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A Theoretical Study of O₂ Activation by Au₇-Cluster on Mg(OH)₂: Roles of Surface Hydroxyls and Hydroxyl Defects

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ABSTRACT: Using density functional theory (DFT) calculations, we investigated O₂ activation by Au₇-cluster supported on the perfect and hydroxyl defective Mg(OH)₂(0001) surface. It is revealed that, hydroxyl groups on the perfect Mg(OH)₂(0001) surface can not only enhance the stability of Au₇-cluster, but also help the adsorption of O₂ molecule through hydrogen-bond interactions with the 2nd-layered interfacial Au sites. Density of states (DOS) analysis shows that the d-band centers of the 2nd-layered interfacial Au atoms are very close to the Fermi level, which thereby reduces the Pauli repulsion and promotes the O₂ adsorption. These two responses make the 2nd-layered interfacial Au atoms favor O₂ activation. Interestingly, the surface hydrogen atoms activated by the 1st-layered Au atoms can facilitate the O₂ dissociation process as well. Such process is dynamically favorable and more inclined to occur in low temperatures than the direct dissociation process. Meanwhile, hydroxyl defects of Mg(OH)₂(0001) locating right under the Au₇-cluster can also shift up the d-band centers of the surrounding Au atoms toward the Fermi level, enhancing its catalytic activity for O₂ dissociation. On the contrary, the d-band

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center of Au atoms surrounding the hydroxyl defect near the Au₇-cluster exhibits an effective down-shift to lower energies, and therefore holds low activity. These results unveiled the roles of surface hydroxyls and hydroxyl defects on Au/Mg(OH)₂ catalyst in O₂ activation and could provide theoretical guidance for chemists to efficiently synthesize Au/hydroxide catalyst.

1. INTRODUCTION

Gold-based catalysts have received considerable attentions in the past decades because of their extraordinary activities in a wide variety of important catalytic conversions.^[1-7] Among them, the catalytic oxidation reactions that use O₂ as oxidant have attracted the highest interest and are most extensively studied.^[8-14] In this field, the general consensus is that the binding and activation of O₂ is the key elementary step with respect to catalytic activity.^[15-17] However, as the most inert transition metal, pure gold surface is quite inactive for O₂ adsorption and activation. In order to improve the catalytic activity, various promotion measures have been investigated, such as the size and morphology control of gold particle,^[18-21] the import of water vapor in the reaction stream,^[22,23] and the optimization of preparation method.^[24,25] Moreover, it is reported recently that the type and morphology of support are also crucial to activity.^[26-30] Therefore, besides the above measures, the choice of suitable support for gold nanoparticles has become a good promoting method as well.

In recent years, gold nanoparticles on different supports have been extensively studied.^[28-34] Among these multifarious types of supports, the hydroxide support is perhaps the most special one, since it provides a unique hydroxyl surface environment

for gold nanoparticles. It is found that the low temperature CO oxidation activity of gold nanoparticles on the hydroxide supports is much higher than that on the traditional oxide supports.^[31-34] Therefore, the synthesis of Au/hydroxide catalysts is growing into new popular fields of study. To date, different promoting mechanisms regarding O₂ activation on Au/hydroxide catalysts have been proposed. On Au/Mg(OH)₂, Haruta et al. conduct X-ray adsorption spectroscopy studies to show that the subnanometer gold clusters on the surface have large contribution to the Mg(OH)₂-supported gold's activity.^[35] By comparing to those typical Au/oxide catalysts (such as Au/MgO^[36], Au/SiO₂^[37] and Au/TiO₂^[38]), experimental studies revealed that the hydroxylation of support surface can effectively enhance the stability of small gold nanoparticles and further promote their catalytic activities.

