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Development of stabilized Ca-based CO_2 sorbents supported by fly ash

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HIGHLIGHTS

- Fly ash stabilized calcium based sorbents were developed for CO_2 capture.
- High CO_2 capture performance is achieved by the fly ash modified sorbents.
- Formation of $Ca_3Al_2O_6$ and $CaAl_2O_4$ accounts for the slow decay of CO_2 capture capacity.
- Detailed mechanism of the utilization of fly ash in sorbents modification is presented.

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ABSTRACT

The rapid decay of CO_2 capture capacity during the calcination/carbonation cycles is one major problem of the calcium looping technology. To improve and maintain excellent CO_2 capture performance of sorbents is of significance, especially in an environmental friendly and cost effective way. Using fly ash, the solid waste captured by collectors from coal combustion systems to modify calcium based sorbents is a potential application to enhance CO_2 capture capacity. Sorbents modified with fly ash presented great reactivity and achieved enhancement in CO_2 capture capacity. After 15 cycles, the modified sorbents achieved a CO_2 capture capacity of 0.27 g CO_2/g sorbent, 5 times as high as that of the original sorbent (calcium carbonate) under severe calcination conditions. The modified sorbent maintained a capacity of 0.180 g CO_2/g sorbent over 80 cycles. The increased surface area and pore volume enabled enhanced CO_2 capture capacity of the modified sorbents. The carbonation kinetics of the modified sorbents was highly increased compared with the original sorbents. The formation of $Ca_3Al_2O_6$ and $CaAl_2O_4$ in the modified sorbents enhanced the sorbents' sintering resistant and slowed the decay in CO_2 capture capacity during the multiple cycles. A promising route to enhance CO_2 capture performance with waste reutilization is highlighted.

1. Introduction

Calcium looping is a potential technology for CO_2 capture because of the large amount of natural, cheap limestone and dolomite available for the sorbents as well as the high temperature capture process operated based on the reversible reaction of CaO and CO_2. The promise of the technology has been presented with some pilot facilities being demonstrated at 1–1.9 MW scale [1–4]. However, the decay of CO_2 capture capacity during the operation is still an issue for further development. Studies have revealed that the reversible reaction between CaO and CO_2 cannot be completely achieved [5,6]. The sintering of sorbents is the main reason for the decay of CO_2 capture capacity during the multiple cycles [5,6]. Many researches have been conducted to enhance CO_2 capture capacity or slowdown the decay with varied methods including operation condition optimization [7–10], sorbent modification with chemicals [11–17], water or steam activation [18–26], sorbents synthesis with different type of support materials [27–31], precursors [32–37] and techniques [38–42], etc. These methods have presented enhancement in CO_2 capture capacity to different extent. However, many of the methods present problems such as potential secondary pollutants [15,26], and the sintering is still severe for those sorbents without supports, etc [20–22,30,33,41]. Thus, it is essential and attractive to develop sorbents of high reactivity as well as strong sintering resistant in a simple and environmental friendly way.

Previous research has reported that limestone doped with SiO_2 or rice husk ash of high silica content greatly enhanced its CO_2 capture

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performance [43–45]. Compounds such as $Ca_{12}Al_{14}O_{33}$, $Ca_3Al_2O_6$ uniformly distributed in CaO enhanced the sintering temperature of sorbents [28,33,34,37,40,42,46,47]. Fly ash, the solid waste captured by pollution control equipment from coal combustion sources, has the majority component of silica and alumina (80–85%) that could be a good source of silica and alumina.

Recently, reports have revealed the utilization of fly ash for CO_2 storage mainly based on its alkaline components such as Ca, Na, Mg and K in wet and dry processes, which worked as the support for sorbents such as amine and Ca-based sorbents to capture CO_2 [12,48–51]. However, there are aspects that were not explained in detail, such as how fly ash is effectively utilized and the mechanism of improved CO_2 capture performance as well as the kinetics, etc. The understanding of above in detail is of great importance to explore the potentials of fly ash modified sorbent for effective carbon capture. Thus, the goal of the paper is to present an environmental friendly route with improved CO_2 capture performance by the use of fly ash. Through the understanding of how modified fly ash as an additive affects sorbents' reactivity and kinetics, the potential for promising CO_2 sorbents development would be convincing with the microstructure analysis as a supplement study.

2. Experimental section

2.1. Materials

The coal fly ash from the Eraring Power Station, Australia was screened to be of less than 120 μm in diameter and employed to modify calcium based sorbents. The chemical composition of the coal fly ash is shown in Table 1. Chemicals such as sodium carbonate (AR, > 99.5%, Na_2CO_3, Sigma Chemical Co.) and calcium carbonate (AR, > 99.0%, $CaCO_3$, Sigma Chemical Co.) were employed to activate the fly ash to effectively modify the calcium based sorbents.

