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Rhenium-promoted selective CO_2 methanation on Ni-based catalyst

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ABSTRACT

Re-doped Ni(111) (Re@Ni(111)) surface was used as a model to investigate the effect of Re on the C—O bond scission and on the selectivity of CO_2 methanation on a Ni-based catalyst. Three pathways, including CO_2 dissociation into CO* followed by CO* hydrogenation, CO_2 reduction through the HCOO* and COOH* intermediates, were analyzed based on the results from the density functional theory calculations. The results indicate that the presence of Re significantly lowers the activation barrier of C—O bond cleavage due to the strong affinity of Re to O but has no significant effect on the hydrogenation steps. Microkinetic analysis showed that the presence of Re greatly increases the selectivity toward CH_4. Analysis of surface coverage of the adsorbed species showed that CO* and H* were the most abundant species on the Ni(111) surface whereas appreciable amount of O adatoms were present on Re@Ni(111) in addition to CO* and H*, with the O adatoms on the Re sites. On both surfaces, increasing H_2 partial pressure resulted in an increase in H* coverage but decreased CO* coverage. The strong affinity of Re toward O makes Re@Ni(111) more effective for C—O bond scission and thereby enhances methane selectivity.

1. Introduction

Catalytic conversion of CO_2 is an effective method to mitigate the excessive carbon dioxide emission and has attracted much attention [1–6]. Carbon dioxide methanation is considered as a key reaction to recycle CO_2, making it a carbon source for high value chemicals [7–10]. The competing reaction to methanation is the reverse water gas shift reaction (RWGS), forming CO as the by-product, as shown in the following reactions:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \text{ Methanation} \quad (1)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \text{ RWGS} \quad (2)$$

Therefore, designing a catalyst that shows high activity and selectivity toward CH_4 is a great challenge.

Metals in group VIII have been investigated for CO_2 methanation and the selectivity toward CH_4 depends on the nature of the metals [11–16]. Supported Ru, Rh, and Ni catalysts were found to promote methanation whereas Pt tends to catalyze the RWGS reaction [17]. The Ru and Rh catalysts have been shown to be more active than Ni but the low cost of Ni makes the Ni-based catalysts attractive for industrial applications [7]. However, coke formation is a serious issue for Ni-based catalysts [18–20]. The addition of a second metal to the Ni-based catalysts has been reported to improve the catalytic performance for CO_2 methanation [8]. Combining Ni with noble metals such as Pt and Pd was reported to enhance metal dispersion and H_2 chemisorption capacity, resulting in superior CH_4 selectivity [21]. Doping a Ni catalyst with Ru also showed high catalytic activity, selectivity, and excellent stability for CO_2 methanation [22,23]. These authors believed that CO_2 was activated and dissociated to C on Ru and C was hydrogenated on Ni to form CH_4 [22]. A density functional theory (DFT) computational screening study predicted that Ni-Fe alloy catalysts could be more active than the pure Ni catalyst [24]. The enhanced activity and selectivity toward CH_4 on Ni-Fe alloy catalysts were confirmed for CO_2 methanation [25–27]. Mg-modified Ni/SiO_2 catalysts were also reported to enhance the capacity of CO_2 adsorption and accelerate the activation of CO_2, making Ni-Mg bimetallics better catalysts for CO_2 methanation than Ni [28]. In all the bimetallic catalysts, the synergistic effect of Ni and the doping metals plays an important role in the enhanced activity and selectivity for the methanation reaction.

Mechanistic studies have been performed to understand the underlying physicochemical origin of CH_4 selectivity in CO_2 methanation [29–33]. A recent DFT study of CO_2 hydrogenation on Ru(0001) suggested that CH_4 production occurs through direct CO_2 dissociation to CO*, followed by sequential hydrogenation of CO* to CHO* and CHO*

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dissociation. The adsorption energy of O adatom was found to be an effective descriptor of selectivity difference toward CO and CH_4. Metals exhibiting a stronger oxygen binding promote deeper CO_2 reduction to CH_4 [32]. Liu et al. proposed that C—O bond cleavage is usually the rate-limiting step in methanation reaction and the methanation can be accelerated by lowering the activation barriers to C—O bond cleavage [34]. Our previous study of bimetallic Ni–Re catalysts for hydrodeoxygenation of phenolic compounds revealed that the Ni–Re neighboring site is the active site for breaking the C—O bond [35]. Ren et al. used data mining technology to screen potential additives to Ni/Al_2O_3 catalysts for methanation and predicted a good performance of Re as a catalytic promoter [36]. However, the role of Re in a Ni-Re bimetallic catalyst for CO_2 methanation is not available.

Herein, we examined the effect of doping Re in a Ni(111) surface on CO_2 methanation as a model for the Ni-based catalysts. We analyzed three possible pathways: (i) CO_2 dissociation into CO* followed by CO* hydrogenation (the direct dissociation pathway), (ii) CO_2 reduction through the HCOO* species (the formate pathway) and (iii) CO_2 reduction through the COOH* intermediate (the carboxyl pathway). We used the results from DFT calculations to construct the potential energy profile and map out the reaction pathways. We then integrated the energetics and mechanism into a microkinetic model to predict reactivity and selectivity as well as follow the coverage of surface species.

