

Substrate effect on the structure and properties of Cu clusters supported on ZnO

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Abstract

To understand the interaction between the Cu clusters and the ZnO substrate, we performed density functional theory (DFT) calculations on the adsorptions of small copper clusters on the ZnO(100) surface. The PBE functional was used in the DFT calculations with a plane wave basis set. The structural changes of the Cu clusters upon adsorption on the ZnO surface were provided. Although a few different adsorption sites are available, a single Cu atom was found to be adsorbed on three positions on a ZnO(100) surface. The adsorption strength of a Cu dimer is increased with respect to the adsorption of a single Cu atom. In the adsorptions of tetramers, and pentamers, three-dimensional configurations of Cu clusters are more favorable than the planer.

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1. Introduction

Finding an efficient, stable, and economical catalyst for selectively activating or coupling C-C, C-H, and C-O bonds is the pinnacle of catalysis for organic synthesis. Many catalytic active nanoparticles of transition metals, such as Pt,^{1,2} Pd,³⁻⁵ Rh,^{6,7} Au,⁸⁻¹¹ Ir,¹²⁻¹⁴ and Cu_n¹⁵⁻²² have been studied extensively for catalysis as well as other applications. For instance, Ir was studied due to their high activities in ethanol oxidation reaction²³⁻³² and Ni for steam reforming of alkanes,³³⁻³⁶ Compared to other transition metals, the abundant and cheap Cu has been used as catalysts for ethanol conversion³⁷⁻⁴⁷ and other applications,⁴⁸⁻⁵⁸ though stability of the catalysts can be a concern.⁵⁹

To overcome stability of Cu clusters, one strategy is to increase the interaction between the cluster and the substrate. Therefore, understanding the interaction between Cu clusters and the substrate is an important area of research. As a common substrate, ZnO has been widely investigated.⁶⁰⁻¹¹⁰ Furthermore, many studies on the Cu/ZnO systems were made.¹¹¹⁻¹⁴⁴ These studies help our understanding of the systems of interest and provides insight into future conversion of organic molecules to different and more useful formats¹⁴⁵ for versatile applications, such as in solar cells,¹⁴⁶⁻¹⁵² have been the driving force in catalyst and related studies.^{153,154}

Despite the advances, there are interesting issues to explore. For instance, when the Cu clusters interacting with ZnO substrate, what is the role of different sites on the adsorption of clusters? and how do the structures of bare clusters change after adsorption? Furthermore, the change of electronic properties of the Cu clusters before and after adsorption is also interesting as electronic properties are critically correlated to the catalytic activities. Therefore, in this work, we chose to study adsorption of single Cu

atom, Cu dimer, and two Cu tetramers and two Cu pentamers on the ZnO(100) surface using density functional theory (DFT) calculations.

2. Computational Details

To study the ZnO support effect on the stability of Cu small clusters, we used ZnO(100) as the supporting surface. In order to determine the adsorption energies and the structures of Cu clusters supported on the nonpolar ZnO surface, we performed the spin-polarized DFT calculations implemented in Vienna Ab-initio Simulation Package (VASP).¹⁵⁵ The electron-ion interactions were described by the projector augmented wave (PAW) method. The exchange and correlation energies were calculated using the Perdew-Burke-Ernzerhof (PBE) functional.¹⁵⁶ The electronic wave functions were expanded in a plane wave basis set with a cutoff energy of 400eV.

We first performed calculations for the ZnO bulk structure. The ZnO bulk consisted of two ZnO dimers in repetitive positions. The size of the unit cell was chosen such that the nearest distance between neighboring images was more than 10Å. Monkhorst-Pack k -point meshes were used.¹⁵⁷ To determine the k -point values for the bulk, several tests were performed. Table 1 summarizes the energies and k -points values obtained from these tests. The data in Table 1 show that the free energies of the ZnO bulk are in the 0.3eV difference when the k -points values changed. Based on these result, the $(5 \times 5 \times 5)$ points were chosen.

Table 1. Free energies as a function of the k -points in ZnO bulk calculations

K-Points	Free Energy (eV)
$5 \times 5 \times 5$	-14.499104
$7 \times 7 \times 7$	-14.309658
$9 \times 9 \times 9$	-14.260910

The initial bulk structure was allowed to fully relax in the DFT calculations. Figure 1 shows the comparison in bond distances between atoms of the bulk before and after full relaxation. There is a 0.017 Å change between the Zn-O bond length before and after relaxation.



