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Study of reaction mechanism of methane conversion over Ni-based oxygen carrier in chemical looping reforming

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ABSTRACT

First-principle calculations based on the density functional theory (DFT) were used to clarify the reaction mechanism of methane conversion over Ni-based oxygen carrier for chemical looping reforming. A systematic investigation about the methane sequential dehydrogenation process was firstly performed. Our calculation results showed that $CH_3 \rightarrow CH_2 + H$ is the rate-limiting step with the activation energy of 2.0 eV. Then the H_2 formation was studied to understand the pathways of H_2 production on NiO surface. It was revealed that the H atom on O-top site could facilely migrate to Ni-top site. We proposed two possible pathways for H_2 formation, path (a) and path (b). The activation energy (2.79 eV) of path (a) is largely higher than that (0.54 eV) of path (b). For path (b), the H diffusion process is identified to the rate-limiting step with the activation energy of 0.59 eV. Finally, we also explored oxygen anion diffusion process in NiO crystal structure. The activation energy (2.23 eV) is very high and this process significantly limits the reaction rate between methane and Ni-based oxygen carrier in CLR process.

1. Introduction

Hydrogen has been considered as an ideal fuel for the future. The hydrogen demand is continuously increasing due to the clean fuel regulations and H_2 is also expected to play a key role in the necessary transition from fossil fuels to a sustainable energy. Currently, the industrial major technology for hydrogen production is the steam reforming of hydrocarbons, mainly natural gas. Although a mature process, the steam reforming is very energy-intensive due to the strong endothermic reforming reaction. Moreover, it is a process with high CO_2 emissions resulting from combustion of fossil fuels to provide the necessary heat load, aggravating global warming. Therefore there is room for the innovative technologies with environmentally friend, low-energy consumption and high hydrogen efficiency. In this context, Chemical Looping Reforming (CLR) was proposed by Mattisson and Lyngfelt [1]. It is based on Chemical Looping Combustion (CLC), where oxygen is transferred by means of an oxygen carrier (OC) without contact between fuel and air and ultimately easy CO_2 capture. The main difference is that the wanted product in CLC is heat from total oxidation of fuel to CO_2 and H_2O, while in CLR it is desirable to exhibit selectivity to CO and H_2. In CLR process the air to fuel ratio is kept low to prevent the complete oxidation of fuel to CO_2 and H_2O. The CLR system mainly consists of two interconnected fluidized bed reactors, an air reactor (AR) and a fuel reactor (FR). In the FR, most of fuel should become oxidized to CO and H_2. The reduced OC is sent to the AR and regenerated by taking up oxygen from the air.

One of the most important issues in CLR is identification of effective OC. The appropriate OC could achieve the selective generation of syngas. While Ni, Cu, Fe, Co and Mn oxides [2–6] have been proposed in literature as potential candidates, Ni-based OC appears to be suitable and promising for CLR. The reduced Ni has excellent catalytic properties for steam methane reforming, water-gas shift and a number of other reactions and Ni-based materials exhibit superior reactivity and thermal stability at harsh operation temperature [6–12]. The researches about Ni-based OC for CLR process have been conducted extensively. Ryden et al. [8] have investigated continuous CLR of natural gas in a laboratory reactor consisting of two interconnected fluidized beds with an oxygen carrier of NiO and $MgAl_2O_4$. The results showed that complete conversion of natural gas and high selectivity towards H_2 and CO was achieved. Subsequently, De Diego et al. [9,13] reported the evaluation of Ni-based oxygen carriers for CLR in a batch fluidized bed reactor and a $900 W_{th}$ circulating fluidized bed reactor under continuous operation. It was found that Ni-based oxygen carrier supported on Al_2O_3 is suitable for a CLR system. Furthermore, Proll et al. [14] tested CLR process with Ni-based OC and natural gas at a scale of 140 kW pilot plant in a dual circulating fluidized bed installation. They found that no carbon

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formation occurred for air/fuel ratios larger than 0.4 even though the steam to organic carbon ratio was less than 0.4. Recently, Antzara et al. [15,16] evaluated the performance of Ni-based OC supported on ZrO_2, TiO_2, SiO_2, Al_2O_3 and $NiAl_2O_4$ in a fixed bed flow unit under conventional reforming and multiple chemical looping steam methane reforming cycle. It was shown that NiO/ZrO_2 exhibited good activity with initial CH_4 conversion higher 80% and excellent stability. Meanwhile, Diglio et al. [17] presented the numerical analysis of the CLR packed-bed reactor with Ni-based OC for hydrogen production. It was concluded that an appropriate choice of both the initial temperature and the length of oxidation and reduction phases is essential prerequisite for the process feasibility and performance. As for CLR process of gas except methane, Jiang et al. [18,19] studied hydrogen production from chemical looping steam reforming of glycerol and ethanol by Ni-based OC in a fixed-bed reactor. They observed that the CLR showed higher glycerol conversion and H_2 yield efficiency in all the tested temperatures compared with conventional steam reforming progress and 20Ni-MMT (montmorillonite) possessed the excellent performance for CLR process of ethanol due to its sintering and coking resistance.

