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CuO supported on manganese ore as an oxygen carrier for chemical looping with oxygen uncoupling (CLOU)

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HIGHLIGHTS

- Oxygen was provided by $CuMn_2O_4$ and CuO in CLOU.
- Oxygen transport capacity of CMO, 3.31%, was obtained after 15 cycles.
- High conversion biochar and carbon capture efficiency were observed below 950 °C.
- CMO shows high reaction reactivity, mechanical strength and magnetic property.

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ABSTRACT

The chemical-looping with oxygen uncoupling (CLOU) is a promising technology that could be used for combustion of solid fuels with inherent separation of carbon dioxide. In this work, manganese ore supported CuO (CMO) oxygen carrier was synthesized. The oxygen transport capacity (*Ro*) and the reaction reactivity of CMO were investigated in TGA. The CLOU tests with biochar as fuel were performed. The reaction reactivity with biochar was enhanced due to the synergistic effect between manganese ore and CuO, and a value of *Ro*, 3.31%, was observed in TGA at 950 °C after 15 redox cycles. In fluidized bed tests, CMO shows excellent cycle performance; full conversions of biochar and the values closed to 100% carbon capture efficiency were obtained in the temperature range of 850–950 °C. However, obvious sintering of CMO was observed when the operating temperature reached 1,000 °C, which was further verified by the SEM, BET and PSD results. From XRD patterns, $CuMn_2O_4$, CuO, Fe_2O_3, and SiO_2 were detected in the fresh CMO sample. The presence of $CuMn_2O_4$ in fresh CMO sample indicated that manganese ore reacted with CuO during calcination. The $CuMnO_2$, Cu_2O and Mn_3O_4 observed in reduced CMO sample indicated that the gaseous oxygen was derived from CuO/Cu_2O and $CuMn_2O_4/CuMnO_2$ systems. The CMO was fully regenerated in air reactor after 10 cycles at 950 °C. In addition, CMO sample showed a higher crushing strength and magnetic property. These results indicated that CMO can be used as a good oxygen carrier candidate for CLOU below 950 °C.

1. Introduction

Carbon capture and storage (CCS) has been regarded as a widely deployed method to reduce CO_2 emissions. CCS consists of capturing CO_2, transporting it, and storing it away from the atmosphere [1]. However, traditional carbon-capture technologies, such as oxy-fuel combustion, pre-combustion and post-combustion, inevitably involve large-scale gas separation, which leads to a high economic cost and energy penalty [2]. Chemical looping combustion (CLC) is a promising technology for low-cost CO_2 capture [3]. In CLC, fuel combustion occurs in a fuel reactor (FR), whose oxygen is provided by an oxygen carrier (OC) instead of by air. The reduced OC in the FR is transferred to an air reactor (AR), where it is oxidized to its initial state. The OC is used to transport the oxygen from the air to the fuel. The fuel and air are never mixed in the CLC process, eliminating the need for gas separation. A high-purity CO_2 stream can be obtained by condensing the flue gas.

Substantial research efforts have focused on CLC with gaseous fuels, such as methane [4,5] and syngas [6,7]. In recent years, CLC with solid fuels has attracted much attention [8]. There are two ways to use solid fuels in a CLC process [3,9]. In the first way, solid fuels are gasified using pure oxygen as a gasifying agent, and then the gasification gas is introduced into the CLC system. The process has a high energy penalty due to the separation of oxygen from air. The second way is introducing

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solid fuels directly into the FR, where the devolatilization and in-situ gasification of solid fuels occur. The main limitation found in this technology is the slow gasification process [10–12]. Because of the slow gasification reaction rate, unreacted char was present in the FR. Thus, the use of a carbon separation system is necessary to avoid the CO_2 emissions in the AR [13]. This has further led to a rise in production the complexity of CLC process. Generally, to some extent, the development and application of CLC with solid fuels is restricted the slow gasification reaction rate.

In this context, chemical looping with oxygen uncoupling (CLOU) was proposed by Mattisson et al. [14]. CLOU requires a special OC to release gaseous oxygen (O_2) in the FR. Subsequently, the solid fuel reacts with the gaseous oxygen, and finally, the reduced OC is regenerated in the AR. Solid fuel is directly combusted during CLOU; hence, the gasification step is omitted and the reaction rates are enhanced. Compared with CLC, CLOU has a higher overall reaction rate, lower circulation rate, and much higher carbon conversion, CO_2 capture efficiency, and combustion efficiency.

OC is the backbone of the chemical looping processes. A perfect OC for chemical looping processes should be environmentally friendly and should have high oxygen transport capacity, high reactivity, thermal stability, and low production costs [3]. The primary OCs that can be used in CLOU including Cu- [15], Mn- [16], Co- [17] and perovskite-based materials [18]. Co-based materials have a low operating temperature and health concerns; perovskite-based materials have low oxygen-carrying capacity; Mn-based oxygen carriers show low fuel conversion and oxidation rates. Although Cu-based OCs tend to sinter and agglomerate, Cu-based materials have been widely studied in the CLOU process, owing to their high oxygen-carrying capacity and excellent thermodynamic characteristics. Various inert support materials, such as Al_2O_3 [19], $CuAl_2O_4$ [20], $MgAl_2O_4$ [21], SiO_2 [22] and ZrO_2 [23,24], have been tested to enhance the performance of Cu-based OCs.

