The Zr-Doped CaO CO₂ Sorbent Fabricated by Wet High-Energy Milling

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Abstract: We fabricated the Zr-doped CaO sorbent for high-temperature CO₂ capture by the wet high-energy co-milling of calcium carbonate and natural zirconium dioxide (baddeleyite) for the first time. The morphology of the material was examined by scanning electron microscopy, energy-dispersive X-ray analysis and X-ray diffraction. Its CO₂ uptake capacity was determined using thermogravimetric analysis. After 50 carbonation–calcination cycles, the Zr-doped CaO sorbent characterized by a high enough CO₂ uptake capacity of 8.6 mmol/g and unchanged microstructure due to CaZrO₃ nanoparticles uniformly distributed in the CaO matrix to prevent CaCO₃ sintering under carbonation. The proposed easy-to-implement CaO-based sorbents fabrication technique is promising for industrial application.

Keywords: CaO; ZrO₂; high-energy milling; CO₂ capture; sorbent

1. Introduction

Carbon dioxide is among the major greenhouse gases promoting global warming leading to climate change. The main anthropogenic CO₂ sources are power plants especially the ones generating energy by burning coal, which is the most carbon-intensive fossil fuel [1–3]. It is predicted that in the next several decades, CO₂ concentration in the atmosphere will continue to increase because fossil fuels will still be the dominating energy source. There are three main methods for large-scale CO₂ capture: pre-combustion, post-combustion and oxy-combustion [3–5]. Post-combustion capture, used to capture CO₂ from flue gas produced by fossil fuel burning, is competitive in cost with the other two approaches, but can be applied in the existing power plants without any major modification. Among post-combustion capture technologies, amine scrubbing, pressure swing adsorption and calcium looping (CaL), also known as the regenerative calcium cycle, are commercially implemented for CO₂ capture [4]. The CaL process employs a low cost CaO sorbent and efficiently operates at temperatures above 600 °C, which are commonly used by power plants to produce saturated steam, in contrast to amine scrubbing and pressure swing adsorption. Besides, the CaL process is less energy-intensive and creates less environmental burden alternative to amine scrubbing [6]. The CaL process involves the reversible reaction CaO+CO₂ ↔ CaCO₃: exothermic carbonation reaction and endothermic calcination reaction. The CaO sorbent, typically derived from natural limestone, is circulated between two reactors called the carbonator and the calciner operating in a temperature range of 650–700 °C and 800–950 °C, respectively. Under multiple carbonation–calcination cycles, CaO sorption ability decreases due to irreversible changes in its structure caused by sintering [7]. Among the approaches used to improve the cyclic stability of the CaO is the development of synthetic sorbents via incorporation of inert thermally resistant oxides (for example, MgO, Al₂O₃, ZrO₂, Y₂O₃, CeO₂ and others) in the structure of CaO [8–12]. The dopant acts as a spacer preventing the sintering of the sorbent and CaO particle growth. ZrO₂ is a frequently used agent because of its high thermal
stability, chemical inertness and proven efficiency. Various synthesis methods, such as sol–gel, flame spray pyrolysis and co-precipitation, are commonly used to fabricate CaO sorbents doped with ZrO$_2$ [8,10,13,14]. These techniques deal with CaO and ZrO$_2$ precursors and give rise to nanosized CaO-ZrO$_2$ sorbents with enhanced CO$_2$ capture performance and cyclic stability. The alternative to ZrO$_2$ precursors is a mineral baddeleyite containing ZrO$_2$ in the range 96.5–98.5 wt% [15]. Baddeleyite is much cheaper than chemically synthesized ZrO$_2$ and its precursors. However, chemical ways of reducing particle size are not efficient when applied to baddeleyite because of its chemical inertness. High-energy milling is a possible approach for baddeleyite processing providing ZrO$_2$ particle size reduction to nanoscale and their mechanoactivation [16]. In [17], it was reported that high-energy milling improved CO$_2$ capture performance of pure limestone, in particular, due to the reduction in particle size. It should be noted that high-energy milling provides not only efficient sorbent and dopant particle size reduction but the effective dispersion of the dopant throughout the sorbent [18].

The aim of this work was to examine the fabrication possibility of an effective Zr-doped CaO sorbent by the high-energy co-milling of calcium carbonate and baddeleyite.

