



Article Catalytic Oxidation of Benzyl Alcohol to Benzaldehyde on Au₈ and Au₆Pd₂ Clusters: A DFT Study on the Reaction Mechanism

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Abstract: Density functional theory calculations were performed to investigate the reaction mechanism of the aerobic oxidation of benzyl alcohol to benzaldehyde catalyzed by Au and Au–Pd clusters. Two consecutive reaction mechanisms were examined with Au₈ and Au₆Pd₂ clusters: (1) the oxidation of benzyl alcohol with dissociated O atoms on metal clusters generating benzaldehyde and H₂O; and (2) oxidation with adsorbed oxygen molecules generating benzaldehyde and H₂O₂. The calculations show that the aerobic oxidation of benzyl alcohol energetically prefers to proceed in the former mechanism, which agrees with the experimental observation. We demonstrate that the role of Au centers around the activation of molecular oxygen to peroxide-like species, which are capable of the H–abstraction of benzyl alcohol. The roles of Pd in the Au₆Pd₂ cluster are: (1) increasing the electron distribution to neighboring Au atoms, which facilitates the activation of O₂; and (2) stabilizing the adsorption complex and transition states by the interaction between positively charged Pd atoms and the π -bond of benzyl alcohol, both of which are the origin of the lower energy barriers than those of Au₈.

Keywords: aerobic oxidation; benzyl alcohol; gold cluster; gold-palladium cluster; DFT

1. Introduction

Bimetallic systems have gained much attention in both academic and industrial research fields because they often exhibit advantageous properties such as catalytic, electronic, and optical properties, compared with those of their pure constituent metals [1–4]. Among the numerous metals that have been investigated in combination, Au–Pd bimetallic nanoclusters were found to be efficient catalysts for a wide variety of chemical reactions because they enable one to perform reactions under mild conditions, providing high selectivity for the desired products [1–7]. For instance, their excellent catalytic performance was shown for the direct synthesis of H₂O₂ [7–11], the synthesis of vinyl acetate [12,13], the epoxidation of alkenes [14,15], the hydrogenation of unsaturated hydrocarbons [16,17], the oxidation of greenhouse gases [18,19], coupling reactions [20–22], and the oxidation of alcohols to carbonylic compounds [23–39].

The oxidation of alcohols, in particular the selective oxidation of primary alcohols to aldehydes, is an important process for the synthesis of fine chemicals and highly valuable intermediates. The oxidation of alcohols is commercially conducted by stoichiometric oxygen donors, such as chromate or permanganate producing aldehydes. However, this



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). produces a large amount of toxic waste, which is environmentally unacceptable [40,41]. In this respect, a series of experimental studies have been devoted to developing catalysts to eliminate this drawback over the past two decades. Gold nanoclusters were reported to be effective catalysts for the selective oxidation of alcohols when used alone; however, significant stability and selectivity improvements were observed with the incorporation of a second metal promoter, such as Pd [5]. It was demonstrated that Au-Pd bimetallic clusters have remarkable catalytic activity for the selective oxidation of benzyl alcohol, which is one of the most frequently employed alcohols for the catalytic activity of a Au-Pd bimetallic catalyst under solvent-free conditions, and is comparable to, or even better than, Au catalysts [23–29]. Regarding mechanistic studies on AuPd bimetallic-catalyzed selective oxidation of benzyl alcohol, two different mechanisms of monometallic Au- and Pdsupported nanoparticles for alcohol oxidation have been proposed experimentally [42–44]: in the case of Au, the rate-determining step involves H-atom abstraction by a superoxo-like oxygen species adsorbed on Au, whereas, for Au–Pd, the rate-determining step is the H_{β} elimination of the adsorbed alkoxide forming the aldehyde [23]. Nevertheless, the precise reaction mechanisms of the Au-Pd bimetallic catalyst, in particular the mechanistic role of Au and Pd atoms in accelerating such reaction, remain the subject of considerable debate and are yet to be fully understood.

