CO-ADSORPTION OF CO, H₂O AND MECHANISM OF WATER GAS SHIFT REACTION ON ZnO (0\(\bar{1}\)0) CATALYST SURFACE: A DENSITY FUNCTIONAL THEORY STUDY

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ABSTRACT

In this work, co-adsorption of CO, H₂O and mechanism calculations of water gas shift reaction (WGSR) on ZnO (0\(\bar{1}\)0) catalyst surface using the density functional theory (DFT) was investigated. Performing the most stable site of co-adsorbed CO and H₂O with configuration and adsorption energy on the catalyst surface were indentified. The carboxyl mechanism of WGSR was proposed and examined then. Based on carboxyl mechanism, the beginning of reaction pathway with the most stable co-adsorbed CO and H₂O configuration as initial state on ZnO (0\(\bar{1}\)0) catalyst surface was considered. The resulted calculations pointed out that the pathway of WGSR mechanisms on the surface was favorable kinetically with rate-determining steps of 1.56 eV.

Keywords: ZnO (0\(\bar{1}\)0) catalyst surface, WGSR, co-adsorption, DFT.

1. INTRODUCTION

Currently, the 80 % approximation of energy resource from fossil fuels was demanded to use in the present world [1]. However, the disadvantage of fossil fuels exert adverse effect on the environment because many pollutants are formed. Conversely, hydrogen energy resource (H₂) burns cleanly, without emitting any environmental pollutants. Further, H₂ exists abundantly in the universe and burns with the highest energy content per unit of weight (i.e, 120.7 kJ/g), comparing to the fossil fuels. Thus, H₂ is known to be the energy carrier of the future and could play an important role in reducing environmental emissions for many practical purposes which have been reported [2-4].
There are many ways to produce H₂ in chemistry scales. However, due to the difficulties in hydrogen storage and delivery, the most favorable way is using the hydrocarbon fuels as a hydrogen carrier. In particularly, methanol is selected to be the best one because of its high ratio of hydrogen to carbon and low reaction temperature, as hydrogen carrier [2,3,5,6]. But, a problem in methanol decomposition to the final H₂ product is the carbon monoxide (CO) production. This molecule is not only harmful to human health but also poison the catalyst of fuel cells [7,8]. Thus, in addition to the toxic CO removal, water gas shift reaction is considered as a promising step for extra hydrogen production. It has been known that many experimental and theoretical calculations of this reaction were investigated in previous works [9-13]. However, the adsorption and mechanism calculations of WGSR on ZnO (1010) catalyst surface fail to show what we will be mainly discussed in this study.

The WGSR refers to the moderately exothermic reaction between CO with H₂O (steam) to form carbon dioxide (CO₂) and hydrogen (H₂). It is considered as a preferable method in CO removal as well as extra H₂ production. It requires low temperatures to achieve a high equilibrium conversion of CO. In fact, WGSR is carried out in two operations corresponding with catalysts. The first is a high temperature step at 350-500°C with iron-oxide based catalyst promoted with chromium oxide for the favorable reaction kinetics [10,14]. The other which is also this research’s objective refers a low temperature step at 180-250°C with copper-zinc oxide-aluminum oxide supported catalyst favoring higher CO conversion [15]. In order to let the WGSR happen faster (kinetically favorable) but still keep up the high amount of production in low temperature (thermodynamically favorable), a construction of a new catalyst for WGSR must be proposed.

Zinc oxide (ZnO) itself is an active catalyst for many important chemical processes on the industrial scale (e.g., de-/hydrogenation and methanol synthesis/conversion) [16-18]. With a hexagonal wurtzite crystal structure and wide direct band gap (~3.37 eV), ZnO has many applications for a wide range of technological uses [19]. In wurtzite crystal structure, ZnO exists mainly four surface directions such as polar surfaces (0001) and (1010), and non-polar surfaces (1010) and (1120). In which, the non-polar ZnO(1010) surface direction is considered as the most stable surface [17,20], because it has been determined to takes up 80 % potential energy of the total surface area [21]. Therefore, in the present works we employed this surface to study WGSR.

