Methane activation on Ni surface: DFT-based insights into catalyst design

Ryan Lacdao Arevalo[a], Susan Menez Aspera[a], Hideaki Kasai[ab], Hiroshi Nakanishi[acd,]*, Syo Matsumura[e]
[a]*National Institute of Technology, Akashi College, 679-3 Nishioka, Uozumi, Akashi, Hyogo 674-8501, Japan*
[b]*Osaka University, 1-1 Yamadaoka, Suita, Osaka 565-0871, Japan*
[c]*Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*
[d]*Institute of Industrial Science, The University of Tokyo, Meguro, Tokyo 153-8505, Japan*
[e]*Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University, Motooka 744, Fukuoka 819-0395, Japan*
**Corresponding author: nakanishi@akashi.ac.jp*

Abstract

Using density functional theory calculations and kinetic Monte Carlo simulations, we investigate the reaction mechanism of methane reforming on Ni surface. Focusing on addressing the “coking” reaction on stepped Ni surface, we found the important electronic factors that govern the selectivity of Ni surface for methane decomposition toward atomic carbon. Results show that carbon adsorption is uniquely characterized by a 5–coordinated bonding with Ni. Interestingly, substituting the specific subsurface Ni atoms with other elements can dramatically change the reaction mechanism of methane decomposition on the surface, suggesting a new approach to catalyst design for hydrocarbon reforming applications. [1]

Keywords: Methane, Density functional theory, Nickel surface.

1. Introduction

Methane activation is one of the most important industrial processes in a modern-day society as it plays a key role in the production of syngas (CO + H_2) that is used to make a wide spectrum of hydrocarbons and alcohols that sustain the energy and chemical needs of humankind. In reforming reactions, methane reacts with H_2O (steam reforming) or CO_2 (dry reforming) to produce syngas shown by the following equations:

$$\mathbf{CH_4 + H_2O \rightarrow CO + 3H_2}$$

$$\mathbf{CH_4 + CO_2 \rightarrow 2CO + 2H_2}$$

Ni is commonly used for these reactions because of its low cost. However, its efficiency is hindered by its high activity for carbon deposition/formation that deactivates the catalyst. In this work, density functional theory and kinetic Monte Carlo simulations are used to identify the various reaction pathways toward atomic carbon and carbon monoxide.

2. Computational Model

Spin-polarized DFT calculations were carried out using the Vienna ab initio simulation package (VASP) within the generalized gradient approximation based on Perdew-Burke-Ernzerhof (GGA-PBE) functional with an empirical dispersion correction of Grimme (DFT-D2). The interaction between ions and electrons was described using the projector augmented wave (PAW) method. Plane wave basis sets were employed with an energy cutoff of 400 eV. Electric dipole correction was used to cut the dipole interactions between the repeated image layer systems. The surface Brillouin zone integrations were performed on a grid of 5×6×1 Monkhorst-Pack k-points using Methfessel-Paxton smearing of $\sigma = 0.2$ eV. Conjugate-gradient algorithm was used to relax the ions into their ground state. The stepped surface of Ni is modeled using fcc (211) facet with 12-atomic layers in a p(1×2) slab. It consists of three-atom-wide terraces with (111) facet structure and one-atom step with (100) character. Vacuum spaces of 14 Å and 10 Å were used to separate the repeated slabs. The optimization of isolated gas-phase molecules was performed with one free molecule within a 25×25×25 Å unit cell with full electric dipole moment correction in all directions. The optimal adsorption configuration of the molecules was determined by exhausting a number of different orientations on the surface with the top two layers of the slab fully relaxed in all directions.

3. Results and discussion

Figure 1 shows the calculated pathways for CH_4 reaction toward atomic C (upper panel) and CO (lower panel). It appears that the subsequent reactions to the conversion of CH_2 determine the selectivity toward C or CO. The reaction pathways show that in order to avoid atomic C, its adsorption energy must be decreased.