In the past decade, quantum chemical calculations have been widely applied to understand the structure and catalytic activity of various nanocluster catalysts, including gold and gold-based bimetallic systems [45–55]. Density functional theory (DFT) calculations with the generalized gradient approximation (GGA) functional have been frequently used because of their low computational cost, but some issues still remain with respect to their validity [54,55]. For example, GGA tends to overestimate the binding energy of O_2 on gold clusters compared with that calculated by CCSD(T) [54] and the reaction energies of the oxidation of methanol by CR-CC(2,3) [56]. However, it was demonstrated that the DFT calculations with M06-L [57] and M06 [58] functionals are practical choices for the theoretical study of nanoscale gold and gold-palladium catalysis [59–64]. Unlike with GGA approximations, the use of these functionals shows how to avoid overestimating the bond energies, leading to an accurate description of the 2D-to-3D structural transition of gold clusters. Karanjit et al. demonstrated that the use of M06 functionals and anionic Au_8 clusters is a suitable model for simulating the aerobic oxidation (oxidation with molecular oxygen) of methanol on PVP (N-vinyl-2-pyrrolidone) supported gold clusters [64]. However, the catalytic activity of Au–Pd clusters for the oxidation of benzyl alcohol has yet to be investigated using suitable modeling.

In this work, we performed a theoretical study to better understand how gold and palladium affect the energetics and the reaction mechanism of the aerobic oxidation of benzyl alcohol over Au_8 and Au_6Pd_2 using DFT calculations with the M06 functional. We examined the low-energy structures of Au_8 isomers and then constructed the low-energy structures of Au_6Pd_2 isomers as a simple model for Au-Pd bimetallic clusters enriched in gold atoms. Next, we investigated the possible reaction pathways as well as the role of Au and Pd in the oxidation reaction of benzyl alcohol to benzaldehyde on both Au_8 and Au_6Pd_2 clusters.

2. Results and Discussion

2.1. Structures of Au_8 and Au_6Pd_2

The Au₈ cluster was chosen as a model catalyst because, firstly, Au₈ is a stable gold cluster that can be detected in low-temperature experiments [65–69], and, secondly, it is one of the most commonly employed Au nanocatalysts in theoretical studies [69,70]. Subsequently, we performed a systematic search for the energetically minimum structures of Au₈ and Au₆Pd₂. AuPd is gold-rich and shows the optimum catalytic activity for the aerobic oxidation of alcohol, such as benzyl alcohol and cinnamyl alcohol without the formation of acid derivatives [27,71]. The lowest-energy structures of Au₈ and Au₆Pd₂ are shown in Figure 1 while other structures and the relative energies are provided in the Supplementary

Material (Figures S1 and S2 and Tables S1 and S2). The most stable of the Au₈ and Au₆Pd₂ structures have D_{4h} and nonplanar Cs symmetry, respectively, in which two Pd atoms of Au₆Pd₂ are located in the adjacent positions. It was found that the introduction of two Pd atoms in the Au₈ cluster slightly increases the partial charge at the neighboring Au atoms due to the lower electron affinity of the Pd atoms. This characteristic of Au₆Pd₂ clusters facilitates orbital interaction between O₂ and apex gold atoms, which induces the binding of O₂ to the Au₆Pd₂ cluster, which is described in the next section.



Figure 1. The lowest-energy structure of Au_8 and Au_6Pd_2 with Mulliken atomic charges, and NBO analysis.

The Mulliken charges presented in Figure 1 indicate that the charge distribution is not uniform over all the Au₈ atoms. High electron densities appear at the apex sites where the gold atoms are less coordinated; the highly coordinated gold atoms have a lower electron density. In the present case, the Mulliken charges provided a more reasonable picture than those obtained by natural bond orbital analysis (NBO). For instance, NBO charges at the apex sites of the metal nanoclusters appear to be positive, which is not reasonable considering the charge distribution and reactivity. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the Au₈ cluster, which are depicted in Figure 2a, reveal that HOMO is localized at low-coordinated gold atoms. This agrees well with the report of Metiu et al. [72], which demonstrates that the valence electrons of the gold cluster are not delocalized over the entire cluster, but localized at the apex, corner, and step. Localization of the HOMO on the apex sites of metal nanoclusters is correlated with the activation of a small molecule, i.e., O_2 , because it facilitates this molecule adsorbing effectively on apex sites. Although it was reported that the complete basis set limit (CBS) beyond the MP2 and CCSD(T) level of theory is required for predicting the dimensionality of the Au₈ cluster [73], the practical choice of DFT calculations with moderate basis sets which reproduce the results of wavefunction theories is useful for simulating the catalytic reactions of gold clusters. Accordingly, the hybrid meta-GGA functional and M06 functional employed in this study provide a similar trend in energetics and electronic properties when compared with previous theoretical studies. Based on the present results together with those of previous studies [59-64], it was reasonable to



adopt the present computational method for further calculations of the aerobic oxidation of benzyl alcohol.