All of those exciting experimental breakthroughs thus invoke many theoretical works aiming to get a clear and detailed explanation for the internal promoting mechanisms of hydroxyl groups. Simulation results have revealed that the generation of Au-OH bonds can enhance the stability of the composite catalyst and lead to effective charge transferring between gold nanoparticles and support.^[39,40] However, there are still many important issues remaining unclear, such as the roles of hydroxyl groups in promoting the activity of gold nanoparticles, the oxygen binding and activation mechanisms on Au/hydroxide catalysts, and the effects of hydroxyl defects. The resolving of these issues will have important implications for the oxidation processes on Au/hydroxide catalysts.

In the present work, the Au/Mg(OH)₂ system is chosen as a model system to

perform density functional theory (DFT) calculations, so as to probe the catalytic roles of surface hydroxyl groups and hydroxyl defects in O_2 activation. Here the $Mg(OH)_2$ support offers an ideal hydroxyl platform to investigate the interactions between gold nanoparticles and hydroxyl groups. The majority of this work is aimed at gaining a detailed theoretical understanding of O_2 activation on the Au/hydroxide catalyst and of the main influence factors on its catalytic activities.

2. COMPUTATIONAL DETAILS AND MODELS

All the DFT calculations were performed by using codes from Vienna Ab Initio Simulation Package (VASP).^[41] The interactions between ions and electrons were described by the projector augmented wave (PAW) method.^[42-44] The Perdew-Burke-Ernzerhof (PBE)^[45] functional was employed for the calculation of nonlocal exchange-correlation energy. A plane wave basis set with a cutoff energy of 400 eV was used for treating valence electrons, and the convergence criterion of energy was 10^{-5} eV. Fully structural relaxation was performed until the forces on all unconstrained atoms were ≤ 0.02 eV/Å. $2 \times 2 \times 1$ and $9 \times 9 \times 1$ κ -point grids determined by the Monkhorst-Pack were used for geometry optimization and DOS calculation, respectively. The transition states for the disassociation of O_2 were searched by climbing image nudged elastic band (CI-NEB) method integrated in VASP.^[46,47]

The optimized bulk $Mg(OH)_2$ primitive cell parameters of $a=b=3.142$ Å, $c=4.766$ Å, were within 1% of the experimental values^[48], $a=b=3.145$ Å, $c=4.769$ Å. The (0001) surface of $Mg(OH)_2$ was modeled using a 5×5 supercell with dimensions of 15.71 Å

$\times 15.71 \text{ \AA} \times 19.10 \text{ \AA}$. The perpendicular direction of the slab was separated by a $15 \text{ \AA}$ vacuum layer which was long enough to screen the self-interaction effects of the periodic boundary conditions. The two-dimensional (2D) Au_7 -cluster which was reported as a highly reactive cluster for CO oxidation^[49] was optimized in a unit cell of $15 \text{ \AA} \times 15 \text{ \AA} \times 15 \text{ \AA}$ and only the Γ -point was used. The initial bond length and bond angle of Au_7 -cluster were referred to the Au(111) surface which was reported as a common exposed surface for Au clusters on $\text{Mg}(\text{OH})_2$ support.^[32,35] During geometry optimization, all the atoms in the slab were allowed to relax.

The binding energies of the adsorbates are calculated following the equation:

$$E_b = E_{\text{sur+ad}} - E_{\text{sur}} - E_{\text{ad}},$$

where

$E_{\text{sur+ad}}$ is the total energy of the slab with the adsorbates on the surface,

E_{sur} is the total energy of the bare slab of the surface, and

E_{ad} is the total energy of the adsorbate species.

Therefore, a positive value of E_b means gaining energy during adsorption.

3. RESULTS AND DISCUSSION

3.1. O_2 Adsorption and Dissociation on the Au_7 -Cluster Supported on Perfect $\text{Mg}(\text{OH})_2$ (0001) Surface. The binding structures of Au_7 -cluster on $\text{Mg}(\text{OH})_2(0001)$ surface are first examined. After trying a variety of possible composite configurations, four stable models were obtained, as seen in Figure 1. The optimized structures show that the generation of Au-OH bonds can significantly enhance the stability of the adsorption state and the binding energy increases with the number of Au-OH bonds,

