



Chemical-looping water splitting over ceria-modified iron oxide: Performance evolution and element migration during redox cycling

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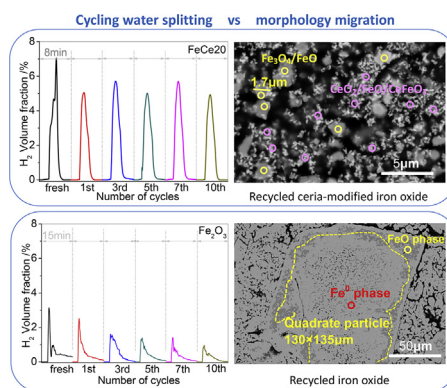
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HIGHLIGHTS

- Fe-Ce mixed oxides exhibited high activity in CLWS process.
- The CeO₂ promotes the oxygen recovery rate of Fe in redox.
- Morphology and element migration of Fe-Ce-O were explored in redox.

GRAPHICAL ABSTRACT



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ABSTRACT

Ceria-modified iron oxide exhibits high redox performance superior to that of pure iron oxide, which can inhibit the deactivation caused by sintering of materials. In the present work, the ceria-modified iron oxide is investigated as an oxygen carrier for hydrogen production via chemical-looping water splitting process (CLWS). To identify the role of CeO₂, the performance evolution and element migration of the mixed oxides during redox cycling were discussed in detail. Comparing the obvious deactivation of pure iron oxide sample, ceria-modified iron oxide shows relative constant production of hydrogen during the successive recycling water splitting. FeCe₂₀ sample with a CeO₂ mole percent of 20% shows the highest average yield of hydrogen (8651 μmol/g) with a Fe average oxygen recovery rate of 67.7% among Fe-Ce mixed oxides with different Ce molar percentage ($x = 0, 10, 20$ and 40%). In spite of materials sintering, the oxygen releasing/acquiring capacity and reactivity of Fe-Ce mixed oxides are three times higher than that of pure iron oxide after redox treatment. This can be ascribed to the preferable dispersion of Ce-based sub-micro particles (CeO₂ and CeFeO₃) and enhanced Fe-Ce interactions generated from active sites at the contact interface between iron oxides (mainly Fe₃O₄ particles) and Ce-based sub-micro particles (CeO₂ and CeFeO₃) after cycling.

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1. Introduction

Hydrogen is well known as one of the most important clean, efficient and safe energies in the world, which does not contain carbon and only generates H₂O during the consumption (Holladay et al., 2009). Chemical looping water splitting (CLWS) process is an emerging hydrogen generation technology via redox cycling (Fan and Li, 2010; Voitic and Hacker, 2016). This process mainly includes reduction and oxidation steps via using a metal oxide as the oxygen carrier, which offers a potentially viable option for carbon-free hydrogen generation coupled with carbonaceous fuels conversion (Fan and Li, 2010). During the reduction step, oxygen carrier donates lattice oxygen for the conversion fuel to chemicals or heat. In the oxidation step(s), the oxygen-depleted oxygen carrier is then re-oxidized by water steam to produce hydrogen. In some cases, water-oxidized oxygen carrier might still need to be oxidized by air (Zeng et al., 2015). Since this technology is largely dependent on the effectiveness of oxygen carrier (Protasova and Snijkers, 2016; Tang et al., 2015), research on development and optimization of suitable oxygen carriers is of significant importance.

Fe₂O₃-based metal oxides are the most promising oxygen carriers in CLWS process due to the high oxygen storage capacity (OSC), superior redox activity and easy availability (Chan et al., 2016; Cho et al., 2015; Jeong et al., 2015; Kathe et al., 2016; Liu et al., 2016; Protasova and Snijkers, 2016; Tang et al., 2015; Zeng et al., 2015). Iron oxides are even explored for chemical looping hydrogen storage and production (Voitic and Hacker, 2016). Nevertheless, iron oxide rapidly deactivates and loses its activity in initial redox cycles due to sintering and agglomeration of metallic iron or iron oxides (Cho et al., 2015; Protasova and Snijkers, 2016; Tang et al., 2015; Voitic and Hacker, 2016). The recent researches mainly focus on the doping and support optimization to enhance the redox stability. Transition metals including chromium, cobalt, nickel, copper, and molybdenum oxides are doped to iron oxides due to their favorable thermodynamics (Otsuka et al., 2003; Scheffe et al., 2011; Takenaka et al., 2005; Wang et al., 2013). The precious metals (Ryu et al., 2008; Takenaka et al., 2004b) and rare earth oxides (Galinsky et al., 2015; Lee et al., 2009; Liang, 2015; Miller and Siriwardane, 2013; Otsuka et al., 1999; Sun et al., 2015; Voitic et al., 2016; Zhu et al., 2014a, 2013) are also doped into iron oxide for enhancing the activity for water splitting. To counter the sintering of iron oxide, numbers of supports including inert oxides (Al₂O₃, ZrO₂, SiO₂ and MgO) (Cho et al., 2012; De Vos et al., 2017; Hafizi et al., 2016; Kidambi et al., 2011; Liu et al., 2012, 2015; Mehdizadeh et al., 2012; Nestl et al., 2015; Zeng et al., 2016), active perovskites (Dueso et al., 2015; He and Li, 2015) and ion conducting oxides (YSZ and GDC) (Kosaka et al., 2015) are investigated.