In terms of theoretical calculations, density functional theory (DFT) has been denoted as a powerful tool for computation systems. Especially, it is employed to study the adsorption or the dissociation on the catalyst surface as well as conversion of the species involved in the process [22-24]. Therefore, using DFT in the mechanism calculations of WGSR on ZnO(1010) surface is needed. In details, the first step of our investigation is the co-adsorption calculations of H₂O and CO on ZnO(1010) catalyst surface to find the most stable site with the configuration and co-adsorption energy obtainments. In the second step, carboxyl mechanism of WGSR are proposed and considered then. Finally, the pathway calculations of carboxyl mechanism on the most stable configuration of catalyst surface are also investigated.

2. MATERIALS AND METHODS

All DFT calculations were performed with the plane wave based package in Vienna ab initio Simulation Package (VASP) [25-29] code. The generalized gradient approximation with
Perdew-Wang 1991 formulation (GGA-PW91) [28, 30] which works well for surfaces, was used to treat the exchange-correlation functional [31]. The cut-off energy of 380 eV was used for geometric optimization in all configurations. The Nudged Elastic Band (NEB) method was employed to locate transition states (TS) for all elementary steps [30, 32], which was constructed by the initial and the final positions along the minimum energy pathway (MEP). In this work, ten configurations corresponding with ten scanned positions were used to locate at each transition state, and an image frequency (IMF) at transition state obtained. All reported results for stable molecules as well as transition states were calculated with the lowest energy conformer of a given species.

Surface model was observed with the parameters in previous experiments and computations, the computed bulk lattice constants of three-dimensional ZnO were \(6.50 \times 10.41 \times 21.57 \text{ Å}\) [33-36]. The optimized \((2 \times 2)\) unit cells of the most stable \(\text{ZnO}(1\overline{1}0)\) surface with six layers were modeled as periodically repeating slabs. The top three layers were free to relax in the calculations of surface adsorption and reaction, and the bottom three layers were fixed at the computed lattice constants to represent the semi-infinite bulk crystal. In order to minimize the interaction between slabs in this infinitely periodic model system, a vacuum region of 15 Å was introduced to separates the top and bottom surfaces of the slabs. Additionally, the Monkhost-Pack mesh was \((4 \times 4 \times 1)\) \(k\)-point for \(\text{ZnO}(1\overline{1}0)\) surface geometric optimization. The model of \(\text{ZnO}(1\overline{1}0)\) surface with parameters has been used previously in our investigations [10, 21].

The adsorption energy was represented to describe the difference between the total energy of coadsorbates-surface system and the sum of surface total energy (\(\text{ZnO}\)) and coadsorbates (CO, H\(_2\)O) total energy, the co-adsorption energy \(E_{\text{coads}}\) per coadsorbates on \(\text{ZnO}(1\overline{1}0)\) surface, defined generally as follow [5],

\[
E_{\text{coads}} = E_{\text{coadsorbate-surface}} - E_{\text{surface}} - E_{\text{coadsorbate}} \tag{1}
\]

where, \(E_{\text{coadsorbate-surface}}\), \(E_{\text{surface}}\) and \(E_{\text{coadsorbate}}\) presented the calculated energy between the coadsorbates and surface, a \(\text{ZnO}(1\overline{1}0)\) surface, and two adsorbates were adsorbed from gaseous phase, respectively. All the energy equations afterwards including either the interaction energy between reactants and products of WGSR or the co-adsorption energy of CO and H\(_2\)O on the most stable \(\text{ZnO}(1\overline{1}0)\) surface were also generated from this general adsorption equation (1). A negative \(E_{\text{coads}}\) referred a gain of energy concludes the thermodynamically favorable adsorption.

3. RESULTS AND DISCUSSION

3.1. Co-adsorption of CO and H\(_2\)O on \(\text{ZnO}(1\overline{1}0)\) catalyst surface

When the co-adsorption of CO and H\(_2\)O on \(\text{ZnO}(1\overline{1}0)\) catalyst surface is performed, we consider the first as adsorbed CO on the surface by either C atom (C down) or O atom (O down) [37 - 40]. 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 [37] indicates that the “C down” orientation was found to be the most stable one. By this, we have performed different orientation of adsorbed CO on the surface and found that the C down is the most stable conformer. Therefore, the “C down” orientations for all the CO adsorption calculation are focused on this study. On the other hand, we try the similar the H\(_2\)O adsorption at positions like CO adsorption on the surface both H atom (H down) and O atom (O down). It turns out that the H\(_2\)O adsorption
by “O down” orientation is the most stable one. Therefore, a co-adsorbed CO with “C down” and H$_2$O with “O down” orientations are calculated then. The results of the most stably-coadsorbed CO and H$_2$O configuration with co-adsorption energy on ZnO (1010) surface is shown in Figure 1.