Figure 1. Comparison of bond distances of bulk before and after relaxation.

The calculated lattice parameters for the bulk are $a = 3.249\text{\AA}$, $b = 3.249\text{\AA}$, and $c = 5.205\text{\AA}$. These computed lattice parameters agree well with Meyer et al. and experimental data, as shown in Table 2. The internal coordinate, u , of the structure determines the relative position of the anion and cation sublattice along the c axis.^{104,105,158} Meyer et al. found that the c/a ratio strongly influences the internal parameter u . They stated that if $u = \frac{1}{4} + \frac{a^2}{3c^2}$ then all of the nearest-neighbored bonds are equal.^{104,105} In the current case, when using this equation the u value is 0.380Å and the calculated u value is 0.383Å, the difference could be from either an over or underestimate of the a and c values.

Table 2. A comparison of the structural parameters for bulk ZnO.

	Our results	Meyer et al. ^{104,105}	Experimental ¹⁵⁸
$a(\text{\AA})$	3.249	3.282	3.250
$c(\text{\AA})$	5.205	5.291	5.207
c/a	1.602	1.612	1.602
u	0.383	0.3792	0.3825

Once the ZnO bulk structure was obtained, we built ZnO(100) surface by cutting the crystal perpendicular to the hexagonal Zn and O layers. There is no mirror symmetry parallel to the nonpolar structure in the ZnO wurtzite structure, meaning that all slabs are Zn terminated on one side and O terminated on the other.^{104,105} For the study of the adsorption of Cu clusters on a ZnO (100) surface, we employ a slab model with a 1×1 surface unit cell consisting of a number of Zn-O bilayers and a vacuum layer of 15\AA separating the slabs to reduce the residual internal electric field.¹⁰⁵⁻¹⁰⁹

In studying the adsorption of the Cu clusters on the ZnO substrate, we used the following equation to calculate the adsorption energy of the Cu clusters on ZnO(100)

$$E_{ads} = - (E_{system} - E_{surface} - E_{cluster})$$

where E_{system} represents the total energy of the whole system consisting of the adsorbed Cu cluster and the surface, $E_{surface}$ represents the total energy of the ZnO surface, and $E_{cluster}$ represents the total energy of the bare Cu cluster.

3. Results and Discussion

3.1. ZnO substrate

To decide how many layers to use as the substrate in our study, two models were studied. A model with eight Zn-O bilayers to represent the ZnO(100) surface with the top three Zn-O bilayers allowed to relax while the bottom five bilayers Zn-O fixed at their calculated bulk positions to mimic the bulk substrate in our calculation of Cu cluster adsorption, as well as, a six Zn-O bilayer surface with the top three Zn-O bilayers allowed to relax while the bottom three layers are fixed. Figure 2 shows an illustration of the eight Zn-O bilayer surface and the six Zn-O bilayer surface.

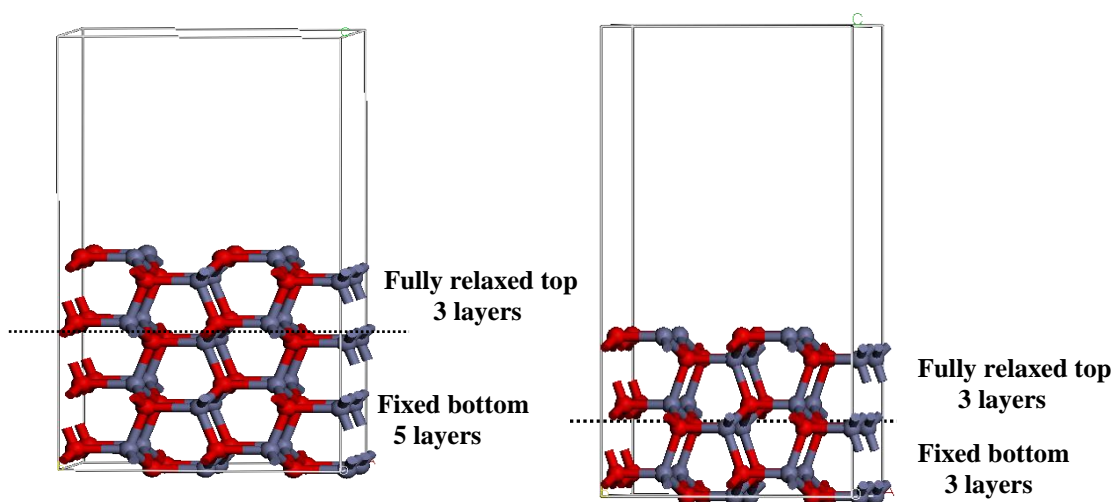


Figure 2. Illustration of eight Zn-O bilayer and six Zn-O bilayer ZnO (100) surfaces.

