

Article

Dissociative Adsorption of O₂ on Ag₃Au(111) Surface: A Density Functional Theory Study

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Abstract: The catalytic efficiency of oxygen reduction catalysts is notably influenced by the dissociative adsorption of O₂. We conducted a systematic investigation into the dissociative adsorption of O₂ on the Ag₃Au(111) surface using ab initio density functional theory (DFT) calculations. Our computational findings indicate that adsorption the configuration designated t-b-t exhibits favorable energetics on the Ag₃Au(111) surface. Regarding the dissociation of O₂, we identified a reasonable dissociation pathway, which proceeds from the initial t-b-t state to the creation of two oxygen atoms that occupy a set of neighboring fcc sites. Furthermore, our analysis indicates that the adsorption of O₂ on the Ag₃Au(111) surface is less favored thermodynamically and more difficult to dissociate than that on the Ag(111) surface. This study furnishes a theoretical framework elucidating the prospective utilization of Ag-Au alloy in the capacity of oxygen reduction catalysts.

Keywords: dissociative adsorption; density functional theory calculations; Ag₃Au(111) surface



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1. Introduction

Binary alloys are widely acknowledged for their remarkable catalytic properties and substantial potential in diverse catalytic reactions, garnering significant attention within the catalysis community [1–3]. These alloy catalysts demonstrate the ability to regulate the density and specificity of active sites on their surfaces to control the dissociative adsorption process in critical reactions, enhancing catalyst activity and selectivity [4–7]. Numerous investigations have highlighted the crucial role of dissociative adsorption of specific intermediates in various catalytic processes, which significantly impact catalytic performance [8]. For instance, Ou et al. [9] conducted an examination into the mechanisms underlying the oxygen reduction reaction (ORR) on palladium and platinum metal surfaces, revealing that the O₂ dissociative adsorption constituted the rate-determining step on both surfaces. This finding can be used to explain the common paradoxical phenomenon observed in the ORR, namely that Pt- and Pd-based catalysts are poorly bound to O₂, yet their catalytic performance is very good. A comparison of the ORR mechanisms on the Pt and Pd surfaces revealed that O₂ dissociative adsorption was more readily achieved on the Pt surface, resulting in enhanced catalytic performance. Maatallah et al. [10] employed density functional theory to assess the capacity of Al alloy clusters to store molecular hydrogen and their performance as catalysts for hydrogenation reactions. The results demonstrated the pivotal role of dissociative adsorption of hydrogen molecules for applications in hydrogenation reactions and hydrogen storage within heterogeneous catalysis. The enhancement in hydrogen storage and catalytic performance of Al alloy clusters can be attributed to the expansion in the number of adsorption sites on the cluster surface. Mortensen et al. [11] conducted thorough energetic calculations of N₂ dissociative adsorption on Fe(111) surfaces, confirming that the rate-limiting step in ammonia synthesis is the dissociative adsorption of nitrogen molecules. Two distinct pathways were identified for the N₂ dissociation. During ammonia synthesis conditions, N₂ dissociation predominantly follows a low-barrier

pathway. However, at the highest synthesis temperature, N_2 dissociation predominantly follows a high-barrier pathway. Liu et al. [12] investigated the activity of Au-Cu alloy nanoparticles as catalysts for CO oxidation. The results indicate that the O_2 dissociative adsorption is a pivotal step that limits the oxidation rate of CO. The alloying of Au with Cu can result in the tuning of the electronic structure of the surface, which in turn affects the dissociative adsorption capacity of gas molecules and the stability of the reaction transition state. By adjusting the alloy compositions and ratios, it is possible to achieve precise tuning of the surface electronic structure in order to optimize the catalytic performance. Therefore, a thorough understanding of these fundamental reaction steps is essential in guiding the design of effective binary catalysts.

