



## Full Length Article

## Influence mechanism of supports on the reactivity of Ni-based oxygen carriers for chemical looping reforming: A DFT study

Yuchuan Feng<sup>a</sup>, Nana Wang<sup>a</sup>, Xin Guo<sup>a,b,\*</sup><sup>a</sup> State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China<sup>b</sup> Shenzhen Institute, Huazhong University of Science & Technology, Shenzhen, Guangdong 518000, People's Republic of China

## ARTICLE INFO

## Keywords:

Density functional theory  
 Supports  
 Reactivity  
 Ni-based oxygen carrier  
 Chemical looping reforming

## ABSTRACT

First-principle calculations based on the density functional theory (DFT) were employed to clarify the influence mechanism of supports on the reactivity of Ni-based oxygen carriers for chemical looping reforming. We firstly built the models of two supported Ni-based oxygen carriers (NiO/ZrO<sub>2</sub> and NiO/MgAl<sub>2</sub>O<sub>4</sub> composites). It was found that NiO cluster is easy to attach to surface of two supports and the forming composites NiO/ZrO<sub>2</sub> and NiO/MgAl<sub>2</sub>O<sub>4</sub> are stable. Then surface reaction between CH<sub>4</sub> and two supported NiO including the steps of CH<sub>4</sub> sequential dehydrogenation (S1), H<sub>2</sub> formation (S2) and CO formation (S3) was investigated. Compared with that for unsupported NiO, both supports addition significantly decreases the energy barrier of S1 process. For both supported NiO, the energy barriers increased in the order of S1 < S2 < S3, suggesting that the S3 process is the rate-limiting step in the surface reaction. The energy barrier (2.77 eV) of S3 process for NiO/ZrO<sub>2</sub> is lower than that (3.07 eV) for NiO/MgAl<sub>2</sub>O<sub>4</sub>, implying that ZrO<sub>2</sub> support is more conducive to the surface reaction. Moreover, our calculation results also found that the Ni<sub>4</sub>O<sub>4</sub>/ZrO<sub>2</sub> OC has a lower the oxygen vacancy formation energy ( $E_{vac}$ ), which showed that the ZrO<sub>2</sub> support makes Ni-O bond weaker than MgAl<sub>2</sub>O<sub>4</sub> support. The C reacts more readily with the oxygen of NiO supported on ZrO<sub>2</sub>. The lower energy barrier of S3 process for ZrO<sub>2</sub> support could be attributed to its higher activity of surface oxygen in the NiO. Therefore, it was concluded that NiO/ZrO<sub>2</sub> oxygen carrier demonstrates relatively better reactivity. Our DFT calculations could provide a detailed understanding of the effect of supports on the reactivity of Ni-based oxygen carrier.

## 1. Introduction

Hydrogen, a clean energy carrier, is considered as an ideal fuel in future energy systems. The current dominating industrial technology for H<sub>2</sub> production is the steam-methane reforming (SMR) process. However, it is a highly energy demanding process with high CO<sub>2</sub> emissions, aggravating global warming. Chemical Looping Reforming (CLR) proposed by Mattisson and Lyngfelt [1] is an innovative technology to produce H<sub>2</sub> while reducing the cost of CO<sub>2</sub> capture. It utilizes the same basic principles as Chemical Looping Combustion (CLC), where the oxygen carrier performs the task of transferring oxygen from air to fuel with inherent CO<sub>2</sub> separation. The major difference is that the wanted product in CLC is heat, while in CLR it is desirable to exhibit selectivity to CO and H<sub>2</sub>. Compared with the complete oxidation, the partial oxidation of the fuel should account for the larger share. In order to prevent fuel from being completely oxidized to CO<sub>2</sub> and H<sub>2</sub>O, low air to fuel ratio is necessary for CLR process.

The selection of effective oxygen carrier is a key issue for CLR technology development. The suitable oxygen carrier should obtain high selectivity to syngas, *i.e.* a gas mixture of H<sub>2</sub> and CO. Even though Ni, Cu, Fe, Co and Mn oxides [2–6] have been proposed as potential candidates, NiO appears to be most promising and appropriate because of their high reaction rate and good selectivity towards H<sub>2</sub> and CO [7]. The CLR process of Ni-based oxygen carriers has been widely investigated in the range from a laboratory reactor [8], a batch fluidized bed reactor [9], a 900 W<sub>th</sub> circulating fluidized bed reactor [10] to a scale of 140 kW pilot plant [11]. The investigation showed that pure NiO exhibits poor performance over multiple redox cycles due to the sintering. To resist the sintering, inert supports such as ZrO<sub>2</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and spinels like NiAl<sub>2</sub>O<sub>4</sub> and MgAl<sub>2</sub>O<sub>4</sub> is usually added [8–10,12–14]. However, experiment studies found that supports addition would impact on the reactivity of Ni-based oxygen carrier in turn. Antzara et al. [14] reported that NiO/ZrO<sub>2</sub> demonstrates good activity with initial CH<sub>4</sub> conversion higher than 80% and excellent stability

\* Corresponding author at: State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China.

