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The search of proper oxygen carriers for chemical looping partial oxidation of carbon

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HIGHLIGHTS

- A method was offered in this work to distinguish the oxidation ability of OCs.
- Three zones were divided by three reactions in the Elliham diagram.
- $CaFe_2O_4$ and $Ca_2Fe_2O_5$ were found to be proper for chemical looping partial oxidation.

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ABSTRACT

Chemical looping partial oxidation process has more advantages over conventional chemical looping process, which can not only completely avoid the problem of greenhouse gas emissions, but also supply syngas products for chemical industry. The aim of the present work is to perform fundamental investigation on chemical looping partial oxidation of solid fuels. Production of CO through chemical looping partial oxidation of carbon was investigated in order to find proper oxygen carrier with good reactivity and high selectivity. A simple and easy to use method based on the zone division of Ellingham diagram was offered to distinguish the oxidation ability of various metal oxides, and three zones including complete oxidation, partial oxidation and inert zones were divided. $CaFe_2O_4$, $Ca_2Fe_2O_5$ and $FeAl_2O_4$ in partial oxidation zone together with Fe_2O_3 in complete oxidation zone were chosen as target oxygen carriers (OCs) for chemical looping partial oxidation of carbon in this work. Of the target metal oxides, $CaFe_2O_4$ and $Ca_2Fe_2O_5$ were found to have fast reaction rate, large oxygen-carrying capacity, high CO selectivity, and good regeneration performance, which made them very attractive for the purpose of chemical looping partial oxidation of solid fuels in real applications.

1. Introduction

The concept of chemical looping combustion (CLC) was first proposed by Ishida et al. [1] in 1987, which divided the combustion process into two successive reactions. Lattice oxygen in oxygen carrier (OC) was used as the reaction intermediate in reduction-oxidation cycles to replace molecular oxygen. The CLC process absolutely avoided the direct contact between reactants and the air, and intrinsically eliminate the dilution of N_2, which led to the enhancement of fuel gas calorific value, and made CO_2 capture or separation much easier than conventional combustion process. Furthermore, CLC process of plastic waste was observed to have the potential advantages of suppressing the formation of PCDD/Fs [2]. Owing to the above unique features, there has been growing interest in the study of CLC, especially in the field of oxygen carrier development, which was thought of as one of key issues for CLC development.

Single metal oxides such as CuO [3], NiO [4] and Fe_2O_3 [5], as well as metal sulfide like $CaSO_4$ [6,7] were widely reported in literature as oxygen carriers due to their favorable thermodynamics and high reactivity [8–10]. Cao and Pan [11] studied chemical looping combustion of solid fuels using various active metal based oxygen carriers. It was found that Cu, Ni, Co based oxygen carriers were the optimum oxygen carriers for the CLC of solid fuels. However, a series of disadvantages were found for single metal oxide: the cost of CuO was much high, NiO would cause serious pollution to the environment, and Fe based oxygen carriers had significant drawbacks of a range amount of heat release in the reducer. According to Huang et al. [12], the order of reactivity

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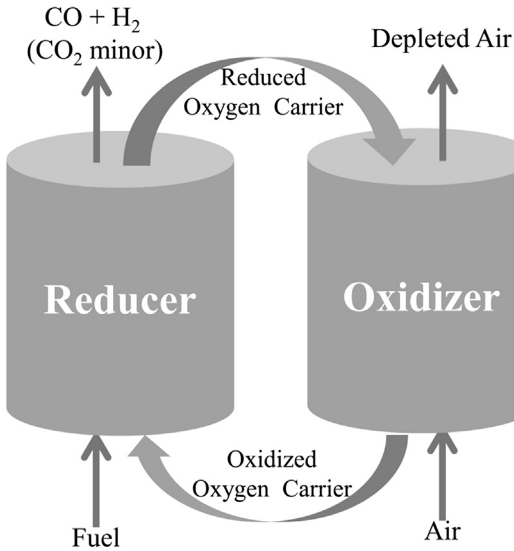

Fig. 1. Schematic diagram of chemical looping partial oxidation.

was speculated as follows: pure oxygen ≈ NiO > H_2O > Fe_2O_3 > CO_2 > Al_2O_3. Recently, mixed metal oxide based oxygen carriers have been attracting significant attention. It was observed that some supported mixed metal oxides demonstrated better reactivity compared with the single counterpart. Tian et al. [13] developed supported Fe-Cu oxygen carriers, whose performance for the CLC process with simulated synthesis gas derived from steam gasification of coal was evaluated. A synergetic effect of Fe-Cu was observed and the presence of Cu promoted the deeper reduction of Fe_2O_3. Recent study on oxygen carrier development mostly focused on the improvement of the reactivity and cycling performance through the modification and adjustment of the existing mixed oxide based materials.

Owing to the joint efforts of researchers all over the world, the research and development on CLC have proceeded from the laboratory scale with big progress in semi-industrial test to the stage of pilot-scale demonstrations. An integrated continuous 25-kWth chemical looping demonstration unit was constructed by Fan and the associates [5,8] for the direct chemical looping combustion of coal using iron-based oxygen carriers. During the 200 h continuous operation, the reaction system showed steady behavior in terms of solid circulation, oxygen carrier reactivity and recyclability, and more than 90% coal conversion with high CO_2 purity (99.5 vol%) in the reducer were confirmed. The detailed evaluation of the chemical looping system of coal and biomass using iron oxides as the oxygen carrier in conjunction with CO_2 capture and storage were applied by Cormos et al. [14].