which is consistent with previous studies^[39]. Therefore, the **(Per-Au₇-4)** state which contains more Au-OH bonds and has the lowest binding energy is chosen as the model system for further O₂ adsorption. From Figure 2, one can see that when the Au₇-cluster is stably adsorbed on the Mg(OH)₂(0001) surface, the d-band center of each Au atom is effectively shifted. It is known that the d-band states of the transition metal have great impacts on the interactions between the adsorbate and cluster.^[28,50] The general rule is that the nearer of the d-band states of the transition metal is to the Fermi level, the stronger are the interactions with the adsorbate states. When the d-band states of the transition metal are up-shifted to the Fermi level, the antibonding states will be pushed above the Fermi level. This response can reduce the Pauli repulsion and make the bond between the adsorbate and transition metal become more stable.^[51] Therefore, the Au₃ and Au₆ atoms whose d-band states are much nearer to the Fermi level will be more favorable for O₂ adsorption than those un-shifted ones.

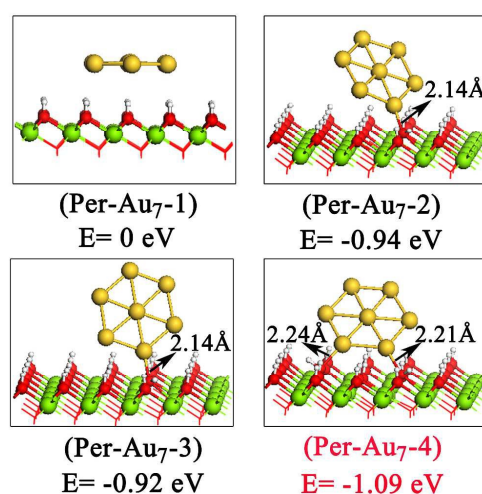


Figure 1. The four stable composite configurations and their relative binding energies of Au₇-cluster on Mg(OH)₂(0001) surface. Color coding: yellow, Au atoms; green, Mg atoms; red, O atoms; white, H atoms.

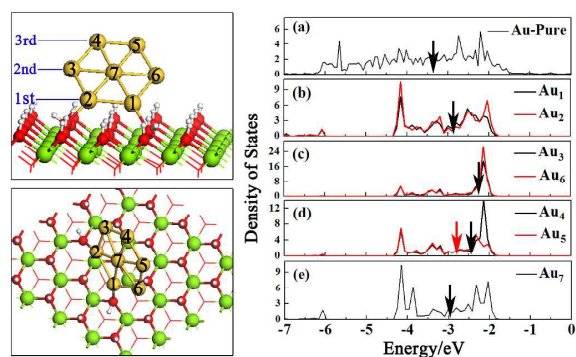


Figure 2. The side and top views of the most stable composite configuration of Au_7 -cluster on $\text{Mg}(\text{OH})_2(0001)$ surface. Projected d-band states of each Au atoms are shown at the right side. The d-band center is marked by black or red arrow. The Fermi level is specified to 0 eV for all Au atoms. See Figure 1 for color coding.

After testing all the possible adsorption sites, the most stable adsorption states of O_2 on the cluster and at the interface between the cluster and the $\text{Mg}(\text{OH})_2(0001)$ surface are obtained, as depicted in Figure 3 (the less stable states are shown in Figure S1). The binding structure in Figure 3-(**Per-O₂-1**) shows that, on the Au_7 -cluster, the main force for anchoring O_2 is provided by the generation of Au-O bonds. However, at the interface (Figure 3-(**Per-O₂-2**)), the bonds lengths of H-O_{II} are 2.00 Å and 2.29 Å. They are close enough to each other to generate hydrogen bonds (about 1.5 Å-2.5 Å) which enhance the stability of the adsorption state. Therefore, at the interface, besides the generation of Au-O bonds, the generation of hydrogen bonds can promote the adsorption of O_2 as well. This just explains the fact that although the d-band center of Au_4 atom is nearly at the same position as Au_6 atom, the binding energy of (**Per-O₂-1**) is 0.15 eV higher than (**Per-O₂-2**). In addition, the O-O bond length in (**Per-O₂-1**) and (**Per-O₂-2**) has both been stretched (from 1.23 Å to 1.34 Å and 1.33 Å, respectively). This means that when O_2 adsorbs on the surface, it will be pre-activated.