2.2. Pathways and Energetics: The Formation of Benzaldehyde and H₂O

The catalytic cycle of the oxidation of benzyl alcohol examined in this work is schematically displayed in Figure 3. The adsorption of O_2 on the cluster is considered a first step for the aerobic oxidation of alcohols. First, we studied the adsorption behavior of O_2 on Au₈ and Au₆Pd₂ clusters. The optimized adsorption complexes are shown in Figure 4, and the structural parameters are provided in Table S3 of the Supplementary Material. In the case of Au₈, the O₂ molecule is most preferably adsorbed at the apex Au atom, which possesses the highest negative charge, followed by coadsorption with a benzyl alcohol molecule. The adsorption of O₂ has been reported as the initial step in the oxidation of methanol on gold clusters [59,60], because it results in a pronounced cooperative effect in the activation of molecular oxygen and catalytic activity for the oxidation of methanol. The O₂ molecule acts as the charge acceptor from Au₈ and Au₆Pd₂. The partial charges at apex Au atoms attached to O₂ decrease from $\delta q = -0.094$ to -0.081 and $\delta q = -0.145$ to -0.068 for Au₈ and Au_6Pd_2 clusters, respectively (Table S3). The partial charge on the O_2 molecule is δq = -0.181 and $\delta q = -0.213$ for Au₈ and Au₆Pd₂ clusters, respectively; the negative charge is enhanced in the Au_6Pd_2 cluster. Considering isolated species, O_2 and metal clusters (Figure 2a) illustrate the adsorption complexes, whereas the adsorbed O_2 illustrates the bent-triatomic bonding with the apex gold atom (Figure 2b). If the adsorption occurred by charge transfer from the Au cluster into a π^* -type orbital (LUMO) of O₂, we would expect that electrons would be gained in a spatial region resembling this orbital. This turned out to occur in the presented adsorption complexes we examined. The example is depicted in Figure 2b. The frontier orbitals of the adsorption complexes suggest that the overlapping of LUMOs between O₂ and apex gold atom readily induce the adsorption process. As a result, the O–O bond of the adsorbed O_2 molecules is increased to 1.29 and 1.30 Å for Au_8 and Au₆Pd₂ clusters, respectively. These O–O bonds are elongated in between the reported experimental values of O_2 (1.207 Å) [74] and O_2^- (1.347 Å) [75]. These results suggest that charge transfer occurs from the cluster to the adsorbed molecular oxygen, leading to the formation of a superoxo-like species, which was experimentally observed as an active species in the selective oxidation of alcohol [76].



Figure 3. Catalytic cycle of the aerobic oxidation of benzyl alcohol to benzaldehyde over Au₈ and Au₆Pd₂.



Figure 4. Frontier orbitals of the adsorption complex of Au₈ and Au₆Pd₂ with benzyl alcohol and O₂.

For the next step, various orientations between and benzyl alcohol on the Au₈ and Au_6Pd_2 clusters were taken into account for initially designed geometries. The most stable geometries optimized at the chosen level of theory are shown in Figures 4–7 and employed for the further step of the transition state search; meanwhile, other adsorption sites and configurations considered in this work are depicted in Figures S3 and S4 of the Supplementary Material. The energy profile from the adsorption of substrates to the generation of benzaldehyde and superoxo species is depicted in Figure 5. The calculated adsorption energy of O₂ and benzyl alcohol on the Au₆Pd₂ cluster is -26.8 kcal/mol, which is much larger than that on the Au₈ cluster of 11.4 kcal/mol. This result can be understood by analyzing the frontier molecular orbitals and the charges on the atoms of the adsorption complexes. The HOMO of the adsorption complexes is delocalized over Pd atoms and the benzene moiety of benzyl alcohol, whereas this characteristic is not observed over Au_8 (Figure 4). Moreover, the Mulliken charge analysis confirms a charge transfer from the benzene unit of benzyl alcohol to Pd atoms, whereby the charges on the Pd atoms decrease from $\delta q = 0.147$ to 0.101. These results suggest that, once the adsorption complex between benzyl alcohol and O_2 on Au–Pd bimetallic surface is formed, the interaction between positively charged Pd atoms and benzyl alcohol via π -bond interaction and the charge transfer from catalyst cluster to O_2 is significant for stabilizing this adsorption complex.