Ag-based binary alloys have garnered extensive utilization across a spectrum of catalytic reactions, including hydrogenation [13], dehydrogenation [14], water–gas shift [15], selective oxidation [16], methanol steam reforming [17], methanol oxidation [18], and others. In the context of the ORR, Pt and Pt-based alloys are considered to be the most efficient ORR catalysts [19]. However, their scarcity in nature and high cost have severely hindered their widespread use in practice [20,21]. In order to obtain cost-effective and highly active ORR catalysts, it is necessary to identify a more suitable catalyst to replace Pt. Currently, Ag is the catalyst that can achieve this goal due to its low cost and acceptable catalytic activity, particularly in alkaline environments where it exhibits high stability. Many previous investigations have established that the catalytic activity of Ag can be significantly enhanced, potentially surpassing that of Pt, by forming Ag alloys [22–24]. Notably, alloying Ag with specific transition metals like Au has demonstrated a substantial augmentation in the electro-catalytic performance of Ag towards the ORR [25,26]. This augmentation is ascribed to alterations in the structure of the metal surface, directly influencing the O_2 dissociative adsorption process at the catalyst surface, thus modulating the rate, selectivity, and stability of the catalytic reaction [27–30]. Despite the recognized importance of the dissociative adsorption step of O_2 in regulating the performance of the ORR, theoretical studies carried out on Ag-based binary catalysts are scarce.

In this study, *ab initio* DFT calculations were employed to explore the dissociative adsorption of O_2 on the $Ag_3Au(111)$ surface. Our computational findings indicate that the adsorption configuration designated t-b-t exhibits favorable energetics on the $Ag_3Au(111)$ surface. Regarding the dissociation of O_2 , we identified a reasonable dissociation pathway, which proceeds from the initial t-b-t state to the creation of two oxygen atoms that occupy a set of neighboring fcc sites. Furthermore, our analysis indicates that the adsorption of O_2 on the $Ag_3Au(111)$ surface is less favored thermodynamically and more difficult to dissociate than that on the $Ag(111)$ surface. The remainder of this article is structured as follows. In Section 2 we present the computational details. In Section 3 we elucidate the results and analysis derived from our investigations, followed by conclusions in Section 4.

2. Computational Details

The periodic DFT calculations were performed using the Vienna *ab initio* simulation package (VASP) [31–33] to iteratively solve the Kohn–Sham equations in a plane-wave basis set. The projector augmented wave (PAW) method [34,35] was used to treat core electrons and their interaction with valence electrons. The exchange–correlation energy was described by the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional [36]. The GGA-PBE functional was selected for the following reasons: Firstly, the GGA-PBE functional has already been used to investigate the O_2 adsorption in the $Ag(111)$ surface [37]. Secondly, the lattice constants of Ag, calculated using the GGA-PBE function, have been found to be quite accurate in comparison with other functions [38]. The Hubbard U correction was disregarded, as the effect on the calculated results of adsorption energies is deemed to be minimal. Spin polarization was taken into account, and the plane-wave cutoff energy optimized at 400 eV. The Brillouin zone was sampled with a $5 \times 5 \times 1$ k-point mesh of the Monkhorst-pack [39]. The converge criteria for electronic self-consistency and force were 10^{-5} eV and 0.02 eV/Å, respectively.

