1. Introduction

Nanoclusters containing 10–1000 atoms have unique optical, magnetic, chemical, and other properties not observed in the corresponding bulk materials and are therefore subject of active research. The properties of nanoclusters, especially smaller-sized ones, strongly depend on the number of atoms in the cluster. This is especially important for catalytic properties: the smaller the size of catalytic particles, the larger the specific surface area of a catalyst.

The first experimental investigations performed with small Au nanoparticles supported by metal oxides (TiO₂, Fe₂O₃, etc.) have shown that they have prominent catalytic activity for many reactions, in particular, for CO oxidation. At room temperature and lower temperatures, they are often superior to classical catalysts such as Pt and Pd. Despite many subsequent studies (see reviews), the mechanisms causing this remarkable enhancement remain poorly understood. Important information about reaction features can be obtained from first-principles calculations.

Gao et al. have studied the catalytic activity and active center locations in gold clusters Auₙ (n ≤ 35). It has been shown that the maximum binding energy is observed at sites with reduced coordination number or with a small angle of the cone formed by adjacent bonds. A correlation has also been found between catalytic activity, adsorption energy, and structural properties through the Sabatier principle and the Brønsted–Evans–Polanyi relationship; the catalytic activity can be well characterized by rather simple structural descriptors. Another way to assess adsorption, and hence catalytic properties, is to study the electronic structure. An increase in the catalytic activity of gold nanoclusters has been observed as the d-band narrows and shifts to the Fermi level. Gold has excellent catalytic properties and long lifespan but is expensive; therefore, finding a cheaper material with similar properties is highly desirable.

Copper catalysts are a well-studied class of materials that have comparable catalytic activity and relatively low priced. Copper is used in a wide range of chemical reactions, including the oxidation of CO. The principal limitation of its...
use is the active oxidation of copper itself,\textsuperscript{20,23} which can be decreased by alloying with various elements (\textit{i.e.} Au, Pt, Pd).\textsuperscript{24–27} Bimetallic or multicomponent clusters are now emerging as a substantial advancement in catalysis.\textsuperscript{18} They usually have a core–shell structure, where only the shell is formed by catalytically active metals. Such a morphology leads to significant cost reduction of a catalyst. In addition, bimetallic nanocatalysts demonstrate a synergistic effect, and are more catalytically active than those formed from pure constituent components.\textsuperscript{28} Specifically, the Cu–Au system is of interest because of its high corrosion resistance,\textsuperscript{22,29} lower cost, and the ability to control its catalytic properties by changing its structural characteristics such as the copper-to-gold ratio.\textsuperscript{10–32}

Moving from one-component to bimetallic catalysts opens the door to a number of reaction mechanisms that exploit component difference. The Langmuir–Hinshelwood (LH) mechanism suggests that both reactants (CO and O\textsubscript{2}) are adsorbed at the catalyst surface where the oxidation reaction takes place. The Eley–Rideal (ER) mechanism suggests the adsorption of only one reactant while the other one remains gaseous. The ER kinetics is close to the LH one when the latter has reactants adsorbed on different sorts of active sites and one reactant is weakly adsorbed.\textsuperscript{33} The feature of the Mars–van Krevelen (MvK) mechanism is that one reactant is adsorbed at the catalyst surface while the other is adsorbed on the top of the first reactant. The LH mechanism has been applied to most studies related to Au nanoparticles and nanoclusters.\textsuperscript{13,34} At the same time, the use of the ER mechanism is limited because of the weak adsorption and dissociation of O\textsubscript{2} on Au. The importance of an oxide layer for the catalytic oxidation of CO has been noted by many researchers.\textsuperscript{4,35–37} In recent years, this observation and the high oxidation of Cu atoms have been constructively used for the fabrication of efficient Cu–Au catalysts. It was found that preliminary annealing in air or oxygen forms a CuO\textsubscript{x} layer at the CuAu surface, which significantly enhances the CO conversion perhaps via the MvK mechanism.\textsuperscript{12,38} Reconstruction of the structure during CuO\textsubscript{x} layer formation was examined in detail by experiments and DFT calculations,\textsuperscript{12,38} while the process of CO oxidation itself is still not well understood as catalyst complexity makes many pathways of the reaction possible. When preliminary annealing is absent, the structure of a CuAu catalyst is not so complicated and the CO conversion is most likely to follow the LH mechanism.

