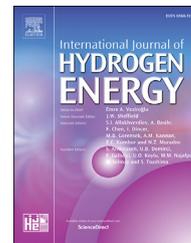


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Characterization of Fe₂O₃/CeO₂ oxygen carriers for chemical looping hydrogen generation

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ABSTRACT

Fe₂O₃ is currently the most proper active metal oxide for chemical looping hydrogen generation (CLHG). However, supports are necessary to improve the reactivity and redox stability. CeO₂ can enhance the oxygen mobility, leading to high redox reactivity and carbon deposition resistance, which can be an excellent alternative support for oxygen carriers. In this paper, Fe₂O₃/CeO₂ oxygen carriers prepared by the co-precipitation method with different Fe₂O₃ loadings were investigated on a batch fluidized bed regarding the hydrogen yield and purity, redox reactivity and stability in CLHG with CO as fuel. The results showed that Fe6Ce4 is the best given comprehensive performance with no CO or CO₂ observed in the obtained hydrogen (detection limit 0.01% in volume). The oxygen mobility property for the reducible support CeO₂ and the physical contact between un-integrated Fe₂O₃ and CeO₂ could improve the reduction of Fe₂O₃. In addition, the formation of the hematite-like solid solution and perovskite-type CeFeO₃ could bring about abundant oxygen vacancies and promote the oxygen mobility, which contributes to the elimination of carbon deposition, counteracts the negative effect of serious sintering and guarantees the reactivity and redox stability of the Fe₂O₃/CeO₂ oxygen carriers. The Fe₂O₃/CeO₂ oxygen carriers were characterized by carbon monoxide temperature-programmed reduction measurement and X-ray diffraction patterns, and Fe6Ce4 was also selected to be characterized by scanning electron microscopy images and energy dispersive X-ray spectrometer analysis.

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Introduction

Hydrogen is a promising fuel and no greenhouse gas emission can be observed in its utilization process. However, hydrogen is a secondary form of energy and it must be produced from other energy sources. Fossil fuels, which still satisfy 80% of the energy demand in the first part of 21st century, should, unfortunately, be employed to generate hydrogen in the near

future, and so CO₂ capture is necessary for the process [1]. Steam methane reforming (SMR) is currently the predominant way for hydrogen production. Nevertheless, it involves complex process and severe reaction conditions, which increases the investment and decreases the energy efficiency of the system. In addition, SMR results in significant CO₂ emission into the atmosphere [2].

Chemical looping hydrogen generation (CLHG) is a promising technology that can produce high purity hydrogen from

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fossil fuels with inherent CO₂ separation [3]. It consists of three reactors, including a fuel reactor (FR), a steam reactor (SR) and an air reactor (AR). Fig. 1 shows the schematic diagram of CLHG process with Fe₂O₃ as the oxygen carrier.

Take CO as fuel and Fe₂O₃ as an oxygen carrier. Fe₂O₃ is first reduced to Fe or FeO by CO in the FR. Then Fe or FeO is oxidized to Fe₃O₄ by H₂O in the SR, resulting in the hydrogen generation. Finally, Fe₃O₄ is oxidized back to Fe₂O₃ by O₂ in the AR. However, CO or CO₂ can be observed in the generated hydrogen due to the carbon deposition derived from the Boudouard reaction in the FR [4], as shown in R1.



Then, the deposited carbon reacts with steam in the SR, leading to low hydrogen purity. CO₂ can be sent into the FR to eliminate the carbon deposition, but it can reduce the fuel conversion [5,6]. H₂O has also been used to eliminate the carbon deposition [7,8]. However, the H₂O can only be used in CLC rather than in CLHG since it would react with FeO or Fe in the FR and decrease the hydrogen yield. Moreover, the inert support can also exert important influence on the carbon deposition [9].

Fe₂O₃ is an excellent metal oxide for CLHG in thermodynamics [10,11]. Nevertheless, the reactivity of pure Fe₂O₃ would deteriorate quickly in a few cycles [12]. Support is needed to improve the reactivity and redox stability. The most widely used supports include SiO₂, Al₂O₃, MgAl₂O₄, TiO₂, ZrO₂, yttrium-stabilized zirconia (YSZ) and perovskites [13,14]. Considerable research efforts have been devoted to the supports for CLC and CLR (Chemical Looping Reforming) related to Fe-based oxygen carriers [15–21]. However, limited attention has been paid to that for CLHG [22–24]. The main difference between CLHG and CLC/CLR is that Fe₂O₃ must be reduced into Fe or FeO in CLHG rather than Fe₃O₄. Nevertheless, Fe and FeO can catalyze the generation of the carbon deposition [25,26]. In addition, FeO can react with some

supports and result in the generation of unreactive compound, decreasing the reactivity and stability of the Fe-based oxygen carriers [7,24].