The eight Zn-O bilayer surface was intensely studied so that the fixed and relaxed layers could be determined. When studying the adsorption of molecules on different surfaces, the surface has to simulate the actual catalytic effect of the bulk. In the actual catalysis effect, most of the top layers of the bulk are the most active, while the layers close to the bulk core remain barely unchanged. This means that when doing surface calculations, a couple of the bottom layers have to be fixed to represent the behavior of

the layers at the center of the bulk structure. To determine how many layers were going to relax to the ground state, we performed calculations varying fixed layers. An eight layer surface with four layers fixed was allowed to relax to the ground state and the energy was calculated to be -70.668 eV. The eight layer surface with five layers fixed was allowed to relax to ground state and the energy was calculated to be -70.662 eV. Next another eight layer surface with six layers fixed was allowed to relax to the ground state and the energy was calculated to be -70.656eV. Based on these results, there was not a significant surface energy change between these three models. It was also found by others that this type of surface was efficient enough to get adequate results that compare to experimental analysis.^{104-106,110} Table 3 shows comparison the free energies of various eight layer surfaces, varying the fixed bottom layers.

Table 3. The free energies of eight layer ZnO (100) with different fixed layers

ZnO(100)	Free Energy (eV)
eight layers (four fixed)	-70.668
eight layers(five fixed)	-70.662
eight layers (six fixed)	-70.656

When compared to one another the free energies per atom for the six layer and eight layer ZnO(100) are somewhat the same. Since there were sixty-four atoms in the eight layers, the free energy per atom is -4.4174eV. Since there were forty-eight atoms in the six layers, the free energy per atom is -4.372eV. When comparing these results there were $\approx 0.5\text{eV}$ between the two ZnO(100) surfaces. Based on these analyses, the six Zn-O bilayer ZnO(100) surface was found to be efficient for this study. Table 4 shows a comparison of free energies of the eight and six Zn-O bilayer ZnO(100) surface.

Table 4. Comparison of free energies of eight and six Zn-O bilayer ZnO(100) surfaces.

Surface Layers	Free Energy (eV)	Free Energy per atom (eV)
Eight Zn-O bilayers (five fixed)	-282.715	-4.42
Six Zn-O bilayers (three fixed)	-209.861	-4.37

3.2 Adsorption of Cu clusters on ZnO(100)

In the study of Cu cluster adsorption to the ZnO(100) surface, various high-symmetry adsorption sites on the ZnO (100) were taken in consideration, mainly focusing more on the atop sites, the face centered cubic (fcc) sites and the hexagonal close packed (hcp) sites. The atop sites would be the regular lattice site for the next atomic layer. The hcp-hollow sites are the positions above the atoms in the second atomic layer. The fcc-hollow sites are the positions above the atoms in the second atomic layer. The fcc-hollow sites are positions within the surface where there are no atoms beneath the Cu clusters, as shown in Figure 3.

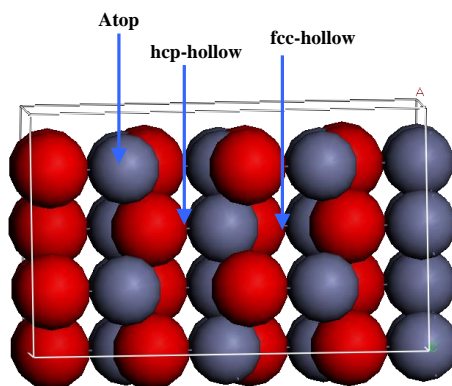


Figure 3. A top view of the high-symmetry adsorption sites on the ZnO(100).

