Experimental study of copper modified manganese ores as oxygen carriers in a dual fluidized bed reactor

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HIGHLIGHTS

- Reactivity of manganese ore was significantly improved by impregnating copper.
- Two 88 h continuous run were performed using both oxygen carriers.
- Attrition data was obtained for both materials based on long operations.

ARTICLE INFO

ABSTRACT

Chemical-looping combustion (CLC) is a developing CO_2 capture technology. CLC makes use of the repeated oxidation/reduction reactions of metal oxide (oxygen carrier, OC) to separate CO_2 from fuel combustion and to obtain a pure CO_2 stream suitable for compression and storage. Low cost materials, such as natural ores, are required for coal-fueled CLC because the lifetime of the oxygen carrier (OC) is lowered by side reactions with the fuel ash or carryover losses. In this study, five manganese ores were examined as oxygen carriers using CO as the fuel gas in a laboratory batch fluidized bed reactor. All five of the ores were impregnated by copper nitrate solution to evaluate the reactivity enhancement of copper impregnation. The period with full CO conversion can be enhanced 2–100 times for different ores in the single fluidized bed test, which indicated that the Cu impregnation may be a general method to enhance the reactivity of manganese ores. Finally, one manganese ore and the corresponding Cu-modified particles were tested in a dual fluidized bed reactor. The attrition rates of both materials were measured as 0.13 wt.%/h during the 88 h operation in the dual fluidized bed. Both the manganese ore and the Cu-impregnated ore exhibited stable and high reactivity during the continuous test in the dual fluidized bed reactor, even at a low temperature (∼310 °C). Copper impregnation had no obvious influence on the attrition property of the manganese ore.

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1. Introduction

Chemical looping combustion (CLC) is a promising technology for inherent CO_2 separation at a low cost [1]. CLC generally consists of two reaction steps: reduction and oxidation. During the reduction step, the fuel is oxidized by the oxygen provided by the reduction of a solid oxygen carrier, typically a metal oxide. In the oxidation step, the reduced oxygen carrier is re-oxidized by air. These two steps are commonly performed in two separate reactors: the fuel reactor and the air reactor, respectively. Both reactors are connected by a circulating stream of solid oxygen carrier. The gases from both reactors never mix, and a stream of H_2O and CO_2 is obtained at the outlet of the fuel reactor, which stays separated from the air nitrogen.

The principle of using a solid oxygen carrier material to provide oxygen for thermochemical fuel conversion was proposed in the 1940s [2] to reform methane. The idea of CLC was patented as a process for CO_2 production from carbonaceous sources in the 1950s [3]. The same principle was proposed during the 1980s with the goal to lower the irreversibility of combustion [4,5]. With the increasing recognition of anthropogenic climate change, the concept was investigated to recover CO_2 from the exhaust of combustion systems for power generation [6,7]. Since then, obtaining CO_2 capture with a low energy penalty for the power sector has been the main driving force for CLC research.

Gaseous fuels [8–10], such as natural gas or syngas, and solid fuels [11–17], such as coal or biomass, have been widely

investigated in the literature as possible fuels for CLC. The application of gaseous fuels is less problematic, whereas for solid fuels, losses of oxygen carriers due to possible side reaction with ash and impurities in the gas stream [18], as well as material withdrawn from the reactor with the ash, may lead to high expected amounts of oxygen carrier makeup [17]. This increases the demand for abundant, low cost and environmental friendly oxygen carrier materials [13]. Possible materials under investigation include natural ores [19–23] and industrial residues or by-products [24–27]. Among the natural ores, ilmenite has been most widely investigated [20,28–31]. Most recently, Arjmand et al. [12,32] investigated several manganese ores as oxygen carriers for CLC, and these manganese ores showed better reactivity than ilmenite. This suggests that manganese ore could be a better choice than ilmenite as an oxygen carrier.

It is generally accepted that low cost oxygen carriers, as mentioned above, tend to have lower conversion rates. Low reactivity of the oxygen carrier directly leads to an increase of the required solids inventory [33]. This in turn leads to a larger pressure drop within the reactor and inevitably to increased power consumption to maintain the solid fluidization [34]. Therefore, it is important to search for oxygen carriers with high reactivity or for methods allowing increased reactivity of the existing low cost oxygen carriers.

Previous research has found that the reactivity of manganese ore can be enhanced by introducing a very small amount of copper ions [35]. The redox stability of the Cu-modified manganese ore and the effects of the loading amount on the reduction reactivity of Cu-modified manganese ore were investigated in a single fluidized bed reactor [35]. However, the more practical use of the oxygen carrier is in a dual fluidized bed reactor in continuous operation. Additionally, more knowledge about the copper impregnation method for improving the manganese ore reactivity would be useful.