CeO₂ is a typical rare-earth metal oxide with a cubic fluorite structure, and it has been widely used in catalyst field, such as exhaust emission control of the motor vehicle, water gas shift reaction, solid-oxide fuel cell and catalytic methane oxidation [27,28]. The catalysis characteristic of CeO₂ can be attributed to its property of storing and releasing oxygen and the resulting oxygen mobility ability. Therefore, CeO₂ has the potential for the resistance to carbon deposition [29,30] and the enhancement of the reactivity and redox stability of the oxygen carriers [31]. It is worth noting that CeO₂, as a reducible “active” support, indeed possesses the capacity for oxygen carrying. However, the amount of oxygen release is too small to be of interest for chemical looping process [32]. Though CeO₂ is not suitable as an independent oxygen carrier in itself, its potential as support or additive for oxygen carriers is promising and encouraging. As to the application of CeO₂ in CLC, Bhavsar et al. [31,32] found that the reducible CeO₂ support can remarkably accelerate the oxidation and reduction kinetics for Ni-based and Fe-based oxygen carriers with H₂ or CH₄ as fuel, and also it allows for complete oxygen carrier conversation relative to Al₂O₃ and SiO₂ supports. Moreover, the CeO₂ support can enlarge the time window for total oxidation of CH₄. Liu et al. [33] concluded that the CeO₂ additive to Fe₂O₃/Al₂O₃ oxygen carrier provided faster oxygen transfer rates from the bulk to the surface of the particle by vacancy diffusion with CeO₂ and Fe₂O₃ solid solution as the prerequisite. Miller et al. [34] revealed that an addition of even 5 wt% CeO₂ could enhance the reactivity for CH₄ combustion by promoting the decomposition and partial oxidation of methane. Furthermore, Fe₂O₃ supported on gadolinia doped ceria or lanthana-doped ceria showed even higher reactivity and oxygen carrying capacity in CLC [35,36]. For CLR, the oxygen carrier Fe₂O₃/CeO₂ could maintain high catalytic activity and structural stability, and show satisfactory selectivity during the conversion of CH₄ to synthesis gas due to the oxygen mobility enhancement derived from the Ce-Fe solid solution [37,38]. There are also investigations on chemical-looping steam methane reforming (CL-SMR) with Fe₂O₃/CeO₂ as the oxygen carrier. Zhu et al. [39,40] showed that Fe₂O₃/CeO₂ was promising in CL-SMR for its high redox activity and desired yields of syngas and hydrogen, in which CeO₂ acted as the oxygen carrier and Fe₂O₃ was used as the additive for CeO₂ doping. In addition, the CeO₂ modified Fe₂O₃ oxygen carrier is a promising material for hydrogen storage and production via cyclic water splitting [41,42]. Furthermore, CeO₂ has also been found effective to eliminate the carbon deposition due to its oxygen buffering capacity in chemical looping process [29,30].

The above reasoning and the encouraging reports motivate our investigations into the performance and mechanism of CeO₂-supported Fe₂O₃ for CLHG. In our previous study, we investigated the effects of CeO₂, ZrO₂, and Al₂O₃ supports on iron oxygen carrier for CLHG [23]. It was concluded that the oxygen carrier supported on CeO₂ demonstrated good reactivity and redox stability with no carbon deposition observed. Therefore, the Fe₂O₃/CeO₂ oxygen carriers deserve to be further researched for CLHG on the basis of our previous research.

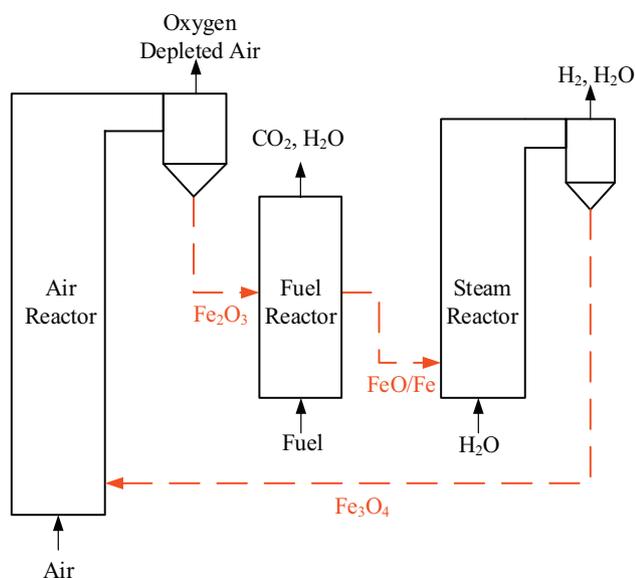


Fig. 1 – Schematic diagram of CLHG process with Fe₂O₃ as the oxygen carrier.

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