2. Materials and Methods

The Zr-doped CaO sorbents were prepared by the mechanical mixing of CaCO$_3$ powder (99.5%, Sigma-Aldrich, Saint Louis, MO, USA) and baddeleyite concentrate powder (99.3%, Kovdorsk GOK, Kovdor, Russia), taken in amounts required to obtain the Zr/Ca molar ratios of 1:10, 2:10 and 3:10 in the sorbent, followed by wet high-energy co-milling in a planetary mill Pulverisette 7 Premium Line (Fritsch, Idar-Oberstein, Germany) for 5 h using 1.5 mm beads of stabilized zirconia. The mass ratio of the mixed powder, distilled water and milling media was 1:3:10. The grinding product was dried in air atmosphere at 80°C for 24 h in an oven OV-11 (Jeio Tech Co., Ltd., Seoul, Korea). The reference undoped CaO sorbent (0:10) was fabricated in the same way. Wet high-energy milling in the planetary mill with the similar parameters was used previously for baddeleyite treatment to prepare nanostructured ZrO$_2$ powder [16].

The analysis of CO$_2$ uptake capacity of the sorbents was performed on the thermal analyzer EXSTAR TG/DTA7200 (SII Nano Technology, Tokyo, Japan) for samples with a mass of 6–8 mg. The sorbent weight was recorded as a function of time. To be activated, each sorbent was preliminary held at 800°C for 20 min under N$_2$ for CaCO$_3$ decomposition. Then, the sorbent was cooled to 700°C at a rate of 10°C/min and held for 30 min in the gaseous stream containing 30 vol.% CO$_2$ and 70 vol.% N$_2$. Flow rates of CO$_2$ and N$_2$ were 30 and 70 mL/min, respectively. After carbonation the sorbent was heated up to 800°C at a rate of 20°C/min and held for 20 min under a N$_2$ flow of 100 mL/min to perform calcination. Preliminary performed differential thermogravimetric analysis showed that carbonation and decarbonation rates were maximal near 700 and 800°C, respectively. The carbonation–calcination cycle was repeated 50 times. For each cycle, CO$_2$ uptake capacity (mmol/g) of the sorbent was determined as the amount of captured CO$_2$ divided by the sorbent weight before carbonation.

Microstructures of the sorbents were characterized using a scanning electron microscope (SEM) Merlin (Carl Zeiss, Oberkochen, Germany) coupled with an energy-dispersive X-ray spectrometer (EDS) INCA Energy 350X-Max 80 (Oxford Instruments, Abingdon, UK) for local elemental composition determination.

Nitrogen physisorption analysis at −196°C was performed with a gas sorption analyzer Autosorb iQ-C (Quantachrome Instruments, Boynton Beach, FL, USA). All samples were degassed under vacuum for 3 h at 300°C before analysis. The specific surface area ($S_{BET}$) was determined with the Brunauer–Emmett–Teller method in a relative pressure range of 0.05–0.35. The pore volume ($V_{sp}$) was determined from the amount of nitrogen adsorbed at the relative pressure of 0.99.

X-ray diffraction (XRD) patterns of the sorbents were recorded in the 20–70° 2θ range by a diffractometer D2 Phaser (Bruker AXS, Karlsruhe, Germany) using CuKα1 monochromatic radiation. The XRD patterns were assigned using the PDF-2 Diffraction Database File compiled by the International
Centre for Diffraction. Phase content was determined from the XRD patterns by the Rietveld method in the TOPAS software (Bruker AXS, Karlsruhe, Germany).

3. Results and Discussion

For all the sorbents, an evaluation of their CO₂ uptake capacity in multiple carbonation–calcination cycles was performed (Figure 1). The pure CaO sorbent showed a rather high initial capacity of 16.1 mmol/g since the stoichiometric capacity of CaO was 17.9 mmol/g. However, after the 3rd cycle, its capacity started to decrease rapidly reaching 1.2 mmol/g in the 24th cycle and then continued to decrease slowly to a steady-state value of about 1.0 mmol/g. Adding ZrO₂ resulted in a sorbent initial capacity reduction. The dopant was inactive for CO₂ capture which reduced the initial CO₂ uptake capacity of the material on a weight basis. The rise in the Zr/Ca molar ratio from 0:10 to 3:10 led to a sorbent initial capacity decrease from 16.1 to 8.1 mmol/g. Although the capacity of the Zr-doped CaO sorbents was initially lower than that of the undoped one, it showed better stability in time with the Zr/Ca molar ratio increase. A decrease in capacity of 15.1, 8.2, 1.9 and 1.8 mmol/g in relation to the initial value was registered in the 50th cycle for sorbents with the Zr/Ca molar ratio of 0:10, 1:10, 2:10 and 3:10, respectively. Among the fabricated sorbents, the one with the Zr/Ca molar ratio of 2:10 (hereinafter referred to as the Zr-doped CaO sorbent) showed the best performance in terms of capacity value and its cyclic stability.

