



Activity and coke formation of nickel and nickel carbide in dry reforming: A deactivation scheme from density functional theory



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ARTICLE INFO

Article history:

Received 10 August 2013

Revised 17 December 2013

Accepted 30 December 2013

Keywords:

Dry reforming

Coke formation

Deactivation

Nickel

Nickel carbide

Methane

CO₂

DFT

Microkinetics

ABSTRACT

Dry reforming is a promising reaction to utilise the greenhouse gases CO₂ and CH₄. Nickel-based catalysts are the most popular catalysts for the reaction, and the coke formation on the catalysts is the main obstacle to the commercialisation of dry reforming. In this study, the whole reaction network of dry reformation on both flat and stepped nickel catalysts (Ni(111) and Ni(211)) as well as nickel carbide (flat: Ni₃C(001); stepped: Ni₃C(111)) is investigated using density functional theory calculations. The overall reaction energy profiles in the free energy landscape are obtained, and kinetic analyses are utilised to evaluate the activity of the four surfaces. By careful examination of our results, we find the following regarding the activity: (i) flat surfaces are more active than stepped surfaces for the dry reforming and (ii) metallic nickel catalysts are more active than those of nickel carbide, and therefore, the phase transformation from nickel to nickel carbide will reduce the activity. With respect to the coke formation, the following is found: (i) the coke formation probability can be measured by the rate ratio of CH oxidation pathway to C oxidation pathway ($r_{\text{CH}}/r_{\text{C}}$) and the barrier of CO dissociation, (ii) on Ni(111), the coke is unlikely to form, and (iii) the coke formations on the stepped surfaces of both nickel and nickel carbide can readily occur. A deactivation scheme, using which experimental results can be rationalised, is proposed.

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1. Introduction

In the last few decades, increasing global warming has become one of the most challenging environmental issues. It is widely believed that one of the main reasons for this climate change is the increasing emissions of anthropogenic carbon dioxide. Furthermore, some non-CO₂ greenhouse gases such as CH₄, N₂O and chlorofluorocarbons may also contribute to the rapid warming [1]. Therefore, it is of great importance to reduce the emissions of greenhouse gases and also to further utilise processes capable of consuming these gases. Dry reforming, which converts CO₂ and CH₄ to H₂ and CO, may be a promising approach to relieve this problem. Furthermore, from an industrial perspective, it produces syngas with a lower H₂/CO ratio than steam reforming, which is more suitable for Fischer–Tropsch synthesis [2].

Numerous-supported metal catalysts have been studied for the dry reforming reaction. It has been shown that many noble metal catalysts, such as platinum [3–6], ruthenium [7,8] and rhodium [9–13], have outstanding catalytic performances. However, considering the cost, the nickel catalyst is regarded as the most promising

industrial catalyst for this process. Nevertheless, deactivation of Ni catalysts due to coke formation [14,15] has been a major obstacle to the commercialisation of dry reforming. Many investigations have been carried out to understand why surface coke forms on nickel catalysts. In a study on the deactivation of dry reforming [14], it is reported that regardless of the pre-treatment conditions, most catalysts exhibit similar activities initially, which may be due to the formation of nickel carbide. They argued that the active phase for the dry reforming is not the metal itself but a carbide form of the metal. Furthermore, in their work, it was suggested that the particles with flat surfaces tend to produce essentially little or no toxic filamentary carbon, while on small and spherical particles, highly toxic encapsulating carbon was found. Moreover, Suh and co-workers [16] found that the formation of carbon was significantly influenced by the metal particle size. The effects of catalyst morphology, structure and particle size on the carbon resistance were also investigated in some other studies [17–20]. Therefore, it is important to investigate the coke formation along with the effects of structure on the reactivity and coke formation in dry reforming.

The mechanism of dry reforming on nickel catalysts is also of great interest, since the elucidation of the mechanism will not only enhance our understanding of the activity and deactivation of this

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reaction, but also may help us to obtain a proper approach to restrain or even eliminate the coke formation. Mirodatos and co-workers [21] reported that the oxidation step of active carbon to CO on the nickel surface is likely to be rate limiting. Using transient isotopic methods, Aparicio [22] suggested that there is no single rate-determining step in methane reforming over Ni catalysts, and under some conditions, the availability of surface oxygen may play a key role in determining the rate. In the work of Wei and Iglesia [23], the activation of the first C–H bond was shown as the sole kinetically-relevant step for the dry reforming on nickel catalysts. In addition, numerical theoretical studies can also be found. Using density functional theory (DFT) calculation, Michaelides and Hu [24–26] investigated the adsorption and dissociation of CH_x on Ni(111), suggesting that a three-centre bonding between carbon, hydrogen and nickel forms in the adsorption of CH_3 on Ni(111). Furthermore, a series of investigations were carried out by Jiao and co-workers [27–33]. They studied the adsorption and dissociation of CH_4 and CO_2 on Ni(111), finding that CH_4 dissociative adsorption is the rate-determining step, and the key intermediate is surface adsorbed CHO [29,30]. They also investigated the CO_2 dissociation on Ni(211) with both direct and H-mediated dissociation mechanisms [28], suggesting that the dissociation of HCOO into CHO and O is unfavourable, while the direct dissociation into CO and O is much easier. Zhu et al. [34] systematically studied all possible reaction pathways in the dry reforming on Ni(111), and their work showed that the oxidation of carbon to CO determines the overall reaction rate at high temperatures, while CH_4 dissociation was found to be the rate-limiting step at lower temperatures. Recently, the dissociation barrier of oxygen on graphene is shown to be very high [35], which suggests that the graphene or graphite like cokes on the nickel surfaces is hard to be removed.

