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Bauxite-modified oxygen carrier for chemical looping combustion: A possible solution to the heat of combustion compensation

Liang Kong[a], *Jinhua Bao*[a], *Liangyong Chen*[a], *Zhen Fan*[a], *Wei Li*[a], *Heather Nikolic*[a], *Kunlei Liu*[a,b,*]

[a] *Center for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington, KY 40511, United States*
[b] *Department of Mechanical Engineering, University of Kentucky, Lexington, KY 40506, United States*

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ABSTRACT

CuO was induced into red mud oxygen carrier materials to balance the temperature difference between the fuel and air reactors in chemical looping combustion. Considering the lower melting point of CuO, surface sintering and agglomeration might be inevitable, and only a low loading was applied in this work. The addition of CuO did not lower the overall redox activity, as demonstrated by both thermogravimetric analysis (TGA) and a bench-scale fluidized bed reactor. Instead, the oxygen transfer capacity was improved. A variety of characterization techniques were used to compare the crystal structure, surface morphology and physical properties before and after long-term reactions. The present results provide a potential strategy for the design and development of oxygen carriers with high stability and reactivity that maintain a lower required circulation rate.

1. Introduction

Chemical looping combustion (CLC) has been considered a promising transformative technology to *in-situ* concentrate CO_2 during fossil fuel conversion due to its low energy penalty and fuel flexibility (Chen et al., 2015; Naqvi et al., 2007; Noorman et al., 2010). With two interconnected but separate reactors, solid oxygen carriers transfer oxygen from the air to the fuel reactor, and direct contact between fuels and air can be avoided; more importantly, power and intermediate syngas for chemical fuels will be simultaneously generated (Siriwardane et al., 2013; Xu et al., 2015; Chen et al., 2017). However, apart from the oxygen carrier selection, one major challenge is the temperature difference between the air and fuel reactors, which results in a shorter contact time between the oxygen carriers and fuels, leading to a lower fuel conversion rate and a higher circulation rate, ultimately necessitating a large oxygen carrier inventory and further increasing the expense of CLC.

During the circulation process of oxygen carriers, heat will be carried along with lattice oxygen transfer, combusted in the air reactor and then recharged in the fuel reactor. Because of the difference between coupled oxygen carrier and fuels, the redox reactions in the fuel and air reactors are heat unbalanced under most circumstances. Therefore, the heat of combustion for fuels and oxygen carriers has become the most important factor in the overall efficiency of chemical looping reactions. In terms of the properties for oxygen carrier materials, we must consider not only their high reactivity during redox reactions, long-term stability, oxygen cyclic capacity, and resistance to attrition and sintering, but also the heat of combustion (Adanez et al., 2012; Sim et al., 2012). Conventional lab-scale fabricated metal oxides including Fe-, Ni-, and Ca-based materials have been thoroughly investigated; nevertheless, contamination by coal ash and the inevitable loss of oxygen carrier during the separation process of ash removal will necessitate continuous make-up of fresh oxygen carrier and greatly increase the cost. Copper-based oxygen carrier materials have emerged as promis-

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[*] *Corresponding author at*: Center for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington, KY 40511, United States.

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ing candidates for chemical looping combustion. CuO oxygen carriers have high oxygen capacity and reactivity, but their mechanical properties tend to seriously degrade after multi-cycle tests due to surface agglomeration, which is ascribed to the relatively lower melting point of copper-containing compounds (Arjmand et al., 2011; Cho et al., 2004). So far, several support materials including ZrO_2, $MgAl_2O_4$, Al_2O_3 and SiO_2 have been utilized to enhance the stability of CuO oxygen carriers (Imtiaz et al., 2014; Wang et al., 2014, 2013; Chuang et al., 2008; Corbella et al., 2006). However, the deposition of CuO onto natural ore has rarely been reported.

The natural ore and materials obtained from chemical waste are of great potential for oxygen carriers due to their cost efficiency. Red mud, being an Fe-based bauxite coproduct of alumina production, has major components of Fe_2O_3, Al_2O_3, SiO_2 and TiO_2 and has been demonstrated as an effective oxygen carrier under both simulated and fluidized bed reactor conditions (Chen et al., 2015, 2014). Considering the introduction of CuO into the oxygen carrier particles will bring up the overall expenses and more importantly, the relatively lower melting point of CuO itself may contribute to undesired agglomeration, a mere 5 wt% CuO was introduced into red mud, with the expectation of balancing the heat difference between the two reactors, in order to avoid substantial amounts of heat transport and the correspondingly high solid circulation rates of the oxygen carrier particles.

In this work, a low amount of CuO was loaded on the surface of red mud oxygen carriers, and the overall performance was evaluated and compared to verify the influence of the CuO. Characterization techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM) and TGA were utilized to compare the overall performance of the CuO-loaded red mud oxygen carriers.