Despite the massive experimental efforts on the reactivity of Ni-based OC, a detailed understanding of reaction process in the fuel reactor for CLR process is still lacking. In fact, the redox reaction process between fuel and Ni-based OC at atomic level and corresponding activation energies, which is highly desirable in order to improve the selectivity toward H_2 and CO, have not been known yet. The knowledge of these mechanisms is of great significance to development of CLR technology. However, the acquisition of required information from experiments is rare and difficult. With its rapid development, first-principle calculation based on density functional theory (DFT) have been increasingly used to investigate the CH_4 dehydrogenation mechanism on pure Ni [20], Co [21], Rh [22,23], Pd [24] surfaces. The electronic properties and behaviors of OC for CLC have also been detected using DFT calculations. Qin et al. [25–27] studied the synergetic effects of Al_2O_3, ZrO_2 and MgO on Fe_2O_3 for CLC of CO. Li et al. [28] demonstrated that TiO_2 can significantly reduce the energy barrier for oxygen anion migration to notably improve the ionic diffusivity for addition of TiO_2 support to iron oxide OC. Our previous studies [29,30] also reported the role of oxygen and H_2S during the reaction process between CO and NiO(0 0 1) surface for CLC with DFT method. Hence, DFT calculations was employed to fill gaps in mechanism understanding in this work.

Of all potential sources of H_2, methane is widely available for CLR process. In our study, we explored the reaction mechanism between methane and Ni-based OC. In CLR process, H_2 is the main desirable product. Therefore, the understanding of pathways of H_2 production at atomic level are very meaningful and urgent. Methane sequential dehydrogenation process on OC surface initially occurs to form H atoms and then the H atoms are combined to generate H_2. Hence, we firstly investigated the methane sequential dehydrogenation reaction on NiO surface to identify the rate-limiting step and to examine the methane dehydrogenation features. Then H_2 formation process was also studied. Moreover, oxygen anion of OC diffuses through bulk solid phases to participate in redox reaction. We finally determined the activation energy for oxygen anion diffusion process within NiO crystal structure. Our calculation results could help elucidate the methane reaction mechanism on NiO surface, improving H_2 yield and efficiency and guiding rational OC design for CLR process.

2. Computational details

NiO(0 0 1) surface is regarded as the near perfect bulk termination according to the experiment technique [31] and previous calculations [32], so this surface was used in present study. All the DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [33–35]. We applied the generalized gradient approximation functional proposed by Perdew, Burke, and Ernzerhof, known as GGA-PBE [36,37] for the treatment of electron exchange and correlation. The projector-augmented wave (PAW) [38] method as implemented by Kresse and Joubert [35] was employed to describe the electron-ion interactions. The plane wave cutoff energy of 400 eV was specified. Considering the strong electron correlation effects that arise from the localized Ni 3 d states, the strong on-site Coulomb repulsion parameter U and the screened exchange interaction parameter J ($U = 6.3$ eV and $J = 1$ eV), in agreement with previously reported values [29,39,40], were implemented. The spin-polarized formalism [29,41] have been performed due to antiferromagnetic properties of nickel oxide. A Gaussian smearing approach with $\sigma = 0.2$ eV [39] was used. The convergence limit of electronic energies was kept at 10^{-5} eV. The force criterion for convergence was set to be 0.03 eV/Å. The local minima was located with the conjugate-gradient algorithm during geometry optimization. The calculated equilibrium lattice constant a_0 for bulk NiO is 4.161 Å, which agrees well with the experiment value of 4.17 Å [42].

We have adopted a six-layer slab with a (2 × 2) periodic supercell to model NiO(0 0 1) surface for all calculations. A 15 Å vacuum region [29,30] was constructed to avoid the interaction between periodic slabs. The top two layers and adsorbates were relaxed, while the remaining four layers were fixed. The Brillouin zone was sampled with a 3 × 3 × 1 Monkhorst-Pack k-point mesh [29,30]. We performed the Climbing Image Nudged Elastic Band (CI-NEB) [43,44] method to identify the minimum energy paths (MEPs) and the transition states (TS). Subsequently, to obtain the accurate TS, the structures were optimized with a quasi-Newton algorithm. Finally, we carried out frequency calculations to check the presence of a single imaginary frequency for all the TS structures.

The adsorption energy (E_{ads}) is determined using the formula:

$$E_{ads} = E_{adsorbates/slab} - (E_{slab} + E_{adsorbates})$$

where $E_{adsorbates/slab}$ is the total energy after adsorption, and E_{slab} and $E_{adsorbates}$ represent the total energy of the clean slab and free adsorbates, respectively. With this equation, a more negative adsorption energy suggests more favorable adsorption.

For each reaction, the reaction energy (ΔH) and activation energy (E_b) are defined as

$$\Delta H = E_{FS} - E_{IS}$$

$$E_b = E_{TS} - E_{IS}$$

where E_{FS}, E_{IS}, E_{TS} represent the energies of the final state (FS), initial state (IS), and TS, respectively.

3. Results and discussion

3.1. CH_4 sequential dehydrogenation on NiO(0 0 1) surface

3.1.1. CH_x ($x = 0$–4) and H adsorption

The geometry optimization of CH_x ($x = 0$–4) and H were performed in a 20 Å cubic crystal cell. The C—H bond length and H—C—H bond angle of CH_4 were calculated to be 1.097 Å and 109.5°, in good agreement with the reported experimental values of 1.096 Å and 109.4° [45], respectively.

The equilibrium configuration of NiO(0 0 1) surface is illustrated in Fig. 1. The CH_4 sequential dehydrogenation process results in the formation of CH_x ($x = 0$–3) and H species. To understand CH_4 dehydrogenation mechanism, we need to know the adsorption process of reactants and products. Thus, the CH_x ($x = 0$–4) and H adsorption with a coverage of 0.25 monolayer (ML) on NiO(0 0 1) surface was firstly investigated. Four high symmetry adsorption sites (Ni-top, O-top, bridge and hollow) have been taken into account. After optimization, the most stable configurations of CH_x ($x = 0$–4) and H adsorption on NiO(0 0 1) surface displayed in Fig. 2 were obtained. Table 1 summarizes the most stable adsorption site and related data.

As shown in Table 1, it is a physical adsorption process for CH_4 with the adsorption energy of −0.02 eV. Previous calculation results

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