High Catalytic Activity of Au Clusters Supported on ZnO Nanosheets

Na Guo,† Ruifeng Lu,§∥ Shuanglong Liu,† Ghim Wei Ho,‖ and Chun Zhang,§†∥

†Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542
‡Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543
§Department of Applied Physics, Nanjing University of Science and Technology, Nanjing, China 210094
∥Department of Electrical and Computer Engineering, National University of Singapore, Singapore, 117546

ABSTRACT: Catalytic activity of metal clusters supported on a two-dimensional (2d) nanosheet has attracted great interest recently. In this paper, via first-principles calculations, we investigate for the first time Au catalysis on recently proposed 2d one-atom-thick ZnO nanosheets. An Au₈ cluster adsorbed on a 2d ZnO sheet (Au₈/ZnO) is chosen as a model catalyst, and the CO oxidation is used as the probe reaction for the catalytic activity. When adsorbed on 2d one-atom-thick ZnO, the Au₈ cluster is found to adopt a planar structure and exhibit high catalytic activities for the CO oxidation with a low reaction barrier around 0.3 eV. The catalyzed CO oxidation highly prefers the Eley–Rideal (ER) mechanism, and the coadsorption of CO and O₂ on the Au₈ cluster plays an essential role in the ER type of reaction in which an additional CO approaches O₂ in a vacuum. The high catalytic activity (low reaction barrier) is due to the charge transfer from Au₈/ZnO to the antibonding 2π* orbital of the O₂ molecule that is facilitated by the coadsorption of a CO molecule. These findings provide new opportunities for the future development of ZnO-based catalysts.

INTRODUCTION

Metal catalysis on two-dimensional (2d) one-atom-thick substrates has attracted great interest recently. Various 2d substrates such as graphene,1−6 hexagonal BN (h-BN),7 and polymeric metal−phthalocyanine,8,9 have been considered in the literature. Unusual effects of these 2d substrates on the catalyzed chemical reactions that could lead to novel applications were reported. For example, it was shown that a moderate mechanical strain on graphene substrate could greatly enhance the stabilization and catalytic activity of the supported metal clusters, implying a possible way to control reversibly the chemical reactions by mechanical force.1 It was also suggested that on graphene or polymeric metal−phthalocyanine substrate, high-performance single-atom catalysts that are highly desired could be realized.2,8,9 These interesting phenomena indicate the great promise of the 2d one-atom-thick support for the design of novel catalysts. However, the difficulty in large-scale production hinders the industry applications of previously proposed systems. Great research effort along this direction has been paid to the search for a better system (a better combination of metal catalysts and 2d substrates) that is efficient yet cheap and easy to fabricate. In this paper, we report for the first time the first-principles investigation of Au catalysis on 2d one-atom-thick ZnO sheets. Our studies offer a new avenue for the future design of 2d substrate-supported catalysts.

ZnO has been regarded as a key material for future technology due to its excellent mechanical, electric, and optical properties as well as its unique ability to form various kinds of nanomaterials,10−13 such as nanowires, nanobelts, nanotubes, and recently 2d nanosheets. Many novel ZnO-based electronic devices such as field effect transistors,14 spintronic devices,15 light-emitting diodes,16 and nanoscale electricity generators17 have been proposed both theoretically and experimentally. A recent experiment demonstrated the evidence of strong interactions between the encapsulated Au cluster and the ZnO outside, which could lead to high catalytic activity.18 Despite the ever-increasing interest in ZnO and also metal nanocatalysis in last several decades, studies pertaining to ZnO-supported metal catalysis still fell short. So far, ZnO has not been considered as a good candidate for substrates of catalysts partly due to the low chemical activity of bulk ZnO. Here, via first-principles calculations, we show the high catalytic activity of Au clusters supported on a 2d one-atom-thick ZnO sheet, suggesting the great potential of the 2d ZnO nanosheets in catalysis chemistry. Interesting effects of the 2d ZnO support on the catalyzed reaction that are different from those of conventional bulk metal oxide substrates are also revealed. We expect these studies to stimulate new experiments along this direction.