The Pd atoms not only enhance the electron density on the neighboring Au atoms and are responsible for the stability of the adsorption complex, but also significantly stabilize the transition state structures in the oxidation reaction. As shown in Figure 5, in the presence of two Pd atoms of Au₆Pd₂, the transition state of H–abstraction by a superoxo-like species (TS_1B) is much more stable than that of Au₈ (TS_1A); the energy barrier of Au₆Pd₂ is lower by 2.4 times than Au₈ (5.5 vs. 13.4 kcal/mol). The 2D to 3D evolution of the Au cluster at TS_1A and thereafter is expected, since the fully relaxed geometry optimization can change the cluster geometry considerably and/or its charge distribution [58] Consequently, the transition state structure reorients to form the interaction between the benzene fragment of benzyl alcohol and Au cluster. The transition state leads to the formation of a hydroperoxyl-like species, AuOOH (Int_1A and Int_1B), which is considered the key intermediate in the oxidation of alcohols [76] The relative energies of these intermediates were estimated

to be -8.1 and -22.6 kcal/mol for Au₈ and Au₆Pd₂, respectively. The difference in the stability of the intermediates is due to the benzylic alkoxide in the latter case occupying a bridge position between two positively charged Pd atoms, resulting in the stronger interaction, which is also indicated by the shorter bond distance of O–Pd compared with O–Au (2.17 vs. 2.25 Å). Subsequently, these key intermediates are transformed to either benzaldehyde and H₂O via H_β–abstraction (Figures 5 and 6) or benzaldehyde and H₂O₂ (Figure 7).



Figure 5. Calculated energy profile and optimized structures for the aerobic oxidation of benzyl alcohol over Au_8 and Au_6Pd_2 generating benzaldehyde and H_2O . All energy values are shown in kcal/mol and the distances are given in Å.

For the next step, the benzaldehyde formation via H_{β} -abstraction (TS_2A and TS_2B) readily occurs on the metal clusters and passes the H_{β} to the neighboring hydroperoxyllike species. Figure 5 shows that this step can be achieved with the energy barriers of 17.9 and 7.2 kcal/mol for Au₈ and Au₆Pd₂, respectively. The calculated activation energies are lower than those obtained from the competitive pathway (21.8 and 12.4 kcal/mol, respectively), which are discussed in the next section. The present result agrees well with the experimental observation in which the use of molecular oxygen as an oxidant in the oxidation of alcohols generates water as a byproduct [43,76]. After overcoming the low-energy barriers, TS_2A and TS_2B, benzaldehyde, and H₂O can be desorbed, leaving chemisorbed atomic oxygen in the bridge positions on Au₈ and Au₆Pd₂.



Figure 6. Calculated energy profile and optimized structures for the aerobic oxidation of benzyl alcohol over Au_8 and Au_6Pd_2 generating benzaldehyde and H_2O (cont'd). All energy values are shown in kcal/mol and the distances are given in Å.

