DENSITY FUNCTIONAL THEORY STUDY OF METHANOL ADSORPTION AND DISSOCIATION ON 2Cu/ZnO (1 0 1 0 ) CATALYST SURFACE

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ABSTRACT

The adsorption and dissociation of methanol (CH₃OH) on the cluster with two copper atoms (2Cu) supported over ZnO(1 0 1 0 ) catalyst surface were investigated using the density functional theory (DFT). The performance of 2Cu adsorbed on ZnO(1 0 1 0 ) surface to obtain model of the 2Cu/ZnO(1 0 1 0 ) catalyst surface. The most stable site of CH₃OH with configuration and energy of adsorption was investigated. The reaction pathway of CH₃OH dissociation via bond scission of the O–H, C–H and C–O to form methoxide, hydroxymethyl and methyl was examined, respectively. The obtained calculations pointed out that O–H bond scission is found to be the most favorable pathway on 2Cu/ZnO catalyst surface.

Keywords: 2Cu/ZnO catalyst surface, methanol adsorption, DFT, methanol dissociation.

1. INTRODUCTION

Methanol is known readily to be the owning renewable energy and as famous fuel for conversion to hydrogen, formaldehyde, methyl formate, dimethyl ether, dimethoxymethane, olefins and alkenes via decomposition, dehydration and partial oxidation [1-4]. Further, CH₃OH is available as an abundant feedstock and largely distributed. Many thermodynamic analysis and experimental observation of primary CH₃OH conversion to hydrogen are shown in previous
works [5-9]. Therefore, the adsorption and dissociation to convert CH$_3$OH has mentioned great interests of researchers.

Because of having advantages as high H/C ratio, CH$_3$OH molecule can be dissociated by three routes including of O–H, C–O, and C–H bonds, respectively. Many previous experiment and calculation investigations of CH$_3$OH dissociation on the surfaces suggested that the O–H scission was proposed as the initial dissociation step [4,10], C–H scission was more favorable than O–H scission [11,12], and the C–O scission suggested to be impossible one for both experimental and theoretical studies [9,11,13-15]. However, CH$_3$OH dissociation through three routes of bond scission on 2Cu/ZnO$\{10\bar{1}0\}$ surface in this present works is not still found.

It has been calculated theoretically in our previous investigation in which the CH$_3$OH decomposed on pure ZnO$\{10\bar{1}0\}$ catalyst surface to final product of CO and H$_2$ was unfavorable [3]. This is requiring that the modification of ZnO surface is needed thus.

Recently, Cu-ZnO based catalysts are active for CH$_3$OH steam reforming and CH$_3$OH dehydrogenation. In addition, it is proven that a catalyst surface with high Cu atom is dispersed on metal oxide surface which it gives higher a conversion and selectivity [10,13,16]. As a result, the target catalyst of 2Cu/ZnO$\{10\bar{1}0\}$ surface model in which 2Cu supported over ZnO$\{10\bar{1}0\}$ using well for water gas shift reaction have been studied in our previous works [15]. With these reasons, it is confident prediction that 2Cu/ZnO$\{10\bar{1}0\}$ surface can be well catalyzed for CH$_3$OH adsorption and dissociation reaction which we are performing.

The powerful tool of theoretical techniques to understand catalytic reactions on the surface has been known as the density functional theory (DFT) and self-consistent periodic calculations [1, 2, 13, 17, 18]. Thus, we employed here to investigate the CH$_3$OH adsorption and dissociation on 2Cu/ZnO $\{10\bar{1}0\}$ catalyst surface. In details, the most stable geometry of CH$_3$OH adsorbed on 2Cu/ZnO(10$\bar{1}$0) surface with configuration and adsorption energy is examined. Hereafter, the CH$_3$OH dissociation with O–H, C–H, and C–O bond scission is performed to compare together, respectively.

2. COMPUTATIONAL DETAILS

All DFT calculations employed with the Vienna ab initio simulation package (VASP) [19-21]. The generalized gradient approximation was used with the functional described by Perdew and Wang (GGA-PW91) [22, 23]. Electron-ion interactions were examined with the use of the projector augmented plane wave method [23], and the non spin-polarized calculations for all of the structural optimizations were performed in this works. Normal-mode analysis was performed to verify the nature of each of these stationary points. The transition state analysis was calculated with ten images, and obtained with one image frequency (IMF) at the first order saddle point. Many here calculations of parameters and equations on 2Cu/ ZnO$\{10\bar{1}0\}$ surface model in computational details were given similarity with our previous works [15].