Accordingly, in this study, five manganese ores were impregnated by copper nitrite solution to examine the effect of the impregnating copper on different manganese ores. Furthermore, both the manganese ore and the Cu-modified manganese ore were evaluated in a dual fluidized bed reactor to examine the long-term chemical stability and attrition properties of the oxygen carriers.

2. Experimental details

2.1. Preparation of oxygen carriers

The five natural manganese ores (designated as Mn1–Mn5) were provided by Mugui Manganese Ore Company from Guangxi Province in China. The ores were first crushed and then calcined in a muffle oven for 4 h at 950 °C and sieved to 125–300 μm. The Cu-modified manganese ores (designated as Mn1Cu2%–Mn5Cu2%) were prepared by impregnation of copper nitrate solution. For every 50 g of manganese ore, solid $Cu(NO_3)_2 \cdot 3H_2O$ (3.8 g) was used as a precursors and was dissolved in water (15 ml) to give the solution. The ore particles were soaked in the solution for 6 h at ambient temperature and were then calcined in air for 2 h at 500 °C. After cooling, all of the particles were sieved to 125–300 μm. The

mass ratio of the copper ion to manganese ore was 2 wt.% and was controlled during preparation.

2.2. Characterization of oxygen carriers

The composition of the manganese ore was analyzed by X-ray fluorescence (XRF), and the results are summarized in Table 1. The corresponding mass fraction of single chemical element can be calculated based on the molecular formula. For example, the mass fraction of Mn can be calculated as 40.45%/71*55 = 31.33%. The BET (Brunauer, Emmett and Teller) surface area and BJH (Barrett, Joyner and Halenda) pore volume of the particles were measured with a Micromeritics micropore analyzer (Autosorb-iQ2-MP, NOVA4000). The crushing strength for all particles was determined using an HP-10 digital force gauge. The value given is the average force in N from 30 individual measurements needed to crush a particle in the size fraction of 125–300 μm. The size distribution was measured by a laser particle size analyzer (Mastersizer 2000). The particles were observed under a scanning electron microscope (SEM, JSM-7001F). The bulk density, BET surface area, BJH pore volume and crushing strength of the particles are listed in Table 2.

2.3. Test of OC in the single fluidized bed reactor

All oxygen carriers were tested in a single fluidized bed. The reactor was made of quartz tube (i.d. 30 mm) and was heated by an electric furnace. The bed material for all the tests was ∼30 g with a size of 125–300 μm placed on the porous distributor. The flow rates of the fluidizing gases for both reduction and oxidation were 2 L/min (STP). Both the reduction and oxidation temperature were 800 °C for the redox cycles. The gas velocity was 0.17 m/s at 800 °C, and the fluidization number U/U_{mf} was 3.3, where U_{mf} was calculated on the basis of the relations by Kunii and Levenspiel [36] with the mean radius of the particle as 212.5 μm. For each test, the bed material was first heated to 800 °C in 10 vol% O_2 (90 vol% N_2). Then, the reducing gas was introduced. The reducing agent was 10 vol% CO (90 vol% N_2). The oxidizing agent was 10 vol% O_2 (N_2 90 vol%). Inert gas (N_2) was introduced between the reduction and the oxidation period. The product gases were introduced into the gas analyzer after passing through a filter.

2.4. Test of OC in the dual fluidized bed reactor

The continuous test was performed in a dual fluidized bed reactor, as illustrated in Fig. 1. The system consisted of an air reactor (AR), a fuel reactor (FR), a riser, a cyclone and two loop seals (LS). The riser was used to transport oxygen carriers from the air reactor to the fuel reactor. The solid circulation rate was controlled by the lower loop seal. The fuel reactor was a bubbling fluidized bed with a length of 1.3 m. The inner diameters of both the air reactor and the fuel reactor were 50 mm. The inner diameter of the riser was 20 mm. The height of the riser was 3.3 m. The secondary air was introduced at the lower part of the riser to assist particle entrainment. The air and fuel reactors were heated by electric furnaces. K-type thermocouples were inserted into the reactor to monitor the

Table 1
Chemical analysis of the manganese ores.

wt.%	MnO	Fe₂O₃	SiO₂	Al₂O₃	BaO	K₂O	P₂O₅	TiO₂	MgO	CaO
Mn1	40.45	7.36	44.09	1.68	4.71	0.23	0.44	–	0.18	0.36
Mn2	54.13	24.71	10.54	7.80	0.09	1.45	–	0.30	0.46	0.21
Mn3	73.37	10.23	7.12	4.01	0.65	0.58	0.22	0.27	0.31	1.61
Mn4	39.41	11.24	32.94	13.09	0.24	1.33	0.29	0.56	0.20	0.22
Mn5	64.75	16.53	5.82	2.33	0.50	0.90	0.06	8.50	0.13	0.07