

First-principles Study of the Extraordinary Sites Effect on Methane Reforming Reaction on Nickel Catalyst

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Highlights

- Extraordinary sites are modeled and compared.
- Local structure affects the adsorption properties of the intermediate species.
- Local structure affects the barriers in methane reforming reaction.
- Step and kink sites have smaller barrier for most reactions.

1. Introduction

In the solid oxide fuel cell (SOFC), hydrocarbon can be directly used as the inlet fuel with internal reforming process in the anode. The study of the elementary reactions in the methane reforming is important both for commercialization of internal reforming SOFC and the basic understanding of catalytic activity. In the high operating temperature of SOFC, metal atoms on the surface of catalyst have high mobility, and the atoms can fluctuate with time. [1] The extraordinary sites such as steps or kinks can be produced at the local positions. In published literatures, the step surfaces have been compared with the terrace models, but only few studies [2,3] have discussed the reactivity of the extraordinary sites of the surfaces with local structures, such as adatom or defect. A systematic comparison of the reactivity of the extraordinary sites has not been studied.

2. Methods

DFT calculations were performed using the Cambridge Serial Total Energy Package (CASTEP) in which a plane wave basis set is used. The generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) were used as the exchange and correlation functional. The cutoff energy of the plane wave was set to 350eV, and the k -points of $4 \times 4 \times 1$ Monkhorst-Pack grids were used.

In the slab model, a (3×3) unit cell with three layers and a vacuum region of 10 Å were used. As shown in Fig.1, we designed four local surface models based on a pure Ni(111) surface with a (3×3) unit cell : i) adatom, ii) defect, iii) pseudo-step, and iv) pseudo-kink.

Adsorption properties of intermediate species in methane reforming were studied, and then the surface reactions on various surface models were calculated.

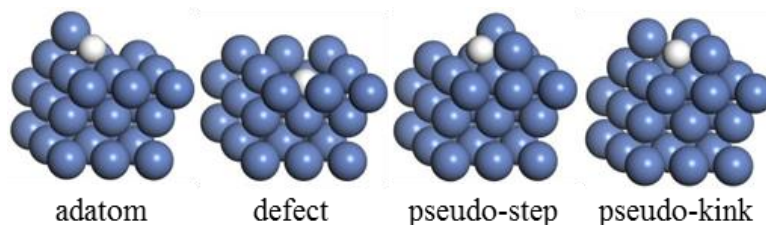


Figure 1. Models of local surface structures with an adsorbate. The blue balls are Ni atoms, and the white ball is adsorbate.

3. Results and discussion

All species are found to bind more strongly on pseudo-step or pseudo-kink surface than on Ni(111) flat surface. H, O, OH, CO, CH₂, and CH₃ are most stable on the bridge sites, while C and CH are more stable by binding more Ni atoms. The adsorption of C, O, CH, CH₂, and OH become stronger by receiving more electrons from the surface, while the adsorption of H, CH₃, H₂O, and CO have little correlation with the

transferred charge. The projected density of states of the d-bands of Ni atoms show that the Ni atoms locating upon the surface can provide more electrons to the adsorbates. In addition, strong adsorption of C atom is found when its p orbital peak shifts toward the lower energy.

The calculated energy paths of the methane dissociation reaction are shown in Fig.2. Based on the transition state calculations, the dominant reaction path of the methane reforming on the Ni catalyst is proposed near the steps of pseudo-step and pseudo-kink models. Micro-kinetic models are necessary for the future study of catalyst performance.

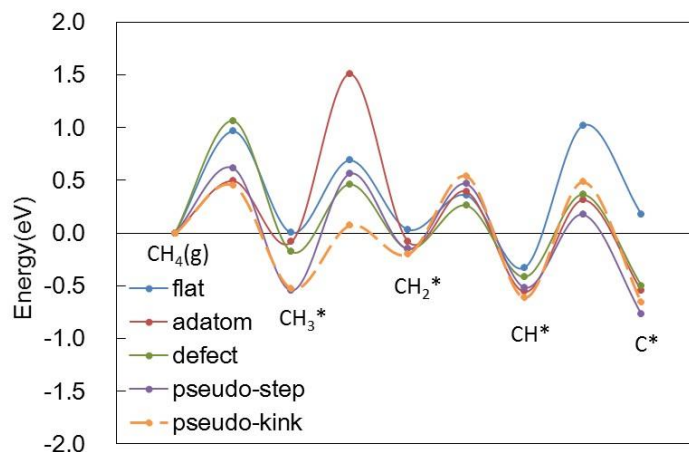


Figure 1. Reaction paths on the different surface models.

4. Conclusions

DFT calculations for the adsorption of hydrocarbon species were carried out using four designed local surface models, adatom, defect, pseudo-step and pseudo-kink surfaces. All adsorbates were found to prefer to be adsorbed on pseudo-step, pseudo-kink surface models. Our adsorption results on the local surface models suggest that surface reactions occur selectively on the extraordinary sites although they exist slightly on the high-temperature surface of the catalyst. It also shows the potential that the surface structure can be changed by the adsorption of the chemical species.

References

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Keywords

First-principles; Methane reforming; Extraordinary site