The resultant chemisorbed atomic oxygen on the cluster (Au8-O and Au6Pd2-O species) can be removed by the reaction with another benzyl alcohol. The energy profile of this route with the intermediate and transition-state structures is shown in Figure 5. This reaction pathway is initiated by the adsorption of benzyl alcohol on the cluster, forming a hydrogen bond between the hydroxyl group and the atomic oxygen with calculated energies of -26.3 and -36.2 kcal/mol for Au₈ and Au₆Pd₂, respectively. The adsorption energies are substantially affected by the charge distribution and the relaxation near the bridge positions of the atomic oxygen. Table S5 in the Supplementary Material shows that the charge distribution of chemisorbed atomic oxygen on Au₆Pd₂ is more pronounced than on Au₈ ($\delta q = -0.663$ vs. -0.612), leading to strong hydrogen bonding and yielding a more stable adsorption complex. In the transition state, the O-H bond of benzyl alcohol is activated by chemisorbed atomic oxygen. In this case, an explanation for the high adsorption energies of this elementary step is the difference in the charge distribution for the atomic oxygen on catalyst clusters. For example, the negative charge on the chemisorbed atomic oxygen of the Int_4A and Int_4B is larger than that on the O1 atom of superoxo-like species in the Ads_A and Ads_B (-0.612 vs. -0.578, and -0.663 vs. -0.580, respectively). In other words, the atomic oxygen on Au₆Pd₂ possesses more basicity than on Au₈. This results in strong hydrogen bonding between the adsorbed atomic oxygen (proton acceptor) and the hydroxyl group of benzyl alcohol (proton donor) in Int_4. Subsequently, the dissociation of the O1–H1 bond and the formation of the O3–H1 bond occur. In this step, the atomic oxygen moves closer to the apex gold atom; meanwhile, the phenyl group of benzyl alcohol is only slightly affected in the course of the reaction. The calculated energy barriers relative to the adsorption complex were 9.5 and 3.4 kcal/mol for Au₈ and Au₆Pd₂, respectively. The resulting benzylic alkoxide occupies a bridge position on Au₈ and Au₆Pd₂, as was found in Int_1A and Int_1B. Subsequently, the H_β atom is transferred to a surface hydroxyl group with the optimized C–H_β distances of 1.28 and 1.19 Å for Au₈ and Au₆Pd₂, respectively; meanwhile, the C–O bond length shortens to 1.34 Å, indicating the characteristic of the carbonyl group produces benzaldehyde and H₂O. Consequently, the products, i.e., benzaldehyde and H₂O, are adsorbed at catalyst clusters with the calculated relative energies of -35.1 and -52.7 kcal/mol for Au₈ and Au₆Pd₂, respectively. These predicted reactions are exothermic; benzaldehyde and H₂O require desorption energies of 20.3 and 22.8 kcal/mol for Au₈ and Au₆Pd₂, respectively.



Figure 7. Calculated energy profile and optimized structures for the aerobic oxidation of second benzyl alcohol over Au₈-O and Au₆Pd₂-O species generating benzaldehyde and H₂O₂. All energy values are shown in kcal/mol and the distances are given in Å.

2.3. The Formation of Benzaldehyde and H_2O_2

As noted above, another possibility exists for the formation of benzaldehyde and H_2O_2 . The H_β -abstractions by oxygen atoms attached to the apex gold atoms occur while the interaction between the benzyl fragment of benzyl alcohol and the metal clusters is formed. Figure 7 shows that the activation energy of this step is 21.8 and 12.4 kcal/mol for Au₈ and Au₆Pd₂, respectively. These values are slightly higher than those obtained from the benzaldehyde formation with H_2O in the previous section. Thus, we finally conclude that the O–H bond cleavage activated by chemisorbed atomic oxygen is kinetically preferable to the superoxo-like species.

Comparing the energy barriers between the proposed reaction pathways, we found that the mechanism of H_{β} -abstraction requires higher activation energies than that of the O–H bond dissociation for both catalysts. Similar trends have also been reported in experimental [43,77–79] and theoretical [80] studies; the presence of a chemisorbed oxygen atom on the gold nanoparticle has a strong influence on the first step of the reaction, decreasing the barrier energy for the deprotonation of the alcohol hydroxyl group, but failing to enhance the dissociation of the C–H_{β} bond. Therefore, the latter step can be considered as the rate-determining step for alcohol oxidation on gold nanoclusters.

Overall, the energy profiles of reactions presented in this study show that the presence of Pd in the Au_6Pd_2 bimetallic cluster can significantly enhance the catalytic activity compared with the Au_8 monometallic cluster. This result agrees well with the reported experimental study whereby enhancements in the selectivity and conversion towards benzaldehyde were observed for gold-rich Au–Pd catalysts, which were maximized for Au_{80} –Pd₂₀ compared with palladium-rich ones [71]. Finally, we believe that the present insights into the reaction mechanism and energetics for the aerobic oxidation of benzyl alcohol to benzaldehyde might be useful for developing bimetallic catalysts for the aerobic oxidation of alcohols.

