DFT study of the formate formation on Ni(111) surface doped by transition metals [Ni(111)-M; M=Cu, Pd, Pt, Rh]

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Abstract. We report on a theoretical study of the formation of formate (HCOO) from the reaction of CO₂ gas and a pre-adsorbed H atom (CO₂(g) + *H → *HCOO) on Ni(111) surface doped by transition-metals [Ni(111)-M; M= Cu, Pd, Pt, Rh] by means of density functional theory (DFT) calculations. This *HCOO formation reaction is one of the most important rate-limiting steps in the methanol synthesis process. We find that the presence of transition metal doping on the first-layer of Ni(111) surface could reduce the activation barrier of this reaction [up to ∼38.4%, compared to clean Ni(111) surface].

1. Introduction

In recent years, research in the synthesis of methanol (CH₃OH) through the hydrogenation of carbon dioxide (CO₂) has become very popular due to potential application of methanol as an alternative fuel [1]. This methanol fuel is interesting because the CO₂ gas which is emitted from the usage of methanol as fuel can be converted back into methanol through the same hydrogenation process. Therefore, this synthesis process could also serve as a way to utilize and reduce CO₂ emission [2].

The synthesis of methanol through the hydrogenation of carbon dioxide (CO₂) is a process which involves very complex reactions. This hydrogenation process also involves multiple high reaction barriers which lead to slow reaction kinetics. Therefore, the presence of a good catalyst is absolutely necessary. At industrial scale, the methanol synthesis is performed by reacting CO₂ and H₂ gases at high pressure (50-120 bar) and at 493-573 K using Cu/ZnO/Al₂O₃ catalyst [3]. However, the rate of CO₂ conversion on this catalyst is still very low. Therefore, the development of new catalysts that have better performance is needed.

To overcome this problem, we try to use Ni-based surface as CO₂ hydrogenation catalyst. The main motivation for choosing Ni as a catalyst is because of its abundance in Indonesia. It is well known that the clean Ni surface by itself is not a good CO₂ hydrogenation catalyst. However, it is also known that the activity of a transition metal surface could be enhanced by alloying or doping the surface with other transition metals. For example, the activity of Cu-Ni bimetal catalyst is found to be
several times better than the clean Cu catalyst [4-6]. A recent theoretical study also shows that the methanol production rate on Cu(111) surface could be enhanced by doping the surface with Ni or Pt [7]. The good performance of these catalysts is originated from the ability of the catalysts to stabilize the adsorption of some important adsorbates and reduce the activation energies of some important hydrogenation steps. Inspired by these facts, we try to use Ni(111) surface doped by transition metals [Ni(111)-M; M = Cu, Pd, Pt and Rh] as candidates for new CO2 hydrogenation catalysts.

As a first study, we perform a theoretical investigation on the formation of of formate (HCOO) from the reaction of CO2 gas and an H atom [CO2 (g) + 1/2 H2 (g) + * → *HCOO] on Ni(111)-M surface by means of density functional theory (DFT) calculations. This *HCOO formation is one of the most important rate-limiting steps in the methanol synthesis process. This *HCOO formation has a relatively slow reaction rate because CO2 molecule is usually difficult to be chemically adsorbed on a catalyst surface. Our results suggest that the presence of transition metal doping on the first-layer of Ni(111) surface could reduce the activation barrier of this *HCOO formation up to ∼38.4%, as compared to the clean Ni(111) surface.

2. Computational Details
In this work we investigate the formation of *HCOO on Ni(111)-M surfaces using density functional theory (DFT) calculations [8, 9]. Spin-polarized density functional theory calculations were performed using Quantum-Espresso package [10]. Exchange and correlation effects were incorporated within the generalized gradient approximation, using the Perdew-Burke-Ernzerhof (PBE) functional [11]. Kohn-Sham eigenfunctions were expanded on plane-waves basis sets where the interaction between the valence electrons and ion cores are described by ultrasoft pseudopotentials[12]. Converged results have been achieved by using cutoff energies of 30 Ry on the plane wave and of 200 Ry on the electronic density. The integration in Brillouin-zone is done on 3x3x1 k-points grid sampled by Monkhorst-Pack scheme [13]. The effect of van der Waals interactions is described using the semi-empirical correction scheme of Grimme, DFT-D2 [14]. Calculation for isolated molecule is done at the gamma point in a 30 x 30 x 30 Å³ cubic cell. All of systems are fully relaxed until the residual force on each atomic component is less than 0.025 eV/Å. Saddle point of some reactions are calculated by the climbing image nudged elastic band method (CI-NEB) [15].

The Ni(111)-M surfaces is modeled by three-layers slab with unit cell size of 3x3 (see Fig. 1). The size of the super-cell corresponds to the 1/9 ML of adsorbates coverage. The adsorbate molecule and the top-most layer were fully relaxed while the rest of the atoms in the slab were fixed on its bulk lattice configuration. One Ni atom at the top-most layer is substituted by an M atom (M= Cu, Pd, Pt and Rh).

