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Insights into the redox reactivity of an inexpensive Fe-based oxygen carrier

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ABSTRACT

Iron-based oxygen carrier (IBOC) is widely used in chemical looping processes (CLP) due to many advantages, and the low-cost ones are prospective for industry application. However, research on the redox properties of the low-cost IBOCs during CLP is still rarely seen, compared to those on the well prepared ones. In this work, an experiment is implemented with a thermo-gravimetric analyzer (TGA) to investigate the reactivity of a low-cost IBOC through several periods of the "three-reactor" loop including hydrogen reduction, steam oxidation, and air combustion. The isothermal approach is used to analyze the TGA data obtained at different temperatures. An X-ray diffractometer (XRD) is used to detect the final forms of iron. It is found that the main forms of IBOC presenting in the "three-reactor" redox cycles are Fe_2O_3, Fe_3O_4 and Fe. The Avrami-Erofeev equations are found to be the most probable reaction mechanisms for the hydrogen reduction and steam oxidation processes. The corresponding reaction kinetic constants for each cycle are calculated. The IBOC reactivity increases with temperature but decreases with the increasing circulation number, and becomes relatively stable within 7 cycles. The final form of iron in IBOC is mainly Fe_2O_3, along with a little Fe_3O_4.

1. Introduction

Chemical looping process (CLP) is a promising approach to capture the greenhouse gas, CO_2, with limited power penalty during syngas and/or power generation [1–3]. This is because CO_2 rich depleted gas can usually be obtained through CLP, which makes it readily for economical CO_2 capture and sequestration [4]. For example, chemical looping hydrogen generation (CLHG) can be efficient to generate pure hydrogen and, in the meantime, sequestrate CO_2 [5].

As the heart of CLP, oxygen carriers play an essential role and, thereby, need detailed and deep investigation. For CLHG, there are generally two different processes. One is composed of two reactors, including a reduction reactor and an oxidation reactor [6], and the other is composed of three reactors, including a reduction reactor, an oxidation reactor and a combustion reactor [7]. For the two-reactor CLHG (2R-CLHG), less fuel is consumed but additional heat is required to sustain the reduction temperature [3]. For the three-reactor CLHG (3R-CLHG), the additional heat can be generated in the combustor and transported by the oxygen carriers to the reduction reactor. Besides, nearly pure nitrogen can be produced as by-product. The 2R-CLHG and 3R-CLHG processes are shown in Fig. 1. For the 2R-CLHG, two reactions can be dominant. Supposing the reducer is H_2 and the highest valence metal oxide is MeO_x, MeO_{x-i} is reduced into MeO_{x-i-j} by H_2 in the reduction reactor like (R1), and then MeO_{x-i-j} is oxidized into MeO_{x-i} by H_2O in the oxidation reactor like (R2).

$$MeO_{x-i}+jH_2=MeO_{x-i-j}+jH_2O \quad (R1)$$

$$MeO_{x-i-j}+jH_2O=MeO_{x-i}+jH_2 \quad (R2)$$

For the 3R-CLHG, three reactions can be dominant. MeO_x is firstly reduced into MeO_{x-i-j} by H_2 in the reduction reactor like (R3). Then, MeO_{x-i-j} is oxidized into MeO_{x-i} by H_2O in the oxidation reactor like (R4). Finally, MeO_{x-i} is further oxidized into MeO_x by air in the combustion reactor like (R5).

$$MeO_x+(i+j)H_2=MeO_{x-i-j}+(i+j)H_2O \quad (R3)$$

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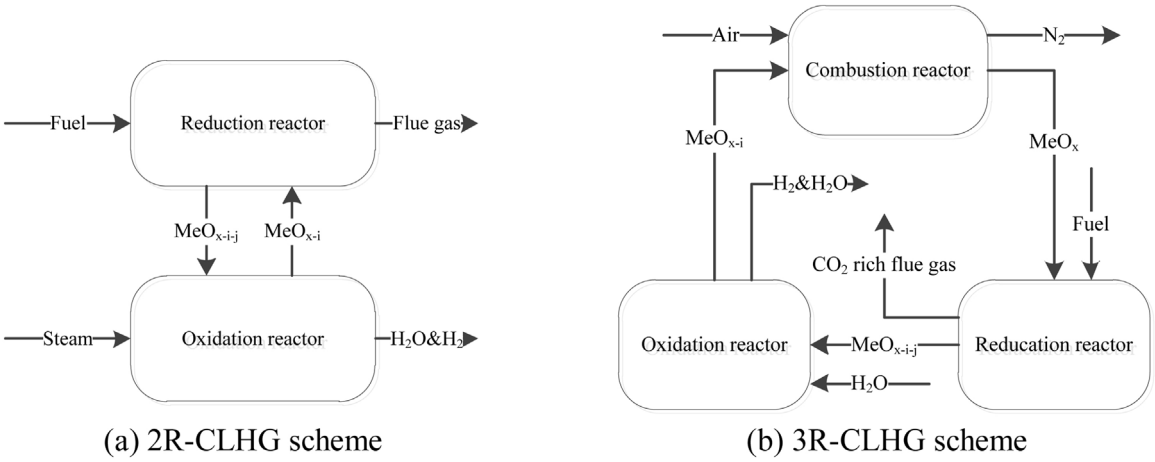