![Figure 1](image-url)

**Figure 1.** The dependencies of the CO₂ uptake capacity of the sorbents with different Zr/Ca molar ratios on the number of carbonation–calcination cycles.

During the multi-cycle carbonation–calcination process, the Zr-doped CaO sorbent prepared by wet high-energy milling showed the CO₂ uptake capacity steady-state value of 8.6 mmol/g exceeding those of the Zr-doped CaO sorbents with the same Zr/Ca molar ratio previously synthesized using a more laborious sol–gel technique [14] and a surfactant-template/ultrasound-assisted method [19].

The microstructure of the fabricated sorbents before and after cyclic tests is illustrated in Figure 2. Figure 2a,b show that fresh Zr-doped CaO and undoped CaO sorbents were macroscopically homogeneous and consisted of agglomerates with size of up to several hundred nanometers. Agglomerates were smaller in size and had clearly defined borders in the case of the Zr-doped CaO sorbent. In both sorbents, randomly disposed agglomerates of nanoparticles formed uniformly distributed cavities of arbitrary shape and size. Significant changes in the microstructure of the pure CaO sorbent were observed after the 50th cycle (Figure 2c). Agglomerates formed a monolithic
structure, which led to porosity reduction. On the contrary, the Zr-doped CaO sorbent microstructure had undergone no noticeable changes (Figure 2d) and was the same as before the 1st cycle.

![SEM images of the virgin sorbents and the same sorbents after the 50 cycle: (a,c) the pure CaO sorbent; (b,d) the Zr-doped CaO sorbent.](image)

**Figure 2.** SEM images of the virgin sorbents and the same sorbents after the 50 cycle: (a,c) the pure CaO sorbent; (b,d) the Zr-doped CaO sorbent.

The specific surface area and pore volume of the sorbents are shown in Table 1. The improvement of the specific surface area as well as the pore volume was observed for the CaO sorbent doped with zirconia. Additionally, after 50 carbonation–calcination cycles, the specific surface area and pore volume of the Zr-doped CaO sorbent only slightly decreased in contrast to a dramatic decrease in the specific surface area and pore volume of pure CaO.

| Sorbent       | Before the 1st Cycle | After the 50th Cycle |
|---------------|----------------------|----------------------|
|               | $S_{BET}, \text{m}^2/\text{g}$ | $V_{sp}, \text{cm}^3/\text{g}$ | $S_{BET}, \text{m}^2/\text{g}$ | $V_{sp}, \text{cm}^3/\text{g}$ |
| pure CaO      | 15.9                 | 0.123                | 2.6                       | 0.025                     |
| Zr-doped CaO  | 21.1                 | 0.149                | 20.5                      | 0.136                     |

The EDS analysis of fresh Zr-doped CaO sorbent revealed that the material contained only calcium, oxygen and zirconium (Figure 3a). The absence of carbon indicated no residual CaCO$_3$ in the fresh Zr-doped CaO sorbent ready to carbonate. No segregated regions of zirconium and calcium were detected by means of EDS mapping. Zirconium and calcium were uniformly distributed in the sorbent (Figure 3b,c).

The XRD patterns of the fabricated sorbents are shown in Figure 4. In the XRD pattern of the pure CaO sorbent, only characteristic peaks of CaO located at 32.2, 37.4, 53.9, 64.2 and 67.4$^\circ$ were observed. No reflections of residual CaCO$_3$ were detected, which is in a good agreement with obtained EDS data. In the XRD pattern of the Zr-doped CaO sorbent, additional peaks appeared at 22.2, 31.5, 45.2, 50.9, 55.5$^\circ$, 56.7 and 65.8$^\circ$, which were identified as characteristic peaks of CaZrO$_3$. The absence of ZrO$_2$ reflections (the most intensive characteristic peaks of ZrO$_2$ phases were at 28.2, 30.1$^\circ$, 30.2 and 31.5$^\circ$) indicated
the complete reaction between ZrO$_2$ and CaO forming calcium zirconate (CaZrO$_3$). Since CaZrO$_3$ was inactive for CO$_2$ capture, this reaction additionally reduced the initial CO$_2$ uptake capacity of the Zr-doped CaO sorbent due to the CaO content decrease. The formation of CaZrO$_3$ is in agreement with previous studies, reporting that CaO reacts with ZrO$_2$ at a calcination temperature of 800 °C [14]. This reaction was probably promoted by preliminary mechanical activation during the Zr-doped CaO sorbent preparation, which provided zirconium incorporation into the CaO lattice just as calcium incorporation into monoclinic ZrO$_2$ lattice, to form tetragonal and cubic ZrO$_2$ phases in [16]. Previously, to incorporate CaZrO$_3$ into CaO as a spacer, such approaches as sol–gel auto-combustion synthesis, flame spray pyrolysis or the surfactant-template/ultrasound-assisted method were used [8,10,19].

