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Redox reaction induced morphology and microstructure evolution of iron oxide in chemical looping process

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ABSTRACT

Oxygen carrier (OC) plays an important role in the successful operation of chemical looping process. A detailed understanding of the structural evolution of the materials is crucial to design high performance OCs for this technology. In this study, Fe_2O_3 particles were used as oxygen carrier to investigate the morphology and microstructure changes induced by redox reaction during chemical looping process, which were performed in the single and multiple redox cycles. X-ray diffraction (XRD), Hg intrusion method and scanning electron microscope (SEM) were used to characterize the changes in phase composition, pore size distribution and morphology.

Our results indicated that the surface area of Fe_2O_3 particles decreased during the redox cycles even though more macro-pores (> 1000 nm) formed for these particles. Sintering was attributed to the surface area decrease of Fe_2O_3 particles in the redox process. Because of the outward Fe cation diffusion, porous structure in the interior of Fe_2O_3 particles was formed, which led to the crushing strength of the OC particles decreased significantly. In the reduction process, the aggregation of unstable Fe_3O_4 could cause the surface sintering of OC particles in the transformation of Fe_2O_3 into Fe_3O_4. Such findings can not only explain the performance of iron-based OCs in redox reaction, but can also provide theoretical guidance for the synthesis of iron-based OCs.

1. Introduction

Chemical looping combustion (CLC) process has recently emerged as a potentially feasible process for CO_2 separation and enrichment [1]. This technology avoids large-scale gas separations, while produces high concentration carbon dioxide stream for storage [2,3]. The CLC process is conducted in a simple manner. Firstly, the oxygen carrier (OC) provides lattice oxygen for fuel combustion in fuel reactor. Then, the reduced OC is re-oxidized by air for lattice oxygen recovery in air reactor. Simplified schematic of chemical looping combustion is shown in Fig. 1.

According to the principle of CLC process, OC material plays an important role in the successful operation and economics of this technology. A lot of studies [4–7] have been conducted to screen oxygen carriers with high potential. In general, a reliable oxygen carrier should follow the selection criteria, such as high reactivity in redox reactions, sufficient oxygen transport capacity, chemical and mechanical stability at high temperatures, high melting temperature, environmental safe and low cost. Up to now, some transition metal oxides, such as Ni [8–10], Cu [11–13], Mn [14–16] and Fe [17–20] were typically investigated in chemical looping process. Among the tested OCs, iron-based OCs are commonly tested in chemical looping process due to their natural abundance, environmental safe, high reactivity and relative high thermal stability [21–23]. Despite iron oxide in metallurgical [24–26] and catalytic [27–29] fields has been extensively studied, the required for reaction temperature, particle size and the types of chemical reactions are usually different from that in CLC process. The reactivity and cycle stability are highly dependent on the microstructure of OC materials [19]. As the oxygen carriers circulates in the CLC reactor, it undergoes the changes in morphology and structure, such as sintering, phase segregation and attrition [30]. These changes might lead to the reactivity of OCs decreasing with redox cycles. Pure iron oxide loses its reactivity rapidly after only a few redox cycles because of the reduction of surface area and pore volume due to sintering [31]. In order to overcome this problem, iron oxides are usually modified with some inert oxides. At present, most of the modifications of oxygen carriers are mostly based on the trial–error method. By adding different inert components, such as Al_2O_3 [32–34], SiO_2 [35–37], MgO [38,39] and TiO_2 [40–42], to improve the activity of the oxygen carriers, the suitable inert components were screened according to the performance of the modified oxygen carriers. However, this process has no clear direction and lack a corresponding theoretical guidance, so it is difficult to select suitable inert components. In this paper, the

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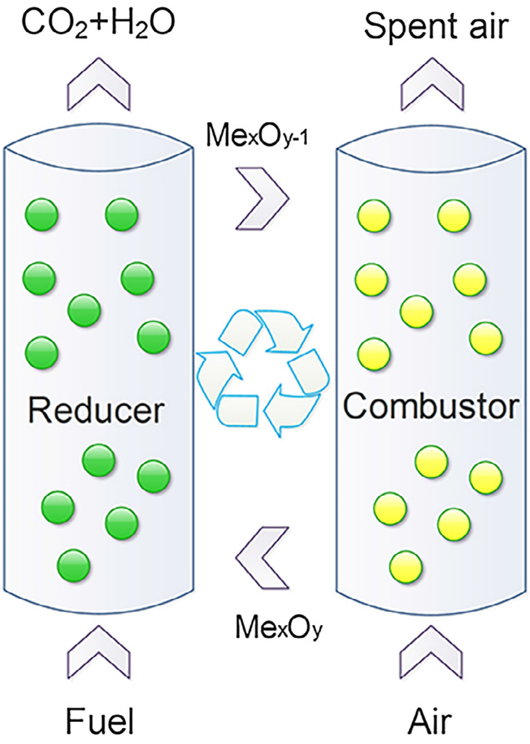

Fig. 1. Simplified schematic of chemical looping combustion.

