Theoretical Study of the Local Structure Effect on Methane Reforming Reaction

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Abstract: We perform density functional theory calculations for the adsorption and surface reactions of hydrocarbon species on designed local structure models based on Ni (111) surface. All species are found to bind more strongly on the pseudo-step or the pseudo-kink surface. H, O, OH, CO, CH_2 and CH_3 are most stable on the up-bridge sites, while C and CH are most stable with a larger coordination number of carbon atom which is embedded into the Ni atoms. Based on the transition state calculations, the dominant reaction path of the methane reforming on the Ni catalyst is proposed near the steps.

Keywords: Methane reforming, First-principles study, Local structure.

1. Introduction

In the high temperature solid oxide fuel cell (SOFC), hydrocarbon can be directly used as fuel with internal reforming process in the anode. The catalyst of the internal reforming reactions is the Ni in the ceramic anode material of Ni/yttria stabilized zirconia (Ni/YSZ). Steam methane reforming reaction (SMR) can occur in the internal reforming process.[1] The operating conditions of the catalytic process are at high temperatures of 800~1100 K. In such a high temperature, metal atoms on the surface of catalyst have high mobility, and the surface fluctuates with time.[2] The extraordinary sites such as steps or kinks can be produced at local positions, so only analysis of reactions on single crystal surfaces is insufficient for the dynamic discussion.[3]

Adsorption and surface reactions on the low index surfaces have been widely studied by density functional theory (DFT) method, such as those on (111), (100), and (211) surfaces. In published literatures, the step surfaces have been compared with the terrace models, but only few studies[4,5] have discussed the reactivity of the extraordinary sites of the surfaces with local structures, such as surfaces with adatom, defect or kink.

2. Theoretical

Local surface models were designed by putting Ni atoms on the slab model or deleting a Ni atom on the top layer of the slab as shown in Fig. 1. One atom added on the Ni surface was used to simulate an adatom; one atom defect on the top layer was used to simulate the defect; two atoms added on the Ni surface was used to simulate a pseudo-step; three atoms added on the surface were used to simulate pseudo-kink.

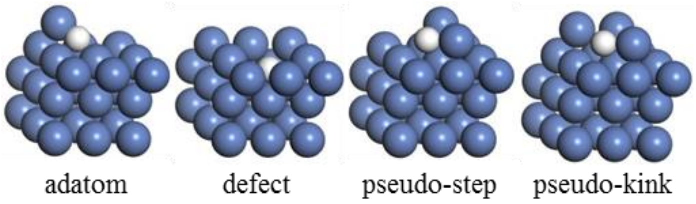

Figure 1. Local surface structure models. Blue balls are Ni atoms, and white ball is adsorbate.

DFT calculations were performed using CASTEP. The generalized gradient approximation (GGA) exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE) was used. The convergence criteria for structure optimization were set to an energy change tolerance of 1.0×10^{-5} eV/atom, a maximum displacement tolerance of 0.001 Å, and maximum force tolerance of 0.03 eV/Å. Spin polarization was considered due to the existence of Ni element. In the transition state calculations, linear synchronous transit

(LST) maximization was followed by repeated conjugate gradient minimizations and quadratic synchronous transit (QST) maximizations until the root mean square (RMS) force convergence was smaller than 0.15 eV/Å.

3. Results and discussion

Adsorption energies of H, O, OH, H_2O, C, CH, CH_2, CH_3, and CO on each adsorption sites were calculated. H, O, OH, CO, CH_2, and CH_3 prefer to be adsorbed on site with two or three bonds with the Ni atoms, while C and CH prefer to have more bonds with the Ni atoms. H_2O prefers the side of one Ni atom.

Fig. 2(a) shows the adsorption energy as a function of the transferred charge of the adsorbed species. All adsorbates except for H_2O are negatively charged after adsorption. The adsorption energies of H, C, O, CH, OH and CH_3 show linear increasing with the amount of electronic charges received from the Ni surface. Fig. 2(b) shows d-band centers of the Ni atoms with different coordination numbers in the surface models. The Ni atoms with smaller coordination numbers have higher d-band centers. The added Ni atoms located on the Ni(111) surface such as in adatom, step, and pseudo-kink models can donate more electrons to the adsorbates and strengthen the adsorption.

The details of the elementary reactions calculations will be shown in the conference.

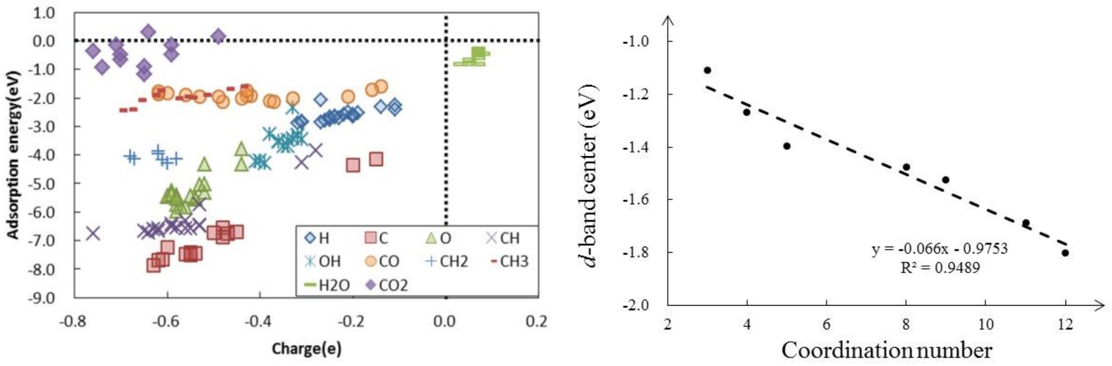

Figure 2. (a)The adsorption energy as a function of adsorbed species charge. (b) *d*-band center as a function of coordination number.

4. Conclusions

DFT calculations for the adsorption of hydrocarbon species were carried out on adatom, defect, pseudo-step and pseudo-kink models. All adsorbates prefer to be adsorbed on pseudo-step or pseudo-kink models. H, O, OH, CH_2, CH_3, and CO are most stable on the up-bridge sites, while C and CH are more stable in embedded sites by interacting with more Ni atoms. The adsorption of H, C, O, OH, CH, and CH_3 is strengthened by receiving more electrons from the Ni surfaces, while the adsorption energies of CH_2 and CO are barely dependent on the electronic charge. The adsorption property of the extraordinary sites can be explained by the *d*-band center shift with the coordination numbers of the added Ni atoms. The added Ni atoms forming adatom, pseudo-step or pseudo-kink models, which have smaller coordination numbers, have higher d-band center, and can provide more electrons to the adsorbates.

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