Previous theoretical studies on the rationalization of catalytic nanoparticles give many important insights into how catalytic properties may be assessed from other characteristics. However, they are focused mostly on model particles with intuitively constructed structures. These studies either considered very small clusters predicted using accurate and computationally demanding methods or used semiempirical approaches for larger particles, with parameters derived from bulk species. For copper–gold nanoclusters, little to no attention has been paid to thorough investigation of reaction pathways—the most comprehensive characteristic of catalytic activity. In this work, we provide an extensive systematic picture of Cu–Au bimetallic nanoparticles with up to 15 atoms, including their equilibrium structures and stability. On the basis of well-known descriptors, we select particles that are both stable and promising for CO oxidation, study them using an accurate \textit{ab initio} analysis of the corresponding reaction pathways and show that copper–gold nanoparticles can be on a par with or even superior to gold nanoparticles in catalytic activity, while being significantly cheaper.

2. Computational methods

The ground-state structures of Cu\textsubscript{m}Au\textsubscript{n} clusters were obtained in a large compositional area using the variable composition technique\textsuperscript{39} for the global optimization of nanocluster structures implemented in the evolutionary algorithm USPEX.\textsuperscript{40,41} This method demonstrated 5–50 times higher speed than the traditional USPEX code for each composition.\textsuperscript{39,42,43}

Global optimization was carried out in two steps. First, we predicted the structures using the Gupta potential\textsuperscript{44} using the evolutionary algorithm USPEX coupled with a large-scale atomic/molecular massively parallel simulator (LAMMPS).\textsuperscript{45} Then, 30 lowest-energy structures for each composition were used as seed structures (known structures of a specific compound for the initial generation in the evolutionary algorithm USPEX) to continue calculations in the evolutionary algorithm USPEX coupled with the VASP code within density functional theory (DFT). Our calculations are spin-polarized and used the projector augmented wave method (PAW)\textsuperscript{46} and the Perdew–Burke–Ernzerhof (PBE)\textsuperscript{47} generalized gradient approximation exchange correlation functional as implemented in the Vienna \textit{ab initio} simulation package (VASP).\textsuperscript{48,49} where we set a planewave energy cutoff of 295 eV and a vacuum layer of 8 Å between the periodic images of the cluster.

Selected catalytically active clusters and all further CO oxidation reactions with them were calculated using dispersion corrections (PBE@MBD)\textsuperscript{50} with an energy cutoff of 600 eV, and the periodic images of a cluster were separated using a vacuum layer of 12 Å in the VASP code.\textsuperscript{38,49} We examined various positions of CO and O\textsubscript{2} molecule attachment for the initial and final states of the CO oxidation reaction and selected the most energetically favorable among them. The adsorption energy is defined as $E_{ads} = E(adsorbate + cluster) - E(cluster) - E(adsorbate)$, where $E(adsorbate + cluster)$ is the total energy of a composite cluster and an adsorbate system, $E(cluster)$ is the energy of a freestanding cluster, and $E(adsorbate)$ is the energy of an isolated adsorbate. The reaction barriers and pathways for CO oxidation were calculated using the nudged elastic band method (NEB)\textsuperscript{51,52} implemented in the VASP code. For all ground states, frequencies were calculated and $3N - 6$ positive frequencies were found ($N$ = number of atoms). Only one significant imaginary frequency was found in each of the transition states.
3. Results and discussion

The most stable structures of all calculated Cu$_n$Au$_m$ clusters ($n + m \leq 15$) are shown in ESI Fig. S1. Some structures important for further analysis are presented in Fig. 1. Our results reproduced previous calculations for smaller clusters$^{53-56}$ or improved on them for Cu$_2$Au$_6$, Cu$_3$Au$_2$, and Cu$_3$Au$_7$ clusters. The ground-state structures of Cu$_n$Au$_m$ clusters with $11 \leq n + m \leq 15$ were found for the first time.

