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Density functional theory study on the reaction between hematite and methane during chemical looping process

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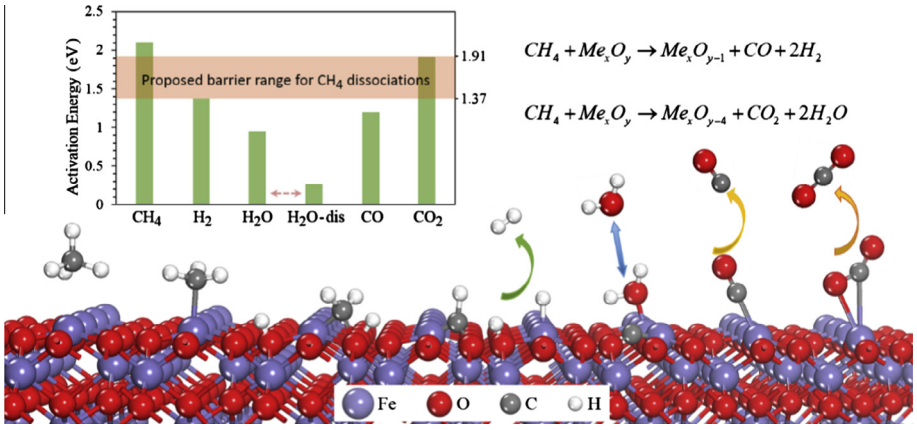
HIGHLIGHTS

- Reaction of α-Fe_2O_3 and CH_4 during chemical looping process was performed by DFT.
- Dissociations of CH_4 are the rate-determining steps with highest energy of 2.10 eV.
- Production and dissociation of H_2O are reversible.
- CO production is more favorable than the production of CO_2.
- Perspectives for designing high reactivity oxygen carriers are proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

We present a first principles study using periodic density functional theory on the reaction between α-Fe_2O_3 and CH_4 during chemical looping process. The sequential processes of methane dissociation, hydrogen formation, water production and dissociation, and carbon selective oxidation on α-Fe_2O_3 (001) surface were explored. It was found that the sequential dissociations of CH_4 were the dominant rate-determining process. Although H_2 production was less favorable than H_2O production, the formed H_2O can be dissociated facilely to increase the surface H concentration at chemical looping conditions. CO production is more favorable than CO_2 production, while CO_2 can also be produced in the high-temperature process. Subsequently, the oxygen migration in α-Fe_2O_3 (001) surface was also investigated, indicating the O migration from inner bulk to surface layer is inherently a high-temperature process. Our results are consistent with the kinetic experiments. In order to improve the CO selectivity in CH_4 chemical looping process for syngas production, we need to find promoters which could decrease the activation barrier of CH_4 sequential dissociation steps and increase the oxygen migration ability of oxygen-carriers.

1. Introduction

Chemical looping processes offer an effective and versatile reduction–oxidation scheme that can convert carbonaceous fuels

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into electricity, hydrogen, liquid fuels and valuable chemicals, while providing CO_2 capture and controlling CO_2 emission at a low cost [1–3]. Chemical looping concept is initially developed for combustion (chemical looping combustion, CLC), which is a cycling process using lattice oxygen instead of molecular oxygen to avoid direct contact between fuel and gaseous oxygen [4,5]. CLC can simultaneously help to improve the power station efficiency and increase the capability for inherent CO_2 capture during the combustion of hydrocarbon fuel [3,6,7]. Using methane as fuel, surface or lattice oxygen in oxygen carriers is used for methane combustion in the fuel reactor (reducer), and total oxidation of methane is targeted to yield a pure stream of CO_2 and H_2O [8,9]. After combustion, the reduced oxygen carriers can be re-oxidized by gaseous oxidant in the air reactor (oxidizer), and the re-oxidized oxygen carriers are then circulated back into the fuel reactor to achieve the looping process [10,11]. Recently, this concept has been introduced into a new technology, chemical looping reforming (CLR) for syngas (a mixture of CO and H_2) production from natural gas, which is more economic than conventional technology [11–15].

CLR process utilizes the same basic principles as chemical looping combustion, as illustrated in Fig. 1, which could be described as a process for partial oxidation of CH_4 where oxygen carriers are used as a source of undiluted oxygen [16,17]. The main difference is that the desired result is not heat from total oxidation, but H_2 and CO from partial oxidation [16,18]. This technique has revived interests in conversion of the abundant supply of available natural gas into syngas that can be used to produce vast arrays of high value chemicals and intermediates.