Fig. 1. Schematics of the 2R-CLHG and 3R-CLHG processes.

$$MeO_{x-i-j}+jH_2O=MeO_{x-i}+jH_2 \quad (R4)$$

$$MeO_{x-i}+i/2O_2=MeO_x \quad (R5)$$

In the reduction reactor, metal oxide is reduced by syngas. The outlet exhausted syngas is rich in CO_2, making it readily for carbon capture and sequestration (CCS). The reduced metal oxide then enters the oxidation reactor where water is split to produce hydrogen. For 2R-CLHG, metal oxide from the oxidation reactor returns to the reduction reactor and begins the next period, while for 3R-CLHG, metal oxide from the oxidation reactor enters the combustion reactor and is further oxidized. In the meantime, nearly pure nitrogen can be produced as by-product. The sensible heat carried by the metal oxide serves as the heat source of the reduction reactor, and that contained in the nitrogen-rich depleted air can be recycled to improve the system efficiency.

Till now, many alternative oxygen carriers, like Ni-, Zn-, Fe-, Co-, Ca-, Cd- and Cu- based ones, have been developed, tested and utilized. Thereinto, Fe-based oxygen carrier is believed promising for CLHG not only because Fe has several valence states, but because it demonstrates higher melting point, better mechanical strength, lower environmental impact and lower cost than the others [8]. In this work, the redox property of Fe-based oxygen carrier for the CLHG process, especially for the 3R-CLHG process, is investigated.

Recently, some researchers have focused on the preparation, characterization and application of different oxygen carriers using the experimental and/or simulation methods. Hafizi et al. [9] recently chose $Fe_2O_3/MgAl_2O_4$ and Fe_2O_3/Al_2O_3 as oxygen carriers and used CaO as CO_2 sorbent to generate highly pure hydrogen. The H_2/CO molar ratio of 16.7 was achieved in their work and high reactivity of the oxygen carrier was obtained during nine cycles for $MgAl_2O_4$ support and Ce/Ca sorbent. Baek et al. [10] recently prepared an oxygen carrier with high content of NiO and Al_2O_3, and found that the oxygen carrier derived from y-Al_2O_3 mixed with MgO showed the best performances. Cho et al. [11] once tested the continuous operation characteristics of a 3R-CLHG system using Fe_2O_3/ZrO_2 as the oxygen carrier in moving beds at 800 °C and found that the oxygen carrier exhibited high durability. Monazam et al. [12] studied the reduction properties of hematite by methane during the chemical looping combustion using a thermo-gravimetric analyzer (TGA). The reaction mechanisms were detected in their work and it was found that the reaction rates would increase with the increasing temperature and methane concentration. Bhavsar et al. [13] evaluated the performance of several iron- and manganese-based mono- and mixed-metallic oxygen carriers during the redox cycles and found that use of ceria as support could result in stable operation. Kathe et al. [14] recently implemented the thermodynamic simulations of hydrogen production from natural gas using an iron-based chemical looping technology. The cold gas efficiency of their scheme was reported to be 5% higher than that of the steam methane reforming. From the literature review, it is found that most of the oxygen carriers tested required time-consuming and costly preparation procedures. Research on the redox characteristics of the low-cost ones like hematite in the 3R-CLHG process, is rarely reported. Thus, complementary research in this field is still necessary.

In this work, a low-cost hematite was used as the oxygen carrier for the 3R-CLHG, and its reactivity was tested in several redox cycles at 800, 900 and 1000 °C, at 1 atm. The reaction mechanisms in the reduction reactor and the oxidation reactor were detected and the reaction rate constants for different processes in each cycle were calculated. The variations of reaction rate constants against temperature and circulation numbers were analyzed. In addition, the final forms of iron were detected at the end of the redox cycles. The results obtained in this work will be helpful for the further preparation and application of the low-cost iron-based oxygen carrier (IBOC).

2. Experimental

Experiments were carried out on a TherMax-500 thermogravimetric analyzer (TGA) made in the Thermo Electron Corporation in America to investigate the reactivity of a common low-cost hematite going through several three-reactor redox cycles. Although for different gasification conditions, especially for different gasification agents, the syngas compositions can differ greatly [15], the typical combustible species in syngas mostly consist of H_2, CO and CH_4 [16]. Thus, carbonaceous fuels, as well as H_2, were utilized as reducer in the primary experiments. However, this trial did not yield precise results mainly due to the decomposition of CH_4 and CO during the reduction process. CO can form carbon deposits through the disproportionated reaction, and CH_4 can form carbon deposits through the cracking reaction at relatively high temperatures [17], as shown by reactions (R6) and (R7).

$$2CO = CO_2+C \quad (R6)$$

$$CH_4= 2H_2+C \quad (R7)$$

Thus, carbon tends to accumulate during the reduction process, leading to increasing sample mass in the thermal gravity (TG) curve, and making the experiment unreliable and hard to control. To avoid this issue, only H_2 was used as the reducer in this work [18]. Actually, for many solid carbonaceous fuel based clean power