Fig. 2a shows the compositional areas with planar and non-planar clusters. Small Cu$_n$Au$_m$ clusters ($n + m \leq 6$) have only planar structures. Structures with $7 \leq n + m \leq 13$ show greater...
than in copper ones. Possible factors responsible for this effect are contributions that dominate in gold clusters (an equal energy of the band top in Cu$_6$ and Au$_6$ is a rare exception). The value of $\Delta_m$ and $\Delta_A$ determines the stability of a cluster against the transfer of atoms. These factors explain the difference of the total energy with respect to the number of atoms and found their minimum:

$$\Delta_m = \min\{\Delta_{Cu}^2, \Delta_{Au}^2\}$$

where

$$\Delta_{Cu}^2 = E(n+1, m) + E(n-1, m) - 2E(n, m)$$
$$\Delta_{Au}^2 = E(n, m+1) + E(n, m-1) - 2E(n, m)$$

and $E(n, m)$ is the ground-state energy of the Cu$_m$Au$_m$ cluster. The value of $\Delta_m$ characterizes the stability of a cluster against the transfer of one atom of each type between a pair of identical Cu$_m$Au$_m$ molecules. In experiments, clusters are synthesized in ensembles, and therefore this value can be a measure of the abundance of a cluster. The results demonstrate the paray effect – enhanced stability of clusters with even numbers of electrons (Fig. 2b). This indicates the tendency of the clusters to have closed-shell electronic structure. One exception is the Cu$_{13}$Au$_{15}$ cluster, which is both stable and open-shell, which can be explained by its high symmetry ($C_{3v}$). Generally, the stability of clusters is determined by two factors: the closed-shell electronic structure and the atomic closed-shell structure.

Having identified stable clusters, we screened them for potential catalytic activity. An obvious way to do so is to calculate the reaction paths and the reaction barriers, but such calculations are extremely computationally demanding. Given the number of clusters considered here, it is highly desirable to find simple descriptors to discard the unpromising cases. One of them is the coordination number, which has been used to approximate adsorption properties and catalytic activity. In general, the following pattern is expected: underbound and low-coordinated atoms have greater catalytic activity. Previous studies have suggested that two- and three-coordinated atoms
serve as catalytically active sites and promote general efficiency. In this study, we evaluated the coordination number of an atom as follows:

\[
CN_i = \sum_j c_{ij}
\]

\[
c_{ij} = \begin{cases} 
\exp\left(-\frac{r_{ij} - R_{sc}}{D}\right), & \text{if } r_{ij} \geq R_{sc} \\
1, & \text{if } r_{ij} < R_{sc}
\end{cases}
\]

where \(i\) is the number of a given atom; \(r_{ij}\) is the distance between atoms \(i\) and \(j\) having sorts \(s = s(i)\) and \(s' = s(j); R_{sc}\) is the reference length of a bond between the atoms of \(s\) and \(s'\) sorts (we took the values of 3.0 Å, 2.85 Å and 2.7 Å for Au–Au, Au–Cu and Cu–Cu pairs); and \(D = 0.37\) Å is the empirically determined parameter. To illustrate the dependence of the minimum coordination number \(CN_{\text{min}} = \min\{CN_i\}\) on the cluster composition, we built an interpolated map of the minimum coordination numbers \(CN_{\text{min}}(n, m)\) for the ground-state clusters of each composition (see Fig. 2c). The coordination numbers of surface atoms in planar and non-planar structures vary from 2 to 3 and from 2 to 4, respectively. In comparison, the core atoms have coordination numbers between 3 and 9.

Using the maps of stability and minimum coordination numbers, we selected stable clusters that have low-coordinated surface atoms, marked with crosses on the maps (Fig. 2), for a more detailed consideration of catalytic properties. We calculated the reaction barriers and pathways for CO oxidation on the selected clusters, which can proceed via two mechanisms: the Langmuir–Hinshelwood mechanism assumes the adsorption of both CO and \(O_2\) molecules on the nanoparticle surface, whereas the Eley–Rideal mechanism suggests the adsorption of only one molecule. In this work, we followed the Langmuir–Hinshelwood mechanism because the adsorption and dissociation of \(O_2\) on Au are hindered by unfavorable kinetics. The mechanism consists of the following elementary reactions:

\[
\text{CO} + \text{cluster} \rightarrow \text{CO}^* + \text{cluster} \quad (R1)
\]