COMPUTATIONAL METHODS

First-principle DFT calculations were performed by utilizing Vienna Ab Initio Simulation Package (VASP) code.19,20 The plane wave basis with the cutoff energy of 450 eV and the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerh (PBE) format21 were used in all calculations.
Relativistic effects were included in the pseudopotential of Au. The structural relaxations were carried out until the Hellmann–Feynman force on each atom is less than 0.01 eV/Å, and the energy convergence criterion was set to 10⁻⁵ eV. A 3 × 3 supercell (Figure 1) and the 3 × 3 × 1 k-sampling in Brillouin zone were employed in all calculations. Along the direction perpendicular to the ZnO sheet, 15 Å of vacuum is included in the supercell to avoid interaction of periodic images. The reaction barrier of the catalyzed CO oxidation was determined by the climbing-image nudged elastic band (cNEB) method.²³–²⁵ Five images and the convergence criteria of 0.01 eV were used in cNEB calculations. The spin polarization is considered in all calculations.

![Image](image_url)

**Figure 1.** Atomic structures of three Au₈ isomers (3d, P1, and P2) before and after the adsorption on ZnO nanosheet. Color scheme: Au in yellow, oxygen in red, and zinc in gray. After adsorption, P2 is the most stable one.

### RESULTS AND DISCUSSIONS

The 2d one-atom-thick ZnO sheet with a honeycomb lattice was first predicted theoretically²⁵ to be an analogue of h-BN where B and N atoms are replaced by Zn and O, respectively. The flat, layered 2d ZnO was then observed in experiments.¹⁰,¹¹ Since then, the mechanical, electronic, and magnetic properties of the 2d one-atom-thick ZnO sheets have been intensively studied,²⁶–²⁹ but the catalytic activity of 2d ZnO-based systems has never been discussed. In this paper, via computational modeling and simulation, we investigated the possibility of using 2d ZnO sheets as substrates for metal nanocatalysts. An Au₈ cluster (which is an often-used Au nanocatalyst in the literature) supported on a 2d ZnO sheet (Au₈/ZnO as shown in Figure 1) was chosen as the model catalyst, and the CO oxidation was used to probe the activity of the catalyst. Note that, in the supercell structure shown in Figure 1, the distance between the Au₈ cluster and its nearest image is around 8 Å, which is far enough to avoid interactions between them. All calculations were done under the framework of density functional theory (DFT).

Au₈ clusters have three different isomers in the gas phase, one three-dimensional (3d) and two planar (P1 and P2) structures, as shown in Figure 1a–c. The predicted geometries of the Au₈ clusters (the Au–Au bond lengths and angles) by our calculations agree well with previously reported results.¹² For the 2d ZnO sheet, our calculations yielded the optimized Zn–O bond length of around 1.9 Å, also in good agreement with literature.¹⁹,²⁰ When adsorbed on 2d ZnO, we found that the P2 adsorption configuration (Figure 1c) is the most stable. The adsorption energy of the P2 configuration is about 0.3 eV higher than the P1 and 3d cases (Note that the adsorption energy is defined here as $E_{ad} = E_{Au} + E_{ZnO} - E_{Au/ZnO}$). For the optimized P2 adsorption configuration, the average distance between the Au and the nearest Zn is estimated to be about 2.6 Å. In Figure 2, we plot the isosurface of the charge difference for the optimized P2 adsorption. From the figure, we can see that after the adsorption, the Au₈ cluster is negatively charged and approximately there are 0.3 electrons transferred from the interfacial region to the cluster.

We then consider the adsorption of an O₂ or CO molecule on P2-Au₈/ZnO, which is the first step of investigating the catalytic activity of the system. For the adsorption of a single O₂, there are four inequivalent adsorption sites (A–D), as depicted in Figure 3a. We have found that there is no stable adsorption of a single O₂ in all these sites. In particular, the O₂ is only weakly adsorbed on sites A–C with adsorption energies of less than 0.1 eV, and there is no adsorption (negative adsorption energy) of O₂ on site D. The most stable adsorption configuration for a single CO molecule. The adsorption energy is around 0.6 eV. (c) The coadsorption of CO and O₂. In this case, the adsorption energy of the O₂ molecule is about 0.6 eV. The carbon atom is in black.

![Image](image_url)

**Figure 3.** Optimized adsorption configurations for O₂ and/or CO: (a) the adsorption of a single O₂. A–D represent four possible adsorption sites. The O₂ molecule weakly binds on A–C with the adsorption energy of less than 0.1 eV. There is no binding on site D. (b) The most stable adsorption configuration for a single CO molecule. The adsorption energy is around 0.6 eV. (c) The coadsorption of CO and O₂. In this case, the adsorption energy of the O₂ molecule is about 0.6 eV. The carbon atom is in black.
amounts of energy. In order to achieve a stable O₂ binding, we examined the coadsorption of O₂ and CO and found that the preadsorption of a CO molecule can greatly stabilize the binding of O₂. We considered various adsorption configurations. The predicted lowest-energy coadsorption configuration is shown in Figure 3c, in which the O₂ binds on the gas-phase value of 1.24 Å. Note that for the coadsorption case, elongated in this case to 1.44 Å compared with the calculated − estimated to be 0.6 eV. The O₂ bond is significantly elongated in this case to 1.44 Å compared with the calculated gas-phase value of 1.24 Å. Note that for the coadsorption case, the adsorption energies of CO and O₂ are almost the same, which is helpful to avoid the notorious CO poisoning problem.