The application of the Scherrer equation to main CaO and CaZrO$_3$ peaks in the XRD pattern at 37.4° and 31.5° allowed the estimation of CaO and CaZrO$_3$ particle sizes of 38 and 20 nm, respectively. The formation of CaZrO$_3$ explained the revealed reduction in the sorbent maximal CO$_2$ uptake capacity with the rise in the Zr/Ca molar ratio due to CaO partial inactivation caused by the reaction with ZrO$_2$ (Figure 1).

According to the obtained data, the influence of the multiple carbonation–calcination process on the CO$_2$ uptake capacity of the fabricated CaO-based sorbents can be explained in the following way. The rapid decrease in capacity of the pure CaO sorbent was mostly associated with CaCO$_3$ sintering. Tammann temperatures of CaO and CaCO$_3$ were 1154 and 533 °C, respectively [20]. The Tammann temperature of CaO was much higher than the used calcination temperature of 800 °C; thereby sintering occurred during carbonation at the temperature of 700 °C, comparable with the Tammann temperature of CaCO$_3$. The fresh pure CaO sorbent prepared by CaCO$_3$ decomposition was porous. During carbonation, CaCO$_3$ was formed, which occupied a larger molar volume than CaO (36.9 cm$^3$/mol instead of 16.9 cm$^3$/mol), which impended CO$_2$ transport due to pore closing. Sintering of CaCO$_3$ additionally blocks pores. Thus, a carbonate layer generated on the CaO particle surface resulted in the trapping of un-reacted CaO inside the particles. The following calcination led to the formation of CaO particles exceeding the initial ones in size. Finally, as cycling proceeded, the rigid interconnected CaO backbone appeared, and only its outer layer was involved in carbonation, while the core stayed out of the reaction.
The Zr-doped CaO sorbent exhibited improved stability compared to pure CaO. The incorporation of inert and thermally resistant CaZrO$_3$ with a high Tammann temperature (1218 °C) [20] created the framework acting as a barrier to CaCO$_3$ sintering, thereby preventing CaO particle growth and the sorbent porosity reduction, that positively affected CO$_2$ access to CaO and consequently prevented a rapid decrease in the amount of CaO ready to carbonate with a rise in the cycle number. Well-dispersed CaZrO$_3$ provided stability of the CaO sorbent microstructure and sorption capacity during multiple carbonation–calcination cycles. However, in order to fabricate an effective Zr-doped CaO sorbent with simultaneously high and cyclically stable CO$_2$ uptake capacity, the quantity of the dopant should be minimized.

4. Conclusions

The Zr-doped CaO sorbent for high-temperature CO$_2$ capture was for the first time fabricated by the wet high-energy co-milling of calcium carbonate and natural zirconium dioxide (baddeleyite). After 50 carbonation–calcination cycles, the Zr-doped CaO sorbent retained high enough CO$_2$ uptake capacity of 8.6 mmol/g, while the CO$_2$ uptake capacity of the undoped one dropped to only 1.0 mmol/g.

Scanning electron microscopy, energy-dispersive X-ray analysis and X-ray diffraction results indicated that the Zr-doped CaO sorbent maintains a high sorption ability due to the formation of an inert and thermally resistant calcium zirconate framework. CaZrO$_3$ nanoparticles with a size of about 20 nm are uniformly distributed in the CaO matrix and impede sintering of low Tammann temperature CaCO$_3$ formed under CaO carbonation, thereby preventing unwanted growth of CaO nanoparticles.

The proposed easy-to-implement CaO-based sorbents fabrication technique is promising for industrial scale production.

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