Theoretical study on copper adsorption on ZnO surfaces for CO2 hydrogenation to methanol

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Theoretical study on copper adsorption on ZnO surfaces for CO$_2$ hydrogenation to methanol

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ABSTRACT

The study of Cu on ZnO surfaces is a topic of ongoing research due to the importance of Cu as a promoter in the low-temperature synthesis of methanol, the water-gas shift process, and methanol steam reforming. The role of ZnO in supporting the stabilization of the Cu atoms and promoting the CO$_2$ hydrogenation reaction is multifaceted and involves a range of physical and chemical factors. In this work, we used density functional theory (DFT) calculations to investigate the Cu adsorption on ZnO surfaces on different sites. Bader charge analysis, adsorption energy, and phonon inelastic neutron scattering (INS) associated with most stable systems were calculated and compared with previous theoretical and experimental results. We found that atomic Cu adsorption on hollow site of ZnO(111) is the most stable site and most favorable site for Cu adsorption comparing to other ZnO surfaces. This is due to the strong metal-oxygen interaction between Cu and the ZnO surface. The results suggest that the Cu/ZnO catalyst with Cu atoms at hollow site is most likely to be active for CO$_2$ hydrogenation. We concluded that further studies are needed to investigate the catalytic activity of this catalyst under realistic reaction conditions with realistic models of Cu supported on ZnO.

Keywords: CO$_2$; Hydrogenation; ZnO; Methanol;
1. INTRODUCTION

ZnO is an inorganic compound made up of zinc and oxygen atoms. It has a hexagonal crystal structure and is thermally and chemically stable. ZnO is a conducting oxide that has astonishing chemical and electrical properties with applications in electronics, pharmaceutical and petrochemical industries [1, 2]. It is known that wurtzite ZnO crystals show four low-index surfaces: (10\overline{1}0), (11\overline{2}0), (0001), (000\overline{1})\), and the zinc blend ZnO crystal show three low-index surfaces: (100),(110), and (111) [3–5]. On the other hand, Cu is a transition ductile metal that shows high thermal and electrical conductivity with various applications on manufacturing of electrical parts, heat exchangers and screw machining products [6–8].

Zinc oxide (ZnO) is commonly used as a catalyst in CO\textsubscript{2} hydrogenation reactions due to its unique properties [9]. It has a high surface area, thermal stability, and can promote the activation of CO\textsubscript{2} and hydrogen molecules [10, 11]. However, ZnO alone is not very efficient in converting CO\textsubscript{2} to methanol. The addition of Cu to the ZnO surface significantly enhances the catalytic activity and selectivity towards methanol production [12, 13]. When Cu is deposited on the ZnO surface, it forms copper-zinc alloy structures or copper oxide clusters [14]. These Cu species act as active sites for the adsorption and activation of CO\textsubscript{2} and hydrogen molecules. The adsorption of CO\textsubscript{2} on the copper species leads to its activation and subsequent hydrogenation to form methanol [15, 16]. In this process, Cu acts as a catalyst to facilitate the reaction between CO\textsubscript{2} and hydrogen (H\textsubscript{2}) to form methanol (CH\textsubscript{3}OH). When deposited onto ZnO surfaces, Cu can undergo surface reconstructions that create additional active sites for CO\textsubscript{2} and H\textsubscript{2} binding [17–19]. For example, Cu(001) surfaces have been found to undergo a surface reconstruction known as the Cu(001)-ZnO structure, which creates a network of Cu atoms and ZnO layers that can enhance the activity of the catalyst [18]. In addition, the presence of ZnO provides a stable support for Cu, preventing its sintering or aggregation during the reaction [20]. Moreover, the electronic properties of ZnO can influence the reactivity of Cu and facilitate the adsorption and activation of reactant molecules. Cu has a relatively low ionization energy and a high electron affinity, which allows it to readily interact with electrons in the ZnO substrate and promote the formation of chemisorbed states. These chemisorbed states can then participate in the hydrogenation reaction.