2. Experimental

2.1. *Oxygen carriers*

Red mud oxygen carriers with 5 wt% CuO loading were fabricated *via* a surface immersion method. Fe-based natural red mud was supplied by Alcoa World Alumina LLC and sieved to the size range between 125 and 355 μm. A stoichiometric amount of $Cu(NO_3)_2 \cdot 5H_2O$ (≥98%, Sigma–Aldrich) was added into the suspension of red mud and deionized water at room temperature under magnetic stirring for 24 h to obtain homogeneity. The slurry was dried in a vacuum freeze dryer followed by calcination at a temperature of 1150 °C for 6 h. The as-calcined samples were sieved, and the particles in the size range from 125 to 355 μm were collected. Pristine red mud oxygen carriers with the same size range were used for comparison.

2.2. *Apparatus*

Coal char derived from Power River Basin (PRB) coal was used as the solid fuel in this work (Bao et al., 2016). To obtain the char, 500 g coal particles were placed in a bench-scale fixed bed reactor at a temperature of 800 °C with a heating rate of 20 °C/min in a N_2 stream of 1.5 L/min (STP). The as-produced coal char with particle size of 125–355 μm was selected for further testing, and the proximate and ultimate analyses results are shown in Table 1.

A laboratory-scale fluidized bed reactor (310 stainless steel, inner diameter of 43 mm and height of 750 mm) was used to evaluate the reactions between coal chars and oxygen carriers. The schematic diagram is shown in Fig. S1. A micro-porous plate was placed 200 mm above the bottom of the reactor and used as a sample holder and gas distributor. The reactor was equipped with temperature control by a K-type thermocouple and a pressure transducer to measure the pressure drop across the gas distributor and fluidized bed materials. The gas feeding system allowed the feed of N_2, air and steam at desired flow rates by using mass flow controllers (MFC, Aeolos QMS403) and a steam generator. A dual piston pump (P-1100, Chrom Tech. Inc.) was used to feed an accurate volume of deionized water to the steam generator, where the feed water was vaporized, and the mixture of feeding gases was preheated to 600 °C before being introduced into the reactor. The feeding of coal char was accomplished with a tube inserted from the top of the reactor. The exit gas passed through a cyclone, high-temperature filter, cooler, and moisture trap in sequence to remove the fine particles and water condensate. A multi-gas analyzer (Rosemount, X-Stream serial) equipped with various channels for the concentration of O_2, CH_4, CO, CO_2 and H_2 continuously measured the exhaust gas composition, and all signals were recorded in the data acquisition system. 150 g of oxygen carriers in the size of 125–355 μm mixed with 100 g fused Al_2O_3 particles (Alfa Aesar) of the same size range were used as bed materials. A constant gas flow rate of 3.0 L/min (STP) of 50% steam and 50% N_2 was applied, the superficial velocity in the reactor, U_0 is about 3.8 times the minimum fluidizing velocity (U_{mf}) of the oxygen carrier particles at 950 °C. When the bed temperature was stabilized, 1.0 g of PRB coal char was introduced to the reactor to initiate the reaction. At the end of the reaction, a combustion step was performed to burn out the unreacted char and to regenerate the oxygen carriers using 2.0 L/min air flow. Stability tests were performed under alternating reduction and oxidation conditions with a 5 min N_2 purge at the interval of every reduction and oxidation process for 65 cycles per sample.

A thermogravimetric analysis (TGA, Netzsch STA 449F3) was used to investigate the reactivity and stability with gaseous fuel. 500 mg oxygen carrier in the size range of 125–355 μm was loaded in a 5 mL alumina crucible. The reaction temperature was maintained at 950 °C with a heating ramp of 20 °C/min, to ensure the complete oxidation of the oxygen carrier before reduction, 20 vol% O_2 balanced by Ar with a total gas flow rate controlled at 200 mL/min (STP) was introduced into the TGA chamber. 20 vol% CO balanced with argon was introduced into the TGA chamber as a reductant after complete oxidation followed by 5 min of Ar purging. The reduction and oxidation proceeded for 30 min each cycle. Attrition tests were performed using a quartz tube (44 mm inner diameter and 533 mm length) as a fluidizing reactor at 950 °C with an air flow rate of 1.5 L/min. The attrition rate (I_{attr}) is defined as: $I_{attr}=m_1/(m_0 \times t)$, where m_1 and m_0 represent the mass of the fine particles (<125 μm) and the initial mass of the sample in the range of 125–355 μm, respectively; t is the reaction time (h).

Table 1 – Proximate and ultimate analyses of Power River Basin coal char.

Proximate analysis (%)				Ultimate analysis (%)					Heating value
Fixed carbon	Volatile matter	Moisture	Ash	C	H	O	N	S	(MJ/kg)
38.09	33.58	23.74	4.59	55	6.47	33.2	0.56	0.18	21.49

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