

# CO-ADSORPTION CALCULATIONS OF CO AND H<sub>2</sub>O MOLECULES ON ATOMIC CU CLUSTER DEPOSITED ZNO (10 $\bar{1}$ 0) SURFACE: A DENSITY FUNCTIONAL THEORY STUDY

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**Abstract.** Calculations of adsorption and reaction mechanism on ZnO (10 $\bar{1}$ 0) surface have been investigated. In this work, the deposition of six atomic copper clusters (6Cu) on ZnO(10 $\bar{1}$ 0) surface (called 6Cu/ZnO(10 $\bar{1}$ 0) model), using density functional theory was employed to calculate for CO and H<sub>2</sub>O co-adsorption. In performance, on ZnO(10 $\bar{1}$ 0) surface, 6Cu were adsorbed to obtain four stable sites of 6Cu/ZnO model, called as 6Cu-I, 6Cu-II, 6Cu-III, and 6Cu-IV. The calculated results found that the 6Cu-IV was the most stable surface model, thus, used to examine the co-adsorption of CO and H<sub>2</sub>O molecules. Further, CO and H<sub>2</sub>O co-adsorption on ZnO(10 $\bar{1}$ 0) surface were calculated also to compare with 6Cu/ZnO(10 $\bar{1}$ 0) surface. Based on co-adsorption energy calculations indicated that CO and H<sub>2</sub>O co-adsorption on 6Cu/ZnO(10 $\bar{1}$ 0) surface were more favorable than on ZnO(10 $\bar{1}$ 0) surface. The studied results will provide an insight into the effective adsorption of cluster on ZnO-based surface by deposition.

**Keywords.** DFT; Co-adsorption; ZnO(10 $\bar{1}$ 0) surface; 6Cu/ZnO(10 $\bar{1}$ 0) surface; 6Cu cluster.

## 1. INTRODUCTION

Interaction of gas molecules on solid surfaces, calling as the adsorption relevant to chemical process is of the importance in industrial, environmental, and medical monitoring [1, 2]. Further, semiconducting metal oxides have been considered for making adsorption processing because of advantages such as low cost, small dimensions, and great compatibility. In adsorption of molecules on emiconducting metal oxide surface, the interacting mechanism is known that the gas molecules charge transfer between the adsorbed gas species (adsorbates) and the surface (adsorbents) occurs. This charge transfer can be increased or decreased the concentration of the major carriers in the metal oxides, depending on the semiconductor type, thereby increasing or decreasing the electrical conductance of the adsorption processing under operating conditions.

Zinc oxide itself is a semiconductor with the hexagonal Wurtzite crystal structure and wide direct band gap (~3.37 eV), which ZnO has a wide range of technological uses [3]. Plus, in combination with other metal particles at the surface, ZnO, in general, has better selectivity and activity performance [4]. In addition, with four main ZnO surfaces, i.e., polar surfaces (0001) and (000 $\bar{1}$ ) and non-polar surfaces (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0), in which the non-polar ZnO(10 $\bar{1}$ 0) surface is considered the most stable one to focus on this study [5, 6].

The theoretical calculations of slusters on the surface as state of matter between isolated molecular species and solids have been investigated [2, 7, 8]. The physical and chemical properties of clusters are that depended on size- particles and been thus tunable. This has an important for adsorption and heterogeneous catalysis by transition metals, to design of modeling characterize adsorbents in the form of well-defined structure on metal oxide surface [9, 10]. By this doing model, Cu-ZnO based surface is considered to be an adsorbent with high Cu content for adsorption process in this investigation.