One of the earlier theoretical studied was conducted by Beltrana et al. (2000) who investigated the interaction modes of the Cu atom on ZnO (10\overline{1}0) surface, and they found that full coverage of Cu atoms on O positions on ZnO (10\overline{1}0), is slightly more energetically favourable than the full coverage over Zn atoms [21]. Furthermore Dai et al. (2008) found that the most favored structures for Cu/ZnO(0001) system are FCC and
HCP hollow sites in term of Cu adsorption, but they didn’t define the charge states of Cu on ZnO surfaces [22]. Many literature studies show that Cu doping into polar terminated ZnO crystals can enhance its physical, chemical and optical properties that affect related applications, but not stability and charge states of and Cu adsorptions on ZnO(111), ZnO(0001) and ZnO(000\bar{1}) surfaces [23, 24]. In addition, there are extensive theoretical studies on the electronic description of ZnO surfaces and different molecular adsorption on those surfaces such as O, N and Ni but not Cu [25–27]. However, there’s still no satisfactory explanation for the stability of which is the key point to understand the production of methanol through Cu/ZnO-based catalyst.

The aim is to investigate the charge transfer of copper on ZnO surfaces and its implications for CO$_2$ hydrogenation to methanol. Another objective is to develop a theoretical model for the adsorption of copper on ZnO surfaces. In addition, the purpose is to investigate the most stable and favorable sites for copper adsorption on ZnO surfaces for CO$_2$ hydrogenation to methanol. The density functional theory (DFT) with Hubbard U correction was employed to calculate the adsorption energy on bridge, hollow, top of Zn and top of O sites of Cu on ZnO(0001), ZnO(000\bar{1}) and ZnO(111) (see figures 1 and 2). This includes using PDOS and the Bader charge analysis to define the charge state of Cu on ZnO(111) and ZnO(0001) on both zinc and oxygen terminated surfaces. Additionally, we investigated the vibration frequencies for the most stable systems via phonon inelastic neutron spectroscopy (INS) to define the types of vibrations modes on those systems. We believe those observations will be important to better understanding of working principle of Cu/ZnO metal interface.

2. Computational Methods

2.1 Adsorption energy

We applied density functional theory (DFT) plane-wave calculations with Hubbard correction (+U) as implemented in ABINIT [28, 29] with the projector augmented wave (PAW) method. The generalized gradient approximation (GGA) with (RPBE) functional exchange-correlation functional was used. For the study of Cu adsorption on ZnO surfaces, we employed slab model with 4 × 4 surface unit cell consisting of 7 layers and a vacuum layer of 15 Å separating the slabs. The top four layers of ZnO bilayers and the adatom H and Cu are allowed to relax while the bottom three bilayers of ZnO are fixed at their bulk positions to imitate the bulk substrate. In addition, the calculations were carried out using the Brillouin zone sampled with (2×2×1) Monkhorst–Pack mesh k-point grids with a cutoff energy of 475 eV, which allows for convergence to 0.01 eV in the total energy. Because regular DFT methods are unable to describe the localization orbitals of the ZnO 3d10 orbital, DFT with the Hubbard U term (DFT + U) was applied for accurate calculations of electronic
structures. After the structures of studied systems were optimized (see table 1 for lattice constants), we have model them with atomic Cu on different sites including top of Zn, top of O, hollow and bridge sites. Then, the adsorption energy was calculated by using the formula below (equation 1):

\[ E_{\text{ads}} = E_{\text{ads/substrate}}^{\text{Total}} - E_{\text{substrate}}^{\text{Total}} - E_{\text{Cu}}^{\text{Total}} \]  

(1)

where \( E_{\text{ads/substrate}}^{\text{Total}} \) is the total energy of the optimized adsorbate Cu interacting with the slab, \( E_{\text{substrate}}^{\text{Total}} \) is the total energy of optimized slab; and \( E_{\text{Cu}}^{\text{Total}} \) is the total energy of the optimized adsorbate.

2.2 Phonon inelastic neutron scattering (INS)

In term of vibrational normal modes, phonon frequencies were computed through ABINIT software with finite differences methods and Gamma point of (0,0,0) in each system. Phonon calculation was weighted with the neutron scattering cross sections included with AbINS in the Mantid software to obtain the spectra [30].

