First-Principles Investigation of Catalytic Activity Improvements with an Electric Field

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Abstract: Some catalytic reactions are activated by an impressed electric field as known as the non-Faradaic electrochemical modification of catalytic activity (NEMCA). We have theoretically investigated the activation mechanism of NEMCA using the density functional theory. We found that all intermediates in CO_2 methanation binds on the Ni surface more strongly as impressing electric field in the normal direction. Dissociative reactions are also accelerated by the effect of electric field, some of them were found as the rate-limiting steps in CO_2 methanation from our kinetic simulations.

Keywords: Density functional theory, Electric field effect, CO_2 methanation.

1. Introduction

In the world, we have faced severe energy problems such as exhaustion of fossil fuel now. We must save energy resources and improve energy efficiency in order to solve this problem. Catalysis is used in most of the energy conversion technologies, so enhancement of catalytic activity is essential for improving energy efficiency. The non-Faradaic electrochemical modification of catalytic activity (NEMCA) with external electric field has attracted attention as one of the methods to improve catalytic activity [1]. The NEMCA was firstly proposed in 1988 by Vayenas et al. [2], and they discussed oxygen anions forced electrochemically to adsorbed on catalyst surface alter the catalyst electric property. However, given electric field also changes the catalyst electric property directly. Breaking down into these effects is difficult with an experimental approach. Therefore, we are trying to investigate the NEMCA using density functional theory (DFT) and clarify the detailed mechanism of NEMCA theoretically. In this study, we focus on the following CO_2 methanation reaction in solid oxide electrolysis cell (SOEC) where NEMCA is also reported [3].

$$\mathrm{CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O, \Delta H^o = \text{-}165kJ/mol} \quad (1)$$

We have calculated the adsorption, surface reaction, and activation energies of hydrocarbons species related the rate-limiting step over CO_2 methanation on Ni surface with electric field proposed by our elementary step mechanism. Based on the knowledge of kinetic mechanism, we discuss why the catalytic activity is enhanced by the electric field. In addition to the direct effect of electric field, the effect of co-adsorbed oxygen anion was calculated and discussed.

2. Theoretical

In this study, catalytic activity improvements with an electric field were computationally investigated using cambridge sequential total energy package (CASTEP) in which density functional theory (DFT) calculations is performed with a plane-wave basis set. Used exchange-correlation functional is the generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE). The plane-wave cutoff energy is set as 450 eV and 630 eV (for the species containing an O atom), Monk-horst-Pack *k*-points are set as 4x4x1. In addition, we utilized the OTFG-ultrasoft as the pseudopotentials. For the slab models, we used 3×3 unit cell with three layers which has a vacuum thickness of 10 Å. Various hydrocarbon species are adsorbed on some Ni catalyst surfaces including (111) facet as the reaction intermediates in CO_2 methanation. When we investigated the effect of impressing electric field, we set electric field of ±0.25, ±0.5 V/Å, where positive values mean (0 0 1) direction and negative values mean (0 0 -1) direction as shown in Fig.1 .

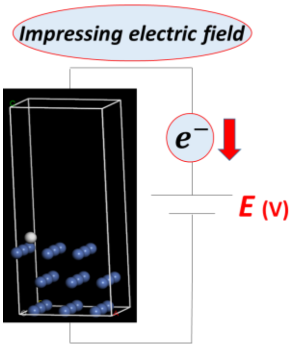

Figure 1. A schematic diagram of the calculated slab model with electric field.

3. Results and discussion

Due to space limitation, just an example of our calculations is shown in this abstract. Table 1 shows the change of adsorption energies of species with external electric field, associated with the following rate-limiting steps on Ni (111) surface proposed our detailed kinetic simulations.

$$CO_2 \rightarrow CO + O \quad (2)$$
$$CHO \rightarrow CH + O \quad (3)$$
$$CH_4 \rightarrow CH_3 + H \quad (4)$$

Here, H, CH, CH_3 species were adsorbed on most stable *fcc* site of Ni (111) surface, while C, O, CO, CHO species were adsorbed on most stable *hcp* site of Ni (111) surface. Also, only CO_2 species was adsorbed on the *top* site of Ni (111) surface. In all species, adsorption energy increases as electric field is stronger regardless of its direction, which means an electric field stabilizes the adsorption of hydrocarbons. This tendency is completely agreed with the reported effect of electric field for sulfur and oxygen atoms adsorption on Ni (111) or Ni (100) surface [4] [5]. In the reactions (2) ~ (4), CO_2, CHO, and CH_4 dissociates into CO and O, CH and O, CH_3 and H, respectively on the surface. Observed tendency with electric field indicates that electric field possibly reduces the reaction energy and activation energy of CO_2, CHO, or CH_4 dissociation due to the production of two adsorbates in each case. At least for reactions (2) and (3), the results lead to the enhancement of CO_2 methanation. Other results will be reported at the poster presentation.

Table 1. The effects on adsorption energy of the electric field.

External field (V/Å)	ΔE_{ad} (eV)							
	H on Ni(111)	C on Ni(111)	O on Ni(111)	CH on Ni(111)	CO on Ni(111)	CH_3 on Ni(111)	CO_2 on Ni(111)	CHO on Ni(111)
0.5	-0.48	-0.45	-0.41	-0.60	-0.36	-0.74	-0.50	-0.59
0.25	-0.12	-0.10	-0.08	-0.17	-0.04	-0.23	-0.11	-0.16
-0.25	-0.13	-0.16	-0.16	-0.09	-0.23	-0.03	-0.17	-0.12
-0.5	-0.50	-0.56	-0.58	-0.44	-0.75	-0.33	-0.65	-0.51

4. Conclusions

DFT was used to study the electric field effects on catalytic activity by making comparison between the calculated information of hydrocarbon species such as adsorption energy with and without electric field on Ni catalyst surface. For example, the adsorption energies of species associated with the rate-limiting steps on Ni (111) surface increases by impressing an electric field. This results indicate that the electric field enhances the stability of the adsorbed species on the catalyst surface. We believe that our research for theoretical mechanism of NENCA will connect to develop more energetically-effective catalysis technology and help to overcome the serious energy problem.

References

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