In this study, we selected $\text{Ag}_3\text{Au}(111)$ to investigate O_2 dissociative adsorption at the Ag-Au surface. The reasons for choosing the (111) surface are as follows: Firstly, the (111) surface is often thermodynamically stable for Ag alloys [38]. Stability is crucial for ensuring that the surface structure remains representative during the course of the experiments or simulations. Secondly, the (111) surface of Ag is often considered to be reactive and plays a crucial role in catalytic processes [40,41]. The O_2 dissociative adsorption may occur preferentially on the (111) surface [37]. Thirdly, the (111) surface is computationally more tractable than higher-index surfaces while still providing valuable insights into surface reactivity [41]. Simulating reactions on more complex surfaces can be computationally expensive, and (111) surfaces strike a balance between computational cost and accuracy. Fourthly, the (111) surface has high symmetry, which can simplify theoretical calculations [42]. High symmetry often leads to fewer surface atoms that need to be considered during simulations, making calculations more computationally efficient. The ordered Ag_3Au bimetallic alloy adopts an L_{12} fcc-type structure. The (111) surfaces of $\text{Ag}_3\text{Au}(111)$ (Figure 1a) and $\text{Ag}(111)$ (Figure 1b) were modeled utilizing periodic four-layer slabs within a $p(2 \times 2)$ unit cell, with each surface layer comprising four atoms. An initial slab cell was augmented with a vacuum layer 15 Å thick. In order to effectively emulate the characteristics of both bulk and surface environments, positional constraints were applied to the atoms within the bottom two layers, while the relaxation was allowed for all other atoms. An O_2 molecule was introduced to the surface of the computational model. In accordance with the Langmuir adsorption model [43], the coverage was determined as the proportion of the solid surface area occupied by the adsorbate relative to the total surface area of the solid. Consequently, the surface coverage of O_2 was calculated to be one-fourth of a monolayer (1/4 ML). In accordance with the standard methods [44], the electric dipole was deemed inconsequential in terms of its impact on the calculated energy values, so it was neglected in our DFT calculation. We determined the bulk lattice constants to be 4.14 Å for Ag_3Au and 4.15 Å for pure Ag through DFT calculations, aligning with findings from prior studies [22,23].

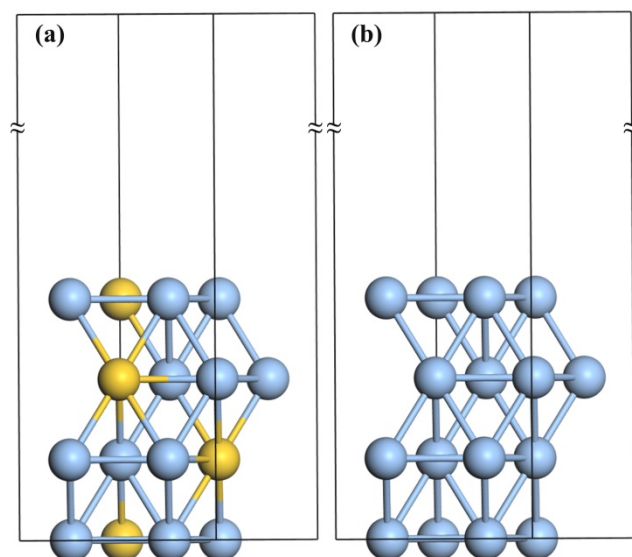


Figure 1. The slab models, which consist of the (a) $\text{Ag}_3\text{Au}(111)$ surface and (b) pure $\text{Ag}(111)$ surface. In the figure, silvery and gold balls represent Ag and Au atoms, respectively.

The adsorption energies ($E_{\text{ads},\text{O}_2}$) at different adsorption sites were calculated from the following expression:

$$E_{\text{ads},\text{O}_2} = E_{\text{O}_2\text{-slab}} - E_{\text{slab}} - E_{\text{O}_2}. \quad (1)$$

In this equation, $E_{\text{O}_2\text{-slab}}$ is the total energy of the adsorbate–surface system, E_{slab} is the total energy of the clean surface, and E_{O_2} is the energy of the isolated O_2 in gas phase.

The climbing-image nudged elastic band (CI-NEB) method is a computational method employed to identify transition states in chemical reactions [45,46]. We used this method to study the transition states and minimum energy path (MEP) for O₂ dissociation on the Ag₃Au(111) surface. The method employs a two-step process. Initially, the reaction path between the initial and final states is identified, and a series of images (representing different conformations) are placed on this path in a uniform manner. Each image is then energy optimized to align with the energy fluctuations along the reaction path and constraints are imposed to ensure that the images remain on the path. The path is further optimized by utilizing the nudged elastic band (NEB) method, which guides each image along the path towards the transition state. Concurrently, the image with the highest energy (representing the potential transition state) is directed along the energy gradient until the transition state is reached. It is important to note that in our calculations, all transition states are determined by frequency calculations, and each transition state corresponds to a single imaginary frequency. The activation energy (E_a) was calculated from the following expression:

$$E_a = E_b^{TS} - E_b^{PS}. \quad (2)$$

In this equation, E_b^{TS} and E_b^{PS} are the total energies of the transition state and the precursor state, respectively.