![Figure 1](image)

*Figure 1. The configuration of the top (a) and side (b) view of CO and H$_2$O co-adsorption on ZnO (1010) catalyst surface. It is noted that the red, blue, grey, and white spheres are noted as O, Zn, C, and H atoms, respectively. Specially, red sphere (1) is atomic O of CO, and red sphere (2) as atomic O of H$_2$O.*

It is observed at site view of Figure 1(b) that the co-adsorption energy of CO and H$_2$O calculated on the catalyst surface is -1.41 eV. In this configuration (Figure 1(b)), both CO and H$_2$O lie vertically on each atomic Zn of the surface ZnO. Whereas, atomic O of H$_2$O (O$_2$) orients to CO, and one H of H$_2$O is to O neighborhood of ZnO, this means that the reaction of CO with H$_2$O (reactant) on the surface is more favorable to form easily COOH intermediate for carboxyl mechanism of WGSR. Observing continuously at the top view of Figure 1(a) is that the C-Zn and O2-Zn distances are found to be 2.14 Å and 2.08 Å, respectively. One H-O2 bond length of H$_2$O is slightly elongated from 1.00 Å to 1.08 Å after co-adsorption on the surface. Our calculations in co-adsorption energy (-1.41 eV) show a better result than from other study on metal surface [11,41]. This is able to say that the performances of WGSR mechanism on metal oxide surfaces (ZnO) in this works are more effectively than that on metal surfaces.

3.2. Proposed carboxyl mechanism

It has been known currently in WGSR that there are three possible routes for initial CO to react with H$_2$O. The first route, the previous studies [9,11] conclude that CO cannot directly react with stable H$_2$O on the surface which we are thus not considering in this study. The second route, causing H$_2$O is dissociated or 2OH recombined to O and 2H on the surface. Then CO is oxidized by O, or 2H get a recombination together back to final product of CO$_2$ and H$_2$. This is the reason why this route is named redox mechanism. A difficulty of the redox mechanism is that OH dissociation or 2OH recombination can be kinetically unfavorable where the previous investigations were calculated with high activation energy [10, 41, 42]. Thus, this mechanism on ZnO (1010) surface is not also considered in here. Finally, the third route as H$_2$O is dissociated to
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hydroxyl (OH), CO reacts continuously with OH to COOH intermediately on the surface, and COOH then is decomposed to final products of CO₂ and H₂. This route is known as carboxyl mechanism in which we considered the most feasible reaction in present work.

To determine the reaction network on carboxyl mechanism, the local minimization energy potential (MEP) of each elementary steps is examined. In MEP calculation, we performed iterative approach, including: (i) the beginning of reaction channels for a given intermediate were first considered; (ii) the calculated reaction barriers (E_a) at transition states with the obtainment of a negative image frequency then, the low-barrier reaction channels only were continued to reach the next new intermediate and reject the too high barrier ones (e.g., the barrier larger than 2 eV); and (iii) as we repeated (i) and (ii) until the target products were yielded. Following this, we have calculated the reaction channels of carboxyl mechanism which resulting MEP calculations with reaction and activation energies are listed in Table 1.

Table 1. The resulted calculations of water gas shift reaction on ZnO (1010) catalyst surface. Including, the reaction energy (ΔE) and activation energy (‡E) for each steps are determined. Where, it notes that the sub-character (a) and (g) are the surface ZnO and gas phase, respectively.

<table>
<thead>
<tr>
<th>Step</th>
<th>elementary reaction steps</th>
<th>ΔE (eV)</th>
<th>‡E (eV)</th>
<th>IMF (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂O(a) → H(a) + OH(a)</td>
<td>0.06</td>
<td>0.07</td>
<td>217i</td>
</tr>
<tr>
<td>2</td>
<td>CO(a) + OH(a) → COOH_cis(a)</td>
<td>0.26</td>
<td>0.31</td>
<td>167i</td>
</tr>
<tr>
<td>3</td>
<td>COOH_cis(a) → COOH_trans(a)</td>
<td>0.11</td>
<td>0.73</td>
<td>532i</td>
</tr>
<tr>
<td>4</td>
<td>COOH_trans(a) → CO₂(a) + H(a)</td>
<td>0.38</td>
<td>0.72</td>
<td>123i</td>
</tr>
<tr>
<td>5</td>
<td>H(a) + H(a) → H₂(g)</td>
<td>-0.24</td>
<td>1.56</td>
<td>869i</td>
</tr>
<tr>
<td>6</td>
<td>CO₂(a) → CO₂(g)</td>
<td>0.09</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.3. Reaction pathway of WGSR on ZnO (1010) catalyst surface