The general steps of AbINS calculation includes using the atomic displacements and frequencies obtained from DFT vibrational calculations and, then the software will calculate a discrete \( S(Q, E) \) using a semi-empirical powder averaging model. AbINS produces \( S(Q, E) \) in scaled units which are related to the correct units barn/cm\(^{-1}\) by a linear factor. With ABINIT data, AbINS uses the values of atomic masses read directly from the phonon file. The resulting scattering neutron is defined as partial differential scattering cross section in which the final energy of \( E' \) between \( (E' + dE') \) of the scattered neutron is defined as the scattered per second times the solid angle \( \Delta \Omega \) and divided by the incident flux \( \Phi \) as shown below (equation 2). It is worth noting that the area is perpendicular to the incident neutron and the partial differential scattering cross section is directly proportional to the scattering function \( S(Q,E) \) [30].

\[ \frac{d^2 \sigma}{d\Omega dE'} = \frac{k_f}{k_i} S(Q, E) \]  

(2)

2.3 Density of state (DOS)

The density of states (DOS) in solid state physics is the measure of number of states available for electron to occupy. The DOS is generally calculated by using first principal methods such as DFT and experimentally using techniques such as photoemission spectroscopy and scanning tunnelling microscopy. The DOS can group very large number of states (levels) at given energy interval as defined in equation (3) below [31]:

\[ \text{DOS}(E) \, dE = \text{number of levels between } E \text{ and } E + dE \]  

(3)
Where $E + dE$ is the number of states in energy range. The DOS can be defined as the number of electron states per unit volume when we modelled the energy of conduction electrons in a metal as trapped in 3D infinite square well. The expression of the number of electron states ($N_s$) per unit volume is defined below (equation 2.3.1):

$$\frac{N_s}{L^3} = \frac{8\pi}{3h^3} \left( \frac{2mE}{\hbar^2} \right)^{\frac{3}{2}}$$

Here, the number of electrons states ($N_s$) up to a threshold energy ($E$), $m$ is the mass of electron and ($L$) is the size of 3D infinite square well. We can find the volume of the sphere in quantum number by calculating the number of electrons states up to a threshold energy. Hence, taking the derivatives of the number of states per unit volume in equation 1.4.6.2 will gives the number of states per unit volume per unit energy [32], which is called density of state DOS as shown below (equation 5):

$$D_s(E) = \frac{dN_s}{dE} = \frac{8\pi}{h^3} m^{\frac{3}{2}} \sqrt{2E}$$

The shape of the DOS graph is determined by the material's electronic structure and the temperature at which it is being measured [31, 33]. The Fermi energy on the DOS indicates state occupation where states below the Fermi energy will be occupied at zero temperature ($T=0$ k) but, states above that will be unoccupied. The total integral of DOS up to the Fermi level is known as the total number of occupied molecular orbitals [31].

The projected density of state (PDOS) is the number of available number of state that electron can occupy projecting on the atomic orbitals (s,p,d,f) at specific energy. The PDOS curve give indication of biggest share for the specific shell (s,p,d,f) and orbital for particular atom. Generally, the PDOS gives information about the different contributions of the different orbitals that computed to then know which states (s,p,d,f) contribution at specific energy.

### 2.4 Bader charge analysis

Previous studies from literature have suggested that there might be a correlation between the adsorption energy (i.e., stability of the system) and the amount of charge exchanged [34–38]. This is because the amount
of charge exchanged affects the electrostatic interactions between the adsorbate and the surface. Hence, Bader charges were calculated by using the scheme proposed by Henkelman et al. to measure the amount of charge exchanged is measured by the Bader charge analysis [39, 40]. Bader charge analysis is a method for partitioning the electronic charge density of a molecule or solid into atomic basins [39]. It was developed by Richard Bader in the 1960s. The basic idea of Bader charge analysis is to define an atom as a region of space where the electronic charge density is a minimum perpendicular to the surface. This surface is called a zero flux surface and the charge enclosed within a zero flux surface is called the Bader charge of the atom [40]. The Bader charge analysis is a non-empirical method, which means that it does not rely on any adjustable parameters. This makes it a reliable way to calculate the charge distribution in molecules and solids. Bader charge analysis has been used to study a wide variety of systems, including molecules, solids, and surfaces. It has been used to investigate the nature of chemical bonding, the distribution of charge in materials, and the reactivity of molecules.
**Figure 1**: The fully optimized structures of Hollow site → Bridge site for both a) ZnO(0001) (Zn-terminated) and b) ZnO(000\overline{1}) (O-terminated). The exposed surface including the adsorbed molecule is shown in ball and stick form, and the rest of the model is represented in the CPK form (Zinc is represented in yale blue, Oxygen in red and Copper in punch pink).
Figure 2: Top view of the ZnO(0001) (Zn-terminated) surface, indicating the studied-symmetry adsorption sites: Bridge, Hollow, and On-top sites. Red and Blue balls represent O and Zn atoms, respectively.

