



Research article

Reduction kinetics of hematite as oxygen carrier in chemical looping combustion



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ABSTRACT

Chemical looping combustion (CLC), which has the characteristic of CO₂ inherent separation, is a novel fossil fuel utilization technology for CO₂ capture with low cost and low energy efficiency penalty. The reduction kinetics of oxygen carrier (OC) is one of the most important issues for CLC reactor design and computational fluid dynamics (CFD) simulation. In this work, well-organized isothermal experiments in a thermogravimetric analyzer (TGA) were first carried out to obtain the kinetics of a hematite as OC reduced by carbon monoxide. The reduction process was identified as two sequential stages, which correspond to the reduction of Fe₂O₃ to Fe₃O₄ and Fe₃O₄ to FeO, respectively. As obtained from the experimental result, the first stage is controlled by gas diffusion in the boundary layer on particle surface while the second stage is mainly controlled by heterogeneous chemical reaction. For the second stage, the activation energy, *E*, is 110.75 kJ/mol and the reaction order, *n*, is 1.5. Then, the same batch of hematite was tested by reacting with the reducing gas of 10 vol.% CO balanced by N₂ in a fluidized bed reactor. The different reaction characteristics in TGA and fluidized bed reactor were analyzed. This work provides a deep understanding on the applicability of the OC reduction kinetics obtained by TGA to the reactor design and CFD simulation of a fluidized bed CLC rig.

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1. Introduction

Chemical looping combustion (CLC) [1,2], which has the characteristic of CO₂ inherent separation [3,4], as an advanced technology of carbon capture and storage (CCS), has attracted widespread attention all over the world. Lattice oxygen atoms in oxygen carrier (OC) instead of oxygen molecules in air are used to oxidize the fossil fuel indirectly. In a typical CLC process, the cascade utilization of chemical energy of fuel is realized, so that a higher energy conversion efficiency can be achieved [5,6].

A typical CLC reactor is composed of an air reactor (AR) and a fuel reactor (FR). The fossil fuel is oxidized via an OC with high oxygen potential (usually metal oxide, Me_xO_y) in the FR, and the resulting products are CO₂, H₂O and reduced OC with low oxygen potential (Me_xO_{y-1}). High-purity CO₂ can be easily obtained from the flue gas through a simple steam condensation process. The high-oxygen-potential OC is re-generated in the AR as the low-oxygen-potential OC is re-oxidized by air. As the high-oxygen-potential OC is further transferred into the FR, a looping is constructed.

Fe-based OC is regarded as a kind of cheap and environmentally friendly OC material, which has gained the most attention. Iron ore as one of the most practical OCs in large-scale CLC systems has been widely investigated. Among these, hematite is a promising OC candidate when

taking economic costs into account. Factually, most of the CLC pilot reactors all over the world are based on natural iron ore oxygen carrier.

There are two foundational issues that need to be addressed in CLC. One is the selection of high-performance oxygen carrier and the other is the rational design of CLC reactor. The two foundational issues are both related to the reactivity of the OC. Elgeassy et al. [7] and Ettabirou et al. [8] investigated the apparent activation energy of Fe₂O₃ monocrystal reduced by CO to Fe₃O₄ or Fe. However, the apparent activation energy cannot be used for characterizing the reactivity of OC solely. Wang et al. [9] studied Fe₂O₃/Al₂O₃ OC through conducting thermodynamic analysis. They concluded that the chemical combination reaction between Fe₂O₃ and Al₂O₃ to form FeAl₂O₄ is detrimental to the reactivity of the OC. Zafar et al. [10] found that Fe₂O₃/MgAl₂O₄ showed high reactivity during the phase transition from Fe₂O₃ to Fe₃O₄ but very low from Fe₃O₄ to FeO. Recently, the reduction kinetics, which act as a quantitative characterization for OC reactivity, has aroused the interest of many researchers. Abad et al. [11,12] systematically investigated the reduction kinetics of synthetic Cu-based, Fe-based and Ni-based OCs reduced by CO, H₂ and CH₄. The obtained kinetic parameters were utilized for the reactor design and computational fluid dynamics (CFD) modeling. Chen et al. [13] conducted an experiment in a micro-fluidized bed reactor to investigate the kinetic parameters of hematite reduced by CO. However, the effect of CO concentration was not considered.