3. Computational Details and Models

All DFT calculations were carried out with the Gaussian09 suit of program [81]. We used hybrid meta-exchange-correlation functionals, the M06 functional, which has been shown to be a reasonably useful functional for studying the structures and catalytic activities of gold clusters, such as the dimensionality of gold clusters and various reactions [61–64]. All-electron calculations for the noble metals in the lower half of the periodic table are difficult; therefore, the scalar relativistic effective core potentials (RECP) for the Au (Xe core) and Pd (Kr core) atoms were applied to describe the core electrons. The LanL2DZ basis sets [82–84] were introduced to describe the outer shell (5s5p5d6s) of the Au atoms and the outer shell (4s4p4d) of the Pd atoms, where pure d and pure f functions were employed for all calculations. The 6-31G(d,p) basis sets were applied for H, C, and O atoms. Since it was reported that the Minnesota functionals are sensitive to the choice of the grid for numerical integrations, the ultrafine integration grid of Gaussian09 was used. In the optimization process, all metal clusters and substrates were allowed to fully relax without any symmetry constraints. The convergence thresholds of the optimization were set to the default values. All the optimized ground state structures were confirmed as local minima, vibrational analysis was performed on the optimized structures, and none of the imaginary frequencies were found. The transition state search was achieved using the QST3 version of the transit-guided quasi-Newton (STQN) method, with 30 images for both the forward and backward direction corresponding to the direction of the transition vector from the TS. All the optimized activated complexes and transition states consisted of only one imaginary frequency. The Mulliken and NBO charge analysis for the most stable structure of Au_8 and Au_6Pd_2 was evaluated using LANL2TZ. The final energy profiles were presented with the Gibbs energy change ($\Delta G^{\circ}_{298,15}$) obtained by frequency calculations with triple-zeta-quality basis sets; the 6-311++G(d,p) basis sets were employed for C, H and O atoms, whereas the LanL2TZ basis set was used for Au and Pd.

4. Conclusions

In this work, we showed how the presence of Pd in Au–Pd clusters can significantly affect the reaction energetics of the aerobic oxidation of benzyl alcohol to benzaldehyde. The results can be summarized as follows:

 The reaction is initiated by the activation of the O₂ molecule on a low-coordinated Au atom forming a peroxide-like species, followed by hydrogen abstraction from the hydroxyl group of benzyl alcohol. Subsequently, C–H_β bond dissociation occurs to produce either benzaldehyde and H_2O_2 or benzaldehyde and H_2O . The Au cluster is an effective catalyst, marking a significant improvement in the stability of the adsorbed substrates, as observed in the Au–Pd cluster.

- (2) The promotional roles of Pd in the Au-Pd cluster involve the enhancement in the electron distribution to the next-nearest-neighbor Au atom, which facilitates the activation of O₂ and substantially affects the stability of the adsorption complex and transition states, yielding low-energy barriers compared with the Au cluster.
- (3) The reaction preferentially proceeds via deprotonation of the O–H bond of benzyl alcohol followed by C–H_β bond dissociation, producing benzaldehyde and H₂O. Another possible reaction pathway for H₂O₂ formation can also be responsible for the reasonable catalytic activity of this reaction because of the low energy barrier.
- (4) The calculated energy profiles show that the activation of the O–H bond of benzyl alcohol is significantly facilitated by the presence of active oxygen species bound to the catalyst clusters (superoxide-like and chemisorbed atomic oxygen species), whereas the effect is reduced by the barrier for $C-H_{\beta}$ bond dissociation that occurs on both Au and AuPd clusters. Thus, the latter step is considered to be the rate-determining step, which is also in agreement with experimental observations.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10 .3390/catal11060720/s1, Figure S1: Optimized structures of Au₈, Figure S2: Optimized structures of Au₆Pd₂, Figure S3: Initial positions of benzyl alcohol, intermediates and products on Au₈ and Au₆Pd₂, Figure S4–S7: Optimized structures for the complexes between benzyl alcohol and O₂ on Au₈ and Au₆Pd₂ clusters, Table S1: The relative energy of the Au₈ isomers, Table S2: The relative energy of the Au₆Pd₂ isomers, Table S3–S7: Tables of structural parameters and Cartesian coordinates of all the species in this work.

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