Table 1: shows the Lattice constants of wurtzite ZnO and zinc blend ZnO

<table>
<thead>
<tr>
<th></th>
<th>Wurtzite ZnO</th>
<th>Zinc Blend ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant</td>
<td>a (Å)</td>
<td>c (Å)</td>
</tr>
<tr>
<td>Our results</td>
<td>3.315</td>
<td>5.309</td>
</tr>
</tbody>
</table>
3. Results and Discussion

3.1 Cu adsorption on ZnO(0001) (Zn-terminated) and ZnO(000$I$) (O-terminated) surfaces

The calculated lattice constants for unit cell of both zinc blend and wurtzite ZnO shows good agreement with previous experimental and theoretical results. In the calculations below, the optimized structures with obtained lattice constants were used for both zinc blend and wurtzite ZnO. Previous studies found that ZnO prevents agglomeration of Cu particles, that leads to the large Cu surface area needed for methanol catalysis and other industrial applications [22, 41–46]. Therefore, we examined the stability of systems with atomic Cu atom adsorbed on different sites (Hollow, Bridge, Top of Zn, and Top of O) for both O-terminated and Zn-terminated ZnO(0001) and ZnO(111) as shown in table 2. In the case of the most stable site of Cu on O-terminated ZnO(000$\bar{1}$), the initial site of hollow that optimized into bridge site shows the lowest adsorption energy (i.e. most stable system) with adsorption energy of -3.206 eV. This site was also the most stable in contrast to other Cu/ZnO(0001) (Zn-terminated) systems. We suggest this occurs because it has the most favorable electronic and structural interactions between the Cu atom and the ZnO substrate compared to other systems. In the hollow site, the Cu atom is located in the center of a six-membered ring of oxygen atoms. This arrangement allows the Cu atom to form strong bonds with the oxygen atoms, which provides a stable foundation for the Cu atom. Additionally, the Cu atom is occupying a position that allows it to interact with the dangling bonds of the ZnO substrate. When we consider most stable Cu adsorption on different sites of ZnO(0001) (Zn-terminated) surfaces, we found that the Cu adsorption located on the initial Bridge site (1.2 Å) shifted into Top of Zn site (1.917 Å) with adsorption energy of -2.504 eV. This result is consistent with the finding by Dai et al. (2008) who found that formation energy of Cu on FCC-Hollow site is -2.54 eV [22] which appears to be more favorable than other sites. Similarly, Cu atom that lactated on Hollow site of ZnO(0001) (Zn-terminated) is the most stable system and the appears to be more favorable than other sites. However, the Cu atom located on top of Zn remains on the same site upon relaxation which also shows the highest adsorption energy comparing to other sites in ZnO(0001) (Zn-terminated) surfaces with adsorption energies of -2.267 and -2.354 eV for top of Zn and top of O respectively.

On the other hand, the Cu on Top of Zn site on ZnO(000$\bar{1}$) (O-terminated) shows the highest adsorption energy with -2.136 eV and the Cu atoms remain in the same position upon the relaxation (1.200 Å to 2.064 Å). The Cu atom donates its electrons to the ZnO surface, which creates a negative charge on the surface and a positive charge on the Cu atom. This charge transfer lowers the energy of the system, making it more stable. The Cu atoms remain in the same position upon the relaxation because they are strongly bonded to
the ZnO surface. The relaxation process only changes the positions of the atoms that are not strongly bonded to the surface. Additionally, the Cu atom is located in a position that allows it to interact with the dangling bonds of the ZnO substrate. Similarly, the Cu atom on Top of O remains on top of O atom upon the relaxations where the distance between the Cu and O atoms is 1.821 Å. However, the shorter length of Cu bond to O (1.821 Å) compared to length of Cu bond to Zn (2.064 Å) for O-terminated ZnO(0001) is further indicates that the interaction of Cu to bond O is stronger than that of Cu-Zn bond. Oxygen is more electronegative than Zn, meaning that it has a stronger attraction for electrons. This means that the Cu-O bond will be more polar than the Cu-Zn bond, with more electron density being donated to the oxygen atom. This results in a stronger bond between the Cu atom and the oxygen atom. This was similar to the DFT study conclusion by both Chen et al. (2019) and Beltrán et al. (2001) who investigated the interaction of Cu with a ZnO by placing one Cu atom on Top of the Zn atom and O atom on the ZnO surface [21, 30].