With respect to heterogeneous gas-solid reaction kinetics, the comprehensive effect of intrinsic chemical kinetics and internal/external

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mass transfer is the most complex and important issue. When establishing the kinetic equations for the reduction reaction of OC, the above two factors must be carefully considered, because the reported rate-controlling step and kinetics (the reaction rate constant and the activation energy) differ, as found in the published literatures. Monazam et al. [14] proposed a two-parallel-reactions-based kinetic model to describe the reduction process of hematite to wustite. The new model is applicable for the volume fraction of gas fuel (methane) ranging from 15 vol.% to 35 vol.% and temperatures ranging from 973 K to 1098 K. For predicting the reduction process of a synthetic Fe-based OC, Abad et al. [11,12,15] adopted the shrinking core model (SCM) as the reaction mechanism of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ with syngas, while Go et al. [16] reported that the reduction of iron oxide by CH_4 is within the diffusion control regime in the temperature range of 1073–1173 K. Piotrowski et al. [17,18] reported that activation energy (E) for the reduction reaction of hematite with syngas composition (CO and H_2) was in a wide range of 25–125 kJ/mol, and the 2-D nucleation growth and first order model was determined as the reaction mechanism. Pineau et al. [19] investigated the reduction reaction of hematite by H_2 in the temperature range 493–1003 K. It was observed from the experiment that there exist two different stages in the reduction process. As a conclusion, the apparent activation energy in the first reduction stage (corresponding to Fe_2O_3 to Fe_3O_4) was determined as 76 kJ/mol, while the second reduction stage (corresponding to Fe_3O_4 to Fe) was calculated as 39 kJ/mol at temperatures higher than 693 K. It was also concluded that the reaction rate at higher temperatures is controlled by phase boundary reaction.

As mentioned above, in the reduction process of hematite, the two reaction stages (Fe_2O_3 to Fe_3O_4 and Fe_3O_4 to FeO) demonstrate different reaction characteristics. When taking both the chemical reaction kinetics and mass transfer into account, the reaction controlling step may differ between the two stages. Usually, a CLC process was designed for operating in a fluidized bed reactor, while the reaction kinetics adopted in reactor design was obtained from thermogravimetric analysis (TGA) in literatures. These two kinds of reaction equipment have different reaction conditions, and the applicability of the reaction kinetics derived from TGA to fluidized bed reactor design is doubtful. In this study, thermogravimetric analysis experiment and fluidized bed experiment were conducted for investigating the kinetic parameters of hematite reduction by CO , in order to provide a deep understanding on the applicability of the reaction kinetics.

2. Experiment

2.1. Materials

The hematite originates from the E'kou Mine, China. This kind of hematite OC was previously adopted in our 5 kW_{th} dual circulating fluidized bed experiment [20,21]. For the concern of continuity and systematism of our work, this kind of hematite was selected as OC in this study. The hematite OC tested in this work has been previously utilized for >300 h in the 5 kW_{th} dual circulating fluidized bed experiments [20,21]. Many characterizations to this material like X-ray diffraction (XRD, X'Pert Pro) analysis, Scanning Electron Microscope (SEM, FEI Quanta 200) analysis and Brunauer–Emmett–Teller (BET) surface area analysis (Micromeritics, ASAP-2020) have been conducted in our previous publications [20,21]. According to the XRD analysis, the Fe element is in the +3-valence state in the fully oxidized OC. The elemental

analysis (as determined using an X-Ray Fluorescence apparatus (XRF, EDAX EAGLE III), see Table 1) shows that the mass fraction of Fe_2O_3 was 66%. By sieving the used hematite OC, the particles in the diameter range of 180–200 μm were collected for the TGA experiment, and the apparent density is 3472 kg/m^3 .

