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Development of CaO-based sorbent doped with mineral rejects–bauxite-tailings in cyclic CO_2 capture

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A highly efficient CaO-based sorbent, using inexpensive materials ($CaCO_3$) and mineral rejects (bauxite-tailings) as reactants, was tested for carbonation conversions for 15 carbonation/calcination cycles in a thermogravimetric analyzer (TGA). The morphology was investigated by scanning electron microscopy (SEM) and the phase composition was determined by X-ray diffraction (XRD). Effects of different bauxite-tailings (BTs)/CaO ratios and thermal pretreatment temperatures on carbonation conversion were investigated in this study. The sorbent doped with 5% BTs (calcined at 900 °C for 3 h) showed superior cyclic stability during 50 carbonation/calcination cycles (being >42% conversions after 50 cycles). Mayenite ($Ca_{12}Al_{14}O_{33}$) in the CaO-based sorbents doped with BTs is responsible for the favorable performance. It can provide a stable framework inhibiting sintering over multiple cycles. In addition, this study may offer the possibility of recycling the BTs from aluminum manufacture.

1. Introduction

Rising concentrations of greenhouse gases in the atmosphere contribute to global warming and climate changes. Carbon dioxide (CO_2) is identified as a key anthropogenic greenhouse gas in particular. In 2010, total CO_2-equivalent emissions were estimated to be 50.1 Gt (Gigatonne) and the emissions form energy sector contributed about 29% to total CO_2-equivalent emissions [1]. To mitigate CO_2 emissions from energy sector especially thermal power generation, CO_2 capture and sequestration (CCS) is being actively studied around the world. Owing to the high CO_2 adsorption capacity (0.786 g CO_2/g CaO, theoretically) and the abundant reserves in the earth crust (3.6%, abundances of the elements), calcium looping is considered to be one of the most feasible ways for CO_2 capture [2]. A calcium looping cycle which involves the exothermic carbonation reaction and endothermic calcination of CaO with CO_2 is based on the reversible chemical reaction described below:

$$CaO(s) + CO_2(g) \leftrightarrow CaCO_3(s)$$

However, extensive studies indicated that CaO-based sorbents suffer from a rapid degradation of CO_2 capture capability during the carbonation/calcination cycles [3,4]. The capacity decay has mainly been attributed to pore blocking, surface area reducing and aggregation of the grain [5]. In order to address this loss-in-capacity, a number of methods were used to improve the regenerability of CaO-based sorbents, such as thermal pretreatment [6], hydration [7,8], inert materials doping [9–11], and chemical modification [12].

Another challenge for capturing flue gases from coal-fired power plants is CO_2 capture cost. The use of inexpensive raw materials will undoubtedly enhance the competitiveness of CO_2 sorbent. Majchrzak-Kuceba et al. [13] synthesized zeolites Na–P1 and Na–A from coal-fly ash by using an alkali fusion method. The Na–A zeolite with large surface area (about 100 m^2/g) and large pore volume (about 0.27 cm^3/g) showed better performance in CO_2 capture (about 5.2 wt%). Using a surfactant as template and rice husk ash as silica source, Hyun et al. [14] prepared the mesoporous MCM-48 silica sorbent. The significant CO_2 adsorption on MCM-48 results from large surface area (about 1024 m^2/g). However, these methods have relatively complex preparation process and high manufacturing cost. Thus, some easy and inexpensive ways to synthesize CO_2 sorbent were developed in recent years. The CaO-based sorbent derived from waste eggshell showed a better CO_2 cyclic stability [15]. To enhance the regenerability and the mechanical strength of CaO-based sorbent in process of cyclic CO_2 capture, Manovic and Anthony [16], using inexpensive calcium aluminate cements as binder, prepared the CaO-based sorbent with higher CO_2 cyclic stability. Li et al. [17] proposed a CO_2 sorbent from hydrate rice husk ash and CaO. In addition, some researchers found that kaolin, an abundant and widespread

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industrial mineral, could improve the stability of CaO-based sorbent [18,19].

Tailings from bauxite consist of mineral rejects from the extraction process mixed with water. The total production of tailings in 2011 was 5.9 million metric tons. At present, bauxite-tailings (BTs) are usually stored in dedicated tailing ponds. The main minerals in bauxite-tailings are diaspore, kaolinite, illite and pyrophyllite. Currently, the research of BTs utilization has involved ceramics [20], sorbents [21], cement and building materials [22]. As it has high alumina content, BTs can be considered as a good candidate to improve the cyclic stability of CaO-based sorbent.

In this work, we attempt to prepare a CaO-based sorbent with high cyclic stability and inexpensive preparation cost as far as possible. Using powdered $CaCO_3$ and BTs as raw materials, CaO-based sorbent was prepared and tested for CO_2 capture during multiple carbonation/calcination cycles. Effects of different BTs/CaO weight ratios and pretreatment temperatures on the adsorption properties were tested.

2. Experimental

2.1. Materials and sample preparation

Calcium carbonate powder (>99% purity, 180 μm, Tianjing, China) was used as the CaO-based sorbent precursor. BTs powder (425 μm, Zhongzhou Branch China Aluminum Co., Ltd.) was used as an additive. The main compositions of the BTs are shown in Table 1. $CaCO_3$ and BTs were weighed and then mixed in a glass beaker, and water was added with stirring to get a mortar. The mixture was blended for 30 min and dried at 80 °C for 3 h. The CaO-based sorbents with different BTs content (5, 10, and 15 wt%) were prepared by calcining the mixture at different temperature (800, 900, and 1000 °C) for 3 h.

