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A highly efficient CaO-based CO_2 sorbent prepared by a citrate-assisted sol–gel technique

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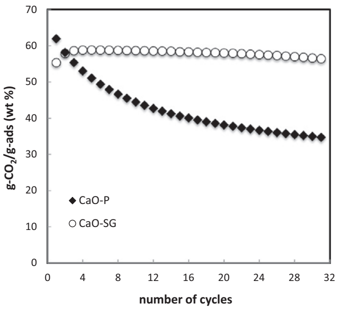
HIGHLIGHTS

- A highly efficient Al-stabilized CaO carbon dioxide sorbent was prepared via sol–gel method.
- Two phases, namely $Ca_9Al_6O_{18}$ and CaO have been identified.
- The superior stability of the current material is due to the high dispersion of $Ca_9Al_6O_{18}$ throughout the CaO matrix.
- A parametric study of CO_2 sorption in mild and severe conditions was achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

This work describes the development of an efficient Al-stabilized CaO sorbent for CO_2 capture. The sorbent (92.5 wt% CaO/7.5 wt% Al_2O_3) was prepared using a citrate-assisted sol–gel technique followed by calcination in two steps, under inert and air atmospheres. The material was tested over 31 cycles of carbonation–calcination under mild and severe operating conditions. Under mild calcination condition (800–900 °C. N_2 flow), the working adsorption capacity was 0.57 g-CO_2/g-ads over 31 cycles without any deactivation. The high stability was attributed to the favorable structural properties and high dispersion of $Ca_9Al_6O_{18}$ binder throughout the CaO matrix. Moreover, a number of parametric studies were performed to investigate the influence of carbonation and calcination temperatures on the activity of the material. Application of severe calcination condition (930 °C in the presence of 100% CO_2) yielded an uptake of 0.33 g-CO_2/g-ads at the end of operation, indicating the superior activity and stability of the current material in comparison to previously reported Al-stabilized CaO adsorbents operated under similar conditions.

1. Introduction

The world temperature has increased significantly due to very large emissions of anthropogenic greenhouse gases (GHGs) to the atmosphere. CO_2 is one of the main components of GHGs, and its mitigation has attracted increased attention over the past decade. Power plants, oil refineries, petrochemical industry and the transportation sector are some of the major sources of CO_2. Flue gas generated in coal and natural gas power plants contains 10–20% CO_2 [1]. Ca-looping (CaL) is an emerging technology to mitigate CO_2 from hot flue gases [2]. This process involves multiple carbonation–calcination cycles at high temperature using basic solid materials, particularly CaO-containing adsorbents. The low cost of CaO, its large CO_2 capture capacity (theoretically 0.786 g-CO_2/g-ads), and the rapid adsorption kinetics at high temperature are the main advantages of CaO-based materials in the CaL process. A challenge in CaL technology is the continuous

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loss of the adsorption working capacity during repetitive carbonation–calcination cycles. Indeed, CaO materials tend to sinter and deactivate at high calcination temperature [3,4]. Several attempts have been made to improve their lifetime [5–7]. Researchers focused mainly on improving the structure and thermal resistance of CaO either by introducing a metal oxide stabilizer phase or exploring different Ca-precursors leading to improved properties. An extensive range of metal oxide stabilizers was used to enhance the stability of CaO, including Zr, Al, Ti and Si oxides [8–16]. A key point toward large-scale application of any CO_2 sorbent is its production cost. Utilizing cheaper metal oxide stabilizers is an effective way to meet the cost minimization target. Aluminum-based stabilizers are suitable candidates due to their low costs. An earlier study by Li et al. [10] demonstrated an improved CaO lifetime during cyclic operation for a mixture of $CaO/Ca_{12}Al_{14}O_{33}$ prepared by wet-mixing technique. Homogenous distribution of $Ca_{12}Al_{14}O_{33}$ (mayenite), with sufficiently high Tammann temperature (~900 °C), throughout the CaO particles could positively retard the structural sintering of CaO during repetitive cycles. The authors reported a CO_2 uptake capacity of 0.4 g-CO_2/g-ads after 50 carbonation–calcination cycles for a sorbent with 75/25 wt% of $CaO–Ca_{12}Al_{14}O_{33}$, which corresponds to a significant improvement in comparison to natural limestone. Following their work, several studies were performed to incorporate Al-stabilizers into the CaO matrix, mainly focusing on optimization of the Ca to Al ratio [17–19], application of different Ca and Al precursors [20,21], and the use of different synthesis techniques [22–24].

The inert phase plays an important role in suppressing the sintering of CaO particles. Depending on the Al and Ca precursors as well as the synthesis technique, various mixed compounds can be formed upon heat treatment, such as $Ca_{12}Al_{14}O_{33}$, $Ca_9Al_6O_{18}$ and $Ca_3Al_2O_6$ [10,20,25]. However, there is no clear evidence of superiority of one over the others, but it is well known that the manner of their distribution among the CaO particles has a distinct role in the sorbent performance. Current research continues to develop suitable synthesis methods to achieve high dispersion of inert phases within the sorbent structure. The material preparation techniques range from simple wet-mixing to relatively complex sol–gel methods [10,17,21,26,27].