The adsorption of a single Cu to the ZnO(100) can take place at various sites as shown in Figure 3. Starting from 6 different adsorption sites, three relaxed adsorptions were found from DFT calculations and they are shown in Figure 4 with the adsorption energies ranging from 1.41-1.64 eV. The most stable adsorption of a single Cu on ZnO(100) is the Cu to form single Cu-O bond as in the configuration of (c) of Figure 4.

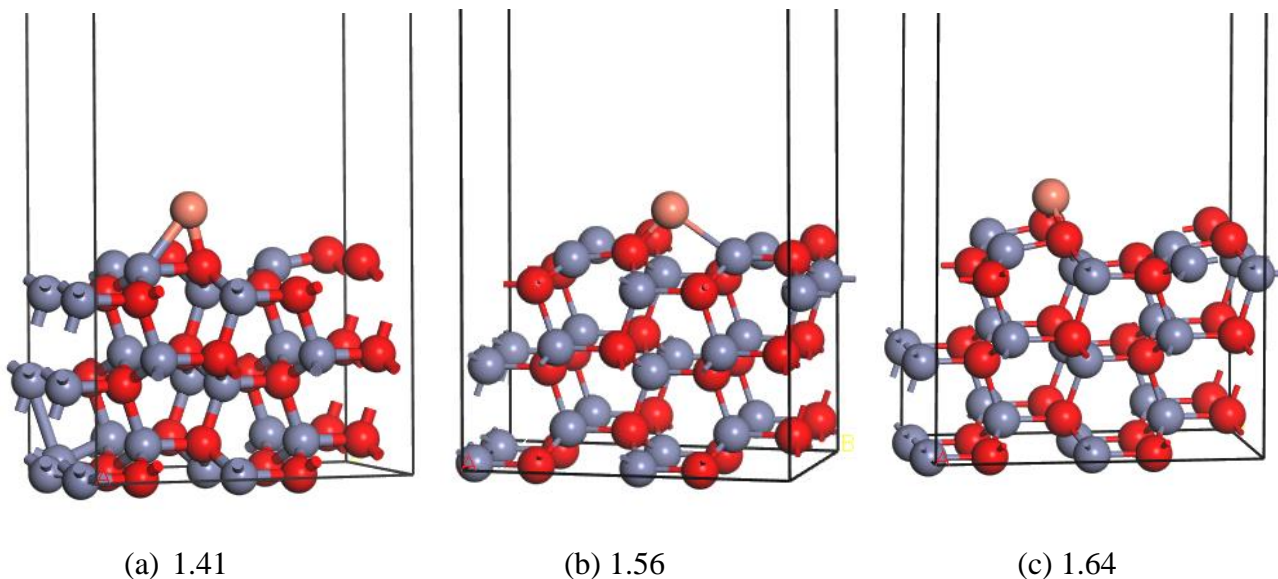


Figure 4. Adsorption configurations and energies (in eV) of Cu atom adsorbed at various positions on the ZnO(100).

The adsorption of a Cu dimer on the ZnO(100) was studied by initially placing it 10 different sites. After DFT calculations, four relaxed adsorptions were obtained and they are depicted in Figure 5 with the adsorption energies ranging from 1.60-2.20 eV. The strongest adsorption of a Cu dimer on ZnO(100) is the Cu dimer to form a single Cu-O bond and two Cu-Zn bonds as shown in (d) of Figure 5. Although adsorption of (a) in Figure 5 has a similar adsorption configuration, the interactions of the Cu dimer and Zn and O are at different locations than as shown in (d) of Figure 5.