E-mail address: [guoxin@mail.hust.edu.cn](mailto:guoxin@mail.hust.edu.cn) (X. Guo).

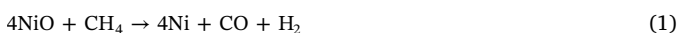
<https://doi.org/10.1016/j.fuel.2018.04.160>

Received 8 February 2018; Received in revised form 26 April 2018; Accepted 28 April 2018  
 0016-2361/ © 2018 Elsevier Ltd. All rights reserved.

under multiple chemical looping steam methane reforming cycles, while low activity (< 50% initial CH<sub>4</sub> conversion) and deactivation rapidly was obtained for NiO supported on SiO<sub>2</sub> and TiO<sub>2</sub>. They also found that NiO/Al<sub>2</sub>O<sub>3</sub> and NiO/NiAl<sub>2</sub>O<sub>4</sub> exhibit similar high initial activity (about 80% initial CH<sub>4</sub> conversion), but high deactivation at the end of the test. Johansson et al. [12] pointed out that NiO/MgAl<sub>2</sub>O<sub>4</sub> could provide higher methane conversion, higher selectivity and lesser tendency for carbon formation than NiO/NiAl<sub>2</sub>O<sub>4</sub> for CLR process.

Although the supports have been extensively studied through massive trial-and-error experiments, the underlying mechanism of the role of supports to the reactivity of Ni-based oxygen carrier is still unclear. It is clear that experimental data alone are not sufficient to provide a complete picture of these mechanism. Theoretical studies, particularly those based on density functional theory (DFT), are often complementary and could provide a more detailed picture. DFT calculations have been successfully employed to detect the characteristics of the Fe-based and Cu-based oxygen carriers [15,16]. In our previous studies [17–19], we have reported the role of H<sub>2</sub>S and oxygen to the reactivity of Ni-based oxygen carrier with DFT method. In addition, the CH<sub>4</sub> conversion mechanism over unsupported Ni-based oxygen carrier for CLR process also has been explored. Therefore, a systematic investigation of DFT calculations could provide a good theoretical support for deeply understanding the influence mechanism of supports on the reactivity of Ni-based oxygen carrier.

Methane is widely used as the fuel for the CLR process. The main reaction between methane and Ni-based oxygen carrier is given below:



In this reaction, CH<sub>4</sub> sequential dehydrogenation process initially occurs on the surface of NiO to generate the C and H atoms. Subsequently, the H atoms are combined to form H<sub>2</sub> and the C atom reacts with the surface O atom of NiO to form CO. Meanwhile, the oxygen vacancies will occur, resulting in a long-range oxygen diffusion within NiO crystal structure from the sub-layers to surface. Therefore, the whole reaction involves the following elementary steps: CH<sub>4</sub> → C + 4H (S1), H + H → H<sub>2</sub> (S2), C + O → CO (S3) and oxygen diffusion (S4) [19–21]. Among four steps, the S1, S2 and S3 processes belong to the surface reaction of oxygen carrier. In this study, a detailed calculation to this key reaction for two supports was performed. We chose ZrO<sub>2</sub> and MgAl<sub>2</sub>O<sub>4</sub> supports as an example considering that they are widely applied to CLR process. Firstly, the models of NiO supported on ZrO<sub>2</sub> and MgAl<sub>2</sub>O<sub>4</sub>, denoted as NiO/ZrO<sub>2</sub> and NiO/MgAl<sub>2</sub>O<sub>4</sub>, were constructed. Then the reaction mechanism between CH<sub>4</sub> and supported NiO (NiO/ZrO<sub>2</sub> and NiO/MgAl<sub>2</sub>O<sub>4</sub>) was investigated. In this work, we just focused on the surface reactions for two supports, including the steps of CH<sub>4</sub> sequential dehydrogenation (S1), H<sub>2</sub> formation (S2) and CO formation (S3). Finally, the CH<sub>4</sub> reactivity of two Ni-based oxygen carriers also was compared to reveal the influence mechanism of supports on the reactivity of Ni-based OC. We proposed a theoretically feasible approach to screen the promising supports for CLR process. Our theoretical results could also provide guidance for rationalizing the design of the high-performance Ni-based oxygen carrier.

