Applied Catalysis B: Environmental 195 (2016) 77–89

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Elucidating the field influence on the energetics of the methane steam reforming reaction: A density functional theory study

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ARTICLE INFO

Article history:
Received 24 February 2016
Received in revised form 12 April 2016
Accepted 14 April 2016
Available online 29 April 2016

Keywords:
Methane steam reforming
Low operating temperatures
Electric fields
Electrocatalysis
Phase diagram

ABSTRACT

To help realize lower operating-temperatures for the highly endothermic Ni-catalytic methane steam reforming (MSR) process, we focused on elucidating the influence of an applied electric field on the energetics of the said reaction. Two aspects were considered in this study: the electric field effects on (i) the adsorption and electronic properties of the MSR-involved species, and (ii) the overall MSR energy profile. Our results show that for Ni-based MSR processes, a positive field strengthens the adsorption of the reactants, promotes product desorption, impedes coke formation, lowers the overall energy profiles and consequently, reduces the temperature requirements for the overall MSR-on-Ni reaction. Based on our phase diagram obtained from first principles, we show that CO can be obtained from the dehydrogenation of COH and CHO at moderate hydrogen partial pressure values with a negative field, while methanol is formed on the surface via hydroxyl oxidation of CH_3 at high hydrogen partial pressures and positive field values. This investigation suggests ways to facilitate the MSR reforming reaction in the presence of an electric field and also points toward a number of elementary reactions that need to be considered for establishing microkinetic model studies.

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1. Introduction

Hydrogen, the energy carrier of the future, can be used in various applications (e.g. vehicles and fuel cells) [1] and cater to our dramatically growing need for sustainable energy resources as well as our ever-present environmental concerns. To generate hydrogen, steam reforming of natural gas (methane) over Ni-based catalysts is widely employed in industry [2,3]. In addition, methane steam reforming (MSR) is a reaction of interest since it can also be performed directly at the anode of a solid oxide fuel cell (SOFC) to generate electric power in the direct internal reforming reaction, which couples steam reforming with subsequent syngas electrochemical oxidation [4–6]. However, the main issue for the said reaction is that methane (CH_4) is very thermodynamically stable and requires a large amount of energy to break its C—H bonds, which makes the MSR reaction a highly endothermic process requiring temperatures of 900 K or higher [7]. Consequently, the Ni catalyst is placed in expensive alloy tubes to tolerate the extremely high thermal fluxes that will occur through the tube walls of the reactor [8,9]. An additional problem related to the high operating-temperature requirements involved in the MSR reaction is the increased occurrence of sintering [10,11] and coking [12–14], which reduces the lifetime of the Ni catalysts. To rationally design catalysts with lower temperature requirements for a methane reformer in industrial or fuel cell applications, it is necessary to understand the thermodynamic properties of the Ni-based MSR reaction at the atomic scale.

The kinetic and thermodynamic properties of methane steam reforming are well studied [15–19]. Jones et al. showed that the dissociative adsorption of CH_4 and the formation of CO are the rate-limiting steps over different transition metals supported by Al_2O_3 and ZrO_2 under MSR conditions from both first principles calculations and experimental investigations [20]. The CO formation barrier is found to be the dominant rate-limiting step at lower temperatures (773 K), while the dissociative adsorption barrier for CH_4 is dominant at higher temperatures above 873 K. Bengaard et al. [21] proposed a possible mechanism over pure Ni catalysts, which is shown in Eq. (1).

$$CH_4 + H_2O \rightarrow C + 4H + H_2O \rightarrow C + 6H + O \rightarrow CO + 3H_2 \quad (1)$$

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http://dx.doi.org/10.1016/j.apcatb.2016.04.026
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Their data indicates that C and CH species are the most stable intermediates on Ni(111) and Ni(211). The overall calculated MSR reaction energy for forming syngas, the total energy differences between the reactant ($CH_4 + H_2O$) and the product ($CO + H_2$) in the gas phase, is 3.03 eV. After correcting the zero-point energies as well as the variation of the enthalpy of the said reaction at T = 298.15 K ($\Delta C_p \Delta T$) [22], the corresponding reaction enthalpy for the said reaction is 2.38 eV, which is in good agreement with the experimental value of 2.14 eV. Using DFT calculations, Blaylock's et al. [23] developed a microkinetic model to investigate the MSR reaction on a Ni(111) surface under realistic conditions. Similar to Rostrup-Nielsen's work [24], they found that CH is the most important carbon-containing reaction intermediate. Wang et al. [25]. studied the stabilities of the intermediates during the CO_2 reforming of CH_4 and found that O, CH_3, CH_2, CH and CHO were key intermediates, in which the most favorable mechanism is as follows:

$$CH_4 + CO_2 \rightarrow CH + 3H + CO + O \rightarrow CHO + 3H + CO \rightarrow 2CO + 4H \tag{2}$$