CO and H<sub>2</sub>O co-adsorption on the surface is the first step in the examination of water gas shift reaction. Many experimental and theoretical studies have been reported to calculate the mechanism of

water gas shift reaction [11-15]. However, to our knowledge, no theoretical studies have been considered co-adsorption of CO and H<sub>2</sub>O on 6Cu/ZnO (10 $\bar{1}$ 0) surface. Thus, in this article, we use a density functional theory (DFT) to study CO and H<sub>2</sub>O co-adsorption on both ZnO (10 $\bar{1}$ 0) surface and 6Cu/ZnO (10 $\bar{1}$ 0) surface. In the details, our performance is the first step to investigate the 6Cu cluster deposition on the ZnO (10 $\bar{1}$ 0), which achieved the most stable configuration of structural 6Cu/ZnO(10 $\bar{1}$ 0) surface. In the second step, the model of 6Cu/ZnO (10 $\bar{1}$ 0) surface then is used to calculate the CO and H<sub>2</sub>O co-adsorption process in finding the most stable co-adsorption configuration. In addition, we also calculate the CO and H<sub>2</sub>O co-adsorption on ZnO(10 $\bar{1}$ 0) surface to compare with 6Cu/ZnO (10 $\bar{1}$ 0) surface. The calculated results in this work will improve the effects of cluster on the metal oxide surface, also the first explore in mechanisms of water gas shift reaction on 6Cu/ZnO (10 $\bar{1}$ 0) where no investigation has been reported.

## 2. METHODOLOGY

### 2.1 Computational details

All DFT calculations were performed with the plane wave based package in Vienna *ab initio* Simulation Package (VASP) [16-20]. The generalized gradient approximation with Perdew-Wang 1991 formulation (GGA-PW91) [19, 21] which works well for surfaces, was used to treat the exchange-correlation functional[22]. The cut-off energy of 380eV was used for geometry optimization. In order to curtail the interaction between the slabs, we introduced a 15 Å of vacuum space in the *z* direction. All reported results for stable molecules were obtained for the lowest energy conformer of a given species.

### 2.2 ZnO (10 $\bar{1}$ 0) surface model

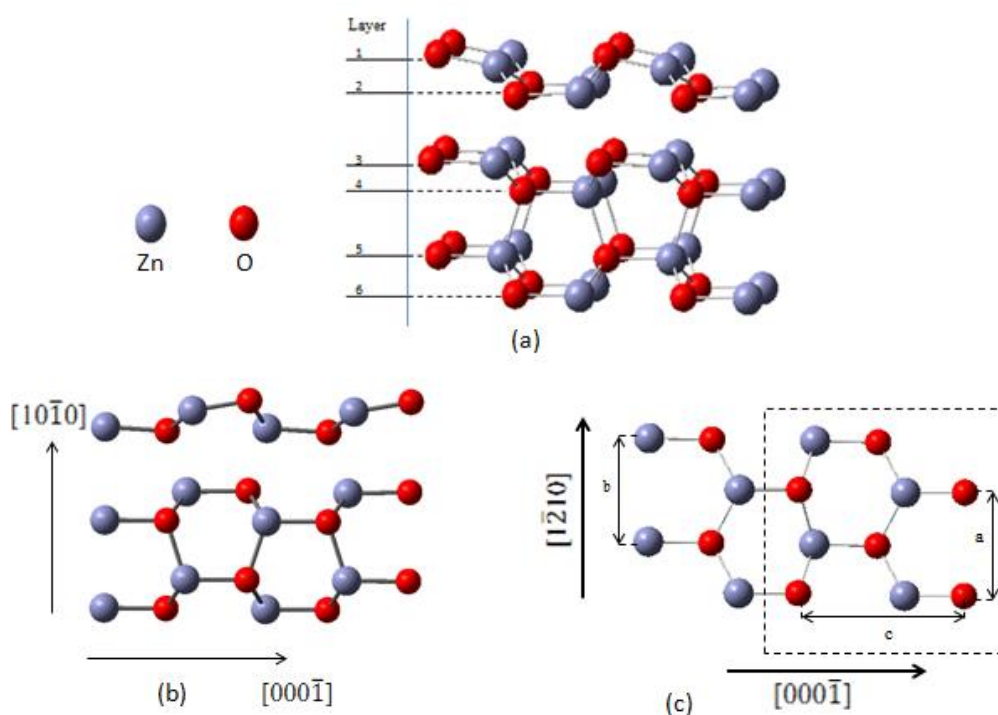


Figure 1. The ZnO (10 $\bar{1}$ 0) clean surface model with three top relaxed layers and three bottom fixed layers: (a) a perspective view with the ball-stick style; (b) a side view of the six-layer surface; and (c) top-view of the first two upper layer, the dashed area represented 1 unit cell with its parameters  $a = b = 3.24\text{\AA}$  and  $c = 5.19\text{\AA}$ ,  $c/a = 1.60$