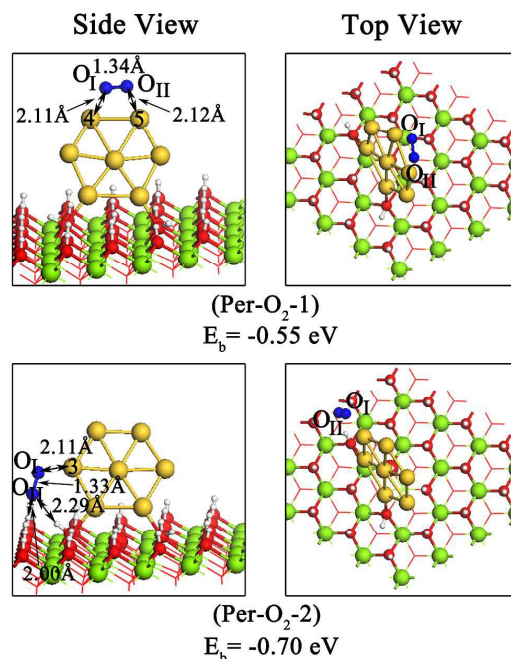


Figure 3. The side and top views of the most stable adsorption states of O₂ on the Au₇-cluster (**Per-O₂-1**) and at the interfaces between the cluster and the Mg(OH)₂(0001) surface (**Per-O₂-2**). Color coding: blue, O atoms in adsorbed O₂; others are the same as in Figure 1.

Having discussed the favorable molecular adsorption, we now turn to explore the dissociative process of O₂. The potential energy profile in Figure 4 shows that the dissociation of O₂ on the Au₇-cluster is an exothermic process, by 0.22 eV, with an energy barrier of 2.15 eV. At the interface, the direct dissociation process of O₂ is similar to the process in Figure 4, as shown in Figure 5-**black line**. However, its energy barrier (1.85 eV) is 0.30 eV lower than the former. This is because when O₂ dissociated at the interface, the O_{II} atom can hardly move and hydrogen bonds exist all through the dissociation process. These enhance the stability of the transition state and lower the energy barrier. In addition, because the dissociated state (**Per-O₂-2-dis**)

is more stable than **(Per-O₂-1-dis)** (0.08 eV lower), the dissociation of O₂ at the interface will be more favorable both dynamically and thermodynamically. From Figure 5-**red line**, one can see that the surface H atoms which are activated by the 1st-layered Au atoms can participate in the reaction process as well (denoted as H-trans dissociation process). Our calculations show this only works for the H atoms in the Au-OH systems. For the other H atoms, no matter how we adjusted their positions, they easily go back to the surface O atoms after relaxation. For the activated H atom transferring on O₂, it needs to overcome an energy barrier of 1.67 eV which is lower than the reaction process on the Au₇-cluster and the direct dissociation process at the interface. Such process is endothermic, by 0.40 eV. The intermediate **(H-trans)** in Figure 5 shows that the O-O bond length has been stretched from 1.33 Å to 1.43 Å. This means that the pre-activation intensity of O₂ in this state has become larger than the molecular adsorption state at the interface **(Per-O₂-2)**. This response makes the further dissociation of O₂ become much easier. The energy barrier is only 1.55 eV, which is even lower than the H atom transfer process. This means that the rate-determining step of the H-trans dissociation process is the transfer of H atoms **(TS 3)**. However, we need to point out that the final state **(H-trans-dis)** is less stable than state **(Per-O₂-2-dis)**, by 0.09 eV. Therefore, it is not difficult to come to a conclusion that the direct dissociation process is more favorable thermodynamically, while the H-trans dissociation process is more favorable dynamically. In other words, when temperature is low and time is short, the O₂ is more inclined to go through the H-trans dissociation process, however, as the temperature become higher and time

become longer, the direct dissociation process will get the upper hand.