\[
\text{CO}^* + \text{O}_2 + \text{cluster} \rightarrow \text{CO}^* + \text{O}_2^* + \text{cluster} \quad (R2)
\]

\[
\text{CO}^* + \text{O}_2^* + \text{cluster} \rightarrow \text{OCOO}^{**} + \text{cluster} \quad (R3)
\]

\[
\text{OCOO}^{**} + \text{cluster} \rightarrow \text{CO}_2 + \text{O}^* + \text{cluster} \quad (R4)
\]

where \(^*\) denotes the species adsorbed on a cluster, \(^{**}\) denotes the adsorption on two sites of a cluster.

For each selected cluster, we modeled the reactions with the CO molecules adsorbed on two- and three-coordinated surface atoms responsible for catalytic activity. The selected cases allowed us to consider different environments of active sites. For example, in the case of \(\text{Cu}_5\text{Au}_7\), there are three possible scenarios: (1 and 2) CO is adsorbed on the three-coordinated Au active site, surrounded by one Au and two Cu neighbors, whereas \(O_2\) is adsorbed on either Au or Cu neighbor; (3) CO is adsorbed on the three-coordinated Au active site, with three neighboring Cu atoms, and \(O_2\) is adsorbed on one of these Cu neighbors. The most thermodynamically and kinetically favorable pathways for each considered cluster are shown in Fig. 3. The calculated pathways for each reaction are shown in ESI Fig. S3.† The activation barriers and adsorption energies are shown in Table 1. The relative energies of intermediates are presented in ESI Tables S1.†

The reaction mechanism starts with the adsorption of CO and \(O_2\) (stages R1 and R2 in eqn (4)). CO adsorption (R1) always proceeds without a kinetic barrier. Seventeen out of the 18 selected clusters have Au atoms as active sites. The corresponding adsorption energies \(E_{\text{ad}}\) vary from \(-0.63\) to \(-1.0\) eV and appear to be independent of the environments of active sites. The remaining case is the \(\text{Cu}_5\text{Au}_3\) cluster with the three-coordinated Cu atom as an active site. It has the strongest adsorption with \(E_{\text{ad}} = -1.11\) eV.

The second stage (R2), the adsorption of the oxygen molecule, usually has no kinetic barrier. The energy gain depends on whether the \(O_2\) is adsorbed on Cu or Au atoms. The adsorption on copper is generally more favorable, with energies from \(-0.58\) to \(-0.34\) eV. For \(O_2\) adsorbed on Au atoms, this range is from \(-0.34\) to \(-0.08\) eV, which can be explained by stronger binding to copper than to more inert gold. We note two outlying cases: \(\text{Cu}_7\text{Au}_6\) and \(\text{Cu}_4\text{Au}_6\). In the former one, \(O_2\) is efficiently adsorbed on the Cu atom of the \(\text{Cu}_7\text{Au}_6\) cluster with an energy gain of 0.92 eV. This may be related to the cluster's higher reactivity due to its open-shell electronic structure. In the \(\text{Cu}_4\text{Au}_6\) cluster, in contrast, the adsorption energy is positive (\(E_{\text{ad}} = +0.18\) eV), meaning that the unbound state is more favorable. This has been observed previously for \(\text{Au}_n\) clusters.

In the next stage (R3), the adsorbed \(\text{CO}^*\) and \(\text{O}_2^*\) molecules bond with each other to form an \(\text{OCOO}^{**}\) intermediate (Fig. 3). This process goes through a transition state TS1 with the activation energy \(E_a\) varying from 0.05 to 0.61 eV. In most cases, it is below \(-0.3\) eV, which is not a significant obstacle in the catalytic pathway, and this transformation can probably proceed under mild conditions. The lowest barriers (\(-0.10\) eV) are observed in \(\text{Cu}_4\text{Au}_5\) and \(\text{Cu}_3\text{Au}_5\) clusters, as well as in the \(\text{Cu}_7\text{Au}_6\) cluster, the only stable open-shell cluster. The latter

![Fig. 3 Computed reaction pathways of \(\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}^*\) on both stable and catalytically active \(\text{Cu}_n\text{Au}_m\) clusters. Here, * denotes the species adsorbed on a cluster.](Image 309x581 to 544x729)
case is consistent with previous results for Au clusters\textsuperscript{34} with odd numbers of electrons.