We consider various possible combinations for the co-adsorption/adsorption sites of CO2, H and HCOO, including the high symmetry sites of the surface. We then compare the calculated total energies of these adsorption configurations and choose the adsorption system that has the lowest total energy (the most stable). The adsorption energy of a molecule on Ni(111)-M surface is defined as:
\[ E_{ad} = E_{\text{tot}} - (E_{\text{surf}} + E_{\text{molecule}}) \, . \]  

where \( E_{\text{tot}} \) corresponds to the total energy of combined system, \( E_{\text{surf}} \) corresponds to the total energy of Ni(111)-M surface and \( E_{\text{molecule}} \) corresponds to the total energy of the isolated molecule. In this formulation, negative adsorption energy refers to stable adsorption and vice versa.

3. Results and Discussions

3.1. \( \text{CO}_2 \) adsorption

Our DFT calculations results show that \( \text{CO}_2 \) molecule is only physically adsorbed on most of Ni(111)-M surfaces with adsorption energies of about -0.2 eV and the closest interatomic distance between \( \text{CO}_2 \) molecule and the surface is of about 3.400 Å. The physisorbed \( \text{CO}_2 \) molecule maintains its linear conformation. There is an exception for Ni(111)-Rh case. While the adsorption energy of \( \text{CO}_2 \) molecule on this surface is almost the same with the other surfaces, \( \text{CO}_2 \) molecule is chemically adsorbed on the Ni-Rh bridge of this surface with a bidendate configuration and with the closest interatomic distance between \( \text{CO}_2 \) molecule and the surface is of about 1.984 Å (see the IS configuration of Ni(111)-Rh/\( \text{CO}_2 \) in Fig. 2). The linearity of \( \text{CO}_2 \) molecule is broken in this bidendate adsorption configuration, indicating a strong interaction between Ni(111)-Rh surface states and the unoccupied anti-bonding orbital of \( \text{CO}_2 \) molecule (\( \pi_u^* \)).

The fact that \( \text{CO}_2 \) molecule is only weakly adsorbed in its linear conformation on most of Ni(111)-M surfaces suggests that the *HCOO formation reaction on these surfaces might not start from the \( \text{CO}_2 \) adsorption. Instead, this reaction might start from the \( \text{H}_2 \) dissociative adsorption since this dissociative process only requires very small activation energy on Ni(111) surface [16]. Since the \( \text{H}_2 \)
dissociation can easily proceed on Ni(111) surface, we assume that this surface [and also the other Ni(111)-M surfaces] can always have some pre-adsorbed H atoms whenever H₂ gases present in the system. In this study, we simplify our reaction model for *HCOO formation on Ni(111)-M surfaces by assuming that this reaction starts from the interaction between a pre-adsorbed H atom and a CO₂ gas (CO₂(g) + *H → *HCOO).

3.2. *HCOO formation

The calculated energy barriers and geometries of initial state (IS), transition state (TS) and final state (FS) for reaction CO₂(g) + *H → *HCOO on Ni(111)-M surfaces are presented in Table 1 and Fig. 2. At the IS, CO₂ molecule is physically adsorbed on the surface [except for Ni(111)-Rh case] while H atom is adsorbed on the fcc-hollow site for clean Ni(111) surface and on the Ni-M-Ni hollow of the hcp-hollow site of Ni(111)-M surfaces. At the TS, H atom interacts with the C atom of CO₂ molecule (forming an H–COO configuration) and break the linearity of O-C-O angle. At the FS, the formed *HCOO stabilizes its adsorption configuration by anchoring its O atoms at the Ni-M bridge of Ni(111)-M surfaces [at the Ni-Ni bridge for clean Ni(111) surface].

The description of the TS configuration suggests that the activation energy for this reaction is consumed by the desorption of H atom from the hollow site and the bending of the O-C-O angle. Therefore, we can assume that the reduction of the activation barrier of this reaction can be achieved by weakening the adsorption strength of H atom while at the same time enhancing the surface-H-CO₂ interaction. Unfortunately, this strategy is not so easy to be realized because these two processes are related to each other and cannot be separated. The mechanism of these processes might be qualitatively explained as follows:

a) When H atom is adsorbed on the surface, derived bonding and anti-bonding states between surface and H atom are created. Depending on the electronic structure of the surface, the energy of some derived states might be located close to π_u* orbital of the physisorbed CO₂ molecule. This situation can facilitate the charge transfer from the surface to the π_u* orbital which will lead to the bending of the O-C-O angle. Therefore, the closer the distance of the derived state to the π_u* orbital, the easier the bending of the O-C-O angle.