The Bader charge analysis for most stable system of O-terminated ZnO(000\bar{1}) shows that the Cu atom donates electrons to the Zn atom, which makes the Zn atom less negatively charged as shown on table 3. The amount of charge transferred from the Cu atom to the Zn atom is 0.061 |e| electrons. This is the difference between the Bader net charges of the Zn atom in ZnO(000\bar{1}) (O-terminated) and the O atom in Cu/ZnO(000\bar{1}) (O-terminated). The Bader net charge of the Cu atom on Cu/ZnO(000\bar{1}) (O-terminated) on hollow site is 0.186 |e|. This means that the Cu atom has a net positive charge of 0.186 electrons. This positive charge is due to the loss of electrons to the O atoms in the ZnO surface. Looking more closely to the CO\textsubscript{2} hydrogenation to methanol through Cu/ZnO-based catalyst, the difference in the Bader net charges of the Zn atom is favorable for the reaction. This occurs because the more electrons that are donated from the Cu atom to the Zn atom, the easier it is for the Zn atom to spill over the hydrogen atom from CO\textsubscript{2}. The positive charge on the Cu atom also helps to activate the CO\textsubscript{2} molecule and make it more susceptible to hydrogenation.

In the case of the most stable system of Cu/ZnO(0001) (Zn-terminated) system, the Bader net charge of O is 1.185 |e| and the Bader net charge of Cu is -0.292 |e| (See table 3). This means that the O atom has gained electrons from the Cu atom, while the Cu atom has lost electrons to the O atom. This charge transfer is due to the difference in electronegativity between Cu and O. Cu is more electronegative than Zn, so it has a stronger attraction for electrons. This means that the Cu atom will tend to take electrons away from the Zn atom, resulting in a positive charge on the Cu atom and a negative charge on the O atom. The Bader net charge of Zn on ZnO(0001) (Zn-terminated) system is 0.953 |e|. This is lower than the Bader net charge of O atom on Cu/ZnO(0001) (Zn-terminated) system, which is 1.185 |e|. This difference is also due to the charge
transfer from Cu atom to O atom. The Cu atom takes electrons away from the O atom, which leaves the Zn atom with a lower net charge. Charge transfer from Cu to O to methanol in the hydrogenation of CO$_2$ via a Cu/ZnO-based catalyst can have several advantages: First, it gives the Cu atom a more positive charge, resulting in higher reactivity. This can lead to the formation of Cu-O bonds, which are important for the catalytic activity of Cu on ZnO. Second, the charge transfer makes the Zn atom more negatively charged, which makes it more stable. This may help prevent Zn atoms from reacting with CO$_2$ or H$_2$ molecules [47].

**Table 2:** Shows the adsorption energy (eV) of atomic Cu on Cu/ZnO(0001) (Zn-terminated), Cu/ZnO(0001̅) (O-terminated), and Cu/ZnO(111)

<table>
<thead>
<tr>
<th>Cu Optimized site</th>
<th>Final Bond length ($\ell$) (Å)</th>
<th>Adsorption energy (eV) on Cu/ZnO(0001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/ZnO(0001) (Zn-terminated) and Cu/ZnO(0001̅) (O-terminated)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O-terminated</td>
<td>Cu$_{\text{OlI-Bdg}}$</td>
<td>$\ell_{\text{Cu-O}}$ 1.949</td>
</tr>
<tr>
<td>Zn-terminated</td>
<td>Cu$_{\text{OlI-Bdg}}$</td>
<td>$\ell_{\text{Cu-Zn}}$ 1.918</td>
</tr>
<tr>
<td>O-terminated</td>
<td>Cu$_{\text{OTop}}$</td>
<td>$\ell_{\text{Cu-O}}$ 1.821</td>
</tr>
<tr>
<td>Zn-terminated</td>
<td>Cu$_{\text{OTop}}$</td>
<td>$\ell_{\text{Cu-O}}$ 2.774</td>
</tr>
<tr>
<td>O-terminated</td>
<td>Cu$_{\text{ZnTop}}$</td>
<td>$\ell_{\text{Cu-Zn}}$ 2.064</td>
</tr>
<tr>
<td>Zn-terminated</td>
<td>Cu$_{\text{ZnTop}}$</td>
<td>$\ell_{\text{Cu-Zn}}$ 2.301</td>
</tr>
<tr>
<td>O-terminated</td>
<td>Cu$_{\text{Bdg-Holl}}$</td>
<td>$\ell_{\text{Cu-O}}$ 2.062</td>
</tr>
<tr>
<td>Zn-terminated</td>
<td>Cu$_{\text{Bdg-ZnTop}}$</td>
<td>$\ell_{\text{Cu-Zn}}$ 1.917</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cu/ZnO(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_{\text{OlI-Holl}}$</td>
</tr>
<tr>
<td>Cu$_{\text{OTop-Holl}}$</td>
</tr>
<tr>
<td>Cu$_{\text{ZnTop-Holl}}$</td>
</tr>
<tr>
<td>Cu$_{\text{ZnBdg-Holl}}$</td>
</tr>
</tbody>
</table>
Table 3: shows the Bader Charger analysis of most stable site on Zn interacting on Cu/ZnO(0001) (Znterminated) and O interacting on Cu/ZnO(0001̅) (O-terminated)