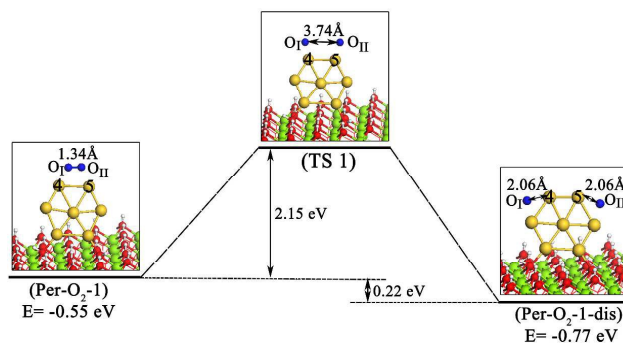


Figure 4. Potential energy profile for the dissociation of O_2 on the Au_7 -cluster supported on the perfect $Mg(OH)_2(0001)$ surface. See Figure 3 for color coding.

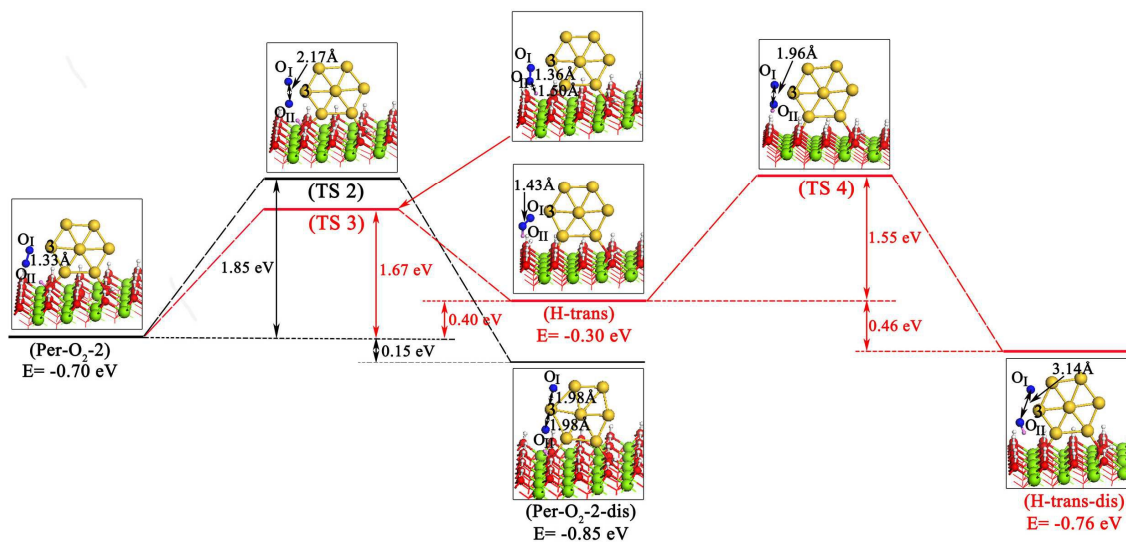


Figure 5. Potential energy profile for the dissociation of O_2 at the interface between the Au_7 -cluster and the perfect $Mg(OH)_2(0001)$ surface. **Black line**: the direct dissociation process; **red line**: the H-trans dissociation process. Color coding: pink, the transferring H atom; others are the same as in Figure 3.