The d-band center is the location of the center of the d-electron band energy of a transition metal surface and is commonly used to describe the catalytic activity of a transition metal surface for chemical reactions, and is calculated as follows:

$$\varepsilon_d = \frac{\int_{-\infty}^{+\infty} E\rho(E)dE}{\int_{-\infty}^{+\infty} \rho(E)dE}, \quad (3)$$

where E and $\rho(E)$ are the given energy and the density of electronic states, respectively.

3. Results and Discussion

3.1. The Adsorption of O₂

According to a previous study [47], it can be found that there are three distinct adsorption sites for O₂ on the Ag(111) surface, which are t-h-b, t-f-b, and t-b-t. In this study, we focus on exploring the adsorption behavior of O₂ at these three adsorption sites. Figure 2 illustrates the stable adsorption configurations of O₂ at these sites on the Ag₃Au(111) surface, with corresponding computational results summarized in Table 1. Observations from Table 1 indicate that O₂ adsorption is most stable at the t-b-t site. The bond lengths of O₂ adsorbed on the Ag₃Au(111) surface are shorter than those adsorbed on the Ag(111) surface, a phenomenon that may be due to the weakened interaction between O₂ and the alloy surface [4,48]. Additionally, the investigation reveals a reduction in the number of electrons acquired by O₂ when interacting with the Ag₃Au(111) surface in contrast to the Ag(111) surface, indicative of alterations in the electronic structure attributed to the alloying of Ag with Au, hindering electron transfer to O₂. Moreover, O₂ adsorption energy on the Ag₃Au(111) surface is found to be lower than that on pure Ag(111). For instance, at the most stable t-b-t site, O₂ adsorption energy on the surface of Ag₃Au(111) is recorded as −0.139 eV, in contrast to −0.243 eV on Ag(111), consistent with prior computational findings [47]. Previous studies [49–51] have highlighted the significance of weak oxygen binding to the catalyst surface in facilitating efficient oxygen reduction reactions, as it promotes rapid electron and proton transfer, thus favoring the reduction of H₂O molecules. Conversely, strong oxygen binding on the catalyst surface impedes protonation and occupies active sites, resulting in elevated overpotentials during the reaction [51]. Therefore, the lower O₂ adsorption energy on the Ag₃Au(111) surface lends further support to the notion that modification of the Ag surface with Au can increase the activity of the ORR.

