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Refractory dopant-incorporated CaO from waste eggshell as sustainable sorbent for CO_2 capture: Experimental and kinetic studies

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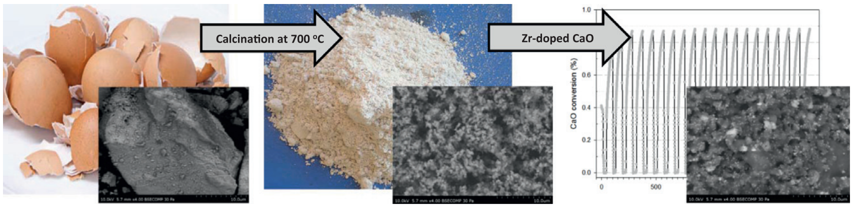
HIGHLIGHTS

- Dopant-stabilized CaO-based sorbents were prepared from waste eggshell for CO_2 capture.
- Ti, Cu, Al and Zr were incorporated within the CaO matrix to obtain robust sorbents.
- Zr-doped CaO showed superior performance with conversion of 88% in 20 cycles.
- Chemical reaction and product layer diffusion contributed to the rate controlling step.
- Intrinsic and diffusional activation energies were calculated as 39.4 and 46.5 kJ/mol.

GRAPHICAL ABSTRACT



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ABSTRACT

This work investigates the development of dopant-stabilized CaO-based sorbents for CO_2 capture and studies the kinetics of the carbonation reaction. Eggshell as biogenesis calcium waste was calcined to obtain low cost CaO powder. Several refractory dopants (Ti, Al, Cu and Zi) were then incorporated within the CaO matrix to prepare robust sorbents. The CO_2 capture performance of the developed sorbents was assessed in some calcination–carbonation cycles performed in Thermogravimetric analyzer (TGA). Among the developed sorbents, Zr-doped CaO exhibited superior performance and durability, where a conversion of around 88% could be sustained within 20 cycles. To have an insight into the rate controlling mechanism and fundamental concept of activation energy, kinetic study was performed on the carbonation reaction of the Zr-doped CaO sorbent. Kinetic results based on the shrinking core model suggested that the carbonation mechanism was controlled by a combination of resistances arising from diffusion of CO_2 through the carbonate layer and its chemical reaction at the CaO–$CaCO_3$ interface. The intrinsic and diffusional activation energies were obtained as 39.4 and 46.5 kJ/mol, respectively.

1. Introduction

The natural greenhouse gas effect is vital for life to thrive on the earth; however, with the ever increasing level of greenhouse gases in the atmosphere the devastating "global warming" would be inevitable. This human provoked climate change requires intellectual solutions to address part of the raised adverse effects. Accordingly, greenhouse gas remediation plants seek ways to remove these gases from the atmosphere and especially notorious gas in this regard is carbon dioxide (CO_2).

Carbon capture and sequestration (CCS) technologies have been widely accepted as promising processes to remove CO_2 from flue/fuel gases to alleviate global scale CO_2 emissions. The current state

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of the art technology for separation of CO_2 is gas scrubbing using aqueous amine solutions which imposes considerable energy costs to the industry for regeneration process and brings about environmental issues due to the high volatility of the solvents [1]. Alternatively, CO_2 sorption using solid sorbents offers the advantage of reduced energy demand. However, the solid sorbent should present a high CO_2 sorption capacity, fast kinetics of sorption–desorption and durable performance under high temperatures and extreme conditions of operation [2].

Calcium oxide (CaO) has been known as a cost-effective sorbent with high sorption capacity close to theoretical value. Recent investigations showed that eggshell derived CaO is a promising sorbent for CO_2 capture. Olivares-Marín et al. [3] studied the influence of particle morphology, porosity and crystal structure of several $CaCO_3$ sorbents from both natural and synthetic origins and found that after commercial CaO, the highest CO_2 uptake was devoted to the eggshell derived CaO. In another investigation carried out by Ives et al. [4], the ability of the CaO sorbents obtained from eggshell, mussel shell and limestone to capture CO_2 from combustion gases was compared. The results showed that the decline in CO_2 capture capacity was slowest for the eggshell, followed by limestone and mussel shell. Castilho et al. [5] utilized several Ca rich shells including eggshell to prepare sorbents for CO_2 capture and found them as potential sorbents to mitigate the anthropogenic CO_2.

In spite of the availability and high capture performance of CaO, this sorbent is highly vulnerable to sintering at high temperatures and its performance is suppressed in several cycles of capture and release of CO_2. To attenuate such decay in cyclic performance of CaO, several refractory dopants have been implemented to incorporate in the synthesis of durable CaO-based sorbents [6–10]. Refractory dopants enhance the resistance to sintering and agglomeration of the sorbent which is the major cause of the depressed cyclic performance of CaO at high temperatures [11].

