Study on the Highly Efficient Reduction of CO₂ to Formate Using Zinc under Mild Hydrothermal Conditions

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Abstract. In this study, the reaction mechanism of CO₂ reduction by using Zn under mild hydrothermal condition was investigated by DFT calculation method. Based on the calculation of the transition state, as well as the IRC and HOMO/LUMO, the Zn-H was considered as a key intermediate for the high formate production from CO₂. This study provides information on the reaction pathway of metal reduction with the metal hydrogen bond under hydrothermal conditions. The energy diagram showed that the Zn-H has high reducing activity, which induced that the formate was easily produced through hydrothermal reactions. From the viewpoint of energy, in the CO₂ reaction system, the HCOO⁻ was easily produced than that in the HCO₃⁻ reaction system. This process provides new concept for the high efficient production of value-added chemicals in the carbon dioxide utilization research area.

Keywords. Carbon dioxide; reduction; hydrothermal reaction.

1. Introduction

Due to the climate change induced by the emission of greenhouse gases, the utilization of CO₂ as a carbon source to form useful chemicals and fuels has attracted much attention [1]. However, the hydrogenation of CO₂ is not easily to be obtained due to the thermodynamic stability. Recently, the photocatalytic and electrochemical approaches have been studied extensively [2, 3]. Unfortunately, these methods have some disadvantages including the low efficiency and high cost. Nowadays, new technology with highly efficient and economical characters is strongly desired for the CO₂ utilization.

Hydrothermal conditions played an important role in the geological process for the fossil fuels production [4-5]. In the hydrothermal reaction process, water acts as a reaction medium, as well as a hydrogen source. Water is the most abundant hydrogen source in the world. Recently, we reported the CO₂ reduction to formate with different metals, such as Zn, Al, Mn, etc. [6] Especially, the formate yields were very high under hydrothermal conditions when Zn was used as the reducing agent. Because Zn could be reused through the reduction of ZnO by concentrated solar energy [7, 8], the Zn showed high potential for the CO₂ utilization through the Zn/ZnO cycle system.

However, the detailed mechanism of CO₂ reduction is still unknown because the reaction took place under high temperature. In our previous study [9], we proposed a reaction approach for the formate production through an SN2-like mechanism. We put forward new concept that Zn-H is a special complex with strong reducing activity for the formate production in the hydrothermal reactions. Zn-H species produced firstly for the production of hydrogen gas. Due to the activity of H atom, the C-H bond was formed subsequently. In this process, HCOO⁻ was assumed as the carbon source for the formate production. M-H was considered as the most active catalyst for the CO₂ reduction [10, 11]. On
the other hand, under hydrothermal conditions, CO$_2$ could be produced in the chemical equilibrium. Therefore, the CO$_2$ reduction directly should be discussed.

Considering that DFT was always used for the investigation of mechanism of chemical reaction, in this study, the ab initio calculation is intended to study the reaction mechanism of carbon dioxide with zinc under hydrothermal conditions including reliable structures of the initial, final and transition states as well as their energies. The proposed reaction pathway could be seen in Scheme 1.

Scheme 1. Proposed reaction pathway for the formate production.

2. Computational Details
By using Gaussian 16 software, PW91PW91 density functional method was employed for the investigation of reaction mechanism. For Zn atoms, LANL2DZ basis set was used. Polarizable continuum model (PCM) with water as the solvent was considered. The vibrational frequency analyses were performed for the structure optimization. IRC computations were carried out to confirm the transition state was plausible or not. The HOMO/LUMO analysis was performed to verify the possibility of electron transfer.