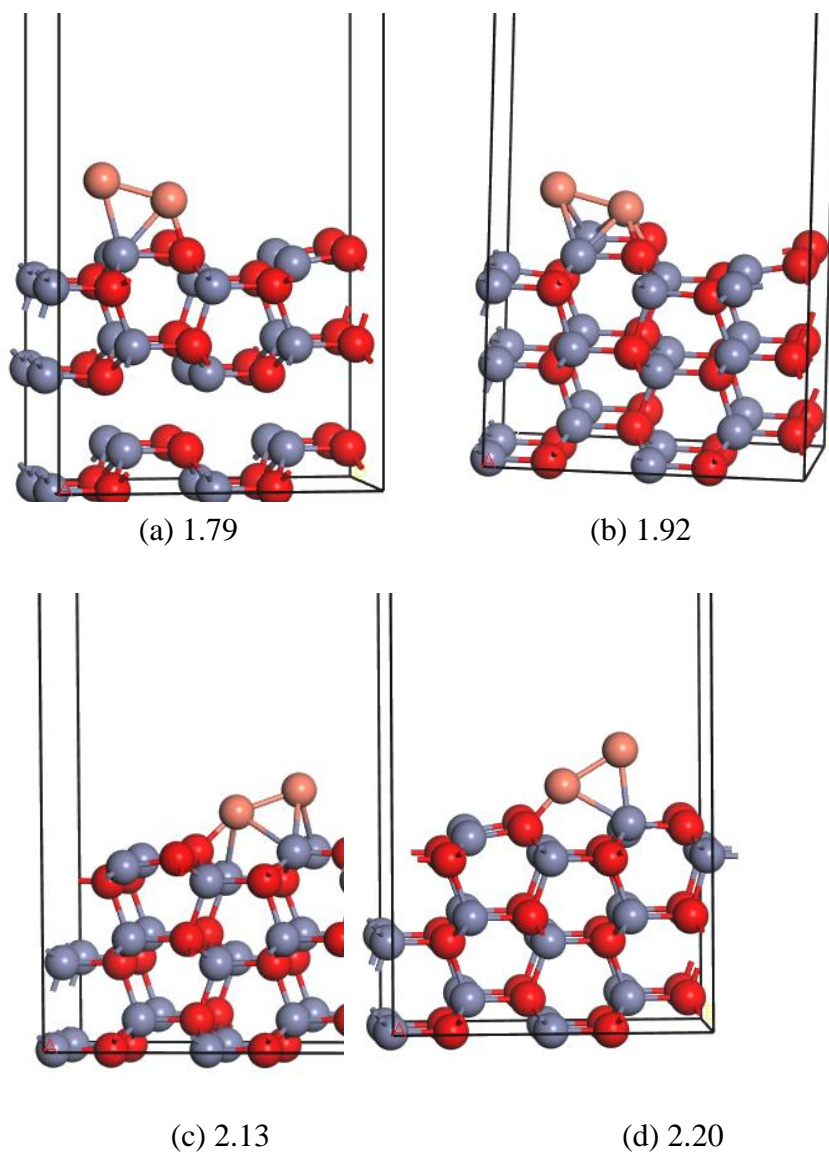
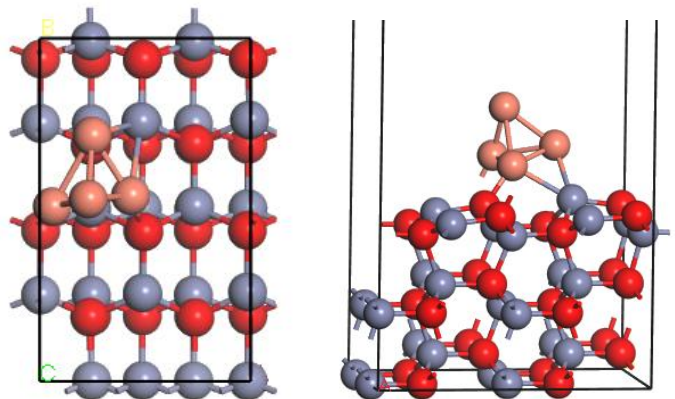
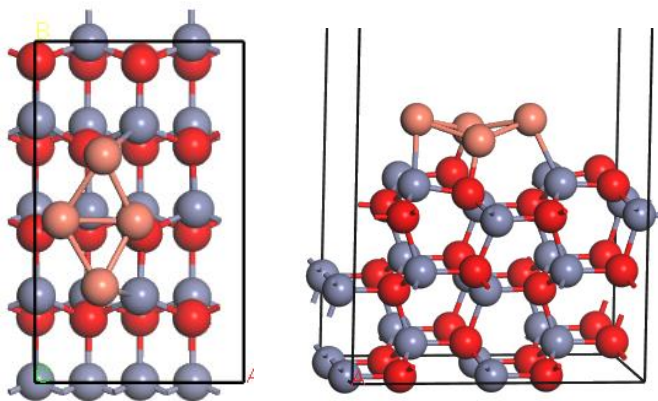


Figure 5. Adsorption configurations and energies (in eV) of a Cu dimer adsorbed at various positions on the ZnO(100).

