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Evaluation of dry reforming reaction catalysts via computational screening

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ABSTRACT

In this work, a computational screening method introduced in a previous report is employed to determine the optimal operating temperature and reactant feed ratio (CO_2/CH_4) for catalysts used in the dry reforming reaction of methane aiming for high reactivity and stability. It is found that changes in temperature would affect the rate of the main reaction, coke formation and coke removal, while changes in the feed ratio could modify the boundary dividing coke formation from removal zones. The increase in CO_2/CH_4 ratio is found to expand the coke removal zone. Four strategies based on stability and reactivity ratings (RT-S and RT-R) of the catalysts are proposed. Type 1, high RT-S and RT-R catalysts benefit from high T and high CO_2/CH_4 since these promote high rate of reaction and coke removal; Type 2, high RT-S but low RT-R catalysts need the same condition as Type 1 except that the maximum achievable reaction and coke removal rate are lower than Type 1; Type 3, low RT-S but high RT-R catalysts which are located in the coke formation zone should be treated first with high CO_2/CH_4 to shift them into the coke removal zone before applying the same treatment as in Type 1 by increasing the temperature. If the shift is not possible, the alternative is to operate at low T and low CO_2/CH_4 to avoid high coke formation; Type 4, low RT-S and RT-R catalysts exhibit the least reactivity and coke-resistance and as a result, the best operating condition that could be used is to operate them at low T and low CO_2/CH_4 to attain lowest rate of coke formation. The ratings concept extended to the interpretation of experimental data in order to predict the stability of the catalysts is demonstrated on four Pt supported (Pt/SiO₂, Pt/TiO₂, Pt/Cr₂O₃ and Pt/ZrO₂) and Rh supported catalysts (Rh/TiO₂, Rh/Al₂O₃, Rh/MgO and Rh/SiO₂). For these catalysts, experimental apparent activation energies of methane consumption were used as input parameters to predict the rate of coke formation. For the Pt catalysts, the predicted trends of coke formation rate trend calculated from temperature-programmed hydrogenation: Pt/SiO₂ > Pt/Cr₂O₃ > Pt/TiO₂ > Pt/ZrO₂. However, in the case of Rh, the measured carbon deposition via the temperature-programmed oxidation could not be well predicted by our extended ratings concept. Thus, the ratings concept is an effective screening tool for reactive and stable DRR catalysts, however further development of the concept via the incorporation of more experimental parameters would make applications to general catalysts achievable.

1. Introduction

Due to concerns over the global warming caused by greenhouse gases, the conversion of CO_2 , one of the most significant greenhouse gases, into more useful products via chemical reactions is of high interest. The dry reforming reaction of methane (DRR) with CO_2 which produces syngas products CO and H_2 is considered one of the solutions towards this issue [1,2]. However, the DRR process performance is inhibited by catalyst deactivation via coking which not only covers the active sites but also blocks the pores leading to both reactivity and stability losses [1]. Hence, screening for reactive and coke-resistant DRR catalysts is crucial. The ratings concept introduced as a DRR catalyst computational screening tool would be beneficial due to the

reduced time and effort in the search for high performance catalysts. The core of the concept intends to determine how reactive and stable catalysts should be designed in order to exhibit high rate of reaction, along with low rate of coke formation and high rate of coke removal. The reactivity and stability of the catalyst are represented by the reactivity and stability ratings (RT-R and RT-S), as different catalyst materials possess unique indexes of RT-S and RT-R [3]. The reactivity rating connects to the activation energies of the first CH_4 dissociation and CO_2 dissociation elementary steps, while the stability rating associates with the activation energies of carbon formation via CH and CO and carbon removal by H and O steps. The concept evaluates the catalysts' reactivity and stability at different RT-R and RT-S indexes on the phase space defined by the reactivity surface (RS) and stability surface

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(SS) variables. In such analysis, the rate of CH₄ consumption is used to construct RS, while the rates of carbon formation and removal are used to establish SS.