b) At the same time, we should also notice that the strength of H atom adsorption depends on the occupancy of these derived bonding and anti-bonding states. The partial/full occupancy of the derived anti-bonding states will weaken the adsorption strength of H atom on the surface. The more these derived anti-bonding states are occupied, the weaker the H adsorption strength is. Unfortunately, this partial/full occupancy means that the derived anti-bonding states are also shifted toward/bellow the Fermi level (ε_f). This shift widens the distance between the derived anti-bonding states of the Surface-*H and π_u* orbital of the physisorbed CO₂ molecule. If the shift is too large, it will hinder the charge transfer from the surface to the π_u* orbital and this of course will make the bending of the O-C-O angle become more difficult. Therefore, weak H adsorption not always results in low activation barrier for the *HCOO formation reaction.
Results in Table 1 show that the activation barrier for \(^{\text{HCOO}}\) formation on Ni(111) surface can be reduced by the transition metal doping. The highest reduction is achieved on Ni(111)-Pt surface [\(-38.4\%\), as compared to clean Ni(111) surface]. The H adsorption energy on this Ni(111)-Pt surface is indeed weaker than that on clean Ni(111) surface (-0.32 eV vs -0.39 eV). However, while the other Ni(111)-M surfaces also have lower activation energies compared to clean Ni(111) surface, the H adsorption energies on these systems are higher than that of clean Ni(111) surface [-0.42 eV, -0.43 eV and -0.51 eV for Ni(111)-Cu, Ni(111)-Pd and Ni(111)-Rh, respectively]. Therefore, as we have explained in the previous paragraph, information of the H adsorption strength alone is not enough to explain the trend in activation energy reduction. We also need to look at the electronic structure of the system to locate the location of the derived bonding and anti-bonding states of Surface-\(^{\text{H}}\) system with respect to the unoccupied \(\pi^*\) orbital of the physisorbed CO\(_2\) molecule. Detail mechanism from the electronic structure perspective will be discussed in our future publication [17].

Before entering to the next section, we comment on the \(^{\text{HCOO}}\) formation on Ni(111)-Rh system. On this system, CO\(_2\) is adsorbed on the surface with bidendate configuration. Therefore, no extra energy is required to bend the O-C-O angle. Without doing any calculation, we can predict that the activation energy for \(^{\text{HCOO}}\) formation on this surface will be lower than that on clean Ni(111) surface, which is indeed true (see Table 1). However, the calculated activation energy for \(^{\text{HCOO}}\) formation on this surface is still higher than that on Ni(111)-Pt surface. This situation arises because H adsorption energy on this system is much stronger than that on clean Ni(111) surface.

4. Summary

We report on a theoretical study of the formation of \(^{\text{HCOO}}\) on Ni(111)-M surfaces using DFT calculations. We find that CO\(_2\) molecule is only physically adsorbed on most of Ni(111)-M surfaces. The fact that CO\(_2\) molecule is only physically adsorbed on most of Ni(111)-M surfaces suggests that the \(^{\text{HCOO}}\) formation reaction on these surfaces might not start from the CO\(_2\) adsorption. Instead, this reaction might start from the H\(_2\) dissociative adsorption since this dissociative process only requires very small activation energy on Ni(111) surface. Therefore, we might simplify our reaction model for \(^{\text{HCOO}}\) formation Ni(111)-M surfaces by assuming that this reaction starts from the interaction between a pre-adsorbed H atom and a CO\(_2\) gas (CO\(_2\)(g) + \(^{\text{H}}\) \rightarrow \(^{\text{HCOO}}\)).

We find that the presence of transition metal doping on the first-layer of Ni(111) surface could reduce the activation barrier of this reaction (up to \(-38.4\%\), compared to clean Ni(111) surface). We also find that Rh doping allows CO\(_2\) molecule to be chemically adsorbed on Ni(111) surface with a bidendate configuration which in turn facilitates the formation of\(^{\text{HCOO}}\).
|       | IS                        | TS                        | FS                        |
|-------|---------------------------|---------------------------|---------------------------|
| Clean | ![Image of Clean IS](image) | ![Image of Clean TS](image) | ![Image of Clean FS](image) |
| doped-Cu | ![Image of doped-Cu IS](image) | ![Image of doped-Cu TS](image) | ![Image of doped-Cu FS](image) |
| doped-Pd | ![Image of doped-Pd IS](image) | ![Image of doped-Pd TS](image) | ![Image of doped-Pd FS](image) |
| doped-Pt | ![Image of doped-Pt IS](image) | ![Image of doped-Pt TS](image) | ![Image of doped-Pt FS](image) |
| doped-Rh | ![Image of doped-Rh IS](image) | ![Image of doped-Rh TS](image) | ![Image of doped-Rh FS](image) |

**Figure 2.** Geometries of initial state (IS), transition state (TS) and final state (FS) of *HCOO formation on Ni(111)-M. Red, yellow, cyan and metallic blue atoms are O, C, H and Ni, respectively. The colors for M atoms are indicated in the figure.

![Diagram of reaction path](image)

**Figure 3.** Schematic for forward and backward reactions.
Acknowledgements
This work is funded by Institut Teknologi Bandung through the "Program Riset dan Inovasi ITB 2015" grant. R.M. is grateful for financial support from MEXT-KAKENHI grants 26287063, 25600156 and that from the Asahi glass Foundation. Calculations were performed using High Performance Computer facility in Institut Teknologi Bandung and in Center for Information Science of JAIST.

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