Ceria is one of the most attractive oxygen transport materials with high OSC and oxygen mobility due to presence of Ce³⁺/Ce⁴⁺ couple in redox processes (Zheng et al., 2016), which is also a new-emerging oxygen carrier material for chemical looping process (Muhich et al., 2013; Scheffe et al., 2014). Oxygen vacancies in ceria could split water for the production of hydrogen (Muhich et al., 2013; Roeb and Sattler, 2013; Scheffe et al., 2014; Zhao et al., 2016). However, the available oxygen amount per mole or gram for pure ceria is relatively low because it is difficult to completely reduce to Ce₂O₃ state and only a certain amount of oxygen vacancies form in most cases. Combination of iron oxide and ceria was proposed to design a redox material with preferable OSC and oxygen mobility for chemical looping process (Bhosale et al., 2016; Dharanipragada et al., 2016; Galvita et al., 2013; Li et al., 2010; Machida et al., 2015; Meledina et al., 2015; Zhu et al., 2014a). We proposed the application of CeO₂-Fe₂O₃ mixed oxides in chemical looping reforming for the production of syngas (Li et al., 2010).

The Ce-Fe-O mixed oxides with a Fe molar content of 30% shows super performance for the selective oxidation of methane to syngas. Interactions (synergistic effect) between Ce and Fe species, including high-dispersed surface iron oxides over ceria and the formation of Ce-Fe solid solution are responsible for the high activity. Ceria-doped iron oxide is also proved to be beneficial for both activity and stability of oxygen carrier for the decomposition of CO₂ to CO via a chemical looping process (Galvita et al., 2013; Meledina et al., 2015). Application of ceria modified iron oxide for CLWS also attracts considerable interest in virtue of high activity towards water splitting reaction (Bhosale et al., 2016; Liang, 2015; Sun et al., 2015; Voitic et al., 2016; Zhu et al., 2014a, 2013). Unlike other complex oxides, ceria modified iron oxide remains relatively satisfactory redox property in spite of sintering (Dharanipragada et al., 2016). The strong Fe-Ce interactions via Ce-O-Fe interfacial linkages could counteract the negative effect of sintering during redox cycling (Zhu et al., 2014a). In this local structure, ceria grains acts an oxygen pathway while iron oxide acts as reservoir, resulting in an enhancement of oxygen release and storage rates (Machida et al., 2015). To summarize, although ceria modified iron oxide has been used as the oxygen carrier for various chemical looping processes, the Fe-Ce synergistic effect of the interface grafting is far from clear. Investigation on the structure and element migration during redox cycling may provide helpful information on understanding the Fe-Ce interaction.

The objectives of this study are to investigate the behavior of ceria-modified iron oxide for CLWS, including the evolution of oxygen carrier in aspects of the activity, microstructure and element during cycling. A serial of Fe-Ce oxygen carriers were studied in CLWS process in combination with the observation on structure and reducibility evolution. Through the detailed information obtained from phase, microstructure, reducibility, and water splitting performance, the Fe-Ce interaction in this oxygen carrier for CLWS are discussed in detail.

2. Experimental

2.1. Preparation of oxygen carrier

Oxygen carriers with 0, 10, 20, 40, and 100 mol% of Ce (x, mole percent of Ce to the total moles of Ce and Fe) in Fe₂O₃-CeO₂ mixed oxides (labeled as Fe₂O₃, FeCe10, FeCe20, FeCe40, and CeO₂, respectively) were prepared by chemical precipitation method. According to the desired mole percent, the starting materials Ce(NO₃)₃·6H₂O and/or Fe(NO₃)₃·9H₂O were dissolved in distilled water to the desired concentration (0.25 mol/L) at the room temperature. Under the fierce stirring, an ammonia 18 wt% aqueous solution was dropped to the mixed solution to adjust pH to 9.5 at the room temperature for the precipitation of Fe and Ce ions. Hereafter, the precipitated sample was separated from the solution by filtering, washed with deionized water, and dried 24 h at 110 °C. After this step, the sample was allowed to cool to room temperature prior to being ground into powder. Finally, the materials were calcined at 300 °C for 5 h and at 500 °C for 10 h under ambient at a heating rate of 5 °C/min. After pressing, grinding and sieving, the samples with particles sizes in 20–40 mesh are obtained and labeled as FeCex.

2.2. Materials characterization

The phase analysis of the Fe₂O₃-CeO₂ mixed oxides was performed using X-ray Diffraction (XRD), equipped with a Japan Science D/max-R diffractometer with Cu K α radiation (λ = 0.1540 6 nm) at 40 kV and 40 mA. The powder patterns were collected in a 2 θ scan range from 20° to 80° with the scanning rate of 5°/min.

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