Most of the current work was aimed to achieve full oxidation of fuels leading to high purity CO_2. Besides complete oxidation, partial oxidation concept has been proposed to produce CO and H_2 from chemical looping process of various fuels [15–17] (Fig. 1). Chemical looping partial oxidation process has more advantages over conventional CLC process, which can not only completely avoid the problem of greenhouse gas emissions, but can also supply syngas products for chemical industry.

Chemical looping partial oxidation of CH_4 to CO and H_2 using CeO_2 as the oxygen carrier was reported by Otsuka et al. [18], it was found that the addition of Pt black could significantly enhance the reaction rate. Kodama [19] experimentally compared the activities of various metal oxides including Fe_3O_4, ZnO, SnO_2, In_2O_3 and WO_3 as oxygen carriers for selectively converting CH_4 to CO and H_2, and WO_3/ZrO_2 was selected as the suitable candidate. Fan and associates [20] found that high-purity syngas could be achieved through the shale gas chemical looping process using Fe-Ti mixed metal oxides as oxygen carriers. According to Tang et al. [21], Fe-based oxygen carrier demonstrated high selectivity toward partial oxidation of CH_4 but possessed low CH_4 conversion, while Ni-based oxygen carrier showed poor selectivity with high CH_4 conversion. It was hypothesized by Bhavsar et al. [22] that an appropriate combination of Fe-Ni mixed oxides could combine the high reactivity of Ni-based oxide with the high selectivity feature of Fe-based oxide and presented an efficient partial oxidation of CH_4.

However, it is rarely reported in the literatures that focus on partial oxidation of solid fuels to produce syngas via chemical looping process. Although applying the concept of chemical looping for solid fuels presented many challenges, it is still with extraordinary significance because of rich deposit of solid fuels. Shen et al. [23] performed experimental investigation on chemical looping partial oxidation of biomass using natural hematite as oxygen carrier in batch and continuous reactors. He et al. [24] investigated chemical looping partial oxidation of biomass using iron ore as an oxygen carrier. Results showed that the oxygen carrier particle can act as a catalyst for tar cracking. Huang et al. [25,26] studied chemical looping partial oxidation of biomass char using $NiFe_2O_4$ and iron ore as oxygen carriers. Results showed that the presence of oxygen carrier apparently improved the reaction rate of char and the carbon conversion in comparison to that of char pyrolysis and steam gasification. Guo et al. [27,28] investigated chemical looping partial oxidation of solid fuels for syngas generation using $CaSO_4$ and iron-based oxygen carrier. It was proved that the presence of oxygen carrier efficiently improved the carbon conversion and the generation of syngas. The optimal temperature for $CaSO_4$ was 850–950 °C, and at 900 °C the equilibrium amount of CO, H_2, H_2O and CO_2 were

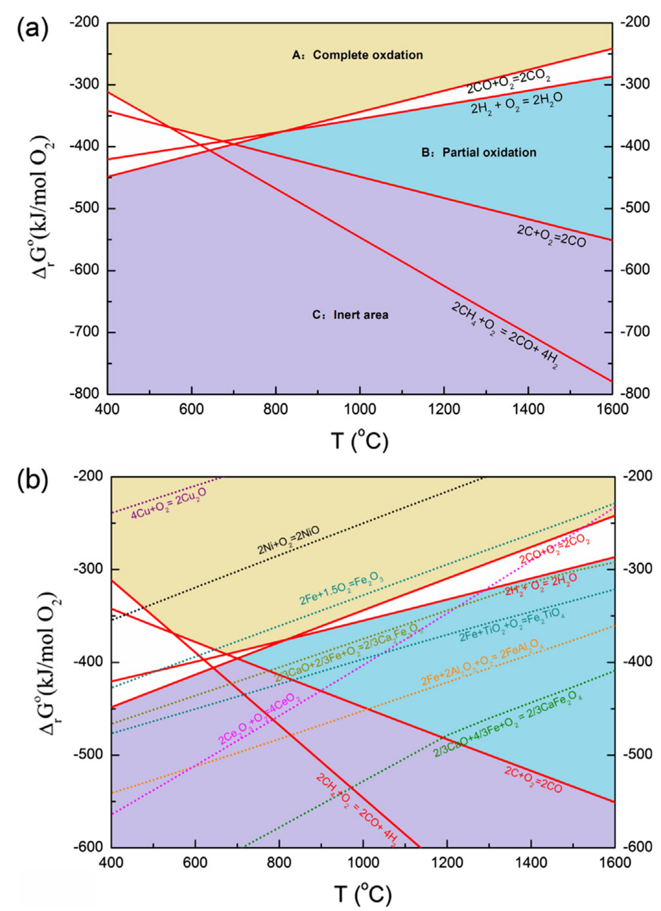

Fig. 2. Ellingham diagram showing the variation of oxidation Gibbs free energy with temperature for oxygen carriers: (a) reaction zone division for chemical looping complete oxidation, partial oxidation and inert area and (b) standard Gibbs free energy changes of related oxidation reactions of some oxygen carrier materials.