morphology and microstructure evolution of iron oxide in CLC were studied, and the essential cause of its deactivation was obtained, which provided guidance for the modification of iron-based oxygen carriers. The results of this paper showed that the Fe cation diffusion had a great influence on the morphology and microstructure of iron oxide. In recent years, the importance of ion diffusion in energy-related fields has been widely realized by the researchers. Zhenchao Sun et al. [43] studied the HCl adsorption using calcium oxide (CaO) as sorbents and the ionic transfer behavior during chloridation reaction. The result showed that the $CaCl_2$ product layer grow inwards to the CaO bulk phase as the gradual transformation of CaO into $CaCl_2$, while the O^{2-} anions diffuse outwards through the $CaCl_2$ product layer and react with H^+ cations at the gas–solid interface. A. Cuadrat et al. [44] studied the behavior of ilmenite in CLC process. The results presented that Fe enriched on the surface of reacted ilmenite particles and porosity improvement were observed. Knutsson et al. [45] also found Fe segregation inside and outside of the ilmenite particles during redox cycles, which would decrease the performance of oxygen carriers. The essence behind Fe segregation is the diffusion mechanism of ions [46]. Such ions diffusion mechanism can not only explain the performance of iron-based OCs in redox reaction, but can also provide theoretical guidance for the synthesis of iron-based OCs.

In previous study, fundamental redox mechanisms in transition oxides (Fe, Cu, Co, Ni, Mn) have been discussed at nanoscale and atomic level [46–48]. Qin [46] studied the nanoscale morphology evolution of single (Fe) and binary metal oxide (Fe-Ni, Cu-Ni) particles undergoing redox cycles. In all researched material systems, the oxidized state of the OC particles presented porous cores due to ion transport. For the Fe-Ti system, porous particles were also formed after redox cycles [47]. According to the atomistic thermodynamics methods and density functional theory calculations (DFT), the energy barrier of Fe ion diffusion to the surface is lower than Ti ion diffusion. Mattisson etal. [22] studied the properties of iron ores with CH_4 during multiple redox cycles at 950 °C. They found that there were cracks and fissures on the surface of the particles after multiple redox cycles. Chern Yean Sim [30] characterized the pure iron oxide particles during the coal chemical looping combustion. Due to the presence of impurity components in coal, it is difficult to observe the structure change of iron oxide particles itself.

However, due to the lack of detailed information about the structural properties of these oxides, the evolution of their microstructure, such as specific surface area, pore size distribution and crushing strength, has not been fully understood. The redox reactivity and performance are intrinsically dependent on morphology, pore structures and crushing strength of oxygen carriers. There is also limited information on the crushing strength properties of oxygen carriers in redox cycles. It is an important requirement due to high strength particles are needed in the redox system to guarantee a good CLC performance. Therefore, it is significant to understand the microstructure and crushing strength of these materials in the oxidation and reduction reaction of oxygen carriers at high temperature.

The goal of this study is to explore the morphology and microstructure evolution of iron oxide under redox cycles. Hg intrusion method was used to characterize the pore structure changes of OC samples, which could provide more comprehensive microstructure information of materials. Besides, the relationship between the microstructure and the crushing strength of these oxygen carrier particles were also taken into account. The results can then be applied in the over design of CLC process.

2. Experimental

2.1. Material

The powder of Fe_2O_3 (30 nm, Aladdin) was first shaped into cylindrical particles with a diameter of 5 cm and a thickness of 3 mm under 30 Mpa, followed by a thermal treatment in air at 900 °C for 2 h. After thermal treatment, the sintered OC sample was crushed and sieved to the size of 250–550 μm. These sieved particles were used as start point in this study. The physical properties of the OC sample were listed in Table 1.

2.2. Experiment setup and test procedure

The schematic diagram of the facility was shown in Fig. 2. The detailed apparatus can be found in our previous study [2].

All experiments were conducted at 800 °C and atmospheric pressure. In a typical run, 1 g OC was loaded in the fixed bed reactor, then the reactor was heated to 800 °C under N_2 stream. Reduction gas (5 vol % H_2 balanced by N_2, total flow rate = 200 ml/min) was introduced to the reactor when the temperature stabilized. After the reduction process, the reactor was purged with N_2 (500 ml/min) for 5 min, and then fed with air (200 ml/min) for oxidation. The all gas volumetric flowrate measurements were performed under 25 °C and atmospheric pressure.

2.3. Characterization

The crystal structure was tested by a Diffractometer Ultima IV with a 2θ range of 10–80° at a speed of 5°/min. The particle size distribution of OC samples were performed using a laser particle size analyzer (Beckman Coulter LS200). The morphology of the oxygen carrier particles was conducted by Hitachi SU3500 scanning electron microscope. Besides the morphology and XRD measurement, the pore size distribution for the OC particles were analyzed by mercury intrusion

Table 1
Physical properties of the OC sample.

d_{50} (μm)	466 (σ = 17.62)
Crushing strength (N)	5.53
Surface area (m^2/g)	2.203

σ: standard deviation.