From the proposed carboxyl mechanism and resulted calculations in Table 1, the outcomes of WGSR in this study were expressed and discussed in two significant points:

The most stable configuration of CO and H₂O co-adsorption on ZnO(1010) catalyst surface was suggested to be initial state (IS) in reaction pathway.

The pathway of WGSR includes three main steps namely (i) CO and H₂O co-adsorption on the surface (see in part 3.1 above); (ii) conversion of CO and H₂O on the surface (see in step from 1 to 4 in Table 1); and (iii) desorption of the products, CO₂ and H₂, out of the surface in gas phase (step 5 and 6 in Table 1). The relative energy corresponding reaction coordinate of each steps with the initial state (IS), transition state (TS), and final state (FS) in reaction pathway are represented as following.

3.3.1. Conversion of CO and H₂O on the surface

The most stable configuration of co-adsorbed CO and H₂O on ZnO (1010) catalyst surface is chosen as IS to identify the WGSR mechanism. The relation between relative energy and
reaction coordinate corresponding with configurations toward reaction pathway are listed in Figure 2.

![Figure 2](image-url) The reaction pathway of WGSR with IS, TS, and FS configurations with relative energies on ZnO (1010) catalyst surface.

The beginning pathway of carboxyl mechanism in WGSR is H$_2$O dissociation to form OH and H on the surface, shown in Figure 2. In TS1, one H of H$_2$O is abstracted to move on neighbor O of ZnO. In this state, O2-H bond length is elongated from 1.08 Å to 1.34 Å, and ZnO-H bond distance from 1.43 Å to 1.20 Å shortened. In FS, H resides on O top site of the surface with O-H bond distance of 1.02 Å, and HO2-Zn bond distance of 2.00 Å. The $^1$E of 0.07 eV with IMF of 217i cm$^{-1}$, and the endothermic $\Delta$E of 0.06 eV in H$_2$O dissociation reaction are calculated and obtained in Table 1 (see step 1 in Table 1).

The step 2 of pathway as COOH$_{cis}$ formation on the surface is determined. Continuously observation in Figure 2 at IS (FS of step 1), both OH and CO reside on each Zn of ZnO. C-Zn bond distance and O2-C bond length are 2.14 Å and 2.65 Å, respectively. In TS2, OH moves to react with CO. Here, O2-C bond length is shortened from 2.65 Å to 1.70 Å. In FS, COOH$_{cis}$ is formed and resided on Zn of ZnO with O2-C bond length of 1.38 Å, and C-Zn bond distance of 2.00 Å shortened. The $^1$E and the $\Delta$E are calculates to be 0.31 eV with IMF of 167i cm$^{-1}$ and endothermic reaction of 0.26 eV, respectively. Hereafter, COOH$_{cis}$ formation has two scenarios of reaction on the surface including, (i) it decomposes to CO$_2$ and H, and (ii) the rotation of COOH$_{cis}$ to COOH$_{trans}$ configuration. However, it has been proved in previous investigations [10,11,42] to conclude that COOH$_{cis}$ rotation to COOH$_{cis}$ configuration is more favorable than COOH$_{cis}$ decomposition. As such, we have consider step 3 as the rotation from COOH$_{cis}$ to COOH$_{trans}$ on ZnO (1010) catalyst surface.

Following step 3, the COOH$_{cis}$ configuration of step 2 as IS, OH are rotated horizontally along ZnO surface, shown also in Figure 2. In this configuration at TS3, bond length of O2-C is
shortened from 1.38 to 1.22 Å. In FS of COOH\textsubscript{trans} formation, H of OH orients to O neighborhood of the surface. The C-Zn bond distance is elongated to 2.78 Å, and O2-C-O bond angle of 147° stretched. The ΔE is endothermic of 0.11 eV, the \(^1E\) of 0.73 eV with IMF 532\(\text{cm}^{-1}\) obtained.