<table>
<thead>
<tr>
<th>System</th>
<th>site</th>
<th>Bader net Charges (e)</th>
<th>Adsorption energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO(0001) (Zn-terminated)</td>
<td>O</td>
<td>0.953</td>
<td>-</td>
</tr>
<tr>
<td>Cu/ZnO(0001) (Zn-terminated)</td>
<td>CuBdg-ZnTop</td>
<td>1.185</td>
<td>-0.292</td>
</tr>
<tr>
<td>ZnO(0001̅) (O-terminated)</td>
<td>Cu</td>
<td>-1.249</td>
<td></td>
</tr>
<tr>
<td>Cu/ZnO(0001̅) (O-terminated)</td>
<td>CuHoll-Bdg</td>
<td>-1.231</td>
<td>0.186</td>
</tr>
<tr>
<td>ZnO(111)</td>
<td>Cu</td>
<td>-1.227</td>
<td>-3.206</td>
</tr>
<tr>
<td>Cu/ZnO(111)</td>
<td>CuHoll</td>
<td>-1.209</td>
<td>0.164</td>
</tr>
</tbody>
</table>

3.2 Cu adsorption on ZnO(111) surface

It is known that the ZnO(111) surface is the most stable surface comparing to other ZnO surfaces as it has the lowest surface energy [48–50]. The reason behind this stability of ZnO(111) is the hexagonal structure in which each atom is bonded to three other atoms either oxygen or zinc atom in the bulk [49, 51–53]. In term of the Cu adsorption on different sites of ZnO(111), it was found that the Cu adsorption on hollow site remain in the same site upon relaxation. The hollow site is the most stable system comparing to other sites on ZnO(111) with adsorption energy -3.640 eV which mean it’s energetically favorable, in contrast to other sites (see table 2). The adsorbed Cu atom in the hollow site can form strong bonds with the six Zn atoms in the site. These bonds are delocalized over the six Zn atoms, which makes them even stronger. According to table 2, the Cu adsorption on wurtzite ZnO surfaces shows higher stability compared to zinc blend ZnO surfaces because of higher sharing of electrons within wurtzite ZnO and higher ability to transfer charge from the Cu to wurtzite ZnO. Another reason is that wurtzite structure has a larger band gap, which make it more difficult for the Cu atom to lose electrons [54–56]. This means that the CO₂ hydrogenation reaction requires the Cu atom to be in a reduced state (Cu+) on ZnO surface.

In order to achieve a better understanding of Cu behavior and to support our finding, we employed Bader charge on hollow site as shown in table 3. The Bader net charge of the Cu atom is 0.164 |e| which signify that the Cu atom has a net positive charge of 0.164 |e| electrons. This positive charge is due to the loss of electrons to the O atoms in the ZnO surface. The difference in the Bader net charges of the O atom of ZnO surface and the O atom of Cu/ZnO(111) system is 0.018 |e|. This means that the O atom in Cu/ZnO(111) has 0.018 |e| electrons less than the O atom in ZnO(111). This difference in charge is due to the presence
of the Cu atom. It is known that Cu atom have a lower electronegativity than O atom which means that the 
Cu atom attracts electrons weaker than the oxygen atom. When the Cu atom is adsorbed on the ZnO surface, 
it donates electrons to the O atom in the surface. This makes the O atom less negatively charged and gives 
the Cu atom a net positive charge. This make it easier for the O atom to dissociate the hydrogen atom during 
CO$_2$ hydrogenation reaction to methanol. Moreover, the amount of charge transferred from the Cu atom to 
the O atom is 0.018 |e| electrons. This is the difference between the Bader net charges of the O atom in 
ZnO(111) surface and the O atom in Cu/ZnO(111) system.