3.2. O₂ Adsorption and Dissociation on the Au₇-Cluster Supported on Hydroxyl Defective Mg(OH)₂(0001) Surface. Hydroxyl defect is an intrinsic defect in metal hydroxides, and it usually plays important roles in the catalytic activity of composite catalysts. On Mg(OH)₂(0001) surface, two typical hydroxyl defects (the defect under (V_{OH}-1) and near (V_{OH}-2) the Au₇-cluster) are investigated, as shown in Figure 6. After relaxation, the initial atomic and electronic structures of the Au₇-cluster have changed. From Figure 7-(V_{OH}-1-Au₇), one can see that when Au₇-cluster adsorbs on the Mg(OH)₂(0001) surface with (V_{OH}-1) defect, the Au₂ atom will be stretched out of the cluster and covers the defect site. This change makes the d-band center of Au₂ atom move much nearer to the Fermi level. Different from the (V_{OH}-1-Au₇) state, the structure of the (V_{OH}-2-Au₇) state has little distortion and the d-band center of the Au₂ atom which is near the hydroxyl defect has an effective down-shift to lower energies. Since the position of d-band center plays important roles in the catalytic activity, the differences between these two Au atoms lead to different activities for O₂.

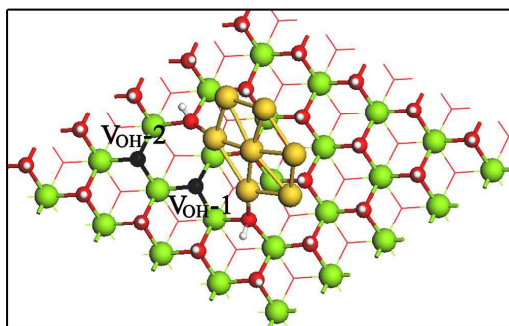


Figure 6. Two typical hydroxyl defects on Au/Mg(OH)₂ catalyst. Color coding: black, the hydroxyl defects; others are the same as in Figure 1.

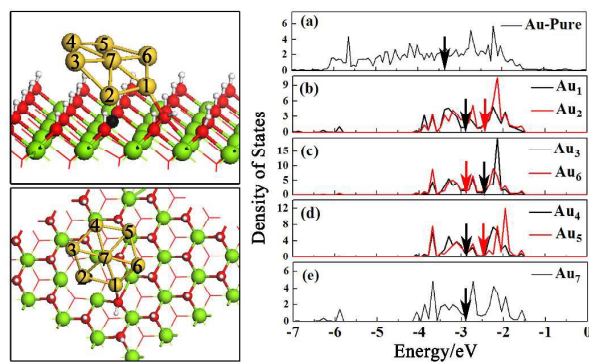
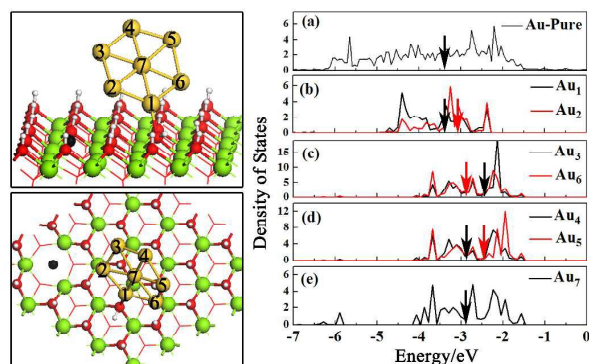
(V_{OH-1}-Au₇)(V_{OH-2}-Au₇)

Figure 7. The side and top views of the optimized configuration of Au₇-cluster on hydroxyl defective Mg(OH)₂(0001) surface. Projected d-band states of each Au atoms are shown at the right side. The d-band center is marked by black or red arrow. The Fermi level is specified to 0 eV for all Au atoms. See Figure 6 for color coding.

After testing various binding forms of O₂ on these two kinds of Au₂ atom, the most stable one on each site is obtained, as depicted in Figure 8. The O₂ adsorption state (V_{OH-1}-Au₇-O₂) is much more stable than state (V_{OH-2}-Au₇-O₂) and (Per-O₂-2) (Figure 3). This can be explained by two main reasons: one is that the O₂ molecule is absorbed by two active Au atoms (Au₂ and Au₃) in state (V_{OH-1}-Au₇-O₂) whose d-band centers are both close to Fermi level; the other is that the hydrogen bond in

state ($V_{OH-1-Au_7-O_2}$) is much shorter and stronger than the hydrogen bonds in other states. The large binding forces between Au_2 and Au_3 atoms in Au_7 -cluster and surface H atom have stretched the O-O bond length from 1.23 Å to 1.44 Å which is even longer than that in the intermediate (**H-trans**). Thus, when O_2 adsorbs on this site, it will be significantly pre-activated as well. As for the other Au atoms, because their d-band centers are not effectively changed, the adsorption behaviors of O_2 on these sites are similar to the corresponding Au atoms in Au_7 -cluster on the perfect $Mg(OH)_2(0001)$ surface (as seen in Figure S2).