2.2. Sorbent testing

A thermogravimetric analyzer (STA 449 F3, Netch Co. Ltd., German) was used for the carbonation/calcination cycles. The gas flow (pure N_2 or N_2/CO_2) rate was 100 mL/min and the temperature, time, and gas flow rate were controlled by NETZSCH-Proteus software. The sample mass was monitored, and conversion was calculated on the basis of mass change, assuming that mass change occurs only as a result of the formation and decomposition of $CaCO_3$. The temperature of the TGA was heated at 750 °C, at a rate of 20 °C/min under a N_2 gas flow of 100 mL/min. Once 750 °C was reached, CO_2 flow of 50 mL/min was introduced into TGA, and N_2 flow was decreased to 50 mL/min. This condition would be kept for 25 min for carbonation. Then the sorbent was heated to 900 °C at a rate of 20 °C/min under N_2 gas flow of 100 mL/min, and this condition was kept for 10 min for calcination. To quantify the extent of CaO utilization, the conversion of sorbent was calculated as follows:

$$X_N = \frac{m_N - m_1}{m_0 \times A} \times \frac{M_{CaO}}{M_{co_2}}$$

where m_0 is the initial mass of sample, A is the initial CaO content, m_N is the mass of sample after N cycles, m_1 is the mass of sample after calcination, and M_{CaO} and M_{co_2} are the molar masses of CaO and CO_2, respectively.

Table 1
The main composition of the BTs.

Component	Al_2O_3	SiO_2	$Total_{Fe}$	TiO_2	CaO	Other
Percentage (wt%)	37.12	25.48	7.53	2.97	0.72	26.28

Phase composition of the sorbent was determined using an X-ray diffractometer (XRD, D/MAX-RA, Rigaku, Japan) at room temperature using a Cu K_α radiation. The morphologies of samples were investigated using a scanning electron microscope (SEM, S-4800, HITACHI, Japan). As CaO is not a conductor material, the sorbents were coated with a layer of gold film to avoid a lack of electrical conductivity. The surface areas and average pore diameter were analyzed by Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry analyzer. The surface area was determined according to N_2 physisorption data at 77 K calculated by the Brunauer–Emmer–Teller (BET) model, while the average pore diameter was obtained using the Barrett–Joyner–Halenda (BJH) model.

3. Results and discussion

3.1. Phase composition of CaO-based sorbents

Fig. 1a showed the XRD pattern of BTs. As shown in Fig. 1a, BTs after pretreatment are composed of Al_2O_3, Fe_9TiO_{15}, SiO_2, Fe_3O_4, and $Ca_{0.986}(Ti_{0.605}Al_{0.349}Fe_{0.023})Si(O_{0.508}(OH)_{0.492})O_4$ phases. Fig. 1b showed the TG curve of BTs under CO_2 atmosphere as shown in Fig. 1b, when CO_2 flow was imported in TGA, change of gas composition may result in the obvious mass loss. But the mass change is not pronounced during isothermal stage, which showed the BTs had almost no adsorption for CO_2. That is, the “CaO” in the BTs is considered to be inactive under CO_2 atmosphere. In the case of Fig. 2, the sorbents showed diffraction peaks belonging to CaO, $Ca_{12}Al_{14}O_{33}$, $Ca_2(SiO_4)$, and Ca_3SiO_5. $Ca_{12}Al_{14}O_{33}$, $Ca_2(SiO_4)$ and Ca_3SiO_5 phases are formed from the reaction between CaO and BTs. Neither ferrum and titanium elements nor their compounds are detected in the synthetic sorbents. It is probably because the content of Fe and Ti or their compounds is below the detection limit of the XRD analysis. On the other hand, it is also possible that amorphous ferrum and titanium were formed during calcination. In the meanwhile, $Ca_2(SiO_4)$ and Ca_3SiO_5 were considered as unfavorable effects for CO_2 capture in previous studies [18,23]. However, the uniform dispersion of $Ca_{12}Al_{14}O_{33}$ in the sorbents provides a stable framework inhibiting sintering of active CaO sites, which was favorable for increasing cyclic durability of CaO-based sorbents [24]. With increasing BTs content, the diffraction peak intensity of $Ca_{12}Al_{14}O_{33}$ increased and more $Ca_{12}Al_{14}O_{33}$ formed to some extent according to the results shown in Fig. 2.

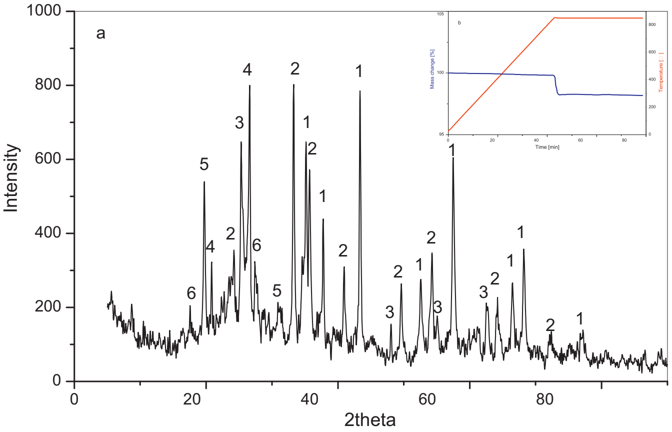

Fig. 1. (a) XRD pattern of the raw BTs; (b) TGA pattern: CO_2 capture of the raw BTs.