Despite the aforementioned studies on the coke formation on nickel catalysts and the mechanisms of dry reforming, there are still some important questions remaining to be answered. These questions are raised from the three most fundamental properties in catalysis: activity, selectivity and stability of the catalyst. Specifically, what is the active site on the nickel-based catalyst, and why is this site favoured over the other sites? What are the main factors that affect an important side reaction which produces carbon depositions on the nickel catalysts? How do these carbon depositions affect the activity and stability of the dry reforming reactions?

In order to answer these questions, DFT calculations and microkinetic modelling were carried out for the dry reforming on flat and stepped surfaces of both nickel and nickel carbide. These surfaces were chosen for the following reasons: firstly, many studies [36–42] have demonstrated that stepped surfaces containing B_5 sites are the active sites for many dissociation reactions. However, to the best of our knowledge, few investigations have been carried out to study the whole dry reforming mechanism on nickel stepped surfaces. Secondly, according to some reports [43,44], the carbon formation from dissociations of CH_4 and CO_2 may undergo dissolution into nickel-forming nickel carbide, which was suggested to be a key step for the growth of carbon whiskers. Some other investigations [14,21] showed that nickel carbide may be the active phase for this reaction. Therefore, it is important to investigate the reaction mechanism on nickel carbide to study the effects of carbide on the dry reforming reaction. In addition, although many calculations of dry reforming on nickel-based catalysts have been reported, few studies were carried out to understand the whole reaction from the kinetic perspective, and thus, a thorough study with kinetic analyses is required.

In this contribution, the mechanisms of dry reforming were obtained on both stepped Ni(211) and flat Ni(111) by DFT calculations. The pathways of dry reforming were also calculated on

both stepped and flat surfaces of Ni_3C ($\text{Ni}_3\text{C}(001)$ and $\text{Ni}_3\text{C}(111)$, respectively), which is a nickel carbide detected by many experimental investigations [14,21,45–49]. The free energy profiles were obtained using thermodynamic analysis, and the catalytic activities of the four surfaces were determined by a microkinetic model [50,51] on all the surfaces mentioned above. Based on the calculation results, a deactivation scheme is suggested to unravel the activity and coke formation on nickel-based catalysts.

2. Theoretical methods

2.1. Density functional theory (DFT)

All the DFT calculations were carried out with a periodic slab model using the Vienna ab initio simulation programme (VASP) [52–55]. The generalised gradient approximation (GGA) was used with Perdew–Burke–Ernzerhof (PBE) [56] exchange–correlation functional. Projector-augmented wave (PAW) method [57,58] was utilised to describe the electron–ion interactions, and the plane-wave basis expansion cut-off was set to 450 eV. Due to the magnetic properties of nickel, the spin polarised effect has been taken into account in our calculations. All the adsorption geometries were optimised using a force-based conjugate gradient algorithm, while transition states (TSs) were located with a constrained minimisation technique [59–61].

Ni(111) was modelled using a periodic 4-layer model with the 2 lower layers fixed and the 2 upper layers relaxed. A $p(3 \times 3)$ supercell (see Fig. 1a) was chosen with $3 \times 3 \times 1$ Monkhorst–Pack k -point mesh sampling for Brillouin-zone integration. While for the modelling of Ni(211), a 12-layer model with $p(1 \times 4)$ supercell (see Fig. 1b) was used with the lower 6 layers fixed and the 6 upper layers relaxed, $3 \times 2 \times 1$ k -point mesh sampling was employed. The Ni_3C crystal was obtained from a structure analysis research of nickel carbide [62]. After optimisation of the crystal, $\text{Ni}_3\text{C}(001)$ and $\text{Ni}_3\text{C}(111)$ were cleaved in order to describe the carbide structures of flat Ni(111) and stepped Ni(211), respectively. A $p(2 \times 2)$ supercell with 8 layers was used for $\text{Ni}_3\text{C}(001)$ (shown in Fig. 2), and k -point mesh sampling was set to $3 \times 3 \times 1$. For the modelling of $\text{Ni}_3\text{C}(111)$, a $p(1 \times 1)$ unit cell (Fig. 3) and $3 \times 3 \times 1$ k -point sampling were used. In the nickel carbide calculation, the upper half atom layers were relaxed and lower half layers fixed as mentioned above for the pure nickel calculation. A $\sim 10 \text{ \AA}$ vacuum region was placed on all the models mentioned above. More details about the modelling and calculations can be found in the Supporting information.

2.2. Thermodynamic analysis

As mentioned in many studies [14,48,49], the dry reforming catalysed by nickel-based catalysts is carried out at a very high temperature, around 1000 K. Therefore, it is highly necessary to take the entropies into account. Herein, like our previous work [50,63], some standard formulas of statistical mechanics were used to calculate the zero-point energy (ZPE), thermal energy and entropy derived from partition functions.

The standard molar Gibbs free energy for each species in dry reforming is obtained by the following:

$$G^\circ = E_{\text{total}} + E_{\text{ZPE}} + \gamma RT \left(1 + \ln \frac{P}{P^\circ} \right) + U^\circ - TS^\circ \quad (1)$$

where E_{total} refers to the total energy obtained from DFT calculation, R is the gas constant, P is the partial pressure of the gas-phase molecule, γ is 0 for surface adsorbed species and 1 for gaseous molecule, and E_{ZPE} , U° and S° are the correction energies from ZPE, thermal

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