The step 4 as COOH\textsubscript{trans} configuration is decomposed to \(\text{CO}_2\) and H on the surface, shown in Table 1 and Figure 2. In TS4 of Figure 2, H of COOH\textsubscript{trans} moves to O neighborhood and \(\text{CO}_2\) is formed on Zn top site of the surface. In FS, H resides at neighbor O. In here, C-Zn bond distance is elongated to 3.60 Å, O-C and O2-C bond length of 1.17 Å and of 1.18 Å shortened, respectively. Simultaneously, \(\text{CO}_2\) transforms from bent to linear configurations with the stretch of O–C–O2 bond angle to 179.9° which these mean that \(\text{CO}_2\) has been desorbed to gas phase. The \(^1E\) in this step calculates to be 0.72 eV with IMF of 123\(\text{i cm}^{-1}\), and the ΔE as endothermic of 0.38 eV.

A summary in conversion of CO and \(\text{H}_2\text{O}\) for mechanism calculations on ZnO(10\(\bar{1}\)0) catalyst surface shows that the reaction pathway is started with \(\text{H}_2\text{O}\) dissociation to OH. Along reaction included as forming CO + OH → COOH → \(\text{CO}_2\) and \(\text{H}_2\) on the surface. The COOH\textsubscript{trans} decomposition to \(\text{CO}_2\) is enclosed along with the desorption of \(\text{CO}_2\) in gas phase. The resulted calculations of \(^1E\) are smaller 1 eV, implying that the reaction steps are more kinetically favorable. However, reaction energies are calculated for each step as endothermic, meaning that reaction steps are unfavorable thermodynamically.

### 3.3.2. Desorption products

Since COOH\textsubscript{trans} configuration is composed to \(\text{CO}_2\) and H on the catalyst surface. \(\text{CO}_2\) has been desorbed enclosing to gas phase. Thus, we calculate only the energy of \(\text{CO}_2\) molecule to determine the ΔE for \(\text{CO}_2\) desorption is 0.09 eV (see step 6 in Table 1).

To desorbed \(\text{H}_2\) performance on the surface, we calculate continuously \(\text{H}_2\) recombination the first (see step 5 in Table 1). The configurations of IS\(\text{H}_2\), TS\(\text{H}_2\), and FS\(\text{H}_2\) in \(\text{H}_2\) recombination reaction on ZnO(10\(\bar{1}\)0) catalyst surface are shown in Figure 3.

![IS\(\text{H}_2\), TS\(\text{H}_2\), and FS\(\text{H}_2\) configurations for \(\text{H}_2\) recombination on ZnO (10\(\bar{1}\)0) surface.](image)

It is an observation at IS\(\text{H}_2\) in Figure 3 that each H resides on each O of ZnO with H-H bond distance of 3.25 Å. In TS\(\text{H}_2\), each H is abstracted out of the surface to react together. In this state, the H-H bond distance is shortened to 1.25 Å. In FS\(\text{H}_2\), \(\text{H}_2\) is formed in gas phase with H–H bond length of 0.75 Å, which is in line \(\text{H}_2\) molecule. The \(^1E\) is calculated to be 1.56 eV with IMF of 869 cm\(^{-1}\), and the exothermic reaction of -0.24 eV (see step 5 in Table 1).
4. CONCLUSIONS

In this research, CO, H₂O co-adsorption and the WGSR mechanism on ZnO(10\bar{1}0) catalyst surface has been investigated by using DFT. Specifically, we have identified the most stable configuration of CO and H₂O co-adsorption on ZnO(10\bar{1}0) catalyst surface which the detailed mechanism of the WGSR was examined then. The carboxyl mechanism of WGSR with the oxidation of CO by H₂O dissociated OH, forming COOH intermediate was found and discussed. The WGSR mechanism on this surface was calculated as kinetically favorable because of smaller activation energy. The reaction pathway was performed to achieve the final products of H₂ and CO₂ in gas phase. The rate–determining step for overall reaction of WGSR on the surface was H recombination with \( \Delta E \) of 1.56 eV. Especially, the steps of COOH cis decomposition and H recombination in WGSR mechanism were performed in corresponding with the steps of CO₂ and H₂ products being desorbed enclosing to gas phase, respectively.

The limitation of this study is that many steps in pathway of WGSR were calculated to be endothermic. This means that the reaction system was unfavorable thermodynamically in which processing reaction was needed to supply the heat from outside system. In addition, an insight to explain the interaction between adsorbates- surface system is still not performed. These limitations are expected to be solved in the future study.

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