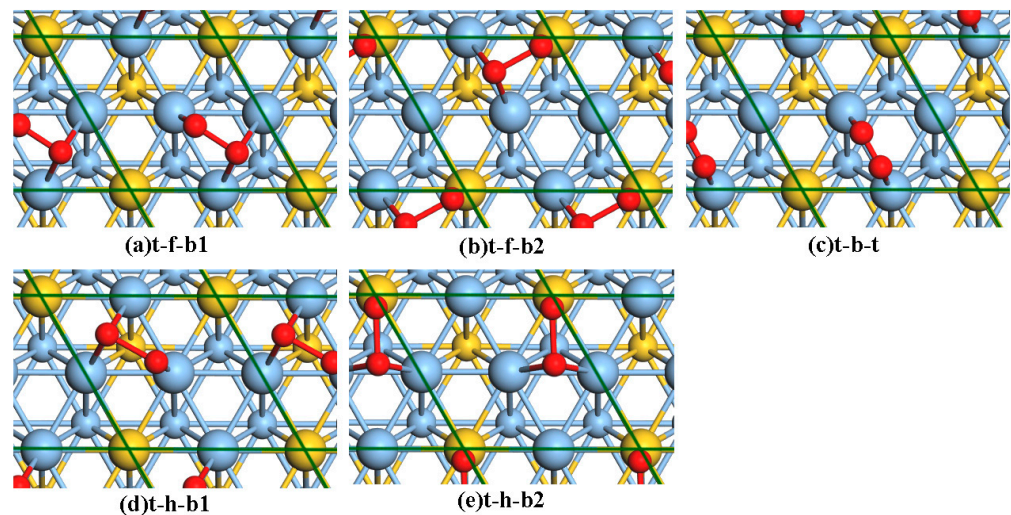


Figure 2. Top view of the stable adsorption configurations of O_2 on the $Ag_3Au(111)$ surface. The silver, gold, and red spheres represent Ag, Au, and O atoms, respectively. For clarity, only the top two atomic layers are shown, and larger spheres are used to represent the atoms in the topmost layer.

Table 1. The DFT-calculated adsorption energies of O_2 (E_{ads} in eV), bond lengths of O_2 (d_{O-O} in Å), and the number of electrons gained by O_2 (N_{chg}) from the Ag(111) and $Ag_3Au(111)$ surfaces.

$Ag_3Au(111)$				Ag (111)			
Site	E_{ads}	d_{O-O}	N_{chg}	Site	E_{ads}	d_{O-O}	N_{chg}
t-f-b1	−0.095	1.308	0.503	t-f-b	−0.196	1.316	0.544
t-f-b2	−0.088	1.307	0.492	t-h-b	−0.189	1.317	0.545
t-h-b1	−0.118	1.305	0.488	t-b-t	−0.243	1.307	0.496
t-h-b2	−0.052	1.304	0.482				
t-b-t	−0.139	1.299	0.455				

3.2. The Electronic Structure of $Ag_3Au(111)$ Surface

In DFT theoretical calculations, the interaction mechanism between adsorbed molecules and surfaces can usually be understood in detail by analyzing the d-band density of states (DOS) [52,53]. This is because during surface adsorption, the interaction between the metal atoms on the surface and the adsorbate leads to the movement of the d-band center. Specifically, when an adsorbate adsorbs to a surface, it affects the electron distribution of the surface metal atoms, leading to a change in the position of the d-band center. This change may affect the chemical reaction activity of the surface metal atoms. For example, when the d-band center moves away from the Fermi level, it increases the energy of the anti-bonding state, which diminishes the interaction strength between the adsorbate and the surface. On the contrary, when the d-band center moves towards the Fermi level, the adsorbate–surface interaction energy may increase, thus enhancing the binding capacity of the adsorbate to the surface. To further understand the interaction between oxygen molecules and the catalyst surface, we conducted calculations of the d-band DOS for Ag atoms situated within the outermost layers of $Ag_3Au(111)$ and Ag(111) surfaces in the absence of gas adsorption. The results are depicted in Figure 3. The observed disparity reveals that the d-band center of Ag on the $Ag_3Au(111)$ alloy surface is more distant from the Fermi level compared to that on the Ag(111) surface. In accordance with the d-band model [54,55], this divergence suggests that the O_2 adsorption energy on the Ag(111) surface exceeds that on the $Ag_3Au(111)$ surface, consistent with our calculations above.

