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Preparation and chemical looping combustion properties of Fe_2O_3/Al_2O_3 derived from metallurgy iron-bearing dust

Zhi-Fang Gao[a,*], Zhao-Jin Wu[b], Wei-Ming Liu[b]

[a] *School of Metallurgy and Resource, Anhui University of Technology, Maanshan 243002, China*
[b] *Key Laboratory of Metallurgical Emission Reduction & Resources Recycling, Ministry of Education, Anhui University of Technology, Maanshan 243002, China*

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ABSTRACT

The Fe_2O_3/Al_2O_3 is prepared from metallurgy iron-bearing dust in the present work, and its feasibility as an oxygen carrier (OC) for chemical looping combustion (CLC) is evaluated by using XRD, SEM-EDX, TGA and others. Experimental results show that the mass percentage of Fe_2O_3 and Al_2O_3 is 86.97% and 4.92%, respectively in the obtained Fe_2O_3/Al_2O_3 sample with specific surface areas of 9.06 cm^2/g. The reaction ratio of the Fe_2O_3/Al_2O_3 reacting with pulverized coal is 44.56% in the first combustion cycle and 24.37% in the fifth cycle, which is similar to that of traditional Fe_2O_3/Al_2O_3 OC. The reason of such a decrease is discussed by means of the thermodynamic phase diagram and ascribed to the increasing agglomeration and sintering of coal ash and Fe_2O_3/Al_2O_3 particles during cycles. The results indicate that the Fe_2O_3/Al_2O_3 material derived from metallurgy iron-bearing dust is a highly reactive and competitive OC for CLC process.

1. Introduction

Recently, the view of strong greenhouse gas effect significantly contributing to the global warming is widely accepted [1,2]. Therefore, reducing the emission of CO_2 becomes the worldwide concern, and many techniques have been investigated to capture CO_2 prior to emission into the environment [3–5]. With the rapid development of social economy, China's CO_2 emission and energy consumption have been increasing dramatically and are now the highest in the world [6,7], which has put great pressure on the environment. Thermal power generation sector is the critical consumer of fuel energy and also the greatest emitter of CO_2 among all the industries [8]. Although the government has been encouraging some optimization of the form of electricity generation by reducing the share of coal-fired power to reduce carbon emissions, the thermal power has always been predominant in China's power industry. Undoubtedly, it is worth studying the new technology of capture CO_2 generated from power industry [9].

Chemical looping combustion (CLC) is a novel, lower energy consumable and efficient combustion technology for CO_2 capture because CO_2 is inherently separated from the other flue gas components (such as N_2 and unused O_2), and thus no gas separation equipment is needed and no energy is expended for the gas separation. So it has recently become an active topic [10,11]. Oxygen carrier (OC) is the important criteria material which is high reactivity and ability to convert the fuel fully to CO_2 and H_2O, low fragmentation, attrition and agglomeration, low cost, risk for health and environment and sufficient oxygen transfer capacity in CLC process [12]. Therefore, most researches of OC are focused on Fe-based OC, including synthetic materials, natural iron ores and industry byproducts [13–16]. Unfortunately, these Fe-based oxygen carriers exhibited a relatively poor performance during CLC process, i.e., low efficiency and high agglomeration in coal conversion or gas conversion [17].

Recently, some researchers found that Fe_2O_3/Al_2O_3 OC exhibits high oxygen transfer capacity and reduction rate because of the introduction of Al_2O_3 [18,19]. Meanwhile, it delivers a good reactivity and less secondary pollution in cycle processing, so that it becomes a hotspot in the research of metal oxides [20]. The researches of Fe_2O_3/Al_2O_3 OC are commonly focused on two ways. One way is to use directly raw resource (such as iron ore or bauxite) for cycle combustion. For example, Gu et al. [21] applied natural iron ore as OC directly in the coal combustion and found that the transfer capacity and conversion rates were low when coal react with the natural iron ore OC, but Mendiara et al. [22] used higher aluminum-containing ore as an oxygen carrier and found that it had a high reactivity and conversion rate. Another way is to develop a combined Fe_2O_3/Al_2O_3 OC from chemical reagents, and the results showed that the synthesis of Fe_2O_3/Al_2O_3 OC has good reactivity and resistance [23]. For example, Wang et al. [24] has

* Corresponding author. Fax: +86 5552311571.
E-mail address: cancan20071007@163.com (Z.-F. Gao).

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Table 1
Chemical composition of the metallurgy iron-bearing dust.

Composition	TFe	CaO	MgO	Al_2O_3	SiO_2	S	P	C	Zn	Pb	Others
Content (wt%)	38.57	4.12	3.78	6.54	10.17	0.33	0.08	24.33	2.17	1.00	8.91

investigated the activity of Fe_2O_3-based oxygen carrier after the introduction of Al_2O_3 and reported its conversion rate of 24.9%. He et al. [25] has studied the Fe_2O_3/Al_2O_3 OC prepared by sol-gel route and methane cycle response characteristics, and proved that Fe_2O_3/Al_2O_3 OC was feasible for chemical looping combustion technology. Guo et al. prepared and characterized Fe_2O_3/Al_2O_3 OC by solution combustion, and indicated that Fe_2O_3/Al_2O_3 OC has good resistance sintering capacity and activity after 5 cycles of combustion test. As an inert carrier, Al_2O_3 can improve the adsorption properties of OC surface lattice oxygen and desorption of oxygen capacity, reduce OC particle sintering in the process of oxidative regeneration [26]. However, the reactivity of Fe_2O_3/Al_2O_3 synthesized by the sol-gel route is superior to natural ore, so the commercialization of Fe_2O_3/Al_2O_3 OC from chemicals has a certain economic cost. In order to achieve the purpose of high value-added utilization of wastes, it is significant to explore some new strategies for using more cheaper raw material or even solid waste to prepare Fe_2O_3/Al_2O_3 OC.

