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Synergistic effects of mixtures of iron ores and copper ores as oxygen carriers in chemical-looping combustion

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Abstract

Iron ore is a cheap and nontoxic oxygen carrier in chemical-looping combustion (CLC). However, it performs good recyclability while low reactivity in the CLC of solid fuels. Copper ore exhibits very high reactivity and oxygen uncoupling behavior, while suffers from tendency towards sintering and agglomeration during consecutive redox cycles at a higher temperature (e.g., 900–1000 °C). In this work, mixtures of hematite and copper ore were used as oxygen carriers for CLC of syngas and coal. Through the isothermal redox experiments at 950 °C in a thermogravimetric analyzer, it is found that there are synergistic effects between iron ore and copper ore, and copper ore could be more efficiently utilized when the mixing ratio of copper ore is maintained 10–20 wt%. As the mixing ratio of copper ore is 20 wt%, the reduction reaction of the mixer OC is no longer endothermic, which is beneficial to the controllability of the fuel-reactor temperature. The fluidized-bed experiments were carried out to verify the reactivity of the mixing ore OCs at 950 °C. It is observed that the mixing OC with 20 wt% copper ore has a better reactivity with the gasification products (especially H₂) of low-volatile anthracite than the pure hematite, and leads to a higher fuel conversion rate and CO₂ yield. The mixtures of iron ore and copper ore are expected to address simultaneously reactivity, recyclability, cost and environmental concerns of oxygen carriers.

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Keywords: Hematite; Copper ore; Oxygen carrier; Chemical-looping combustion; Coal

1. Introduction

The present CO₂ capture technologies have the disadvantage of the large energy penalty while separating CO₂ from flue gas. Chemical-looping combustion (CLC) is an innovative combustion

technology for heat and power production with inherent CO₂ capture [1], thereby avoiding the need for costly separation processes. In a CLC system, fuel-reactor (FR) and air-reactor (AR) are interconnected while isolated from each other in reaction atmosphere [2]. The oxygen required for the fuel combustion is provided by an oxygen carrier (OC) which is reduced in the FR and regenerated by oxidation with air in the AR. The flue gas leaving the FR just consists of CO₂ and H₂O while the fuel is oxidized by OC

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completely, then pure CO₂ is obtained for storage or application after steam condensation.

The OC is critically important for CLC. Suitable OCs for gaseous and solid fuels should have the following characteristics: high reactivity to convert fuel to CO₂ and H₂O; sufficient oxygen transport capacity to reduce the solid inventory in the reactors; high resistance to agglomeration, sintering, fragmentation and attrition; low cost and environmental friendliness [3]. At present, the OC is usually manufactured by pure chemicals whose cost is too high to be used in the large-scale CLC plants. Iron ore (e.g., hematite, ilmenite), which is inexpensive, abundant, environmental friendly, has been widely studied as OC in CLC [4–6], however it still exists several disadvantages, i.e., if Fe₂O₃ (the main component of iron ore) is only reduced to Fe₃O₄, its oxygen transport capacity will be lower; if the reduction phase contains FeO or Fe, thermodynamic limitation for FeO and Fe will prevent full conversion of CO and H₂ into CO₂ and H₂O [7,8]. Additionally, the reduction rate between iron ore and fuels is not rapid enough, which in return contributes to the increase of bed inventory. Thus it is necessary to improve the reactivity of iron ore through, e.g., doping with high-reactivity metal oxides (e.g., CuO [9,10], NiO [11]). However, the modified iron ore OCs were limited by complex preparation process and high price of the active metal. On the other side, in the case of CLC of coal, the char gasification is a rate-limiting step [12], resulting in a low CO₂ capture efficiency and coal combustion efficiency using iron ore as OCs. Therefore, accelerating the char gasification is important to fast and complete conversion of solid fuels in the FR. Some researches aimed to improve the char gasification rate through adding catalysts into OC. The catalysts are usually alkali metals or alkaline earth metals [13–15]. However, the loss of catalysts during the multiple redox process and the sintering/agglomeration of OC particles due to the low melting points of alkali components should be in particularly solved.

Copper ore, which is a respectively cheaper material compared with chemicals of active metal oxides, exhibits very high reactivity and oxygen uncoupling behavior (which is able to release gaseous O₂ in the oxygen-deficient FR to avoid the rate-limiting gasification step in the in-situ gasification CLC processes), which leads to higher overall reaction rate, higher carbon conversion, higher CO₂ capture and combustion efficiencies, and much less OC inventory and lower solid circulation rate. Furthermore, the reaction of copper ore and coal gasification products is exothermic (by the way, the reaction of iron ore and fuels is endothermic), which will helps to fulfill the heat balance over the system. However the copper ore is still more expensive than iron ore and copper materials have rather low melting points

(1083 °C for Cu, 1235 °C for Cu₂O and 1326 °C for CuO) [9,16], which is easy to sinter and agglomerate at high temperatures.

The mixtures of iron ore and copper ore as OCs may exhibit synergistic effects in improving reactivity of iron ore and resistance to sintering/agglomeration of copper ore. The synthetic mixed copper-iron oxides OCs have been studied by different researchers [9,17,18]. The mixed OCs showed favorable performance and synergistic effects. The objective of this study was to design a natural combined OC with optimized mixing ratio of iron ore and copper ore to attain high reactivity and stable reaction performance in CLC. The mixture of iron ore and copper ore was also expected to address cost and environmental concerns of OCs.

2. Experimental

2.1. Experimental material

In this work, the OCs were prepared from a hematite and a nature copper ore of China. In order to improve the mechanical strength, they were calcined at 500 °C for 5 h and then 1000 °C for 10 h in an air-atmosphere muffle oven. Finally, the ore particles after calcination were ground and sieved to 0.18–0.28 mm to obtain the fresh OC products. Based on the X-ray fluorescence (XRF, EDAX EAGLE III) measurement and X-ray diffraction (XRD, X' PertPRO) analysis, the chemical analysis of the two ores is shown in Table 1. The coal used in this work was GaoPing (GP) anthracite from China. The particle size of coal was in the range of 0.3–0.5 mm and the proximate and ultimate analyses of coals are shown in Table 2.

2.2. Experimental procedure and fluidized-bed reactor

At first, the copper ore and hematite were mixed with the mass ratio of 0/10, 1/9, 2/8, ..., 10/0 as the primary samples. The samples were labeled as Hem, 1Cu9Hem, 2Cu8Hem, ..., Cu-ore, respectively. Then, the isothermal redox experiments were conducted in a thermogravimetric analysis (WCT-1D, TGA) with these samples.

Table 1
Chemical analysis of the hematite and copper ore OC.

Hematite wt%		Copper ore wt%	
Fe ₂ O ₃	81.89	CuO	21.04
SiO ₂	8.42	CuFe ₂ O ₄	70.05
Al ₂ O ₃	8.37	SiO ₂	5.53
Others	1.32	Al ₂ O ₃	1.08
		Others	2.29

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