

Theoretical Research of Catalytic Activity Improvement with Electric Field

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Highlights

- Hydrocarbon species on Ni surface were calculated by DFT method w/o electric field.
- Adsorbed species are more stable on Ni catalyst surface by impressing electric field.
- Oxygen anion co-adsorption effects were investigated.
- Theoretical mechanism of NEMCA was investigated.

1. Introduction

All the countries of the world have severe energy problem such as exhaustion of fossil fuel now. We have to 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 adsorb 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 NEMCA using density functional theory (DFT) and clarify the detailed mechanism of NEMCA theoretically. In this study, we focus on CO₂ methanation reaction in solid oxide electrolysis cell (SOEC) where NEMCA is also reported [3]. We have calculated the adsorption, surface reaction, and activation energies of hydrocarbon species related CO₂ methanation on Ni surface with electric field. Based on the knowledge of kinetic mechanism, we discuss why the catalytic activity is enhanced by the electric field. In addition to the effect of electric field, the effect of co-adsorbed oxygen anion was calculated and discussed.

2. Numerical details

In this study, we performed density functional theory (DFT) calculations using Cambridge Sequential Total Energy Package (CASTEP) in which a plane-wave basis set is used. We utilized the generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) as the exchange and correlation functional, 440 eV or more as the plane-wave cutoff energy, and 4×4×1 Monkhorst-Pack grids as the *k*-points. As a slab model, we used 3×3 unit cell with three layers which has a vacuum thickness of 10 Å (It is noted that parts of the calculation were performed with 2×2 unit cell and 6×6×1 *k*-points.). Various hydrocarbon species are adsorbed on some Ni catalyst surfaces including (111) facet as the reaction intermediate in CO₂ 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 .

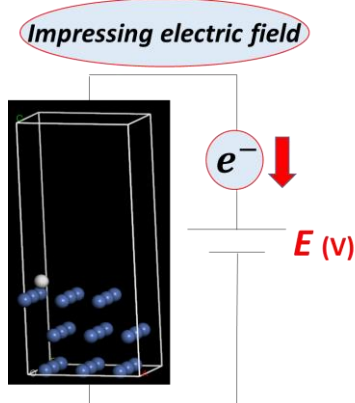


Figure 1. A schematic diagram of the calculated slab model with electric field.

3. Results and discussion

Due to space limitation, just an example of our calculations are shown in this abstract. Table 1 shows the change of adsorption energies of H and C atoms on Ni (111) surface with external electric field. Here, H and C species were adsorbed on most stable *fcc* site of Ni (111) surface. In both H and C atoms, adsorption energy increases as electric field is stronger regardless of its direction, which means electric field stabilizes the hydrocarbon adsorption. This tendency is completely agreed with the reported effect of electric field for sulfur atom adsorption on Ni (111) and (100) surface [4]. For the CO₂ methanation, CO₂ dissociation into CO and O on the surface is considered as one of the rate limiting reactions. This tendency indicates that electric field possibly reduces the reaction energy and activation energy of CO₂ dissociation due to the production of two adsorbates and leads to enhancing the catalytic activity of CO₂ 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)
0.5	0.48	0.16
0.25	0.12	0.02
-0.25	0.13	0.09
-0.5	0.50	0.30

4. Conclusions

DFT method 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 H and C atoms on Ni (111) surface increases by impressing 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 effective catalysis in various situations and help to overcome the serious energy problem.

References

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Keywords

“Density functional theory; Electric field; Hydrocarbon species; Oxygen co-adsorption”.