Metallurgy iron-bearing dust, containing 30–80% Fe, 5–10% Al and a variety of trace transition metals (Zn, Mn, Ni, Mo, V, and Cr, etc.), are valuable metallurgical secondary resources. Improper disposal of the dust not only produces a waste of valuable secondary resources, but also causes serious environmental pollution [27]. At present, the most use of metallurgical dust is returned to steel production for Fe recovery [28]. In addition, extraction of some single valuable elements as well as building materials doped application are used in other areas. Meanwhile, it was found that a large number of metallurgy dust containing iron oxidation are the components for preparing Fe_2O_3/Al_2O_3 OC with relief sintered body [29–31]. If the appropriate methods is used to prepare Fe_2O_3/Al_2O_3 OC from metallurgy iron-bearing dust instead of chemical reagents, a variety of components in metallurgy dust are not only taken full advantage, but also used to prepare the synergetic Fe_2O_3/Al_2O_3 OC with better combustion characteristics. In addition, the studies of Fe_2O_3/Al_2O_3 OC prepared by the complex system of solid waste are generally scarce [32,33]. However, the question is how to simultaneously recover some wanted amount of Fe and Al from the dust, excluding the undesired elements in the meantime, to prepare Fe_2O_3/Al_2O_3 OC?

In this study, the metallurgy iron-bearing dust is used to prepare Fe_2O_3/Al_2O_3 OC by co-precipitation, and the samples were characterized by XRD, SEM-EDS and TG-MS. The reactivity and mechanism of the dust-derived Fe_2O_3/Al_2O_3 OC were discussed with the aid of Factsage thermodynamic software. The aim of the current study is to investigate the reduction and oxidation reactivity of the dust-derived Fe_2O_3/Al_2O_3 in CLC process.

2. Experimental

2.1. Materials

In this study, the metallurgy iron-bearing dust and coal was obtained from Ma'anshan Iron & Steel Company Limited of China and Shanxi province, respectively. The chemical compositions and densities of the metallurgy iron-bearing dust are listed in Table 1. The Industrial, ultimate and ash analysis of coals are given in Table 2. Based on the characteristics of the raw materials shown in Table 1, the metallurgy iron-bearing dust has an average particle size of 17.93 μm, a specific surface area of 13.38 m^2/g, 38.57 wt% TFe(the total amount of Fe, Fe_2O_3, Fe_3O_4), 6.54 wt% Al_2O_3, and the other components. SiO_2 is abundant in the dust, which can be separated by co-precipitation method. Table 2 shows the 85.58 wt % fixed carbon in the coal which can meet the minimum requirements for chemical looping combustion. While the ash in the coal includes SiO_2 and Al_2O_3, and more SiO_2 particles have certain effects on the properties of OC in CLC process.

Based on XRD analysis results, the main mineral components of the metallurgy iron-bearing dust are hematite (Fe_2O_3), coke (C), fayalite ($2FeO{\cdot}SiO_2$), $MgO{\cdot}SiO_2$, $FeO_2Al_4Si_5O_{18}$ and others.

2.2. Methods

2.2.1. Preparation of Fe_2O_3/Al_2O_3 OC

The preparation of Fe_2O_3/Al_2O_3 OC was conducted under the following conditions. The metallurgy iron-bearing dust samples (100 g) were milled to 200 mesh, which were put into 100 mL hydrochloric acid solution rising to 80 °C and the undissolved precipitate were removed by filter. 80 °C sulfuric acid solution was added to the above solution, while the distilled water was added to keep the solution constant in volume, and the reaction completed after 2 h. After filtering and washing the filter cake, the solution was added hydrogen peroxide and heated to 70 °C, regulating its pH value to 4 by dropping ammonia solution, and the solvent evaporated and the solute deposited. After filtering, the filter cake (the precursor of Fe_2O_3/Al_2O_3 OC) was washed several times and heated in a muffle burner to 900 °C at 20 °C/min and holding for 1 h to ensure the production of Fe_2O_3/Al_2O_3 OC [23]. The temperatures selected in each experimental stage were based on the previous text conditions researched by authors.

2.2.2. Oxygen excess number Φ

The OC is very important to operate the CLC system economically. According to the industrial and ultimate analysis

Table 2
Industrial, ultimate and ash analysis of the coals (%, ω).

Industrial analysis	Mt	A_{td}	S_{td}	V_{td}	V_{daf}	FC_{daf}	Caloric value (MJ/kg)
	8.77	7.48	1.67	33.19	36.03	58.94	31.56

Ultimate analysis	C_{daf}	H_{daf}	O_{daf}	N_{daf}	S_{td}	C/H	C/O
	85.58	3.88	5.34	1.46	0.37	21.19	14.72

Ash analysis	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	SO_3	Others
	42.27	0.84	25.34	11.43	1.13	5.88	0.38	0.705	4.89	4.20

Note: Mt, A, daf is denoted total moisture of coal, ash of coal, and dry basis, respectively.