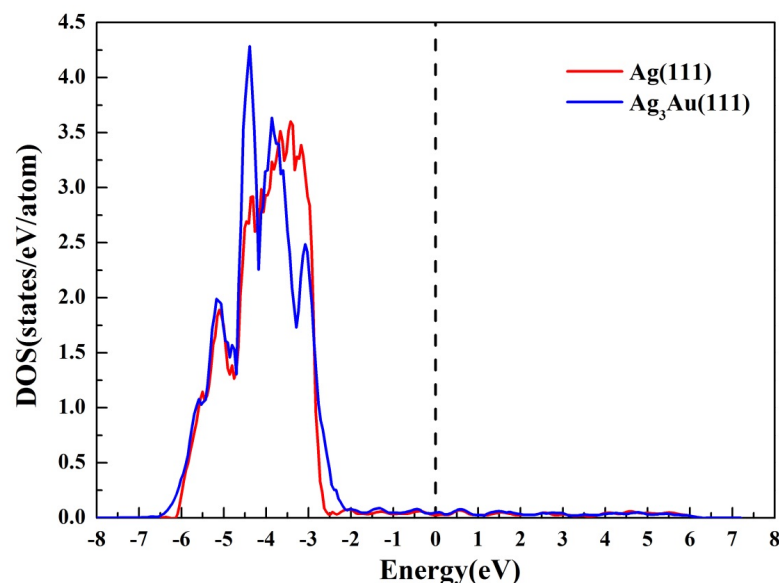


Figure 3. The d-band DOS for Ag atoms situated within the outermost layers of Ag₃Au(111) and Ag(111) surfaces in the absence of gas adsorption.

There are two main factors that can affect the d-band center, which are the ligand (electronic) effect and the strain (geometrical) effect [56–58]. In order to investigate the influence of the ligand effect on the O₂ adsorption behavior, a Bader charge analysis was conducted on the Ag₃Au(111) and Ag(111) surfaces. The calculations indicate that Ag atoms situated in the outermost atomic layer of Ag₃Au(111) receive a greater number of electrons compared to the corresponding Ag(111) surfaces. These electrons are primarily derived from their neighboring Au atoms. However, the accumulation of excess electrons on the alloy surface leads to the enhancement in electrostatic repulsion [59], which indirectly leads to a decrease in the adsorption strength of O₂ on the alloy surface. This finding is consistent with the calculations in Table 1. Therefore, the ligand effect will be a factor affecting O₂ adsorption behavior on the Ag₃Au(111) surface. In order to investigate the influence of strain effect on the O₂ adsorption behavior, the Ag–Ag interatomic distances were investigated. Since the radii of Ag and Au atoms are equal, this would result in the Ag–Ag interatomic distances on the surface of Ag₃Au(111) being almost equal to the Ag–Ag interatomic distances on the surface of Ag(111). Therefore, the strain effect has little influence on the change in the d-band center of the Ag atoms on the alloy surface. Another factor (ligand effect) will be the main controlling factor affecting the O₂ adsorption behavior on the Ag₃Au(111) surface.

3.3. The Dissociation of O₂

In surface-catalyzed reactions, the transition state plays a pivotal role. The transition state is the critical state between reactants and products in a chemical reaction, representing an intermediate state in the transformation of reactants into products. In catalytic reactions, the formation of the transition state necessitates overcoming an energy barrier, which reflects the energy required for the conversion of reactants into products. The formation and stability of the transition state directly influence the rate and selectivity of the reaction. Catalysts facilitate the reaction by lowering the energy barrier required for the conversion of reactants to transition states. Active sites on the surface of a catalyst can provide a suitable environment for reactants to combine and form transition states on its surface, thus lowering the energy barrier for the reaction. In addition, the chemical properties of the catalyst surface can also interact with the reactants to change the structure and energy of the transition state, further affecting the rate and selectivity of the reaction. Consequently, for surface-catalyzed reactions, a comprehensive understanding of the structure and properties

of the transition states is crucial for the design of efficient catalysts and the optimization of reaction conditions.