In this work, we employ the ratings concept and propose strategies to achieve optimal operating conditions that promote reaction and coke removal and suppress coke formation. Detailed construction of the concept can be found in the supplementary document. In the first part, this concept is limited to the evaluation of theoretical data for model catalysts. Then, we extend the investigation of the ratings concept to include experimental data. We show that by knowing the apparent activation energy of the catalysts representing their overall reactivity, the stability could be evaluated by the predicted carbon formation rate at steady state. The reliability of this prediction is checked by comparing it with the measured carbon deposition from temperature-programmed hydrogenation (TPH) in the case of Pt [4,5] and temperature-programmed oxidation (TPO) in the case of Rh catalysts [6].

2. Methods

2.1. Density functional theory

Spin-polarized periodic DFT calculations are performed using the Vienna ab initio simulation package (VASP) [7–10], where the Kohn–Sham equations are solved via self-consistent algorithms. The construction of basis functions describing the core electrons utilizes the Projector Augmented Wave pseudopotentials (PAW) [11], while the valence electrons are described by plane wave basis sets with a cutoff energy of 450 eV for all systems. The exchange-correlation functional is described within the generalized gradient approximation (GGA) with the Perdew, Burke and Ernzerhof (PBE) functional [12,13]. The Brillouin zone integration is constructed through a Monkhorst-Pack [14] grid of 4 × 4 × 1 sampling for all models. The first order Methfessel-Paxton smearing method [15] with 0.2 eV smearing width is used for partial occupancies. Convergence criteria of 10^{−4} and 10^{−3} eV are used for successive electronic and ionic steps, respectively. The climbing nudge elastic band method (cNEB) [16,17] using 6 images between initial and final images is employed to obtain the activation energy of elementary steps. The adsorbate structures are optimized at their most stable adsorption sites for every selected elementary step with the setups used in our previous cluster model work [18].

2.2. Slab model construction

The slab models representing the Ni catalyst during the DRR are constructed as metallic Ni(111), carbide Ni₃C(001) and oxide NiO(111)-p(2 × 2) phases of Ni as illustrated in Fig. 1. The Ni(111) is modelled as a 5-layer slab cleaved from the optimized bulk Ni following our reported procedure [19,20]. For the Ni carbide, a Ni-terminated Ni₃C(001) of 9-Ni-C-layer slab are constructed, where the surface was cleaved from the optimized rhombohedral R-3Ch (hexagonal) bulk system [21,22]. The NiO(111)-p(2 × 2) is an O-terminated 6-Ni-O-layer slab with the assumption of the octopolar reconstructed surface that is reported to be the most stable NiO(111) surface [23–25].

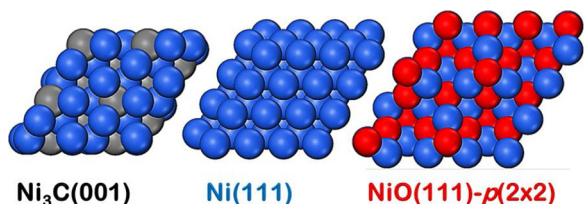


Fig. 1. Top view of slab models. From left to right: Ni₃C(001), Ni(111), and NiO(111)-p(2 × 2) surfaces. (color code: blue = Ni, grey = C, red = O) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 1

Elementary steps and rate equations of the 8-step DRR mechanism.