To understand the effects of CO preadsorption on binding of the O₂ molecule, we performed the Bader charge analysis for different adsorption cases (adsorption of single O₂ or CO and the coadsorption). In Table 1, we show the change of net charges on the adsorbed molecules (O₂ or CO) and the Au atoms bonded with the molecules after the adsorption. It can be clearly seen from the table that when CO and O₂ are coadsorbed, compared with the single-molecule adsorption, the CO molecule loses significant amounts of electrons (~0.7 e⁻), and the O₂ molecule gains nearly the same amount of electrons. The CO-assisted electron transfer to the O₂ molecule greatly enhances the binding of O₂. In Figure 4, we plotted the calculated reaction path with the barrier around 0.3 eV. In the initial state (IS), the distance between the C atom of the CO in vacuum and the nearest O atom of the adsorbed O₂ (d_{CO-O₂}) is 3.0 Å. The transition state (TS) features a peroxo-type O—O—C—O intermediate complex with a d_{O—O} of 1.7 Å. The O—O bond length in TS is about 1.6 Å. The low reaction barrier of 0.3 eV clearly suggests that the Au₈/ZnO under study is an excellent catalyst for CO oxidation. In the second step of the reaction, the remaining O atom is removed by another CO molecule that completes the cycle of the reaction. Our calculations gave a low reaction barrier of around 0.27 eV for the second step of the reaction. The calculated reaction path for the second step is shown in Figure S2 in the Supporting Information. It worth mentioning here that CO₂ is weakly adsorbed on single-layer ZnO with the adsorption energy of less than 0.2 eV.

<table>
<thead>
<tr>
<th>atom</th>
<th>CO adsorption</th>
<th>O₂ adsorption</th>
<th>CO + O₂ Coadsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au1</td>
<td>−0.05</td>
<td>0.03</td>
<td>−0.19</td>
</tr>
<tr>
<td>Au2</td>
<td>0.01</td>
<td>−0.26</td>
<td>0.02</td>
</tr>
<tr>
<td>Au3</td>
<td>0.11</td>
<td>−0.17</td>
<td>0.17</td>
</tr>
<tr>
<td>CO</td>
<td>0.03</td>
<td>N/A</td>
<td>−0.65</td>
</tr>
<tr>
<td>O₂</td>
<td>N/A</td>
<td>0.70</td>
<td>1.47</td>
</tr>
</tbody>
</table>

“The positive/negative value denotes the gain/loss of electrons. N/A = not applicable.

In conclusion, we report for the first time the first-principles investigations of Au catalysis on 2d one-atom-thick ZnO nanosheets. An Au₈ cluster adsorbed on a 2d ZnO sheet (Au₈/ZnO) is chosen as a model catalyst, and the CO oxidation is used as the probe reaction for the catalytic activity. We found that, when adsorbed on 2d ZnO sheets, the Au₈ cluster adopts a planar structure (P2) and exhibit high catalytic activities for the CO oxidation reaction with a low reaction barrier of around 0.3 eV. The catalyzed CO oxidation highly prefers the Eley—Rideal (ER) mechanism, and the coadsorption of CO and O₂ on the
Au₈ cluster plays an essential role in the ER type of reaction in which an additional CO approaches O₂ in a vacuum. These findings provide new opportunities for both the design of heterogeneous metal catalysts and the future applications of ZnO-based materials.

**ASSOCIATED CONTENT**

2 Supporting Information

The reaction path of the Langmuir–Hinshelwood mechanism for the first step of CO oxidation (Figure S1) and the reaction path of the Eley–Rideal mechanism for the second step of CO oxidation (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: phyzc@nus.edu.sg.

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We acknowledge the support from Ministry of Education (Singapore) and NUS academic research funds (Grant Nos. R-144-000-325-112 and R-144-000-298-112). Computations were performed at the Graphene Research Centre and the Centre for Computational Science and Engineering at NUS.

**REFERENCES**