In the fuel reactor, methane is initially decomposed over an oxygen carrier to form hydrogen atoms and carbon atoms [19]. Subsequently, the H atoms recombine to produce H_2 or are oxidized by lattice oxygen to generate H_2O, while C atoms are oxidized by lattice oxygen to generate CO or CO_2. Meantime, the oxygen carrier (Me_xO_y, a metal oxide) is reduced by the following general reaction:

Fuel reactor:

$$CH_4 + Me_xO_y \rightarrow Me_xO_{y-4} + CO_2 + 2H_2O \quad (R1)$$

$$CH_4 + Me_xO_y \rightarrow Me_xO_{y-1} + CO + 2H_2 \quad (R2)$$

In the air reactor, the reduced compounds (Me_xO_{y-n}) are regenerated by taking up oxygen from the air [20], and the re-oxidized carriers will recirculated to the fuel reactor for a new cycle.

Air reactor:

$$Me_xO_{y-4} + 2O_2 \rightarrow Me_xO_y \quad (R3)$$

$$Me_xO_{y-1} + 0.5O_2 \rightarrow Me_xO_y \quad (R4)$$

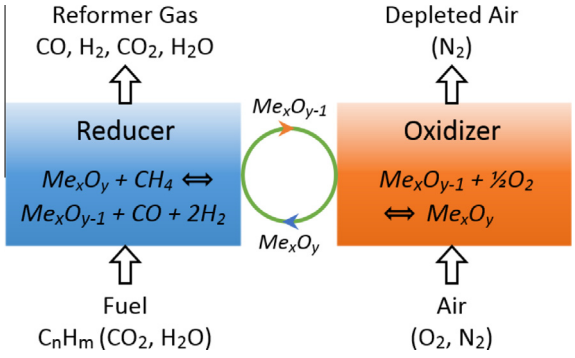

Fig. 1. The basic principles of CH_4 chemical-looping reforming.

Outlet gas from the fuel reactor may contain a gas mixture of CH_4, CO_2, CO, H_2O and H_2 [10,16,21]. Selection of appropriate oxygen carriers and controlling the relative amount of carbon (CH_4) and oxygen (Me_xO_y) in the fuel reactor can achieve selective generation of syngas [17,22]. Therefore, as carriers of oxygen and heat, the suitable oxygen carriers with high activity, selectivity, and redox stability for methane selective oxidation play an important role in the CLR process [23].

Several transition metal oxides of Ni, Cu, Fe, Co, and Mn have been proposed as oxygen carrier candidates in CLR process [23,24]. To improve the structure, dispersion, durability and oxygen mobility of oxygen carriers, these suitable metal oxides are usually combined with various support materials, such as Al_2O_3, SiO_2, TiO_2 and CeO_2 [10,13,23,25,26]. According to the review work [27] that summarized recent advances in the development of oxygen carriers, among these metal oxides, iron oxides are promising candidates for their comparatively cheap price, large natural reserves and low toxicity [11,28,29]. Moreover, high thermal stability is an important property of iron oxides, making them suitable for CLR applications at high temperature [23].

Reactivity studies of iron oxide as oxygen carriers for CLR process and the reduction of iron oxides by methane have been conducted extensively [13,30,31]. The literature data suggests that activation energy obtained by reducing iron oxides with methane varies from 49 to 271 kJ/mol [28,32–34]. Ghose et al. [19] measured the reduction of iron oxide (Fe_2O_3) with 100% methane in the temperature range of 800–1025 °C. The apparent activation energy was obtained as 206 kJ/mol in the temperature range of 800–950 °C and 105.7 kJ/mol in the temperature range of 950–1025 °C. Monazam et al. [35] studied the reduction of hematite in methane atmosphere over the range of 700–825 °C with CH_4 concentrations of 15%, 20%, and 35% in N_2, they found that most of the CH_4 was totally oxidized into CO_2 and H_2O at the early stages of the reduction period. As the reaction proceeded, a minor amount of CO and H_2 were released due to partial oxidization of some CH_4 [30]. Cho et al. [36] observed very little or no carbon formation using an iron-based oxygen carrier. By tailoring the composition of oxygen carriers and controlling the supply of oxygen, such as adding small amount of Ni to iron oxides, could increase the reactivity and selectivity for partial oxidation of CH_4 [13]. It was observed that the redox reactivity of the oxygen carriers is improved by Ni addition because synergic effect may occur between NiO and Fe_2O_3/Al_2O_3 [30].

The knowledge of the reaction between iron oxides and methane is of great importance in the design of a chemical looping process, and many experimental investigations have been performed on the reactivity of iron oxides with methane. Nevertheless, a detailed understanding of the reaction mechanism between iron oxides and methane by theoretical research is still lacking. Therefore, we present a first principles study using density functional theory (DFT) to model chemical looping reaction in the fuel reactor with methane as fuels and iron oxides as oxygen carriers. The elementary processes of this reaction will be systematically examined, including the sequential process of methane decomposition, hydrogen formation, water production and dissociation, carbon selective oxidation on α-Fe_2O_3 (001) surface and oxygen migration in α-Fe_2O_3 (001) surface. The objective of this study is to provide useful insight into the detailed reaction processes at the atomistic scale, in order to design more efficient oxygen carriers or to optimize the current process.

2. Computational model and method

All DFT calculations were performed with the generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhof (PBE)