Finally, the OCOO\textsuperscript{**} complex undergoes O–O bond breaking and decomposes into an isolated CO\textsubscript{2} molecule and an adsorbed O* atom (stage R4). The activation energy for the corresponding transition state TS2 strongly depends on the coordination of the remaining oxygen atom at the moment of CO\textsubscript{2} detachment: if O* is bound to one atom (Au or Cu), then \( E_a \) is between 0.32 and 0.75 eV, whereas when O* is bound to two atoms one of which is Cu, the barrier drops to extremely low values of several meV. Such a reduction of the barrier, indicating high catalytic activity, is observed in Cu\textsubscript{5}Au\textsubscript{3}, Cu\textsubscript{3}Au\textsubscript{5}, Cu\textsubscript{5}Au\textsubscript{3}, Cu\textsubscript{5}Au\textsubscript{5}, Cu\textsubscript{5}Au\textsubscript{7}, Cu\textsubscript{6}Au\textsubscript{6}, and Cu\textsubscript{7}Au\textsubscript{6} clusters (Table 1). Typical examples of mechanisms with two different coordinations of O* at the moment of CO\textsubscript{2} detachment, together with corresponding energetics, are shown in Fig. 4.

In the final stage of the reaction, the adsorbed O* atom is bonded with two or three atoms of Cu and Au. The adsorption

\begin{table}
\centering
\begin{tabular}{cccccccc}
\hline
\textbf{N} & \textbf{Cluster} & \textbf{Atom for CO} & \textbf{E\textsubscript{ad} (CO), eV} & \textbf{Atom for O\textsubscript{2}} & \textbf{E\textsubscript{ad} (O\textsubscript{2}), eV} & \textbf{First activation energy\textsuperscript{a}, eV} & \textbf{First reaction energy, eV} & \textbf{Second activation energy\textsuperscript{a}, eV} & \textbf{Second reaction energy, eV} \\
\hline
1 & Cu\textsubscript{5}Au\textsubscript{3} & Au (atom 6) & –0.82 & Cu (atom 1) & –0.54 & 0.61 & –0.42 & ±0 & –1.56 \\
2 & Cu\textsubscript{5}Au\textsubscript{3} & Cu (atom 4) & –1.11 & Cu (atom 5) & –0.58 & 0.31 & –0.15 & 0.38 & –2.49 \\
3 & Cu\textsubscript{5}Au\textsubscript{3} & Au (atom 4) & –0.87 & Cu (atom 3) & –0.50 & 0.41 & –0.65 & 0.71 & –1.72 \\
4 & Cu\textsubscript{5}Au\textsubscript{3} & Au (atom 8) & –0.92 & Cu (atom 3) & –0.54 & 0.32 & –0.16 & 0.32 & –1.70 \\
5 & Cu\textsubscript{5}Au\textsubscript{3} & Au (atom 8) & –0.92 & Au (atom 6) & –0.24 & 0.53 & –0.39 & ±0 & –2.22 \\
6 & Cu\textsubscript{5}Au\textsubscript{3} & Au (atom 8) & –0.79 & Au (atom 10) & –0.19 & 0.20 & –0.44 & 0.38 & –1.91 \\
7 & Cu\textsubscript{4}Au\textsubscript{6} & Au (atom 10) & –0.99 & Cu (atom 3) & –0.34 & 0.21 & –0.23 & 0.10 & –1.87 \\
8 & Cu\textsubscript{4}Au\textsubscript{6} & Au (atom 10) & –0.99 & Au (atom 8) & 0.18 & 0.18 & –0.95 & 0.75 & –2.20 \\
9 & Cu\textsubscript{4}Au\textsubscript{6} & Au (atom 8) & –0.73 & Cu (atom 4) & –0.41 & 0.31 & –1.13 & ±0 & –2.03 \\
10 & Cu\textsubscript{5}Au\textsubscript{3} & Au (atom 9) & –0.96 & Cu (atom 4) & –0.34 & 0.08 & –0.62 & 0.54 & –2.40 \\
11 & Cu\textsubscript{5}Au\textsubscript{3} & Au (atom 9) & –0.68 & Cu (atom 3) & –0.53 & 0.27 & –0.58 & 0.49 & –1.71 \\
12 & Cu\textsubscript{5}Au\textsubscript{3} & Au (atom 6) & –0.76 & Cu (atom 2) & –0.55 & 0.21 & –0.92 & ±0 & –1.48 \\
13 & Cu\textsubscript{5}Au\textsubscript{3} & Au (atom 11) & –0.71 & Cu (atom 5) & –0.49 & 0.26 & –0.43 & 0.37 & –1.73 \\
14 & Cu\textsubscript{5}Au\textsubscript{3} & Au (atom 11) & –0.71 & Au (atom 12) & –0.08 & 0.11 & –1.03 & 0.17 & –1.87 \\
15 & Cu\textsubscript{4}Au\textsubscript{6} & Au (atom 11) & –0.63 & Au (atom 8) & –0.34 & 0.29 & –0.70 & 0.52 & –1.55 \\
16 & Cu\textsubscript{4}Au\textsubscript{6} & Au (atom 11) & –0.63 & Cu (atom 5) & –0.58 & 0.58 & –0.80 & ±0 & –3.03 \\
17 & Cu\textsubscript{4}Au\textsubscript{6} & Au (atom 10) & –0.75 & Cu (atom 3) & –0.92 & 0.10 & –0.26 & 0.36 & –1.77 \\
18 & Cu\textsubscript{4}Au\textsubscript{6} & Au (atom 10) & –0.75 & Cu (atom 3) & –0.43 & 0.05 & –0.22 & ±0 & –1.87 \\
\hline
\end{tabular}
\caption{Calculated activation and adsorption energies for CO and O\textsubscript{2} in CO oxidation on clusters that are both stable and catalytically active. \( N \) – number of the pathway. Numbers in parentheses indicate the number of the atom in the XYZ coordinates (see the ESI\textsuperscript{†}).}