3. RESULTS AND DISCUSSION

3.1. Surface model
The behavior model of 2Cu adsorbed on ZnO(10\(\bar{1}0\)) surface is systemically calculated. Five top view configurations with average \(E_{\text{ads}}\) and surface \(E_{\text{Cu-ZnO}}\) energies of 2Cu adsorption on surface are detailed in Figure 1 and Figure 2.

![Figure 1. The site view configurations and adsorption energy of 2Cu adsorb on ZnO(10\(\bar{1}0\)) surface. It is noted that all negative values (minus) of \(E_{\text{ads}}\) and \(E_{\text{Cu-ZnO}}\) referred a gain of energy conclude the thermodynamically favorable adsorption.](image)

It is an observation the adsorption energy from site A to site D in Figure 1 are determined by average and surface energies, which it is lower than that of site E in Figure 2. This means that site E is the most stable one. Therefore, the catalyst surface of site E model is used in CH\(_3\)OH adsorption and dissociation reaction. And the side view configuration of site E is shown in Figure 2.

![Figure 2. The most stable site E presents as site view configuration. Shaded blue and high-red spheres represent Zn and O atoms of ZnO surface, the low-red spheres are the Cu atoms.](image)

Looking at Figure 2 to see that, 2Cu adsorb to the ZnO surface through one Cu is vertical sitting on top site of Zn with Cu-Zn bond distance of 2.45 Å. Another Cu is bound to ZnO dimmer with Cu-O bond distance of 1.90 Å and Cu-Zn distance of 2.45 Å. In this case, 2Cu supported over ZnO (1 0 1 0) surface is determined as two active sites; one is at top site of 2Cu
atoms, where it is richer Cu⁺ ion; one is between interfacial Cu and ZnO. This is to say that 2Cu/ZnO catalyst surface will be more active than pure ZnO catalyst surface. In addition, our previous investigations were concentrated that[15] the 2Cu adsorbed ZnO surface through Cu donation to become Cu⁺ ion. As a result, CH₃OH adsorption on 2Cu/ZnO(1 0 1 0) catalyst surface of site E is examined continuously as following.

3.2. Methanol adsorption

The formation of CH₃OH adsorption, six modes of adsorbed CH₃OH on 2Cu/ZnO(1010) catalyst surface are found. The configurations in Figure 3, parameters and energy of CH₃OH adsorption in Table 1 are obtained and calculated, respectively.

![Figure 3. Configurations of CH₃OH adsorbed on 2Cu/ZnO(1010) surface at six different adsorption sites. It is noted that shaded white spheres represent as hydrogen atom, the grey ones of the carbon atoms, and the red ones of O atoms.](image)

It is an observation in Table 1 that calculations of the general parameter and energy such as bond length, bond distance, and bond angle are changed after CH₃OH adsorption for comparison with CH₃OH in gas phase. This means that there is an existing interaction between CH₃OH and the catalyst surface. We observe continuously the E_ads in Table 1 that site A (-1.20 eV) is the most stable one, whereas site F is the most unstable one (-0.11 eV). This is caused as the elongation of C-O and O-H bond length to site A become strong interaction, comparing with that on site F. Further, an observation of configuration finds that site A is formed by chemical bond between oxygen atom (O_ads) of CH₃OH and atomic Zn of ZnO on 2Cu/ZnO surface, whereas site F is between atomic C and atomic Cu. These follow us to conclude that the interaction of
CH₃OH on the surface in site A is stronger than in site F. Similar to that, site A is also more stable than from site B to site E. Specially, we observe previous configuration of site A and site B in Figure 3 that the Oₐd in site A is to Zn on the surface. However, valuable $E_{\text{ads}}$ of site A (-1.20 eV) is higher than of site B (-0.67 eV). This is to say that 2Cu/ZnO catalyst surface in which Zn active site adsorbed CH₃OH is better than Cu active site. Further, the $E_{\text{ads}}$ of site A on 2Cu/ZnO catalyst surface in this work is higher given than on pure ZnO catalyst surface in our previous works[3], this is to say that the contribution of 2Cu electrons to ZnO surface which it makes Zn to be more active.

