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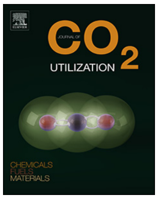

Calcium precursor from stirring processes at room temperature for controllable preparation of nano-structure CaO sorbents for high-temperature CO_2 adsorption

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ABSTRACT

Nano-structure CaO crystals with an average size of 480 nm × 255 nm (length and width) were prepared by simply roasting $CaCO_3$ precursors at 900 °C for 2 h. The $CaCO_3$ precursors with a pure vaterite crystalline phase were readily synthesized by a room temperature stirring method using $Ca(NO_3)_2$ and CO_2 storage material (CO_2SM). The CO_2SM played an important role in providing CO_3^{2-} source and structure controlling. The effects of CO_2SM dosage, Ca^{2+} concentration, and stirring time on the crystallization of $CaCO_3$ precursors were investigated. In addition, the CO_2SM was successfully regenerated by simply exposing the filtrate from the preparation process to CO_2 for further preparing $CaCO_3$ precursor. The as-obtained CaO crystals exhibited a strong CO_2 adsorption capacity up to 17.18 mmol g^{-1} under 0.1 MPa at 700 °C.

1. Introduction

CO_2 emission is a major contributor to global warming and climate change [1,2]. A variety of strategies, such as liquid absorption [3,4], solid adsorption [5–7], and membrane separation [8–10], have been developed for CO_2 capture. CaO powder is an excellent solid adsorbent candidate of CO_2 capture due to its reversible reaction with CO_2 to form $CaCO_3$ ($CaO + CO_2 \rightleftharpoons CaCO_3$) [11–15]. Hence, many advanced techniques have been developed for the production of CaO, such as precipitated calcium carbonate (PCC) [16,17], dry planetary ball-milling method [18], self-assembly template synthesis (SATS) [19], and sol-gel method [20,21] Among them, roasting $CaCO_3$ precursor can yield highly thermal-stable CaO with excellent activity. However, the synthesis of $CaCO_3$ precursors usually requires templates or additives, and long reaction process [22–25].

In the present work, a template- or surfactant- free method was developed for the preparation of morphology controllable $CaCO_3$ precursors via the reaction of CO_2SM with $Ca(NO_3)_2$. The produced $CaCO_3$ was used to prepare CaO crystals by 2 *h* roasting at 900 °C. The CO_2SM, a white powder, was prepared by absorbing CO_2 with equimolar ethylenediamine (EDA) and EG solution [26]. The influences of CO_2SM dosage, Ca^{2+} concentration, and stirring time on the crystallization of $CaCO_3$ precursors were systemically investigated. The filtrate from the preparation process was successfully recycled at least five times to capture CO_2 for further preparing $CaCO_3$ precursors with uniform morphology. Our work provided a new strategy for preparing CaO crystals with strong reduction performances and high CO_2 capture capacity up to 17.18 mmol·g^{-1} under 0.1 MPa at 700 °C. Fig. 1 shows the entire preparation process.

2. Experimental section

2.1. Materials

Analytical grade EG was purchased from Beijing Reagent Company (Beijing, China). Analytical-grade EDA and $Ca(NO_3)_2{\cdot}4H_2O$ were purchased from Tianjin Reagent Company (Tianjin, China). Compressed CO_2 (99.999 vol %) was purchased from the Standard Things Center (Beijing, China). The CO_2SM was derived from the equimolar system EDA + EG up-taking CO_2. All other chemical reagents were analytical grade and did not require any treatment.

Formation of CO_2SM. Pure compressed CO_2 was continuously bubbled through the EG + EDA system (molar ratio = 1: 1). In this process, the EG + EDA system showed a white sticky solid at t = 20 min and the solution completely changed to solid CO_2SM at t = 105 min. The solid CO_2SM was washed three times with ethanol.

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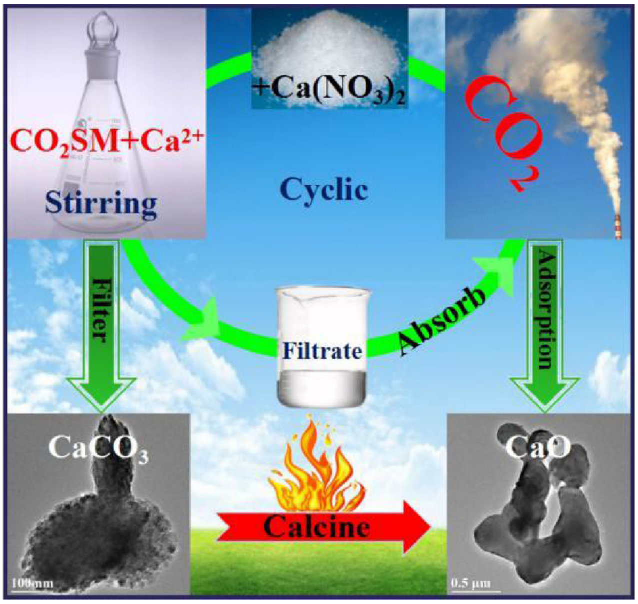

Fig. 1. Controllable preparation of nano-structure CaO crystals and it's adsorption for CO_2. In this process, the $CaCO_3$ precursor with a pure vaterite crystalline phase was readily synthesized by a room temperature stirring method with $Ca(NO_3)_2$ and CO_2SM.

After washing, the solid CO_2SM was vacuum dried at 60 °C for 5 h and stored at room temperature.