2. Computational details

All calculations were performed using the Vienna Ab Initio Simulation Package (VASP) [37,38]. Projector augmented wave (PAW) potentials were used to represent the effective cores [39,40]. The Perdew − Burke − Ernzerhof (PBE) functional was used to calculate exchange and correlation energy [41]. The cutoff energy of the plane wave basis set is 400 eV. The atomic structures were relaxed using either the quasi-Newton scheme or conjugate gradient algorithm implemented in the VASP code. The convergence criterion for electronic self-consistence was set at 5×10^{-6} eV and for ionic relaxation at 1.0×10^{-4} eV, corresponding to the maximum force on the movable atoms < 0.03 eV/Å in the optimized configuration. We included spin polarization in this study because Ni displays ferromagnetic behavior.

The optimized lattice constant of bulk Ni is 3.52 Å with the k-points (6 × 6 × 6), which is consistent with the experimental values [42] and previous computational studies [43]. The Ni(111) surface is constructed from the relaxed bulk Ni and simulated with a four-layer slab in a p (3 × 3) surface unit cell. The Re@Ni(111) is modeled by replacing one of the nine Ni atoms in the first layer of the slab. A vacuum space of 15 Å has been used in both Ni(111) and Re@Ni(111) models. In the geometry optimization, the atoms in the bottom two layers were fixed at their corresponding bulk positions, and the top two layers together with the adsorbates were allowed to relax. A (3 × 3 × 1) k-point grid was used to generate the K-point.

The adsorption energy was defined as:

$$E_{ads} = E_{adsorbate/slab} - E_{slab} - E_{adsorbate} \tag{3}$$

where $E_{adsorbate/slab}$, E_{slab}, and $E_{adsorbate}$ represent the total energies of slab with the adsorbate, the optimized clean slab, and the adsorbate species in the gas phase, respectively. A positive value corresponds to an endothermic process, whereas a negative value indicates that the adsorption is exothermic. The reaction energy ($\triangle E$) and the activation barrier (E_a) were obtained by the following equations:

$$\triangle E = E_{FS} - E_{IS} \tag{4}$$

$$E_a = E_{TS} - E_{IS} \tag{5}$$

where, E_{IS}, E_{TS}, and E_{FS} represent the total energy of the initial state, transition state and final state on the slab, respectively. Possible transition states were selected from the images generated from the interpolation between the reactant and product states. The selected possible transition states were relaxed using the quasi-Newton method in VASP. The resulting transition state configuration was then subjected to frequency analysis to make sure it has only one imaginary frequency correspond to the bond making/breaking step. Similar approach has been used in previous studies [44,45]. All energies reported in this paper had been corrected by Zero-Point-Energy.

A microkinetic analysis based on the mean-field microkinetic model was performed to predict reaction rate of elementary steps and the coverage of species. For surface reaction, the forward rate constants were estimated using transition state theory:

$$k_f = \frac{k_B T}{h}\frac{q_{TS,vib}}{q_{IS,vib}}e^{-E_a/k_B T} \tag{6}$$

where k_B, h and T are the Boltzmann constant, Planck's constant and reaction temperature, respectively. E_a is the ZPE-corrected activation barrier for the forward reaction obtained from DFT calculations. And $q_{TS,vib}$ and $q_{IS,vib}$ are the vibrational partition functions for the transition state and the initial state, respectively. The vibrational partition functions are determined based on:

$$q_{vib} = \prod_i \frac{1}{1 - e^{-hv_i/k_B T}} \tag{7}$$

where v_i is the vibrational frequency for "i" vibrational mode of the adsorbed intermediate, i runs to N-1 and N for the transition state and initial state, respectively. The reverse rate constant (k_r) was estimated similarly.

Adsorption of CO_2 is an activated process and the adsorption rate constant for CO_2 adsorption needs to be estimated using the transition state theory. The adsorption for other gas species was assumed to be nonactivated and the rate constants for adsorption were calculated based on collision theory [46–48].

$$k_f = \frac{A\sigma}{\sqrt{2\pi m k_B T}} \tag{8}$$

here, m, k_B and T represent the molecular mass, Boltzmann constant and temperature, respectively. The sticking coefficient σ was assumed to be 1.0 for the adsorbing species. A is the area of each adsorption site and the typical value of A is 5.365×10^{-20} m^2 for Ni(111) [49]. The rate coefficients for desorption steps were calculated as follows:

$$k_r = k_f/K_{eq} \tag{9}$$

After determining the rate constant, a microkinetic model was developed as a set of algebraic differential equations:

$$\frac{d\theta_j}{dt} = \sum_i v_{j,i} r_i = 0 \tag{10}$$

$$\theta^* = 1 - \sum_j \theta_j \tag{11}$$

here, index i loops over all reactions, θ_j is the coverage of adsorption species and θ^* denotes the coverage of empty sites on the surface. The surface coverage was obtained by solving the differential-algebraic equations using the SciPy Python package. With the surface coverage at steady state, the reaction rate of each elementary step can be obtained and the product selectivity can be calculated.

3. Results and discussion

3.1. Adsorption of reaction intermediates

In order to study the mechanism of CO_2 methanation, we first determined the adsorption structure and energy of the reaction intermediates. The adsorption sites on the Re@Ni(111) and Ni(111) surface are marked in Fig. 1. For each adsorbate, the most stable adsoprtion sites and energies on Re@Ni(111) and Ni(111) are shown in Table 1. The optimized structures of each reaction intermediate on Re@Ni(111)

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