From the information that was observed in previous experiments and computations, the computed bulk lattice constants of three-dimensional ZnO were 6.50 x 10.41 x 21.57 Å [23-26]. The optimized (2 x 2) unit cells of the most stable ZnO (10 $\bar{1}$ 0) surface with six layers were modeled as periodically repeating slabs as Figure 1 [27, 28]. The top three layers were free to relax in the calculations of surface adsorption and interfacial reaction, and the bottom three layers were fixed at the computed lattice constants to represent the semi-infinite bulk crystal [29]. In order to minimize the interaction between slabs in this infinitely periodic model system, a vacuum region of 15Å ( see in Figure 2) was introduced to separates the top and bottom surfaces of the slabs [28]. Additionally, the Monkhost-Pack mesh was (4 x 4 x 1) *k*-point for ZnO (10 $\bar{1}$ 0) surface geometric optimization. In order to construct a developed ZnO-based catalyst, we proposed to let 6 Cu atoms adsorb on the first layer of the ZnO (10 $\bar{1}$ 0) surface.

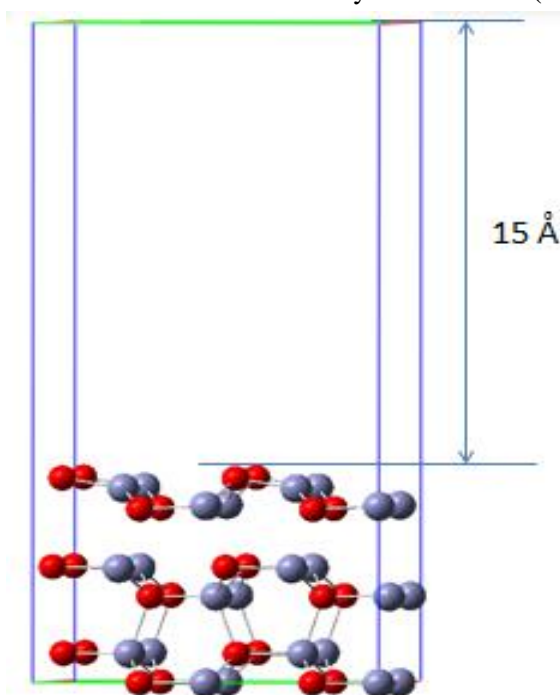


Figure 2. A side view of the optimized ZnO (10 $\bar{1}$ 0) surface with the 15Å vacuum slab

### 2.3 Energy equations

Different possible adsorption sites on ZnO (10 $\bar{1}$ 0) surface resulted in various cases of 6Cu cluster deposited on the clean ZnO (10 $\bar{1}$ 0) surface. It has different initial structures were optimized and obtained. To describe the difference between the total energy of adsorbate-surface system and the sum of surface total energy and adsorbates total energy, the adsorption energy ( $E_{ads}$ ) per adsorbate on ZnO (10 $\bar{1}$ 0) was defined generally as follow [27]:

$$E_{ads} = E_{adsorbate-surface} - E_{surface} - E_{adsorbate} \quad (\text{Eq. 1})$$

Where,  $E_{adsorbate-surface}$ ,  $E_{surface}$  and  $E_{adsorbate}$  represented the calculated interface energy between the adsorbates and surface, a clean surface, and a molecule adsorbed from gaseous phase, respectively. All the energy equations afterwards including either the interaction energy between Cu-ZnO or the co-adsorption energy of CO and H<sub>2</sub>O on the most stable 6Cu/ZnO (10 $\bar{1}$ 0) surface were also generated from this general adsorption equation (Eq.1). A negative  $E_{ads}$  referred a gain of energy concludes the thermodynamically favorable adsorption.