However, thus far, the influence of the environment on the underlying reaction mechanism over heterogeneous catalysts is still largely unexplored. One possible route to achieve lower operating-temperature requirements for the MSR reaction is to study the effects of the electric field on its mechanism [26–28]. Gorin et al. applied interfacial electric fields, generated from a parallel plate cell with a voltage source, to the Al_2O_3 catalytic rearrangement of *cis*-stilbene oxide. The results showed that the reaction conversion of the cis-stilbene oxide to the aldehyde and ketone products increased up to 10 times higher in the presence of an interfacial electric field as compared to when such as field is absent. Further, the aldehyde to ketone product ratio increased from 1:4 (without electric fields) to 17:1 (in the presence of an electric field) [26]. Sekine et al. investigated the electric field effects on the methane steam reforming over Pd/CeO_2, Ru/CeO_2 and Pt/CeO_2 catalysts, so called "electro-reforming" [27,28]. The methane conversion was largely enhanced with an electric field over all catalysts as well as the hydrogen production yields. Furthermore, our previous work concluded that a positive field could significantly reduce pure carbon deposits over Ni catalysts by decreasing the stabilities of pure carbon atoms and increasing the activation energy barrier for CH dissociation. In addition, the presence of a positive field strengthened the adsorption of H_2O, while a negative electric field had an opposite effect. Moreover, we examined methane and water dissociation over flat and stepped Ni surfaces and found similar electric field effects on both Ni surfaces for the above-mentioned reactions [29–31].

There are several approaches to apply an electric field in the theoretical work, such as the Neugebauer and Scheffler's method [32] (NS) and the double reference method of Neurock and coworkers [33,34]. For the NS approach [32], one inserts a dipole sheet in the middle of the vacuum of a supercell to polarize the metal surface. The polarization induces opposite charges on the top and bottom of the metal surfaces and thereby generates a uniform electric field (F) at a given specified value. With this approach, the interaction between the metal and the adsorbate depends on the effective dipole moment and the effective polarizability of the system. Large electric fields, on the order of ±1 V/Å, can rearrange the molecular or atomic orbitals of the intermediates, which can directly alter the stabilities of the reaction intermediates and consequently change the underlying reaction mechanism [35–37]. To relate the applied field to the electrode potential, a rough approximation based on a Helmholtz model proposed by Janik and coworkers was proposed [38,39]:

$$F = \frac{(U - U(PZC))}{d} \tag{3}$$

where d is the distance between the electrode surface and counter-ion charge plane (i.e. the thickness of the Helmholtz layer of a fuel cell system). U(PZC) is the potential of zero charge, which varies from one metal surface to another and for different ion compositions. U(PZC) is often approximated to be 0 on the reversible hydrogen electrode (RHE) scale. Therefore, for an electric field of 0.5 V/Å within a Helmholtz layer of 3 Å, the electrode potential is 1.5 V_{RHE}. However, such an approximation cannot capture the impact of the adsorbate in shifting the metal work function, which especially needs to be improved when an adsorbate/electrode system has a large dipole moment. On the other hand, adjusting the number of electrons within the unit cell and adding a compensating homogeneous background charge in the double reference method [39] can change the surface potential and generate an electric field at the electrode-electrolyte interface [38]. The electric field is related to the electrode potential (V_{NHE}) by:

$$V_{NHE} = \phi/e - 4.6 \tag{4}$$

where ϕ is the calculated work function referenced to vacuum, e is the charge of an electron and 4.6 V is the estimated potential of the vacuum of the normal hydrogen electrode (NHE) scale in fuel cells [40]. In addition, to generate electrode potentials above 1.1 V (or below 0.5 V), the top of the metal slab is positively charged (or negative charged) by selectively adding (subtracting) a number of electrons to the system. This relates to the calculated system in the presence of a simulated positive field (a simulated negative field) in the NS method since such a system includes a positively charged (a negatively charged) metal slab.

In this present paper, by using the NS method, we will show the significance of the electric field effects on the energetics of the MSR-on-Ni reaction. Several researchers have proposed [41–43] that surface OH and O species can be key intermediates that react with the surface CH_x species. Thus we examined mechanisms for the overall MSR reaction that include both CH_xOH and CH_xO species (given in Fig. 1). To identify the relative equilibrium stabilities of the MSR intermediates under realistic conditions, we also provide a first-principles-based phase diagram for the CH_xOH and CH_xO species as a function of the hydrogen chemical potential and the applied electric field. Based on our previous studies, we also anticipate that many of the results obtained here on a Ni(111) flat surface will be applicable to stepped surfaces as well [29–31]. The paper ends with the significant findings on the field effects on the heterogeneous reaction and an outlook on the remaining challenges of field-dependent heterogeneous reactions.

2. Methods

Our DFT calculations were performed with the Vienna *Ab Initio* Simulation Package (VASP). For adsorbates/late transition metal system, it was recently found in a benchmarking study that the Perdew-Wang 91 functional is of comparable accuracy to the PBE, PBEsol and RPBE functionals when examining a large variety of adsorption systems [44]. As a result, for all calculations we used the Generalized Gradient Approximation with the PW91 exchange correlation functional (GGA-PW91) [45–47]. The projector-augmented wave method was applied to solve the Kohn-Sham equations [48]. The choices for the k-point mesh (4 × 4 × 1), the lattice constant of Ni (3.521 Å), the plane-wave energy cutoff (400 eV), the vacuum size (11 Å) [31,49], and four-layer Ni slab was tested in our previous work [29–31]. An increase in the energy cut-

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