Table 1. The bond length (R, in Å), bond distance (d, in Å), bond angle ($\phi$, in degree), and adsorption energies ($E_{\text{ads}}$, in eV) for CH₃OH adsorption on 2Cu/ZnO (1010) surface with different adsorption sites.

<table>
<thead>
<tr>
<th>Sites</th>
<th>R (C-H)</th>
<th>R (C-O)</th>
<th>R (O-H)</th>
<th>$\phi$ COH</th>
<th>d(Zn…Oₐd)</th>
<th>d(Cu…Oₐd)</th>
<th>$E_{\text{ads}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.10</td>
<td>1.45</td>
<td>1.12</td>
<td>117.92</td>
<td>2.00</td>
<td>-</td>
<td>-1.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(-1.14)a</td>
</tr>
<tr>
<td>B</td>
<td>1.10</td>
<td>1.44</td>
<td>1.07</td>
<td>111.19</td>
<td>-</td>
<td>1.96</td>
<td>-0.67</td>
</tr>
<tr>
<td>C</td>
<td>1.10</td>
<td>1.43</td>
<td>1.01</td>
<td>110.64</td>
<td>2.14</td>
<td>-</td>
<td>-0.60</td>
</tr>
<tr>
<td>D</td>
<td>1.10</td>
<td>1.44</td>
<td>1.00</td>
<td>107.07</td>
<td>2.15</td>
<td>-</td>
<td>-0.55</td>
</tr>
<tr>
<td>E</td>
<td>1.10</td>
<td>1.44</td>
<td>0.97</td>
<td>108.71</td>
<td>-</td>
<td>2.20</td>
<td>-0.31</td>
</tr>
<tr>
<td>F</td>
<td>1.10</td>
<td>1.41</td>
<td>0.99</td>
<td>106.80</td>
<td>-</td>
<td>-</td>
<td>-0.11</td>
</tr>
<tr>
<td>CH₃OH gas phase</td>
<td>1.09</td>
<td>1.43</td>
<td>0.97</td>
<td>109.50</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*The CH₃OH adsorption energy on ZnO (1010) surface was calculated by Cong et al [3].

Previously the configuration of site A in Figure 3 is that the CH₃OH adsorbs vertically on 2Cu/ZnO surface in which Oₐd interact to Zn via electrons transfer from lone pair of Oₐd to Zn. The bond distance of d(Zn…Oₐd) is found to be 2.00 Å (see in Table I). The $E_{\text{ads}}$ is calculated as -1.20 eV, C-O bond length of 1.45 Å and O-H bond length of 1.12 Å elongated which is much longer than that from site B to site F. This is to confirm that strong interactions between CH₃OH and 2Cu/ZnO surface on site A is found to be most stable adsorption. Further, the geometrical parameters in this work are in good agreement with the experimental [4, 24, 25], which gives us more confident on method employed in this study.

3.3. Methanol dissociation

The CH₃OH dissociation is begun with the adsorption step of CH₃OH onto the 2Cu/ZnO (1010) catalyst surface. The CH₃OH adsorption is performed then via three different kinds of
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bond scission, namely C–H, C–O, and O–H. The possibility of reaction mechanism for CH₃OH adsorption and dissociation on 2Cu/ZnO (1010) catalyst surface will be as follows,

$$\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OH}_2$$  \hspace{1cm} (1)

$$\text{CH}_3\text{OH}_2 \rightarrow \text{CH}_3\text{OH}_2 + \text{H}_2$$  \hspace{1cm} (1a)

$$\text{CH}_3\text{OH}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2$$  \hspace{1cm} (1b)

$$\text{CH}_3\text{OH}_2 \rightarrow \text{CH}_3\text{OH} + \text{OH}_2$$  \hspace{1cm} (1c)

where, (g) sub-character means that methanol in gas phase, and (a) sub-character notes as active site on the surface; step (1) is denoted CH₃OH adsorption; step of (1a), (1b), and (1c) present the C–H, O–H, or C–O step, respectively.

Previously, the reaction mechanisms of CH₃OH dissociation with the C–H, O–H, or C–O bond on the surfaces have been investigated theoretically and experimentally [6,9-13]. In the present work, we perform only the configuration of site A as initial state (ISₐ) to calculate mechanism for CH₃OH dissociation on 2Cu/ZnO (1010) catalyst surface. The activation barrier of bond scission on site A via C–H, O–H, or C–O is determined, respectively. The resultant transition state (TSₐ) and final state (FSₐ) along the reaction pathways of site A are illustrated in Figure 4.