In recent years, natural minerals, such as olivine [25], copper ore [26], and iron ore [27], have been used as active supports or OCs in the chemical looping process. Generally, natural minerals have advantage of abundance and low cost, moreover, some can be used in chemical looping processes due to their specific properties. For example, olivine has been used in biomass chemical looping processes on account of good catalytic activity for biomass gasification, while copper ore and iron ore can provide a certain amount of oxygen for chemical looping processes. Like copper ore and iron ore, the use of manganese ore as an OC in chemical looping processes was investigated [28–30], and the oxygen-uncoupling property of manganese ore was reported [31]. However, relatively few studies have been devoted to the use of manganese ore as an active supporting material in CLOU.

In this study, CuO supported on calcined manganese ore was evaluated in CLOU. The reaction reactivity and oxygen transport capacity of the OC were investigated by thermogravimetric analysis (TGA). The CLOU experiments were conducted in a fluidized-bed reactor using biochar as fuel. The carbon conversion (χ_c), carbon capture efficiency (η_c) and gas products were measured. The cyclic tests of OCs with biochar were further examined. Finally, physical properties of OC samples were characterized using various techniques.

2. Experimental

2.1. Solid fuel

The fuel used in this work was biochar. This was obtained from Wuhan United Venture Reproducible Energy Co., Ltd. in Wuhan City, Hubei Province, China. The biochar particle size used in this study was 70–150 μm. Ultimate and proximate analyses of the biochar are shown in Table 1.

Table 1
Properties of biochar sample.

Ultimate analysis (dry basis, wt%)					Proximate analysis (dry basis wt%)		
H	C	N	S	O[a]	Ash	Fixed Carbon	Volatile
0.51	76.6	2.56	0.08	6.23	14.02	80.50	5.48

[a] By difference.

2.2. Preparation of the oxygen carrier

Natural manganese ore was supplied by Lei yang Daji Manganese Industry Co., Ltd. in Changsha City, Hunan Province, China. The natural manganese ore was crushed and then calcined at 1,000 °C for 6 h. The resulting sample was cooled and sieved to 75–430 μm. An X-ray fluorescence (XRF) microprobe apparatus (EAGLE III, EDAX Inc.) was used to obtain the chemical composition of calcined manganese ore (MO) sample. The MO was mainly composed of 51.73 wt% SiO_2, 35.24 wt% Mn_2O_3, 9.71 wt% Fe_2O_3, 2.15 wt% K_2O, 0.38 wt% TiO_2, and 0.79 wt% Al_2O_3, as shown in Table 2.

CuO/manganese ore (CMO) with a mass fraction of 30 wt% CuO was synthesized by the impregnation method as follows. First, $Cu(NO_3)_2\ 3H_2O$ and MO were accurately weighed with a mass ratio of $Cu(NO_3)_2\ 3H_2O$/MO of 1.30. Next, $Cu(NO_3)_2\ 3H_2O$ (reagent grade) was dissolved in a small volume of deionized water to obtain a nitrate aqueous solution, which was then transferred to a beaker containing MO powder. The mixture was stirred slowly at 80 °C for 10 h in a magnetic stirrer, dried at 105 °C for 48 h in a drying oven, and calcined at 950 °C for 6 h in a muffle furnace. Finally, the CMO sample was cooled to room temperature, crushed, and sieved into particles with a size range of 75–430 μm for use.

2.3. Thermogravimetric analyzer (TGA) tests

2.3.1. Reactivity with biochar

The reaction reactivity of CMO and biochar was investigated in a TGA (SDT Q600, TA Instruments). MO and CuO/SiO_2 (CSO) samples were used as comparisons in the tests. The CSO was obtained by supporting CuO on SiO_2 powder using the same preparation method. In each run, biochar powder and OCs were mixed thoroughly in a mortar at a mass ratio of 1:10. Mixture samples of 10–15 mg were added to a ceramic crucible and heated from room temperature to 950 °C at a heating rate of 30 °C/min in the presence of nitrogen (80 ml/min). They were maintained at 950 °C for 20 min.

2.3.2. Oxygen transport capacity (Ro) in CLOU

The *Ro* of CMO was measured using the TGA. The experimental procedures are as follows. A CMO sample (about 15 mg) was placed in a ceramic crucible and heated from room temperature to 950 °C at 30 °C/min in air (consisting of 20.8% O_2 in N_2). At the same time, the carrier gas was switched to nitrogen and kept for 60 min. Subsequently, air was introduced in the reactor to regenerate the OC for 45 min. The flow rates for air and nitrogen were controlled at 80 ml/min. A total of 15 redox cycles were performed.

2.4. Fluidized-bed tests

CLOU experiments were conducted in a laboratory-scale fluidized-

Table 2
Chemical analysis of the calcined manganese ores.

Oxide	Al_2O_3	SiO_2	K_2O	TiO_2	Mn_2O_3	Fe_2O_3
Wt%	0.79	51.73	2.15	0.38	35.24	9.71