O–O–CO is weaker compared with that of the original O2 molecule. In the third transitional state (TS3), PDOS of this O atom is decreased further at the main hybridization peak, which indicates that the O–O bond is almost broken. In Fig. 9(g), the extensive hybridization of the 2p electrons only happens among the other three C and O atoms, which confirms the complete dissociation of O2 and formation of CO2 in the final state (FS).

Discussion of the reaction mechanisms of CO oxidation on Au–Cu nanoparticles

The reaction mechanism of CO oxidation on Au–Cu nanoparticles can be explained based on our simulation results. In contrast to the Cu alloy, O2 adsorption and CO oxidation on Au nanoparticles only occurs at vertex sites.40 However, these under-coordinated sites occupy a very small proportion of the nanoparticle surface,23,26 which reduces the probability of O2 adsorption and further reactions with CO. Oxidation resistance experiments indicate that at 110 °C, the transformation of Cu nanoparticles to Cu2O and CuO aggregates only requires several tens of minutes.48 Inert CuO surfaces cannot provide effective adsorption for reactants. CO oxidation cannot be carried out on Cu2O surfaces because their active CuCUS sites are far apart. The oxidation rates of Au–Cu alloy nanoparticles are much lower than those of pure Cu ones.44 To catalyze CO oxidation on Au–Cu nanoparticles, CO molecules are first adsorbed on their surface Au sites. Owing to the introduction of O2, some Cu atoms of the particles are oxidized to form numerous local Cu3O surface oxide layers. Simultaneously, coherent interfaces are generated between Cu2O and the unoxidized Au layers. O2 activation and CO oxidation can occur on these Cu3O–Au interfaces. For traditional nanogold catalysts, interfaces between Au and oxide substrates are used for O2 activation and CO oxidation. However, for these Au–Cu binary nanoparticles, CO and O2 can directly react on surfaces, and this does not depend on the substrates. Considering the catalyst design for CO oxidation reactions, O2 cannot be activated and dissociated on pure Au and Pt nanoparticles. In contrast, Cu, Rh, Ni, Ru, and Co nanoparticles are easily oxidized and lose their surface active sites for O2 adsorption. Via alloying techniques, binary nanoparticles can avoid being completely oxidized and offer active sites for O2 adsorption and further CO oxidation.

Conclusions

On AuCu(111), CO is stably adsorbed on the top of the Cu site and O2 prefers to be located at the Cu2 edge in the tilted-tbt state. The O2 dissociation barrier on the unoxidized AuCu alloy surface is as high as 0.74 eV. Because CO and O2 are adsorbed on the separate Cu sites, they cannot readily combine to generate CO2 on AuCu(111). On Cu2O/AuCu(111), CO is strongly adsorbed on the top of the CuUNC site and O2 prefers to be located at the Cu3 fcc hollow in the tft-CuUNC top state. CO cannot react with the lattice oxygen of the Cu2O surface oxides. The direct O2 dissociation on oxidized AuCu alloy surfaces is difficult because of the high dissociation barrier value of 0.90 eV. The reaction of CO + O2 on Cu2O/AuCu(111) is impossible as the reactants cannot move together in adsorption states. On Cu3O/AuCu(111), O2 prefers to be located near Cu2O–Au interfaces rather than inside the Cu2O surfaces. CO can be adsorbed on Au surfaces, moderately. When CO diffuses to the Au site near Cu2O–Au interfaces, it can easily react with O2 due to the small reaction barriers of 0.07–0.35 eV. After this reaction, the remaining O atom on the AuCu2 hcp hollow can also react with CO on the neighboring Au site and the corresponding reaction barrier is 0.42 eV. The Hirshfeld population and bond length analysis indicate that O2 near Cu2O–Au interfaces can obtain more charge, transferred from the substrates and shorter Cu–O adsorption bonds, which causes its lower adsorption energy value. In addition, PDOS results show that the electronic hybridization of the O–O bond in O2 weakens and eventually disappears after it combines with CO to form O–O–CO and CO2 + O.
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Notes and references