\textsuperscript{a}In cases where a reaction involves several barriers, one has to carefully determine which barrier limits the reaction rate.\textsuperscript{62} In all cases studied here there are two barriers, and the highest one is the rate-limiting one.

Fig. 4 Mechanisms of OCOO* decomposition: (a) with usual barriers; (b) with ultralow barriers.
energy varies from $-1.6$ to $-2.1$ eV, which is in close agreement with the results obtained by Chepkasov et al.$^{32}$

In the calculated potential energy surfaces, turnover frequency (TOF)-determining intermediates$^{62}$ (the intermediates which have the lowest energy) and TOF-determining transition states$^{62}$ (the highest TS following the rate-determining intermediate) follow immediately one after another, so the limiting stage of each pathway is the step with the highest activation barrier. The median limiting activation barrier of the whole reaction (R1–R4) is not higher than 0.4 eV and can be overcome under mild conditions. We also found special clusters with extremely low activation energies (several meV): Cu$_5$Au$_5$, Cu$_5$Au$_7$, and Cu$_7$Au$_6$ have a low first barrier; Cu$_2$Au$_3$, Cu$_2$Au$_5$, Cu$_5$Au$_7$, Cu$_6$Au$_6$, and Cu$_7$Au$_6$ have a low second barrier. The Cu$_4$Au$_6$ cluster has both extremely low first and second barriers (0.05 and 0.02 eV). Another crucial parameter is the total reaction energy $E_r$, which varies from $-3.3$ to $-5.04$ eV. The most energetically favorable path, on Cu$_8$Au$_{16}$, is $\sim 1$ eV lower than all the other ones. This higher gain in the energy comes from the rearrangement of metal atoms to a much more symmetric structure during stage R4.

The median activation barrier of the reaction is more than 3 times lower than the effective activation energy $\sim 1.3$ eV of the non-catalytic reaction.$^{62}$ We also compared our results with the corresponding values in the pure gold and copper clusters and surfaces.$^{13,14,60,64,65}$ The results demonstrate that our values of limiting activation barriers are comparable with those in pure gold nanoclusters ($\sim 0.4$ eV) and are lower than barriers in pure copper nanoclusters ($\sim 0.5$–0.6 eV). Surfaces of bulk gold catalysts have lower barriers ($\sim 0.2$–0.3 eV), but some of our clusters (Cu$_n$Au$_m$, etc.) have the lowest barriers. Structure reordering, which might occur during the reaction, may affect not only the reaction energy but also other aspects of the catalytic cycle. For example, in the CO oxidation on the Cu$_4$Au$_5$ cluster, rearrangement takes place during stage R4, causing migration of the O* atom from the copper to the gold atoms and thereby facilitating the subsequent recovery of the catalyst.