3.3 PDOS analysis

To better understand the origin of adsorption properties, we analyze the projected density of state (PDOS) 
of the most stable site which is the adsorbed Cu on bridge site of ZnO(000$\bar{1}$) (O-terminated) with adsorption 
energy of -3.206 eV comparing to other ZnO(0001) surfaces. On analyzing partial density of states (PDOS) 
we found significant overlap between Cu s (u) and Zn p (u) orbitals at -4.5 eV (see figure 3). This overlapping 
is due to the fact that these orbitals have different symmetries, and it reveals why the adsorption energy of 
Cu atom on ZnO(000$\bar{1}$) (O-terminated) is low and stability of the system is high as the electrons are 
transferred from the Cu s orbital to the Zn p orbital. This transfer of electrons creates a negative charge on 
the Cu atom and a positive charge on the Zn atom. The electrostatic attraction between these opposite 
charges holds the Cu atom to the ZnO surface. Hence, the strong bonding between Cu and ZnO is 
responsible for the high activity of Cu/ZnO catalysts for CO$_2$ hydrogenation as the Cu s (u) orbital is the most 
reactive orbital, and it is also the most exposed to the surface. When CO$_2$ molecules approach the Cu/ZnO 
surface, they are attracted to the negative charge on the Cu atom [57–59]. This attraction weakens the bonds 
between the carbon and oxygen atoms in the CO$_2$ molecule, making it easier for the hydrogen atoms to break 
these bonds and form methane [60–62]. The symmetry of the PDOS for Cu s (u) and Cu s (d) orbitals is 
determined by the symmetry of the orbitals themselves and the symmetry of the crystal lattice as shown in 
figure 4. The Cu s (u) orbital is a spherically symmetric orbital, which means that it has the same shape in all 
directions. The Cu s (d) orbitals are dumbbell-shaped orbitals, which means that they have a donut-shaped 
cross section.

The analyzing partial density of states (PDOS) for optimized hollow site for Cu adsorption on ZnO(111) 
system shows overlapping between the Cu s (u) and Zn p (u) orbitals at energy level of -7 eV with adsorption 
energy -3.640 eV (see Figure 6). This overlap is responsible for the strong bonding between the Cu atom 
and the ZnO surface. The Cu s (u) orbital is the outermost orbital of the Cu atom, and it is responsible for the
bonding between the Cu atom and the ZnO surface. The Zn p (u) orbital is also exposed to the surface, and it has the same symmetry as the Cu s (u) orbital. This results in a strong overlap between the two orbitals, which leads to a strong bonding and high stability of Cu on ZnO(111) surface. This is essential for the reaction mechanism that can be used to design better catalysts by tuning the bonding characteristics of the Cu/ZnO catalyst. Therefore, hollow site for Cu adsorption on ZnO(111) is the most favorable site for Cu adsorption and that the Cu/ZnO catalyst with Cu atoms at this site is most likely to be active for CO₂ hydrogenation.

3.4 Phono Inelastic Neutron Scattering (INS) analysis

The computed phonon INS spectrum for atomic Cu adsorbed on the optimized bridge site of ZnO(000\(\bar{1}\)) (O-terminated) system shows peak of Cu-Zn stretching mode at energy transfer (frequency) of 620 (eV) (see Figure 5). This peak corresponds to the stretching vibration of the Cu-Zn bonds and it is similar to the reported mode through Raman scattering spectra by Tan et al. (2016) [63]. The wavenumber of the Cu-Zn stretching mode is affected by the bonding environment of the Cu-Zn bonds. In the bridge site, the Cu atom is bonded to two Zn atoms and two O atoms. This bonding environment is different from the bonding environment of the Cu atom in the bulk ZnO crystal, where the Cu atom is bonded to four O atoms. The different bonding environment in the bridge site results in a shift in the wavenumber of the Cu-Zn stretching mode to lower wavenumbers. This shift is due to the increased electronegativity of the O atoms compared to the Zn atoms. The O atoms pull electron density away from the Cu atom, which weakens the Cu-Zn bond and lowers the wavenumber of the stretching mode. It is worth to mention that the ZnO(000\(\bar{1}\)) (O-terminated) system atoms were fixed except the atomic Cu bounded with Zn atom during first-principle phonon calculations.