Since we consider the CH₃OH dissociation on site A as ISₐ, the O-H bond scission is shown in Figure 4. An observation of TSₐ(O-H), at reaction beginning, the atomic H moves toward the top site of surface Zn, accompanied by an elongation of O-H bond length to 1.49 Å. In FSₐ, H sits on the top site of Zn adjacent at the surface, with H-Zn_distance bond distance of 1.58 Å. Whereas, CH₃O group resides at Zn top site on 2Cu/ZnO catalyst surface, with CH₃O-ZnO bond distance of 1.93 Å. The reaction energy and activation barrier of O-H bond scission is calculated to be exothermic of 0.05 eV and 0.26 eV, respectively, with an image frequency (IMF) of 970i cm⁻¹ obtained at transition state. Inhere, the calculated results indicate that the pathway of O-H bond scission is kinetically favorable, in which this calculation is in agreement with previous studies on MoS₂(0001) [25], CuCl(111) [1], and Au(111) [4] surfaces. Similar to that, C-H bond scission on site A as ISₐ is performed continuously that H in CH₃ group of CH₃OH is abstracted to move to 2Cu of the catalyst surface. In TSₐ(C-H), H sits on top site of surface Cu, with C-H bond length is elongated to 1.89 Å. In the FSₐ, H resides on the top site of Cu at the surface, with H-Cu bond distance of 1.48 Å. And, the CH₃OH group resides on Zn top site of 2Cu/ZnO catalyst surface, with CH₃OH-ZnO bond distance of 1.98 Å. The reaction energy and activation barrier of C-H bond scission are calculated to be the endothermic of 1.70 eV and 1.27 eV, respectively, with the IMF of 2926i cm⁻¹ at transition state. Finally, the C-O bond scission on site A is performed also as ISₐ that CH₃ group is abstracted to move on 2Cu of the catalyst surface. In TSₐ(C-O), CH₃ sits on top site of surface Cu, with C-O bond length is elongated to 2.75 Å. In the FSₐ, CH₃ group resides on the bridge-site of 2Cu at 2Cu/ZnO surface, each the CH₃-Cu bond distance as 2.00/2.00 Å. Whereas, OH group resides on Zn top site of the surface, with OH-ZnO bond distance as 1.86 Å. The reaction energy and activation barrier of C-O bond scission are the exothermic of 0.27 eV and as 4.69 eV, respectively, with an IMF of 1114i cm⁻¹ at transition state.
Figure 4. The reaction pathway and configuration of CH$_3$OH dissociation on site A present via C-O, C-H, and O-H bond scission on 2Cu/ZnO (10\overline{1}0) surface. In which, IS$_A$, TS$_A$, and FS$_A$ denote as initial, transition, and final states of site A, respectively. It is calculated that the minus sign of TS$_A$ and IS$_A$ gives the value of activation barrier, whereas of FS$_A$ and IS$_A$ is reaction energy value.

It is here a summary that depending on activation barrier and reaction energy, we found that the reaction pathway of O-H bond scission on site A is the most favorable one. This gives agreement with previous works [2,3,8,11]. This helps us to be confident in CH$_3$OH decomposition continuously on site A to final products as CO and H$_2$ on 2Cu/ZnO catalyst surface in the research future.

4. CONCLUSIONS

CH$_3$OH adsorption and dissociation on 2Cu/ ZnO (10\overline{1}0) catalyst surface using DFT method have investigated. From resulted investigations, we have several conclusions in the following:

1) Six modes of CH$_3$OH adsorption with configuration and adsorption energy on 2Cu/ZnO (10\overline{1}0) catalyst surface are calculated, in which the site A configuration is found as the most stable one.

2) On 2Cu/ZnO (10\overline{1}0) catalyst surface, since the calculated CH$_3$OH adsorption of site A is more stable than of site B. This indicates that Zn active site is more activity than Cu active site.

3) Depending on activation barrier and reaction energy, the CH$_3$OH dissociation of site A is found that the pathway starting with O-H bond scission is the most favorable one on 2Cu/ZnO (10\overline{1}0) catalyst surface.
It is that the CH$_3$OH decomposition to final product as CO and H$_2$ on site A starting with O-H bond scission on 2Cu/ZnO (1010) catalyst surface will be continued in next research.

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REFERENCES