Step i	Elementary step i	Rate equation of step i
1	CH _{4(g)} + 2* ↔ CH _{3*} + H*	r1 = k _{1Y} CH ₄ θ _* ² - k ₋₁ θ _{CH₃} θ _H
2	CH _{3*} + * ↔ CH _{2*} + H*	r2 = k ₂ θ _{CH₃} θ _* - k ₋₂ θ _{CH₂} θ _H
3	CH _{2*} + * ↔ CH* + H*	r3 = k ₃ θ _{CH₂} θ _* - k ₋₃ θ _{CH} θ _H
4	CH* + * ↔ C* + H*	r4 = k ₄ θ _{CH} θ _* - k ₋₄ θ _C θ _H
5	CO _{2(g)} + 2* ↔ CO* + O*	r5 = k _{5Y} CO ₂ θ _* ² - k ₋₅ θ _{CO} θ _O
6	C* + O* ↔ CO* + *	r6 = k ₆ θ _C θ _O - k ₋₆ θ _{CO} θ _*
7	H* + H* ↔ H _{2(g)} + 2*	r7 = k ₇ θ _H ² - k _{-7Y} H ₂ θ _* ²
8	CO* ↔ CO _{2(g)} + *	r8 = k ₈ θ _{CO} - k _{-8Y} CO ₂ θ _*
total	CH _{4(g)} + CO _{2(g)} ↔ 2H _{2(g)} + 2CO _{2(g)}	r _{DRR} = r ₁ + r ₂ + r ₃ + r ₄ + r ₅ + r ₆ + 2r ₇ + 2r ₈

2.3. Microkinetic modelling

To ensure that there is no over-counting in the DRR mechanism, the following assumptions were made. As step 5, 6 and 8 in Table 1 of DRR mechanism are shared by both the DRR and the Boudouard reactions, each of the steps are assumed to contribute equally to both reactions. Thus, the following rates for DRR, Boudouard, and reverse-Boudouard reactions are derived.

$$\text{DRR rate} = r_1 + r_2 + r_3 + r_4 + [(0.5)(r_5)] + [(0.5)(r_6)] + 2r_7 + [(0.5)(2r_8)]$$

$$\text{Boudouard rate} = [(0.5)(r_{5R})] + [(0.5)(r_{6R})] + [(0.5)(2r_{8R})]$$

$$\text{Reverse-Boudouard rate} = [(0.5)(r_{5F})] + [(0.5)(r_{6F})] + [(0.5)(2r_{8F})]$$

The Matlab software was utilized in solving all sets of equations, where the 8-step mechanism shown in Table 1 was considered. In this paper the mechanism accounts for the DRR reaction including the Boudouard and reverse Boudouard reaction illustrated in Table 2 as additional coke formation and removal reactions [26], where the assumptions and simplification of the DRR mechanism were reported in our previous work [3]. In addition, it was assumed that the surface reaction is the rate limiting step and the mass transfer of reactants and their diffusion through the catalyst pore together with the adsorption and desorption steps is fast.

The transition state theory (TST) was applied to each elementary step to determine the forward and reverse rate constants, k_i and k_{-i}, respectively from the following Eyring equation [27]:

Table 2

Elementary steps and rate equations of the 3-step Boudouard (BD) and reverse-Boudouard reaction (RBD).

Step i**	Elementary step i	Rate equation of step i
8 reverse	CO _(g) + * → CO*	r _{8R} = k _{-8Y} COθ _*
6 reverse	CO* + * → C* + O*	r _{6R} = k ₋₆ θ _{CO} θ _*
5 reverse	CO* + O* → CO _{2(g)} + 2*	r _{5R} = k ₋₅ θ _{CO} θ _O
8 forward	CO* → CO _(g) + *	r _{8F} = k ₈ θ _{CO}
6 forward	C* + O* → CO* + *	r _{6F} = k ₆ θ _C θ _O
5 forward	CO _{2(g)} + 2* → CO* + O*	r _{5F} = k _{5Y} CO ₂ θ _* ²
Boudouard	2CO _(g) + * → CO _{2(g)} + C*	r _{BD} = 2(r _{8R}) + r _{6R} + r _{5R}
reverse-Boudouard	CO _{2(g)} + C* → 2CO _(g) + *	r _{RBD} = 2(r _{8F}) + r _{6F} + r _{5F}

k_i = rate constant of step i (negative i means reverse of step i).

y_i = mole fraction of gaseous species i equals to its partial pressure over total pressure (p_i/p_{total}).

θ_i = surface coverage of surface species i (* = free site, others are as designated).

** step i refers to the forward and reverse step of DRR step in Table 1 and r_i = r_{iF}-r_{iR} (for example, r₅ = r_{5F}-r_{5R}).

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