In this work, we focused on fabricating a Al-stabilized CaO sorbent for CO_2 removal using a citrate-assisted sol–gel technique to achieve efficient dispersion of inert material within CaO structure with improved sorbent physical properties as well as CO_2 capture behavior. The material was investigated for CO_2 capture cycling under mild and severe regeneration conditions. Our findings were compared to literature data collected under similar operating conditions.

2. Experimental

2.1. Materials and synthesis

Anhydrous citric acid ($C_6H_8O_7$), aluminum isopropoxide (Al(O-iPr)$_3$), calcium acetate monohydrate ($Ca(C_2H_3O_2)_2{\cdot}H_2O$), calcium hydroxide ($Ca(OH)_2$, >99%) and Pluronic P123 ($(C_3H_6O{\cdot}C_2H_4O)_x$ (Mn = 5800) were purchased from Sigma–Aldrich. Isopropanol (C_3H_7OH) was obtained from Fischer.

A citrate-assisted sol–gel technique was used to synthesize the CO_2 sorbent. Citric acid (chelating agent), P123 (surfactant) and Al(O-iPr)$_3$ were dissolved in distilled water, followed by addition of isopropanol. The desired amount of calcium acetate was then added to the solution. The molar ratios of citric acid and water to total metal cations (Al and Ca) were 1:1 and 135:1, respectively. The mass ratios of isopropanol and P123 to water were set as 0.12:1 and 0.09:1, respectively. The solution was strongly stirred overnight at 60 °C in a temperature controlled oil bath. The obtained gel was further aged for 8 h at room temperature followed by drying overnight at 60 °C. The obtained cake was crushed, then calcined in a furnace under controlled atmosphere using the two-step method [28], which consists of an initial ramp from ambient temperature to 900 °C (10 °C/min) in N_2 flow, then switching to air atmosphere for 2 h. The collected powder was crushed and sieved (particles size of <140 μm). As often reported in the literature [18,20–22] a CaO/Al_2O_3 weight ratio (%) of 92.5/7.5 was used for the prepared sorbent. The sorbent was labeled as CaO-SG. Pure CaO (CaO-P) was obtained by calcination of calcium hydroxide precursor ($Ca(OH)_2$) as a reference to evaluate the performance of the proposed sorbent.

2.2. Characterization

The sorbents were characterized by X-ray diffraction (XRD) using a Rigaku Ultima IV instrument (CuKα source, $\lambda = 0.15418$ nm), scanning electron microscopy (SEM) using a JEOL JSM-7500F instrument and N_2 physisorption data using a Micromeritics ASAP 2020 gas analyzer. The samples were outgassed at 200 °C for 3 h prior to N_2 adsorption measurements. The total pore volume and pore size distribution were estimated using the BJH equation [29], whereas the surface area was calculated using the BET model. The crystallite sizes were calculated from XRD data using the Scherrer equation [30].

2.3. CO_2 adsorption/desorption measurements

The performance of the proposed CO_2 sorbent was measured by thermogravimetry using a Q600 TGA instrument (TA Instruments). A small amount of sample (~10 mg) was loaded into a platinum sample holder and heated to 800 °C at a ramp rate of 10 °C/min under pure N_2 flow (50 mL/min), followed by a 10 min hold at 800 °C for the complete activation of material. The carbonation step was conducted using pure CO_2 (50 mL/min) for 30 min at different temperatures (600, 650 and 700 °C). The calcination step was performed in pure N_2 (50 mL/min) for 10 min at 800, 850 and 900 °C or in pure CO_2 (50 mL/min) for 5 min at 930 °C, for mild and severe calcination operations, respectively. For the mild calcination procedure, a temperature ramp rate of 10 °C/min was used during the heating and cooling steps. A ramp rate of 100 °C/min (maximum limit of the furnace) was utilized during severe calcination operation to minimize unwanted CO_2 uptake during the heating step.

3. Results and discussion

3.1. Material characterization

The XRD data (Fig. 1) of CaO-SG showed the occurrence of CaO (active phase, JCPDS 37-1497) and $Ca_9Al_6O_{18}$ (binder, JCPDS 70-0839) upon heat treatment at 900 °C. Assuming that aluminum reacted quantitatively, the nominal CaO and $Ca_9Al_6O_{18}$ contents may be calculated as 80 and 20 wt%, respectively. The crystallite sizes of CaO and $Ca_9Al_6O_{18}$ were estimated to 39 and 37 nm. Depending on the aluminum and calcium precursors, different calcium aluminate phases may be produced, including $Ca_{12}Al_{14}O_{33}$, $Ca_3Al_2O_6$ and $Ca_9Al_6O_{18}$. Al-rich phase of calcium aluminate ($Ca_{12}Al_{14}O_{33}$) is less thermodynamically stable at high temperature compared to the Ca-rich phase ($Ca_9Al_6O_{18}$). Zhou et al. [20] described a mechanism for producing these two mixed-oxide phases. Basically, $Ca_{12}Al_{14}O_{33}$ is formed at a lower temperature, and upon increasing the temperature, calcium ions diffuse into the CaAlO matrix to form $Ca_9Al_6O_{18}$. However, depending on the