The CI-NEB method is employed to identify transition states in molecular dynamics, with particular relevance to chemical reaction pathways. Prior to utilizing the CI-NEB method, it is essential to define the initial and final states of the reaction. These two states serve as a foundation for identifying the optimal transition state. In this chemical reaction, we choose the most stable t-b-t configuration as the initial state without considering other stable configurations (e.g., t-f-b1, t-h-b1, t-f-b2, t-h-b2). The reasons for this are as follows: Firstly, using the most stable structure as the initial state ensures that the calculated reaction paths and transition states are the most probable and most relevant paths [6]. Secondly, the most stable initial state provides a clear energy reference for the entire reaction path [2]. Thirdly, starting the calculation from the most stable structure allows for faster convergence to the correct transition state. Fourthly, starting with the most stable structure is more consistent with physical and chemical reality [4]. Fifthly, choosing the most stable initial state reduces the problem of path bifurcation encountered during calculations. As O₂ molecules adsorb onto the surface of the alloy and undergo dissociation, the resultant oxygen atoms are inclined to occupy adjacent fcc sites, thereby establishing the final state. This results in an O₂ dissociation pathway as shown in Figure 4, i.e., a dissociation pathway that starts from the t-b-t state and ends with the 2 × fcc state. In this dissociation pathway, the O₂ adsorbed at the t-b-t site rotates and two oxygen atoms occupy the bridge site, forming a transition state (TS). The energy barrier associated with this transition state was calculated to be 1.12 eV. Subsequently, with the horizontal stretching of the O-O bond, two O atoms move from the bridge sites to the neighboring fcc sites, which finally completes the dissociation process.

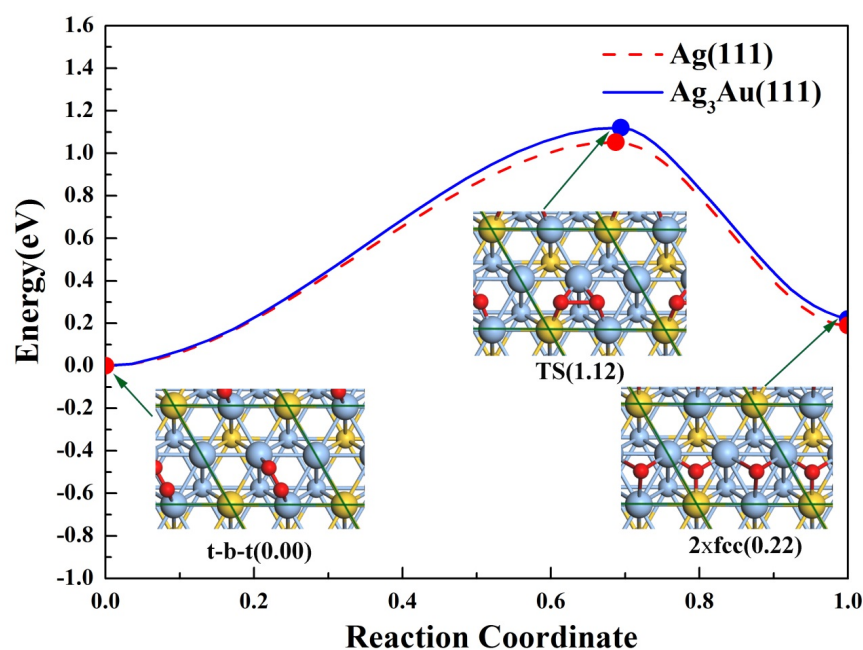


Figure 4. The O₂ dissociation pathway on the Ag₃Au(111) and Ag(111) surfaces. The pathway starts from the t-b-t state and ends with the 2 × fcc state.

As illustrated in Figure 4, the formation of a transition state typically necessitates the surmounting of an energy barrier, which is defined as the energy difference between the reactants and the transition state. This energy barrier typically manifests as an additional energy requirement that must be absorbed in order for the reaction to proceed to the transition state. Consequently, the formation of the transition state during an electro-catalytic reaction is significantly endothermic. To ascertain whether the entire catalytic reaction process is endothermic or exothermic, it is necessary to calculate the energy

differences between the products and reactants. When the values are negative, this indicates that the entire catalytic reaction process is exothermic. Conversely, when the values are positive, this indicates that the entire catalytic reaction process is endothermic. As illustrated in Figure 4, the dissociation of O_2 on the surface of $Ag_3Au(111)$ is endothermic. This indicates that the dissociation process of O_2 is energetically unfavorable and requires an external energy supply in order to proceed. Such reactions typically necessitate external energy inputs, such as electricity, light, or heat, under industrial and laboratory conditions.