The Cu-Zn stretching vibration is important for the CO₂ hydrogenation reaction because it allows the Cu atom to interact with the CO₂ molecule. The Cu-Zn stretching mode can be weakened by the presence of hydrogen atoms. This is because the hydrogen atoms can donate their electrons to the Cu atom, which weakens the Cu-Zn bonds. The weakening of the Cu-Zn bonds can make it easier for the Cu atom to interact with the CO₂ molecule and catalyze the CO₂ hydrogenation reaction. Moreover, the presence of hydrogen atoms can weaken the Cu-Zn bonds, which will result in a lower intensity peak. However, the value of 0.6 for the intensity of the peak is still relatively high, suggesting that the Cu-Zn bonds are not too weak. This suggests that the Cu atoms are still able to interact with the CO₂ molecule and catalyze the CO₂ hydrogenation reaction. However, the reaction may not be as efficient as it would be if the Cu-Zn bonds were stronger.
Figure 3: PDOS for the Zn d (u), Zn d (d), Cu s (u) and Cu s (d) on bridge site of Cu/ ZnO(000\(\overline{1}\)) (O-terminated) system, the energy is relative to Ef.

Figure 4: PDOS for Cu s (u) and Cu s (d) orbitals of Cu on bridge site of Cu/ZnO(000\(\overline{1}\)) (O-terminated) system, the energy is relative to Ef.
Figure 5: Shows phonon INS for atomic Cu on bridge site of Cu/ZnO(000̅1) (O-terminated) system.

Figure 6: PDOS on the Zn d (u), Zn p (u), Zn s (u) and Cu s (u) on hollow site of Cu on ZnO(111) system, the energy is relative to Ef.
4. Conclusion

In this study, we employed density functional theory calculations to investigate the adsorption of Cu on different sites of ZnO(111), ZnO(0001) and ZnO(000\bar{1}) surfaces for the purpose of enhancing the CO$_2$ hydrogenation reaction. We used PDOS and the Bader charge analysis to define the charge state of Cu on ZnO(111) and ZnO(0001) on both zinc and oxygen terminated surfaces. It was found that optimized Cu atom on bridge site of ZnO(000\bar{1}) (O-terminated) is the most stable system, and it appears to be more favorable than other sites on both ZnO(0001) and ZnO(000\bar{1}) surfaces. The PDOS shows significant overlap between Cu s (u) and Zn p (u) orbitals at -4.5 eV because these orbitals have different symmetries as the electrons are transferred from the Cu s orbital to the Zn p orbital. The Bader charge analysis for most stable system of O-terminated ZnO(000\bar{1}) shows that the Cu atom donates electrons to the Zn atom, which makes the Zn atom less negatively charged. However, we found that the hollow site of ZnO(111) is the most stable and favored site for Cu adsorption comparing to all studied surfaces of both wurtzite ZnO and zinc blend ZnO. This means that hollow site for Cu adsorption on ZnO(111) is the most favorable site for Cu adsorption and that the Cu/ZnO catalyst with Cu atoms at this site is most likely to be active for CO$_2$ hydrogenation.

These findings have important implications for the development of highly efficient CO$_2$ hydrogenation catalysts, as they suggest that the incorporation of Cu into ZnO supports could lead to improved catalytic activity and selectivity. Future studies should aim to consider the effects of reactant and product molecules on the adsorption of Cu and the CO$_2$ hydrogenation reaction by investigating the reaction kinetics and mechanisms of the CO$_2$ hydrogenation reaction. In addition, further studies are needed to investigate the catalytic activity of this catalyst under realistic reaction conditions with realistic models of Cu supported on ZnO through INS. Although, the present study demonstrates the potential of transition metal-based catalysts for enhancing the CO$_2$ hydrogenation reaction.
5. References


Declarations

Ethics approval and consent to participate
Comply with ethical standards.

Consent for publication
Not applicable

Data Availability and materials
The data that support the findings of this study are available on request from the corresponding author.

Conflict of interest
On behalf of all authors, the corresponding author states that there is no conflict of interest.

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MA: Formal analysis, Data Curation, Writing-Original Draft, Software, Methodology, and Validation.
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