### 3. RESULTS AND DISCUSSIONS

#### 3.1 6Cu/ZnO (10 $\bar{1}$ 0) surface

Based on the chemical sense, the distribution of 6Cu cluster was oriented at possible sites on ZnO (10 $\bar{1}$ 0) surface. Thence, several configurations of 6Cu cluster disposed on ZnO (10 $\bar{1}$ 0) surface (denoted as 6Cu/ZnO (10 $\bar{1}$ 0)) optimized and investigated. Among the calculated models of 6Cu/ZnO (10 $\bar{1}$ 0), the four most stable structures (having the highest adsorption energy) were obtained and presented in Figure 3.

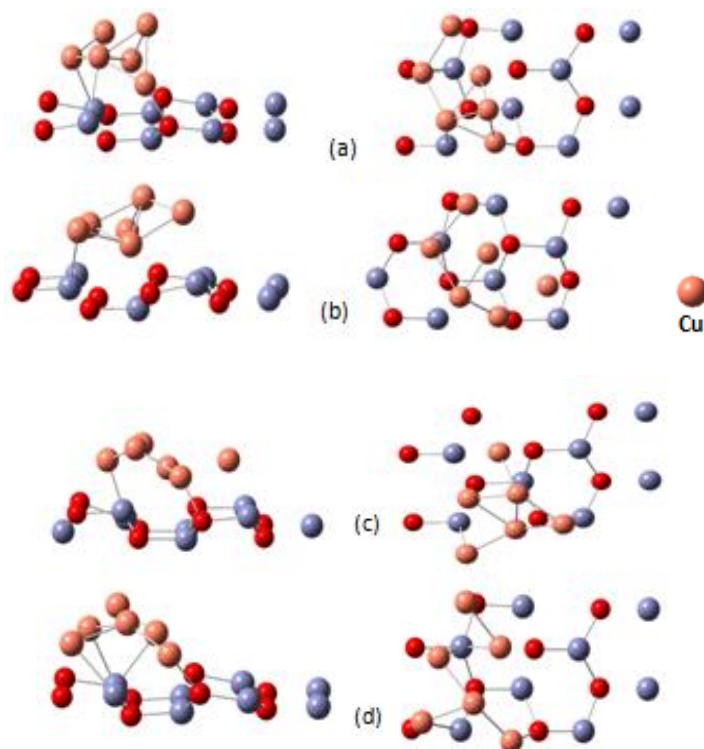


Figure 3. The side view (left) and top view (right) of the optimized geometries of 6Cu adsorption on ZnO (10 $\bar{1}$ 0) clean surface: (a) 6Cu-I, (b) 6Cu-II, (c) 6Cu-III, (d) 6Cu-IV.

As illustrated in Figure 3, all four stable structures yet the 6Cu-III had the tendency of adsorbing on the most top Zn atom. It was favorable for the later adsorption of CO on the surface due to the fact claimed by Hung and his partner (2009), the vicinity of the top most O ion is purely repulsive to CO molecule [27].

Table 1 presents the interaction energy of per Cu atom on the ZnO (10 $\bar{1}$ 0) surface ( $E_{int}$ ), the contribution of Cu-ZnO surface interaction ( $E_{Cu-ZnO}$ ) and the average bond length between two Cu atoms ( $d_{Cu-Cu}$ ) corresponding with each case. Their equations are basically based upon the equation (Eq. 1) but replace with  $n = 6$  instead. They are expressed as follows:

$$E_{int} = -[E(Cu_6/ZnO) - E(ZnO) - 6E(Cu)] / 6 \quad (\text{Eq. 2})$$

$$E_{Cu-ZnO} = -[E(Cu_6/ZnO) - E(ZnO) - E(Cu_6)] / 6 \quad (\text{Eq. 3})$$

Where,  $E(Cu_6/ZnO)$  is the total energy of the ZnO (10 $\bar{1}$ 0) surface with 6Cu cluster ( $Cu_6$ ), while  $E(ZnO)$  and  $E(Cu)$  are the total energy of the ZnO (10 $\bar{1}$ 0) surface and a single Cu atom gaseous phase, respectively.