Some clusters considered in this study have more than one active site, and different reaction paths can be realized on one cluster. The prevailing path may depend on the environmental conditions, particularly the temperature. At lower temperatures, the system is likely to undergo the reaction with the lowest barrier. If the temperature is high enough to overcome the barriers, the preferred reaction is determined by the largest overall energy gain. A good example of such competition is the Cu$_4$Au$_5$ cluster, where for one reaction path, the overall energy decrease and the largest barrier are 3.4 and 0.32 eV, respectively, whereas for the other path, the corresponding values are 3.8 and 0.71 eV (cases 3 and 4 in Fig. 3). The first path has a lower barrier and the second one has a larger energy decrease. Similar behavior was also observed for Cu$_5$Au$_6$ and Cu$_5$Au$_7$ clusters. In some studies, in nanocatalysis the activation energy $E_a$ and total reaction energy $E_r$ are considered linearly dependent (relying on the Brønsted–Evans–Polanyi (BEP) statistical principle$^{14}$); if a path has the lowest barrier, it should have the highest energy gain. The BEP principle is known to be valid for reactions occurring on the same catalytic surface, but often applied to other systems like nanoclusters.$^{14}$ In this study, an apparent violation of the BEP principle was observed for Cu–Au clusters, which we suggest can be due to a different nature of active sites at the cluster surface. One should also keep in mind that the BEP principle is valid only as a statistical trend and is often violated when looking at individual cases.

4. Conclusions

We performed a systematic study of CO oxidation on Cu–Au nanoclusters. First, the ground-state structures of Cu$_m$Au$_n$ clusters were determined in a wide area of compositions ($n + m \leq 15$) using the USPEX method combined with density-functional theory calculations. On the basis of the energies of the optimal clusters, we assessed the local stability for each one through the minimum second derivative of their energy with respect to the number of atoms of each kind. To estimate potential catalytic activity, we found the lowest coordination number in all considered structures. Next, we selected nine promising candidates, which are suggested to be both stable and catalytically active and considered 18 different reactions of CO oxidation on these clusters. For each reaction, we calculated the adsorption energies of CO and O$_2$, energies of the transition states, and of the intermediates along the minimal energy pathway. We showed that the activation energies are often not higher than $\sim 0.4$ eV, which can be overcome under mild conditions, and thus it might be expected that most part of the experimentally synthesized ensemble of clusters would have high catalytic activity. In some cases, extremely low activation barriers (0.02–0.11 eV) were found, which can be due to the characteristic features of the reaction mechanisms; for example, the second barrier strongly depends on the coordination of an adsorbed O* atom when CO$_2$ is desorbed from a cluster. We also found an often-occurring structural rearrangement of clusters during the reaction, which can affect the energy gain and facilitate desorption of oxygen from the cluster. We showed that the activation energies of catalytic CO oxidation on Cu–Au clusters are equal to or lower than those in pure Au clusters. In addition to the lower cost of copper, this makes copper–gold clusters a new promising class of catalysts.

Author contributions

Anastasia A. Mikhailova; conceptualization, methodology, data curation, investigation, writing – original draft, writing – review and editing, and visualization. Sergey V. Lepeshkin; methodology, formal analysis, investigation, writing – original draft, and visualization. Vladimir S. Baturin; methodology, formal analysis, investigation, writing – original draft, and visualization. Alexey P. Maltsev; investigation, formal analysis, and writing – original draft. Yurii A. Uspenskii; conceptualiz-
ation and writing – review and editing. Artem R. Oganov; conceptualization, supervision, and writing – review and editing. All co-authors contributed to the discussion of the data. All authors have given approval to the final version of the manuscript.

Conflicts of interest
The authors declare no competing financial interest.

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