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Chemical looping with oxygen uncoupling of high-sulfur coal using copper ore as oxygen carrier

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Abstract

Chemical looping with oxygen uncoupling (CLOU) has been viewed as a promising candidate for solid fuel combustion with inherent CO_2 separation at considerably low energy penalty. This work aimed to investigate the sulfur evolution behavior and performance of copper ore oxygen carrier (OC) within the CLOU process using a typical high-sulfur content coal in Sichuan (SC), China as fuel. Experiments at different temperatures and oxygen to fuel ratios were conducted in a laboratory-scale fluidized bed reactor and comparisons have been made between SC coal and Gaoping (GP) anthracite with low sulfur content. It was found that both the increase of temperature and decrease of oxygen to fuel ratio can enhance the generation of sulfurous gases. There were two SO_2 peaks during the CLOU process of both SC and GP coals, due to the two relatively independent stages of coal combustion process: volatiles combustion and coal char combustion. The second peak was generally more sensitive to temperature, and a higher temperature would contribute to much more SO_2 generation. Cyclic redox experimental results of SC coal in fluidized bed reactor showed stable sulfur evolution trend and moderate reactivity of copper ore OC. Moreover, calcium oxide (CaO) was introduced as desulfurizing agent to remove the sulfurous gases generated in the CLOU process of SC coal and the desulfurization efficiency was achieved as high as 98%. XRD and XPS analyses showed that no metallic sulfide was detected on the surface of the reduced OC samples and ESEM images indicated that no serious sintering problem occurred to the used particles.

Keywords: Chemical looping with oxygen uncoupling (CLOU); Copper ore; High-sulfur coal; Sulfur evolution; Oxygen carrier

1. Introduction

Emission of CO_2 into the atmospheric environment has long been considered as the biggest contributor to the increasingly severe greenhouse effect [1]. Among possible candidates of the state of the art for carbon capture within fossil fuel combustion processes, chemical looping combustion (CLC) was proposed as a promising technique to inherently separate CO_2 at low energy penalty [2]. A CLC system generally consists of two reactors: air reactor (AR) and fuel reactor (FR), in which oxidation and reduction processes take place, respectively. A kind of solid particle, namely oxygen carrier (OC),

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travels to and fro between the AR and FR to provide active lattice oxygen needed for fuel conversion. The outlet gas of AR is mainly of O_2 depleted air; while FR theoretically contains only CO_2 and H_2O, so that high-purity CO_2 stream could be easily obtained after a simple moisture removal process. A variant of the CLC process, known as chemical looping with oxygen uncoupling (CLOU), was initially proposed by Mattisson et al. [3], which still retains the merits of the CLC technique. Distinctively, CLOU involves the use of a special OC which is able to release gaseous oxygen at the appropriate temperature window in FR. Consequently, much higher combustion efficiency and coal conversion rate could be acquired.

The appropriate OCs for CLOU should not only have the capability of releasing gaseous oxygen at suitable reaction conditions, but also exhibit stable physiochemical structure and good reactivity under severe cyclic redox processes. Among available or proposed oxygen carrier systems, i.e., Mn_2O_3/Mn_3O_4, Co_3O_4/CoO and CuO/Cu_2O, Cu-based OC is the most promising choice for the CLOU process of solid fuel and has been extensively studied in previous publications [4–11]. Several pairs of synthetic Cu-based OCs, like $CuO/CuAl_2O_4$, $CuO/MgAl_2O_4$, CuO/ZrO_2 and CuO/Al_2O_3 have been investigated in laboratory-scale fluidized bed reactors as well as continuously-operated pilot plants, which showed very good performance and were considered to be promising for adapting to CLOU process [5–7]. Conversion characteristic of coals with different ranks in CLOU process was evaluated in a 1.5 kW_{th} unit by the *C.S.I.C.* group [5]. Complete coal conversion to CO_2 and H_2O was achieved in all tests, while the CO_2 capture efficiency was significantly dependent on FR temperature and coal type. Afterwards, copper ore, as a kind of relatively cheap natural mineral, was proposed as an appropriate OC candidate for CLOU process [8–10,11]. Due to the complicated compositions, copper ore generally shows relatively poorer reactivity than synthetic Cu-based OCs. Nevertheless, combustion efficiency of higher than 96% was still achieved with GP coal as fuel [9]. To be noted, slight sintering and agglomeration phenomenon was observed for copper ore OC, especially when using lignite as fuel at elevated temperature [10]. To address the sintering problem of copper ore OC at high temperatures, Wen et al. [8] suggested a kind of copper ore with typically low CuO content (5.82 wt. %) as OC, while Tian et al. [10] proposed to add cement into copper ore and an optimum cement loading ratio of 20 wt.% was established.

Sulfur evolution within chemical looping process should be carefully addressed, which mainly affects the CLC system in two aspects. Firstly, OC contamination by forming metallic sulfides or sulfates, which will degrade the OC reactivity and make the OC more prone to sintering, since sulfides and sulfates generally exhibit relatively low melting point [12,13]. Secondly, sulfurous gases mixed in FR exhaust lowered the CO_2 capture efficiency and the existence of which is also unfavorable for subsequent CO_2 compression and purification [14]. Several studies have been carried out to investigate the sulfur fate in typical CLC process [15–20], mainly including thermodynamic calculation, effect of sulfur contained in gaseous fuel on OC reactivity and sulfur evolution during continuous operation. Generally, Cu-based materials are sulfur sensitive when H_2S concentration is high, while Fe-based OCs are highly sulfur resistant materials, even with gaseous fuel contained high concentration of H_2S [19]. However, up to now, investigations on sulfur evolution behavior during coal-derived CLOU process are quite few. Adanez-Rubio et al. [14] investigated the sulfur fate in a 1.5 kW_{th} CLOU unit using lignite as fuel and $CuO/MgAl_2O_4$ as OC. It was found that most of the sulfur content in coal released as SO_2 in FR and high carbon capture efficiency could still be obtained within the CLOU process.

The objective of this work was to evaluate the sulfur fate and performance of copper ore OC within CLOU process, using a typical high-sulfur content coal as fuel. Effects of temperature and oxygen to fuel ratio on sulfurous gases generation as well as OC reactivity were investigated in a laboratory-scale fluidized bed reactor. 5 cyclic redox experiments were performed to examine the sulfur evolution trend and copper ore OC performance under sulfurous gases-contained condition. Finally, calcium oxide (CaO) was introduced within the CLOU process of SC coal to evaluate its desulfurization efficiency.

2. Experimental

2.1. Copper ore OC and coal particles

A kind of refined copper ore from Zhongtiaoshan, China was used in this work, the same batch of which has been comprehensively tested in our previous works [9–11]. The ore was calcined in a muffle oven to totally eliminate the inherent sulfur content [21] and enhance its mechanical strength. Then it was crushed and sieved to the size range of 0.125–0.18 mm. As obtained from X-ray diffraction (XRD, X'Pert PRO) and X-ray fluorescence (XRF) spectrometry (EDAX EAGLE III) analyses, the ore after calcination contained 70.05 wt.% $CuFe_2O_4$, 21.04 wt.% CuO, 5.53 wt.% SiO_2, 2.29 wt. % $CaSO_4$ and 1.08 wt.% Al_2O_3 (See Table S1 and S2 in Supplemental Material (SM) for more details of the chemical and physical properties of the copper ore OC). Two typical Chinese coals, Sichuan (SC) coal and Gaoping (GP) coal, with nearly the same volatile and fixed carbon contents but obvious difference in sulfur content, were