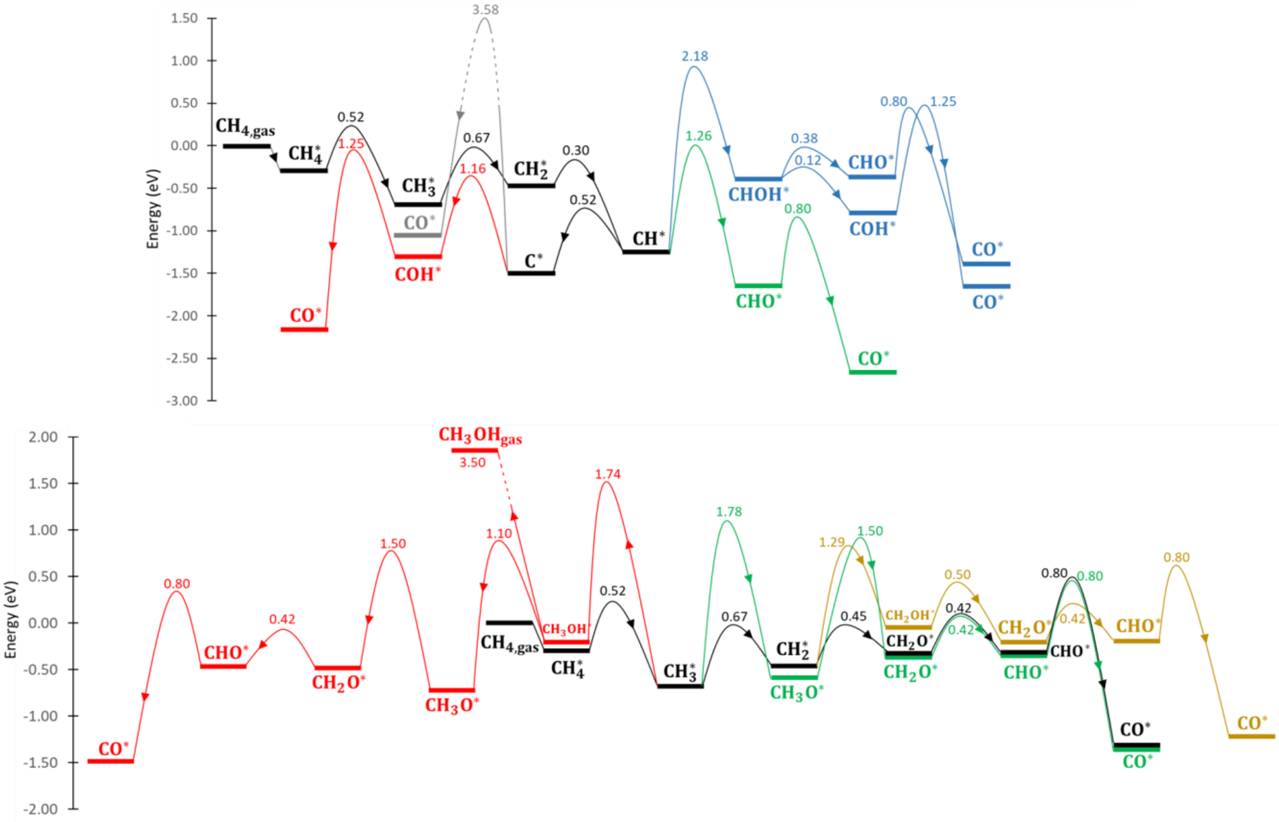

Figure 1. Energy diagram for methane reforming process. The black curves show the low activation barrier paths.

Analysis of the electronic factors that govern the high stability of atomic carbon on the surface points that its adsorption on stepped Ni surface is uniquely characterized by a 5–coordinated C–Ni bonding that involves Ni atoms from both the surface and subsurface layers. Interesting, substituting a specific subsurface atom of stepped Ni surface discriminately reduces the adsorption energy of atomic C, thereby changing the reaction pathway for methane decomposition on the surface. This suggests a new approach to catalyst design aimed at avoiding the “coking” reaction for hydrocarbon reforming processes.

4. Conclusions

Density functional theory calculations revealed the various reaction pathways for methane reforming. Results suggest a mechanism for avoiding the pathway for methane decomposition to atomic carbon that leads to catalyst deactivation via “coking”. By substituting a specific subsurface atom of stepped Ni surface, the unique 5–coordinated C–Ni bonding that characterizes the strong adsorption of carbon on the surface can be avoided, thereby weakening its adsorption on the surface.

Reference

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