2.2. Sorbents preparation

The comparative sorbent CaO was produced by calcination of analytical calcium carbonate ($CaCO_3$) in a muffle furnace at 850 °C in air for 30 min. The sorbents modified with coal fly ash (denoted as M-CaO) were prepared according to the procedures presented in Fig. 1. First of all, 100 g fly ash, 120 g $CaCO_3$ and 90 g Na_2CO_3 was carefully mixed and calcined at 900 °C in air for 2 h. Next, the mixture was hydrated in Milli-Q water (1000 ml) with a stirrer mixing for 20 min at room temperature. Then, the slurry was filtered to separate the supernatant and the slag. While, a small amount of lime was added into the supernatant with stirrer mixing for 10 min, the slag after rinsed (its composition is shown in Table 1) was used as raw materials for cement production. The liquid was further filtered to get the clear supernatant; and CO_2 was introduced to form a precipitate. Then, the precipitates were rinsed with Milli-Q water for 3 times and dried at 120 °C. Finally, the dry precipitates (namely modified fly ash) mixed with calcium carbonate with different mass ratio and calcined at 1000 °C for 30 min to get the sorbents ready for experiment. The sorbents calcined with a mass ratio of 1:4 (precipitates: calcium carbonate) is expected to have 60 wt% $Ca_3Al_2O_6$/40 wt% CaO denoted as M-CaO-1 and sorbents developed with mass ratio of 1:5 and 1:10 were denoted as M-CaO-2 (45 wt% $Ca_3Al_2O_6$/55 wt% CaO) and M-CaO-3, (25 wt% $Ca_3Al_2O_6$/75 wt% CaO), respectively. The free CaO content for M-CaO-3 tested referred to the literature [44] was to be ~71%, very close to the calculation value.

2.3. TGA tests

Both the cyclic CO_2 capture performance and carbonation kinetics of the sorbents was investigated in a thermogravimetric analyzer (Q600, TA instrument, USA) which is capable of working at temperature up to 1500 °C. The Q600 features a reliable, horizontal furnace encased in a perforated stainless steel enclosure with a platinum pan standing on balance beams inside the furnace. Based on the preliminary tests, around 10 mg of sample (particle size less than 120 μm) with a thin thickness was placed in the pan for each run that is suitable to avoid the diffusion effect and sintering effect during the experiment. After calcined in 60 ml/min CO_2 at 950 °C for 5 min, the temperature of the sample was dropped down to 700 °C in compressed air. Then, reacting gas mixture of 15% CO_2/N_2 balance at a flowrate of 60 ml/min was introduced into the furnace and reacted with the sorbents for 15 min. After carbonation, the temperature was increased up to 950 °C at a rate of25 °C/min in CO_2. It should be mentioned that the calcination started to take place after 900 °C till it is completed at 950 °C for 5 min. Temperature and weight were continuously recorded by a computer. Plots of conversion versus time were obtained through measuring weight gain, assuming that $CaCO_3$ was the only product of carbonation. Thus, the results of carbonation conversion and observed rates of carbonation obtained did not need to know the actual content of CaO in the sorbents.

2.4. Characterization

The X-ray fluorescence (XRF) was employed to examine the main compositions (in the form of oxides) of the fly ash and slag after they were fused in a glass disc prior to analysis. X-ray diffraction analyzer (XRD, X'Pert Pro) was used for the determination of crystalline phase of the fly ash and sorbents by using Cu Kα radiation in a range of 5–90° with an accelerating voltage of 45 kV and tube current of 40 mA. The Micromeritics TriStar 3000 Analyzer (Micromeritics Instrument Corporation, USA) which employs nitrogen as an adsorbate at 77 K was used to measure the pore structure of the sorbents. The surface area was determined by the Brunauer-Bmmet-Teller (BET) equations and pore volume was calculated by the Barrett-Joyner-Halenda (BJH) method. The morphologies of the fly ash and sorbents before and after carbonation were measured by FESEM (Nova NanoSEM 450) equipped with a Bruker SDD-EDS detector, which enables the analysis of elemental composition and dispersion determination.

3. Results and discussion

3.1. Understanding of the modification

As presented in Table 1, the majority compositions of fly ash are SiO_2 and Al_2O_3, with minorities including Fe_2O_3, CaO, K_2O, Na_2O, TiO_2, MgO, etc. as well as a small amount of carbon measured by the loss on ignition (LOI) of 2.40. It is obvious that the amount of above compositions in the slag (fly ash after modification) is changed. Specifically, SiO_2 and Al_2O_3 is dropped from 63.92 wt% and 23.78 wt% to 32.98 wt% and 7.80 wt%, respectively, while, CaO is largely increased from 2.16 wt% to 36.25 wt%, and Na_2O is increased from 0.77 wt% to

Table 1

Chemical composition determined by XRF analysis for the Eraring coal fly ash and slag (wt.%).

Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	SO_3	TiO_2	P_2O_5	Other	LOI[1]
Fly ash	2.16	0.67	63.92	23.78	3.69	0.77	1.45	0.06	0.95	0.31	0.43	2.40
Slag	36.25	0.38	32.98	7.80	1.95	11.30	0.53	0	0.52	0.13	0	8.16

[1] Loss of ignition.