## 2. Computational details

All the DFT calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) [22]. The projector-augmented wave (PAW) [23] approach as implemented by Kresse and Joubert [22] was used to describe the electron-ion interactions with the generalized gradient approximation functional proposed by Perdew, Burke, and Ernzerhof (GGA-PBE) [24] for the treatment of electron exchange and correlation. The plane wave cutoff energy specified in all calculations was 400 eV. A 3 × 3 × 1 Monkhorst-Pack k-point mesh was applied to the Brillouin zone sampling. A Gaussian smearing approach with σ = 0.2 eV was employed. The electronic energies and force criterion for convergence were set to be 0.03 eV/Å, 10<sup>-5</sup> eV. We located the

**Table 1**

The lattice parameters of NiO, ZrO<sub>2</sub> and MgAl<sub>2</sub>O<sub>4</sub> unit cell.

Support (space group)	Calculation	Experiment
NiO (FM-3M)	a = b = c = 4.16 Å; α = β = γ = 90°	a = b = c = 4.17 Å; α = β = γ = 90° [26]
ZrO <sub>2</sub> (P42/NMC)	a = b = 3.63 Å; c = 5.25 Å; α = β = γ = 90°	a = b = 3.64 Å; c = 5.27 Å; α = β = γ = 90° [27]
MgAl <sub>2</sub> O <sub>4</sub> (FD-3M)	a = b = c = 8.10 Å; α = β = γ = 90°	a = b = c = 8.09 Å; α = β = γ = 90° [28]

local minima with the conjugate-gradient algorithm for the geometry optimization. For NiO, we have adopted the spin-polarized formalism due to its antiferromagnetic properties. In addition, to accurately describe the strong electron correlation in the localized Ni 3d states, the strong on-site Coulomb repulsion parameter U and the screened exchange interaction parameter J (U = 6.3 eV and J = 1 eV), consistent with previously reported values [25], were introduced. More detailed discussions about computational method were seen in our previous study [19]. The unit cell of NiO, ZrO<sub>2</sub> and MgAl<sub>2</sub>O<sub>4</sub> were optimized and the calculated lattice parameters are in good agreement with the experimental data [26–28], as listed in Table 1.

In this work, we selected the stable low-index surfaces, ZrO<sub>2</sub>(1 0 0) and MgAl<sub>2</sub>O<sub>4</sub>(1 0 0), as the support surfaces. As shown in Fig. 1, four-layer (2 × 2) ZrO<sub>2</sub>(1 0 0) and three-layer (2 × 1) MgAl<sub>2</sub>O<sub>4</sub>(1 0 0) [16] were constructed. A 20 Å vacuum region was used to prevent the interaction between periodic slabs. The top layer and adsorbates were relaxed, while the remaining layers were fixed for ZrO<sub>2</sub>(1 0 0) and MgAl<sub>2</sub>O<sub>4</sub>(1 0 0) surfaces. The calculated surface energies of ZrO<sub>2</sub>(1 0 0) and MgAl<sub>2</sub>O<sub>4</sub>(1 0 0) in this work were 1.77 and 2.12 J/m<sup>2</sup>, which are in agreement with the reported literatures of 1.69 [29] and 2.25 J/m<sup>2</sup> [30], respectively. The NiO nanocluster was used to represent the active phase that adhered to supports. The geometry optimization of NiO cluster were performed in a 20 Å cubic crystal cell.

The adsorption energy ( $E_{ads}$ ) is calculated as below:

$$E_{ads} = E_{adsorbates/slab} - (E_{slab} + E_{adsorbates}) \quad (2)$$

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

The Climbing Image Nudged Elastic Band (CI-NEB) [31] method was performed to determine the transition states (TS) for each reaction. Subsequently, the structures were optimized with a quasi-Newton algorithm to obtain the accurate TS. The reaction energy ( $\Delta H$ ) and energy barrier ( $E_b$ ) are defined as

$$\Delta H = E_{FS} - E_{IS} \quad (3)$$

$$E_b = E_{TS} - E_{IS} \quad (4)$$

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

## 3. Results and discussion

### 3.1. The models of NiO/ZrO<sub>2</sub> and NiO/MgAl<sub>2</sub>O<sub>4</sub> composites

To understand the interaction between NiO and supports of Ni-based oxygen carriers, the models of NiO/ZrO<sub>2</sub> and NiO/MgAl<sub>2</sub>O<sub>4</sub> composites firstly need to be constructed. Although the NiO contents in real oxygen carriers vary in a large range (10–60 wt%) [8–10,13,14,32–34], the NiO and supports are connected by the interaction between the atoms at the atomic level. The actual NiO particles with a high degree of NiO dispersion on the supports could achieve the molecule-sized clusters. Therefore, the Ni-based oxygen carriers could be simplified as the adhesion of NiO nanocluster to the supports grain

Download English Version:

<https://daneshyari.com/en/article/6630677>

Download Persian Version:

<https://daneshyari.com/article/6630677>

[Daneshyari.com](https://daneshyari.com)