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Research article

Kinetics of sintering induced surface area decay of iron oxide in the reduction process of chemical looping combustion

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ABSTRACT

The chemical looping combustion (CLC) is an advanced combustion technique that can separate carbon dioxide (CO_2) simultaneously. The recyclability and stability of oxygen carriers is very important for the economical efficiency of CLC. The major factor for the deactivation of oxygen carriers is sintering. For most CLC studies, the focus were all on the reactivity of the oxygen carriers, but very few effort was contributed to the sintering properties of the oxygen carriers. This article addressed the characteristic and decay kinetics of surface area for iron oxide in the reduction process of CLC. The results showed that increasing the reaction temperature accelerated the decrease rate of surface area for iron oxide. In addition, with the reduction degree deepening, the grain size of iron oxide increased. Sintering kinetics of surface area decay based on a power law expression model was investigated. The activation energy for surface area decrease of iron oxide in the reduction process was calculated as 89.94 kJ/mol. Sintering and oxygen vacancies creation were the two causes for microstructural variation of iron oxide during the reduction process. Sintering leads to the decrease of surface area for iron oxide, while oxygen vacancies creation results in the porous structure forming.

1. Introduction

Facing the increasing pressure of global warming over the last twenty years, various technologies to reduce CO_2 emissions from large-scale power generation had been proposed or under extensive development [1], including post-combustion capture, pre-combustion capture, oxy-fuel combustion capture and chemical looping combustion. Among these technologies, chemical looping combustion (CLC) is considered one of the most promising technique due to its nature of in-situ CO_2 capture with extremely low energy penalty. CLC process avoids the costly gas separation process, but produces a high purity of CO_2 stream ready for sequestration [2,3]. As a result, CLC technique was identified as one of the most advanced power generation technologies in the CO_2 constrained scenario by the U.S. Department of Energy (DOE) [2]. CLC is conducted in a simple manner between two reactors, an air reactor and a fuel reactor. In the fuel reactor, oxygen carrier (OC), providing lattice oxygen in the CLC process, is reduced by fuel following the global reaction scheme:

$$(2n + m)Me_xO_y + C_nH_{2m} \rightarrow (2n + m)Me_xO_{y-1} + mH_2O + nCO_2 \tag{1}$$

where Me_xO_y stands for oxygen carrier in fully oxidized form and Me_xO_{y-1} represents the oxygen carrier in the oxygen depleted form.

And the oxygen depleted carrier is then transferred to the air reactor and re-oxidized by air for oxygen recovery, which undergoes the chemical reaction seen below:

$$Me_xO_{y-1} + \frac{1}{2}O_2 \rightarrow Me_xO_y \tag{2}$$

Simplified schematic of chemical looping combustion is shown in Fig. 1.

Oxygen carriers play an important role in the CLC process, which determine the product components and process efficiency of chemical looping. A lot of studies [4–7] have been carried out to develop reliable oxygen carriers. Briefly, a desirable oxygen carrier should have high reactivity with fuel and oxygen, high recyclability in long term operations, low sintering, low cost and easily available. Up to present, numerous types of oxygen carriers, such as synthetic metal oxides [8–10], industry wastes [11–13] and natural minerals [14–17] were tested or developed in CLC process. Among these types of oxygen carriers investigated, iron oxides [18–20] seem to be the most suitable to meet the requirements of chemical looping process because of their low cost and non-toxic, good reactivity and relatively high melting points. The recyclability and stability of oxygen carriers is very important for the economical efficiency of CLC. The major factor for the deactivation of

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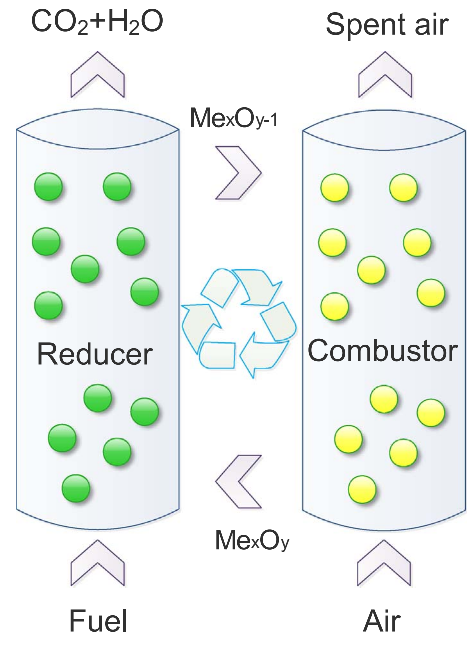

Fig. 1. Simplified schematic of chemical looping combustion.