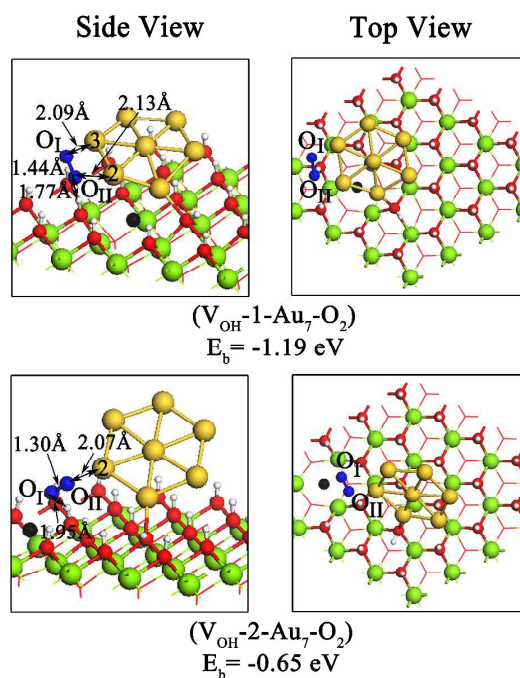


Figure 8. The side and top views of the most stable adsorption states of O_2 on Au_7 -cluster supported on two kinds of hydroxyl defective $Mg(OH)_2(0001)$ surface. See Figure 3 and Figure 6 for color coding.

We have then investigated the dissociative process of O_2 on the defective surfaces.

The potential energy profiles and the corresponding transition states are shown Figure 9. It can be seen that the energy barrier of O_2 dissociation on the (**V_{OH}-1**) defective surface is only 1.24 eV which is much lower than the rate-determining step of H-trans dissociation process (**TS 3**). This is because in **TS 5** the hydrogen bond and the large binding forces of Au_2 and Au_3 atoms both have significant promotion for the stability of O_I and O_{II} atoms in O_2 . Moreover, this process is exothermic, by 0.15 eV, and the stability of the final dissociated state (**V_{OH}-1-Au₇-O₂-dis**) is much higher than that on the perfect surface as well (the binding energy is 0.49 eV lower than (**Per-O₂-2-dis**) state in Figure 5). Therefore, the generation of (**V_{OH}-1**) defect will make the dissociation of O_2 more dynamically and thermodynamically favorable than the perfect surface. For the dissociation process on the (**V_{OH}-2**) defective surface, the V_{OH} site will become a good site for anchoring O_2 . However, the dissociation of O_2 needs to overcome an energy barrier of 2.23 eV which is similar to **TS 1** in Figure 4 and this process is endothermic, by 0.38 eV. Thus, the catalytic activity of the Au atom near the (**V_{OH}-2**) defect is barely promoted.

From the above discussions, one can see that the hydroxyl defects under the Au_7 -cluster can significantly enhance the catalytic activity surrounding Au atoms, while the defects near the cluster have little effect. Therefore, the hydroxyl defects generated on the synthesized $Au/Mg(OH)_2$ catalyst can barely promote the catalytic activities of Au nanoparticles. Therefore, one should keep more hydroxyl defects on the support before Au clusters were deposited, so as to synthesize the most effective $Au/Mg(OH)_2$ catalysts for O_2 activation.