CO_2 sorption using sustainable CaO-based materials have been reported extensively. These researches span the aspects of either durable sorbent development or CO_2 capture process optimization. However, few studies are found in the open literature focusing on the kinetics of CO_2 capture using dopant-incorporated CaO-based sorbents. Most available published works report the kinetics of carbonation of pristine CaO with CO_2. Bhatia and Perlmutter [12] investigated the kinetics of CaO–CO_2 reaction using random pore model (RPM). Grasa et al. [13] also applied the RPM to estimate the intrinsic rate parameters for carbonation reaction of CaO–CO_2 and developed a kinetic expression as a function of number of cycles, CO_2 partial pressure and temperature to calculate the particle conversion with time. In another study, Li et al. [14] developed a rate equation to describe the kinetics of CaO–CO_2 reaction using the nucleation-growth gas–solid reaction model. Johnsen et al. [15] used shrinking core model (SCM) to describe the carbonation reaction rate of dolomite-CO_2. Dou et al. [16] also applied the SCM to determine the rate limiting step and governing kinetics in the carbonation reaction of CaO–CO_2. In another investigation performed by Mostafavi et al. [17], a thermodynamic and kinetic study was performed on the carbonation reaction of dolomite and CaO based on grain model as an improved version of SCM. López-Periago et al. [18] modeled the diffusion of reactants through product layer, as the rate controlling step in slow gas–solid reaction, using Jander equation to describe the carbonation kinetics of supercritically precipitated calcium carbonate.

It is well understood that unique morphology and feature of each sorbent dictates its kinetics parameters including reaction rate constant, diffusion rate constant, intrinsic and diffusional activation energies as well as rate limiting steps. Use of kinetic values from the literature for the specific sorbent at hand could lead to huge errors and misunderstanding of the process. Having this in mind and considering the importance of kinetic studies in proper design and operation of carbonation reactors, this work aims to study the kinetics of CO_2 capture using dopant-incorporated CaO sorbents whose data are scarcely found in the literature.

In this study, eggshell as a very rich source of calcium carbonate ($CaCO_3$) which is available as waste material of alimentary and bakery industries was used to obtain low cost CaO. The first objective of this work was to develop high performance dopant-incorporated CaO-based sorbent for CO_2 capture. For this purpose, different refractory dopants were incorporated in the eggshell derived CaO. The performance of the developed sorbents was assessed in some carbonation–calcination cycles. As the second objective of this work, the kinetics of the carbonation of the best doped-CaO sorbent was studied. An approximate solution of the shrinking core model was used to determine the rate parameters, rate limiting step and intrinsic and diffusional activation energies.

2. Materials and methods

2.1. Preparation of the sorbents

Eggshells were collected from residential wastes. The shells were washed and the inner membrane was separated from the shells. They were air dried and then ground using a mortar and pestle. The powdered shell was calcined in a muffle furnace at 700–900 °C for 1–2 h. Upon the completion of the calcination, a chalky-white fine powder was obtained.

Different refractory dopants including Zirconium (Zr), Titanium (Ti), Copper (Cu) and Aluminum (Al) were used to synthesize dopant-incorporated CaO-based sorbents using solid-state method. The dopant precursors (ZrO_2, TiO_2, CuO and Al_2O_3) were mixed with predetermined quantities of eggshell derived CaO. The notation of D/Ca (x:y) (D = Zr, Ti, Cu and Al) was used to present the specific dopant-incorporated CaO-based sorbent, where (x:y) represents the molar ratio of a specific dopant over Ca. For example, the notation of “Zr/Ca (3:10)” represents the sorbent which was prepared by doping of ZrO_2 into the CaO lattice, with Zr/Ca molar ratio of 3:10. The resultant mixtures were properly blended to ensure the perfect mixing of the materials. The so obtained dry mixtures were calcined at 700 °C for 30 min to obtain the corresponding dopant-incorporated sorbents.

2.2. Sorbents performance tests

To evaluate the performance of the developed sorbents, CO_2 capture experiments were carried out in a Thermogravimetric analyzer (TGA, SDTQ-600). A 10–12 mg of the sample was loaded in a ceramic pan and heated under a N_2 flow rate of 100 ml/min to the pre-set calcination temperature. The sorbent was calcined for 20 min, after which the temperature was reduced to the desired carbonation temperature (see Fig. 3). At the onset of the carbonation, N_2 was switched to CO_2 at the same flow rate to commence the CO_2 capture test. The variation in the sample weight and temperature as a function of time was recorded continuously to calculate the molar CaO conversion was follows:

$$x_{CaO}\% = \frac{W_{CaO}\%}{0.786 \times \alpha_{CaO}} \quad (1)$$

where $W_{CaO}\%$ represents the weight percentage change of the sorbent during CO_2 capture, 0.786 is the stoichiometric uptake of CO_2 by CaO and α_{CaO} denotes the weight fraction of CaO in the sorbent. Since the dopant does not show any (or only limited) affinity for CO_2 capture, the conversion was calculated just based on the conversion of CaO to $CaCO_3$. Some of the critical CO_2 capture tests