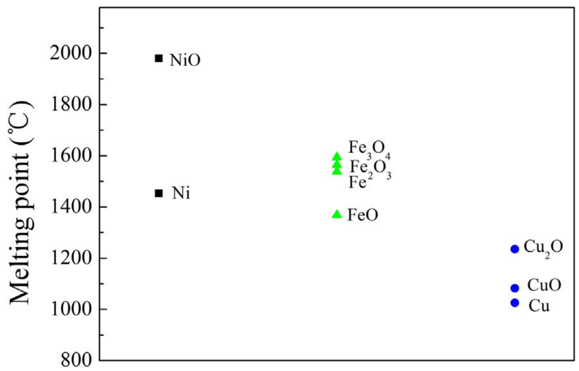

Fig. 2. Melting point of some common used oxygen carriers.

oxygen carriers is sintering. In general, Tammann temperature, empirically as half of melting point of the bulk solid, which is used to characterize the resistance of thermal sintering [21]. Sintering is a thermal degradation caused by the high reaction temperature, which lead to both the specific surface area and the porosity decreased and the density increased. Fig. 2 show the melting point of some common used oxygen carriers. The operating temperature range of a CLC system is 800–1200 °C, which often lead to the sintering of oxygen carriers. Therefore, the sintering of iron oxide is inevitable at high operating temperatures. Previous studies [22–24] indicated that pure iron oxide can lose their reactivity quickly due to sintering of the particles in the first few redox cycles.

The dominant driving force of sintering is the decrease of high surface energy of iron oxide above Tammann temperature by forming larger particles [25]. Sintering is a complex physical and chemical process, which is influenced by temperature, particle size, atmosphere and chemical components. It is well known that sintering could lead to the microscopic morphology changes of solid particles, such as the reduction of surface area and the growth of grain size. Therefore, previous researches into sintering [26–28] were mainly concentrated in the microstructure characteristics such as surface area, porosity and grain size. Because the reactivity of a solid is generally based on these physical structure. For example, surface area and grain size could influence the reaction rate. And porosity could affect the diffusion of gas reactants and products in the internal surface of solid reactants.

Since sintering is an important cause of oxygen carriers deactivation. Detailed understanding of the sintering characteristics is crucial, both to predict the extent of deactivation, and to derive new strategies to limit the effect of these processes. For most CLC studies, the focus were all on the reactivity of the oxygen carriers, but very few effort was contributed to the sintering properties of the oxygen carriers.

The surface area is a very sensitive parameter to study sintering properties of oxygen carriers. The objective of this research is to investigate the evolution of surface area and to obtain the decay kinetics in the reduction process of chemical looping combustion where iron oxide was used as OC. The microstructure evolution during the reduction process was also taken into account.

2. Material and methods

2.1. Material

Pure Fe_2O_3 power provided by Shanghai Aladdin Chemical Reagents Co. Ltd., was used as OC samples. Prior to the experiment, the Fe_2O_3 sample was subjected to a thermal treatment at 900 °C for 2 h in air. These sintered OC sample was used as starting point to investigate the phenomenon of surface area evolution during CLC process.

2.2. Experimental equipment and procedure

The schematic diagram of experimental set-up was shown in Fig. 3. In this study, the experiment was conducted in a fixed bed reactor, which had an inner diameter of 12 mm and a length of 400 mm. There was a porous plate was placed at 200 mm from the bottom of the fixed bed reactor, which was used as gas distributor and sample holder during experiment. The fixed bed reactor was equipped with an electric furnace system and the bed temperature was controlled by a K-type thermocouple.

The reactant gas was 5% H_2 balanced by N_2 at a total flow rate of 200 ml/min. The volumetric flow of reaction gas was controlled by a mass flow controller. In each experiment, 1 g sample was loaded on the porous distributor, then the reactor was heated to the desired temperature under the N_2 atmosphere. In the reduction stage, sample was exposed to the reducing (200 ml/min) atmosphere. When the reduction stage ended, 500 ml/min N_2 was used as purging gas to replace the reducing atmosphere in the reactor.

2.3. Characterization

The BET analysis was conducted using an ASAP 2020 surface area Analyzer. The specific surface area and pore size distribution were

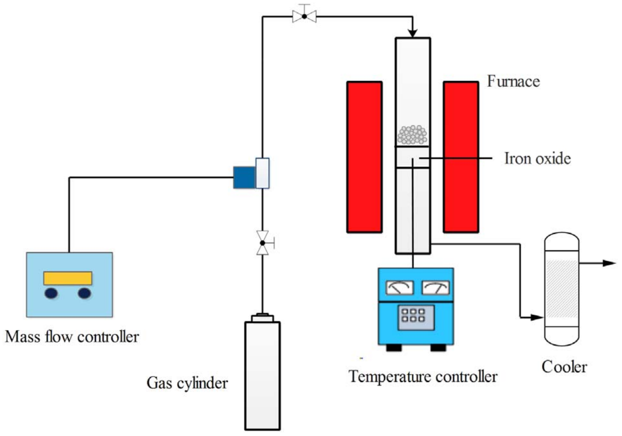

Fig. 3. Setup of the fixed bed system.