In order to deepen our comprehension of the dissociation mechanism of O_2 on the $Ag_3Au(111)$ surface, we conducted an additional investigation into the dissociation process of the $O_2/Ag(111)$ system, with the findings presented in Figure 4. Examination of the figure reveals a notable similarity between the dissociation pathways of the $O_2/Ag(111)$ and $O_2/Ag_3Au(111)$ systems. In this dissociation pathway, the O_2 adsorbed at the t-b-t site also rotates and two oxygen atoms occupy the bridge site, forming a transition state (TS). However, the dissociation energy barrier observed for the $O_2/Ag(111)$ system is comparatively lower, measuring 1.05 eV, a result consistent with prior research [47,60]. This phenomenon is also frequently observed in Pt alloys when the ORR is being investigated. Previous ORR mechanism studies have identified two dissociation mechanisms for O_2 molecules adsorbed on the catalyst surface. The first mechanism is the direct dissociation of O_2 molecules into two O atoms, while the second mechanism is the combination of O_2 molecules with H ions to produce OOH. Among these two mechanisms, the level of the dissociation energy barrier determines the O_2 dissociation mechanism. In comparison to the $Ag(111)$ surface, the O_2 molecule on the $Ag_3Au(111)$ surface exhibits a higher dissociation energy barrier. This indicates that the second mechanism is more favorable for the O_2 dissociation. Consequently, it is quite difficult for O_2 to dissociate directly into two O atoms on the $Ag_3Au(111)$ surface. Instead, O_2 is more likely to combine with H ions to form OOH during the oxygen reduction reaction. This further explains that, despite the O_2 dissociation energy barrier being higher on the $Ag_3Au(111)$ surface than on the $Ag(111)$ surface, alloying Ag with Au is observed to enhance the catalytic performance of Ag alloys in experimental studies [25,26].

4. Conclusions

We employed ab initio DFT calculations to explore the dissociative adsorption of O_2 on the surface of $Ag_3Au(111)$. Computational findings reveal that the t-b-t sites were identified as the most stable for O_2 adsorption on both $Ag_3Au(111)$ and $Ag(111)$ surfaces. Their adsorption energies were -0.139 and -0.243 eV, respectively. The bond lengths of O_2 adsorbed on the $Ag_3Au(111)$ surface are shorter than those adsorbed on the $Ag(111)$ surface; this may be due to the weakened interaction between O_2 and the alloy surface. Bader analysis indicates a reduction in the number of electrons acquired by the adsorbed O_2 on the $Ag_3Au(111)$ surface, possibly due to alterations in the surface's electronic structure resulting from alloying, which could impede electron transfer to O_2 . The analysis of the electronic structure shows that the d-band center of Ag on the $Ag_3Au(111)$ alloy surface is more distant from the Fermi level compared to that on the $Ag(111)$ surface. This suggests that O_2 adsorption energy on the $Ag(111)$ surface exceeds that on the $Ag_3Au(111)$ surface. Furthermore, upon analysis of the factors influencing the center of the d-band in the alloy catalysts, it is evident that the reduced stability of O_2 adsorption on the surface of $Ag_3Au(111)$ may be attributed to the ligand effect. Regarding the dissociation of O_2 , we identified a reasonable dissociation pathway, which proceeds from the initial t-b-t state to the creation of two oxygen atoms that occupy a set of neighboring fcc sites. Notably, O_2 has a higher dissociation energy barrier on the surface of $Ag_3Au(111)$ than on the surface of $Ag(111)$. This indicates that the adsorption of O_2 on the $Ag_3Au(111)$ surface is more difficult to dissociate than that on the $Ag(111)$ surface, and also well explains the ORR mechanism, namely that the OOH is the first reduction product due to the high activation energy barrier for the O_2 dissociation. This study furnishes a theoretical framework elucidating the prospective utilization of Ag-Au alloy in the capacity of oxygen reduction catalysts.

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