Table 1. The calculation parameters for 6Cu atoms adsorption on ZnO (10 $\bar{1}$ 0) : interaction energy of per Cu atom ( $E_{int}$ ), the stability of the adsorbed 6Cu cluster ( $E_{Cu-ZnO}$ ) and the average bond length between two nearest Cu atoms corresponding with each case.

Sites	$E_{int}$ (eV)	$E_{[Cu-ZnO]}$ (eV)	$d_{Cu-Cu}$ (Å)
6Cu-I	2.86	1.86	2.55
6Cu-II	2.81	1.81	2.44
6Cu-III	2.74	1.78	2.42
6Cu-IV	2.94	1.94	2.66

The data in Table 1 explained the models illustrated in Figure 3. It was observed that the higher Cu-ZnO surface interaction, the longer the Cu-Cu bonds. This observation consisted with understanding that when Cu atoms adsorbed on the surface, interaction between atoms and surface became higher, leading to the weaker connection among atoms. Hence, they were apart from each other and resulted in their long bond length. Another considerable parameter was the interaction energy which was obtained based upon (Eq. 2). According to the comparison among four stable 6Cu/ZnO (10 $\bar{1}$ 0) configurations, the model 6Cu-IV (Figure 3) had most stable structure with the highest interaction energy of 2.94 eV. Its six Cu atoms were arranged in zigzag before adsorbed on clean surface with the longest average bond length between two nearest Cu atoms of 2.66 Å. Therefore, the configuration 6Cu-IV was used to study the CO and H<sub>2</sub>O co-adsorptions on the 6Cu/ZnO (10 $\bar{1}$ 0) surface.

### 3.2 Co-adsorption of CO and H<sub>2</sub>O molecules on the 6Cu/ZnO (10 $\bar{1}$ 0) surface

CO adsorbed on the ZnO surface either by C atom (C down) or O atom (O down) [30-33]. It is well known that, the surface area in the vicinity of the topmost O ion is purely repulsive for both the “C down” and “O down”. Previous study [30] indicated that “C down” orientation was found to be the most stable one. We also performed different orientation of CO adsorbed on ZnO surface and found that the C down is the most stable conformer. Therefore, we considered “C down” orientation for all the other calculations in this study. Similarly, we considered only C down orientation of the adsorbed CO to interact with the Cu cluster deposited over ZnO surface.

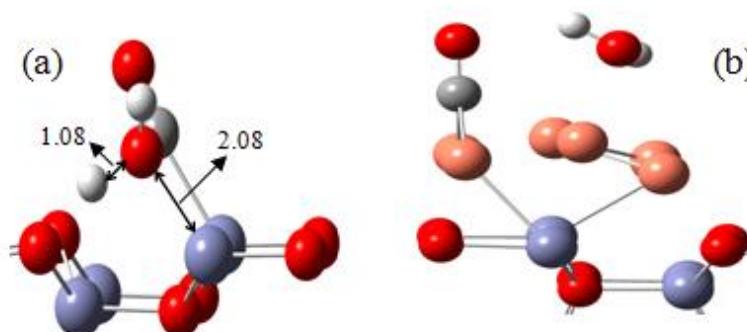


Figure 4. Side view configuration of the optimized CO and H<sub>2</sub>O molecule co-adsorption on the studied ZnO (10 $\bar{1}$ 0) surface (a) and 6Cu/ZnO (10 $\bar{1}$ 0) surface (b).

The previous investigation [34-36] shown that the most stable configuration of H<sub>2</sub>O adsorption on the surfaces were atomic O of water oriented to metal oxide surface. Therefore, adsorbed H<sub>2</sub>O molecule on surfaces in this study, we let also O of the H<sub>2</sub>O molecule orient to Zn on ZnO surface and to Cu cluster on 6Cu/ZnO surface, respectively. As a result, the most stable configuration of CO and H<sub>2</sub>O co-adsorption on ZnO(10 $\bar{1}$ 0) surface and 6Cu/ZnO(10 $\bar{1}$ 0) surface are shown in the Figure 4.