2.2. Experimental procedure

The isothermal reduction experiments were first conducted in a thermogravimetric analyzer (WCT-1D). In the preliminary experiment, five different sample masses (50 mg, 30 mg, 20 mg, 10 mg and 5 mg) and four different gas flow rates (20 mL/min, 50 mL/min, 80 mL/min and 95 mL/min) were employed to investigate the effect of gas diffusion in crucible on the reduction rate of hematite. The reducing gas was 10 vol.% CO balanced by high purity N_2 and the temperature was 950 $^\circ\text{C}$. It was found that when the sample mass was smaller than 10 mg and gas flow rate was higher than 80 mL/min, the effect of the gas diffusion in crucible on the reduction rate can be eliminated. In this sense, the experimental conditions of sample mass at 10 mg and gas flow rate at 80 mL/min were adopted in subsequent formal TGA test. The formal experiment can be divided into 16 cases depending on four different CO concentrations (5 vol.%, 10 vol.%, 15 vol.% and 20 vol.%) and four different reaction temperatures (850 $^\circ\text{C}$, 900 $^\circ\text{C}$, 950 $^\circ\text{C}$ and 1000 $^\circ\text{C}$).

Afterwards, reduction experiment was conducted in a fluidized bed reactor to investigate the reactivity of hematite OC. The hematite with the mass of 6 g was chosen as the active OC materials and 20 g silica sand was chosen as the inert bed materials. Reducing gas of 10 vol.% CO balanced by N_2 was aerated to the reactor with the flow rate of 800 mL/min in the reduction period, and the temperature was maintained at 900 $^\circ\text{C}$. The schematic view of the fluidized bed reactor rig is shown in Fig. 1. The diameter of the reaction chamber is 26 mm and the exhaust gas was detected by the on-line gas analyzer. Detail description of fluidized bed reactor can be found in our previous publications [23–25].

3. Analysis and results

3.1. Data processing method

In TGA experiments, the instantaneous weight of the OC sample was measured and saved automatically. Transient conversion of the OC sample can be calculated as,

$$X_i = \frac{m_{\text{ox},i} - m_t}{m_{\text{ox},i} - m_{\text{re},i}} \quad (1)$$

where m_{ox} and m_{re} is the weight of the sample at the fully oxidized and reduced state, respectively; m_t is the weight of the OC at time t ; i represents the different reduction stages. To be more specific, for the first reduction stage, $m_{\text{re},i}$ equals to the sample weight when the Fe_2O_3 content in the ore was completely reduced into Fe_3O_4 ; while for the second reduction stage, $m_{\text{re},i}$ equals to the sample weight when Fe_3O_4 in the OC were fully reduced to FeO .

In fluidized bed reactor experiment, the flow rate of the exhaust gas and the volume fraction of CO_2 in the exhaust gas were on-line detected. Considering the fact that no carbonaceous gas was observed in the oxidation process, i.e., no carbon deposition occurred in the reduction process, the transient conversion of the OC can be expressed as,

$$X = \frac{\int_{t_0}^t F_{\text{ex}} y_{\text{CO}_2} dt}{\int_{t_0}^{t_{\text{total}}} F_{\text{ex}} y_{\text{CO}_2} dt} \quad (2)$$

where F_{ex} is the flow rate of the exhaust gas; y_{CO_2} is the volume fraction of CO_2 in the exhaust gas.

Table 1
Elemental analysis of the hematite [22].

Element	Wt.%	At.%	Element	Wt.%	At.%
Fe	73.38	57.85	S	00.61	00.84
Si	18.73	29.35	K	00.13	00.15
Al	04.52	07.38	Ca	00.33	00.41
Mg	02.14	03.88	Ti	00.15	00.14

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