2.2. Preparation of $CaCO_3$ precursor and CaO crystals

$CaCO_3$ precursors was prepared by stirring 6–60 g/L CO_2SM in 50 mL 0.02–0.5 mol/L water solution of $Ca(NO_3)_2$ at 1000 rpm at room temperature for 0.25 min-2 h. The precipitates were filtered by vacuum filtration, washed with double-distilled water and ethanol three times, and dried at 120 °C for 2 h to afford $CaCO_3$ precursor. The produced $CaCO_3$ precursor was heated in air to 900 °C at the heating rate of 5 °C min^{-1} in 2 h to afford CaO crystals.

2.3. Characterization

The $CaCO_3$ precursor's images were observed using the scanning electron microscopy (SEM, Quanta FEG 650, China) with an accelerating voltage of 20 kV and high magnification transmission electron microscopy (HR-TEM, JEM-2100, Japan) with an accelerating voltage of 200 kV. Their X-ray diffraction (XRD) patterns were collected on a powder X-ray diffract meter (Siemens D/max-RB) with Cu Kα radiation at the scanning rate of $0.05°·S^{-1}$. Fourier transform infrared spectroscopy (FTIR) was recorded on a Nexus 670 infrared spectrophotometer. Isotherms were analyzed using 3 H-2000PS2 BET instrument with the Barrett-Joyner-Halenda (BJH) theory to give the pore parameters, including Brunauer-Emmett-Teller BET surface area ($m^2\ g^{-1}$), total pore volume ($cm^3\ g^{-1}$), and average pore size (nm). Thermogravimetry analysis (TGA, Entzsch-Sta 449) was employed to measure the weight percentage of $CaCO_3$ precursors.

2.4. Temperature-programmed reduction (TPR)

The H_2-TPR of CaO crystals was conducted by a TP-5080 apparatus equipped with a thermal conductivity detector (TCD). CaO crystals (50 mg) were put in a quartz tube reactor with an i.d. of 6 mm, pretreated at 400 °C for 30 min under N_2 gas flow (30 $mL·min^{-1}$) to remove physically adsorbed H_2O and/or CO_2, and cooled to room temperature. The crystals were then reduced with 30 $mL·min^{-1}$ 5 vol% H_2/N_2 with the temperature linearly increased from room temperature to 900 °C at the heating rate of 10 °C min^{-1}. The H_2 consumption of CaO crystals was recorded with the TCD.

2.5. Temperature-programmed desorption (TPD)

The alkalinity of CaO crystals was measured by CO_2-TPD using the TP-5080 apparatus equipped with the TCD. The CaO crystals (100 mg) were put in a quartz tube reactor, heated at 900 °C for 30 min under He gas flow (30 ml min^{-1}) to remove moistures and other adsorbed gases, and cooled to room temperature, 50 °C, 600 °C, 700 °C or 800 °C, respectively. The pre-treated CaO crystals were then exposed to pure CO_2 at the corresponding temperature for 30 min, and subject to TPD test under a constant He gas flow (30 mL min^{-1}) as heated from room temperature to 1000 °C at the heating rate of 10 °C min^{-1}.

3. Results and discussion

3.1. Characterizations of CO_2SM

According to XRD, FTIR, and ^{13}C NMR technologies, the solid CO_2SM was confirmed as an alkylcarbonate salts [26].

3.2. $CaCO_3$ precursor

In this section, the effects of CO_2SM dosage, Ca^{2+} concentration, and stirring time in the crystallization process were investigated in detail.

3.2.1. CO_2SM dosages

$CaCO_3$ precursor was prepared by stirring different dosages of CO_2SM ranging from 6.0 g/L to 60.0 g/L in 50 mL 0.1 mol/L water solution of $Ca(NO_3)_2$ with at 1000 rpm at room temperature for 1 h. The pH values of reaction solution before and after the reaction, average diameter of crystals and $CaCO_3$ precursor crystal forms are listed in Table 1 (Samples A–F). The as-prepared $CaCO_3$ precursors was then characterized by SEM, XRD and FTIR.

As shown in Fig. 2 for the SEM images of the as-obtained $CaCO_3$ precursors, the average size of spindle-like $CaCO_3$ particles increased from 0.68 μm to 0.80 μm (Fig. 2A–C) along with aggregation, and gradually decreased to 0.51 μm (Fig. 2D–F) with the increase of CO_2SM dosage. The minimum particle size (0.51 μm) was found in sample F that was prepared with 60 g/L CO_2SM. The reaction solutions before the reaction were alkaline with the pHs of 8.24-8.31. Therefore, it can be concluded that CO_2SM solution was alkaline, and the alkalinity of reaction solution increased with the increases of EG and EDA contents. After the reaction, pH value of the reaction changed to 6.70, 6.76, 6.85, 6.92, 7.25 or 7.42, respectively, depending the dosage of Ca^{2+}.

Fig. 3 shows the XRD patterns and FTIR spectra of the as-prepared $CaCO_3$ precursor. All samples exhibited peaks at $2θ = 21.004°$, 24.900°, 27.047°, 32.778°, 42.759°, 43.848°, 49.098°, 50.077°, and 55.805° corresponding to (004), (110), (112), (114), (008), (300), (304), (118), and (224) planes, respectively, with no impurity diffraction peaks found

Table 1
As-prepared $CaCO_3$ precursor under different CO_2SM dosages (6 g/L, 10 g/L, 16 g/L, 20 g/L,40 g/L and 60 g/L CO_2SM dosages), 50 mL 0.1 mol/L $Ca(NO_3)_2$ solution and stirring speed at 1000 rpm for 1 h at room temperature.

Sample	CO_2SM (g/L)	pH Before	After	Average diameter (μm)	Crystal form of $CaCO_3$
A	6	8.24	6.70	0.68	Vaterite
B	10	8.24	6.76	0.71	Vaterite
C	16	8.26	6.85	0.80	Vaterite
D	20	8.26	6.92	0.77	Vaterite
E	40	8.28	7.25	0.65	Vaterite
F	60	8.31	7.42	0.51	Vaterite