Adsorptions of two Cu tetramers on ZnO(100) were studied using DFT here. The final adsorption configuration and the relative energy of the two adsorptions are shown in Figure 6. Like Au^{8,10} and Cu tetramer clusters,¹⁵ the adsorbed Cu tetramer prefers a planer configuration, which allows maximum interaction with the substrate.



(a) 0



(b) 0.30

Figure 6. Adsorption configurations of the top (left) and side (right) views and the energy difference (in eV) of the Cu tetramers (a) and (b) adsorbed on the ZnO(100).

The adsorption configurations of two Cu tetramers on the ZnO(100) were investigated and the results are shown in Figure 7. Unlike tetramers, the three-dimensional structures of the Cu cluster seem to be dominant. This may be due to the mismatch of the lattice parameters and the Cu-Cu bond lengths that may induce some constraints between the adsorbed Cu cluster and the substrate.

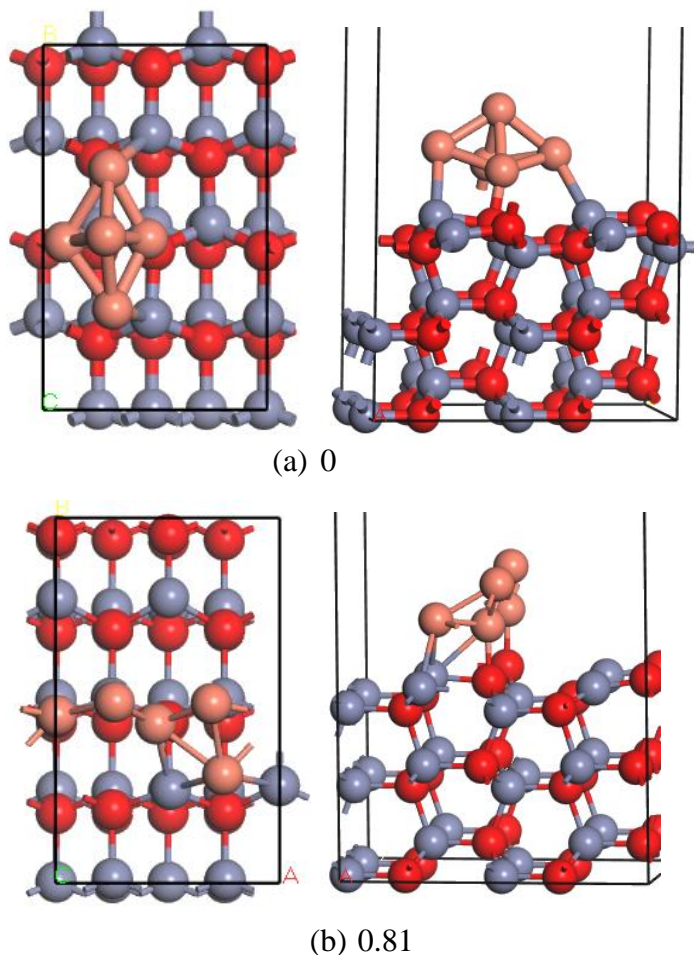


Figure 7. Adsorption configurations and the energy difference (in eV) of the Cu pentamer (a) and (b) adsorbed on the ZnO(100).

We note that more studies of adsorption of Cu clusters on the ZnO(100) surface are necessary to further understanding of the adsorption process. For instance, surface defect effect on adsorption¹⁵⁹ as well inclusion of U in the DFT treatment are interesting research for future studies to understand the adsorption.

4. Conclusions

The overall goal of this research is to develop new catalysts for more efficient hydrogen production or synthesis of new energy carriers from coal gasification. In the

process of synthesizing syngas, catalysts that can minimize methanol formation from coal gasification will be desirable. As the first step of the project, we performed DFT calculations for the study of the adsorption of small copper clusters on the surface of zinc oxide. The DFT calculations with PBE functional were carried out in VASP. The structural changes of Cu clusters upon their adsorption at different surface coverage on ZnO surface were studied. Although a few different adsorption sites are available, a single Cu atom was found to be adsorbed on three sites on a perfect ZnO(100) surface. Adsorptions of Cu dimer are stronger than the adsorption of a single Cu atom. In the case of adsorptions of tetramers, and pentamers, the DFT results predicts that three-dimensional configurations of Cu clusters are more favorable than the planer.

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