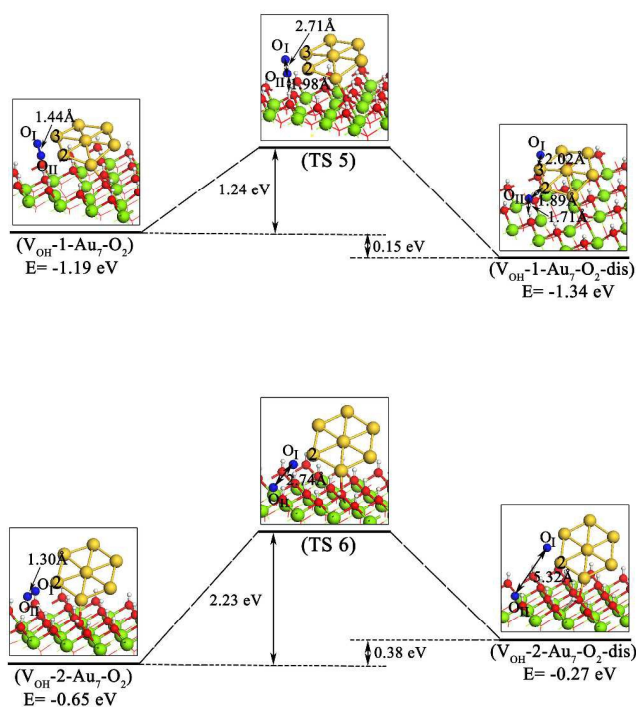


Figure 9. Potential energy profiles for the dissociation of O_2 on the Au_7 -cluster supported on the two typical hydroxyl defective $Mg(OH)_2(0001)$ surfaces. Up: (V_{OH-1}) ; down: (V_{OH-1}) . See Figure 3 for color coding.

4. CONCLUSIONS

This work represents our theoretical attempt to rationalize the O_2 activation process on $Au/Mg(OH)_2$ catalyst, focusing on how surface hydroxyls and hydroxyl defects affect the reaction microscopically. The results show that the d-band states of the Au atoms play important roles in O_2 adsorption and activation. Because the 2nd-layered interfacial Au atoms hold d-band centers are close to the Fermi level, the antibonding states of these Au atoms will be pushed above the Fermi level. Such response decreases the Pauli repulsion and enhances the stability and activity of the adsorbed

O₂. Therefore, the 2nd-layered interfacial Au atoms are more active for O₂ activation.

The hydroxyl groups on Mg(OH)₂(0001) surface can both enhance the stability of Au₇-cluster and promote the adsorption and pre-activation of O₂ on the interfacial Au atoms. Furthermore, the hydrogen atoms activated by the Au atoms can directly participate in O₂ dissociation process as well. The energy barrier of this process is 0.18 eV lower than that of the direct dissociation process. Thus, the H-trans dissociation process will be more favorable dynamically. The hydroxyl defect right under the Au₇-cluster can lead to significant up-shifts of the d-band center of the surrounding Au atoms, making them more favorable for O₂ activation. The hydroxyl defect near the Au₇-cluster, however, offers little promotion effect for the surrounding Au atom.

In summary, our results demonstrate that the surface hydroxyl groups and hydroxyl defects on the Au/hydroxide catalysts are very influential for O₂ adsorption and activation. To synthesize the most efficient Au/hydroxide catalysts for O₂ activation, one should prepare more interfacial Au atoms (making the Au clusters have thin and flat structures) and generate more hydroxyl defects on supports before Au clusters were deposited.

Supporting Information Available: The less stable adsorption states of O₂ on the Au₇-cluster and at the interface between the cluster and the perfect Mg(OH)₂(0001) surface, and the less stable adsorption states of O₂ on the Au₇-cluster supported on the (V_{OH}-1) and (V_{OH}-2) defective Mg(OH)₂(0001) surface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Acknowledgment

This work is supported by the Natural Science Foundation of Guizhou Province (no. QKJ[2015]2129), the Construction Project for Guizhou Provincial Key Laboratories (Z[2013]4009), the GZNC startup package (no. 14BS022). We thank Prof. J. Jiang and W. H. Zhong for helpful discussions.

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