3. Results and Discussion
3.1. Structural Optimizations of Initial and Final States
At first, the structure of the initial and final states was optimized by DFT calculation. The results could be seen in Figure 1. As shown in Figure 1, the charge distribution was illustrated. It can be seen clearly that in the reaction process of Zn and H$_2$O, which can produce hydrogen, Zn-H could be assumed as a intermediates. The H has the negative charge, which number was -0.327. Therefore, it can be considered that the active negative H attacked the carbon atom of CO$_2$. In the final state, the HCOO$^-$ was produced. Because the HCOO$^-$ was ion in the aqueous phase, the Zn could attracted with OH$^-$, which could form the Zn(OH)$_2$. In the end, the ZnO was produced due to the dehydration effect. The Zn$_5$ cluster was used for the calculation due to the forming trigonal dipyramidal structure [12]. It should be noted that the CO$_2$ was used as the complex in the calculation of Zn$_5$/fragments complexes.

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\text{Initial State} \quad \text{Final State}
\]

Figure 1. The charge distribution of the initial state and final state.
3.2. Energy Calculation of the Transition State

Based on the structural optimizations of initial and final states, the transition state of the formate production was calculated. In figure 2, the energy diagram of the initial, transition and final states was showed. As shown in figure 2, the energy of transition state was not very high, therefore the reaction process took place easily under hydrothermal conditions. It should be noted that the calculation was performed with the reaction temperature 300°C. It could be proposed that the H of Zn-H was strongly active. As we know, the reaction of Zn and H$_2$O was an exothermic reaction, which produced hydrogen and a lot of heat simultaneously. Comparing with the initial state, the final state, when the HCOO complex was produced, was very stable. The distance between Zn and H bond is about 1.807 Å. Comparing with our previous study, the Zn–H bond distance is 1.94 Å. Considering that the calculation parameters are little different, the results was very similar. The charge of H atom in the Zn-H bond is -0.329. This charge illustrated that the zinc hydride was produced instead of proton. Comparing with our previous study, the charge of H atom was -0.221. The charge is a little different. Anyway, the negative charge means that the Zn-H has strong activity. Therefore, the energy of transition state is smaller than our previous study. These results were consistent. From the viewpoint of energy, in the CO$_2$ reaction system, the HCOO was easily to be produced than that in the HCO$_3$ reaction system.

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\begin{align*}
\text{Zn}_5, \text{H}, \text{OH}, \text{CO}_2 & \quad \text{TS} \quad \text{Zn}_5, \text{OH}, \text{HCOO} \\
\text{TS} & = 0.0 \quad 4.80 \quad -33.63
\end{align*}
\]

Figure 2. Energy diagram of the initial state, transition state and final state.

3.3. IRC, HOMO/LUMO of the Transition State

The IRC results could be seen in figure 3. As shown in the figure, the reaction energy barrier for the formate production was low, which means that the H atom has strong reducing activity under this reaction condition. Once the C-H bond was formed, the energy was very lower, which means that the HCOO complex was more stable than CO$_2$+H complex. The HOMO/LUMO results could be seen in figure 4. As shown in figure 4, the occupied HOMO shows a bonding interaction between the C atom and the H atom. As the H atom moved from the Zn$^5$ surface to the C atom, the interaction of C and H atoms was stronger. Considering the optimized structure of final state, i.e. the produced HCOO, the HCOO was adsorbed on the Zn$_5$ surface. The charge then changed to positive, instead of negative. Then the structure was more stable. The IRC and HOMO/LUMO calculation results illustrated the transition state was plausible.
4. Conclusions

In this study, the reaction mechanism of CO$_2$ reduction by using Zn under mild hydrothermal condition was investigated by DFT calculation method. Based on the calculation of the transition state, as well as the IRC and HOMO/LUMO, the Zn-H was identified species as a key intermediate for the high formate production from CO$_2$. The theoretical study performed in this study presents findings the reaction pathway of metal reduction with the metal hydrogen bond under hydrothermal conditions. The energy diagram showed that the Zn-H has high reducing activity, which induced that the formate was easily produced through hydrothermal reactions. From the viewpoint of energy, in the CO$_2$ reaction system, the HCOO$^-$ was easily to be produced than that in the HCO$_3^-$ reaction system. We propose that this reaction pathway would provide new concept for the high efficient production of value-added chemicals in the carbon dioxide utilization research area.

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