In order to compute the total energy of CO and H<sub>2</sub>O co-adsorption on the studied surface, all relevant parameters including the energy of CO adsorbate ( $E[CO]$ ) as well as H<sub>2</sub>O adsorbate ( $E[H_2O]$ ) in gaseous phase individually, the energy of ( $E[surface]$ ), and the energy of CO-H<sub>2</sub>O on the surface ( $E[CO.H_2O/surface]$ ) which was obtained by calculating the geometry in Figure 4, had to be ready for the energy equation (Eq. 4). The co-adsorption energy  $E_{coads}$  in this works was expressed in table 2 as,

$$E_{coads} = E[CO.H_2O/surface] - E[surface] - E[CO] - E[H_2O] \quad (\text{Eq. 4})$$

Table 2. The calculation parameters for CO and H<sub>2</sub>O co-adsorption energy ( $E_{coads}$ ) on ZnO(10 $\bar{1}$ 0) surface and 6Cu/ZnO(10 $\bar{1}$ 0) surface

Parameters (Å)	ZnO	6Cu/ ZnO
CO	1.14	1.19
OC-Zn	2.12	/
OC-Cu	/	1.92
H <sub>2</sub> O-Cu	/	2.25
OH <sub>2</sub> -O <sub>s</sub>	1.43	/
$E_{coads}$ (eV)	-1.42	-1.67

It is an observation in Table 2 that CO bond lengths on both ZnO and 6Cu/ZnO surfaces are elongated after co-adsorption, which is likely due to the formation of the chemical bond between CO and surfaces (see in Figure 4). Further, CO bond length of 1.14 eV on ZnO surface is lower than that of 1.19 eV on 6Cu/ZnO surface, implying that Cu cluster on ZnO surface is more active than Zn on the ZnO surface in adsorption process. In addition, CO bonds to Zn with bond distance of 2.12 eV, whereas, to Cu with bond distance of 1.92 eV, this is to say that CO interaction on 6Cu/ZnO surface is stronger than that on ZnO surface. Those follow us to conclude that the CO adsorption on 6Cu/ZnO surface is more effective than ZnO surface.

Continuously observation in Table 2 is H<sub>2</sub>O adsorption on 6Cu/ZnO surface that O of H<sub>2</sub>O interacts directly to Cu (Figure 4b) to form chemical bond with the H<sub>2</sub>O-Cu bond distance of 2.25 eV. Whereas, H of H<sub>2</sub>O is bonded to O of ZnO (O<sub>s</sub>), formed H bond (Figure 4a) with OH<sub>2</sub>-O<sub>s</sub> bond distance of 1.43 eV. This indicates that the H<sub>2</sub>O adsorption on 6Cu/ZnO is more active than on ZnO surface. As a result, it clearly that CO and H<sub>2</sub>O co-adsorption energy on 6Cu/ZnO(10 $\bar{1}$ 0) surface is calculated to be -1.67 eV, which higher than that on ZnO(10 $\bar{1}$ 0) surface with -1.47 eV. It means that CO and H<sub>2</sub>O co-adsorption on Cu cluster deposited ZnO surface is more effectively to compare with ZnO surface. This helps us to predict that chemical reactions occurrence on 6Cu/ZnO surface will be more favorable ZnO surface.

#### 4. CONCLUSION

Based adsorbed 6Cu cluster on ZnO (10 $\bar{1}$ 0) surface, we have identified the most stable 6Cu/ZnO (10 $\bar{1}$ 0) surface structure. Further, the most structural configuration of CO and H<sub>2</sub>O co-adsorptions on ZnO surface and cluster 6Cu/ZnO are calculated, respectively. The resulted calculations of co-adsorption energy on 6Cu/ZnO surface are more effective than on ZnO surface.

This study is the first step in designing more effective ZnO-based catalysts for chemical reactions computationally. To further investigate the improved properties of the 6Cu/ZnO (10 $\bar{1}$ 0) surface, it is suggested the water gas shift reaction mechanism on this surface will identified in next our research.

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