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The Zr-Doped CaO CO_2 Sorbent Fabricated by Wet High-Energy Milling

Vyacheslav V. Rodaev * and Svetlana S. Razlivalova

Institute for Nanotechnology and Nanomaterials, Derzhavin Tambov State University,
Internatsionalnaya Street 33, 392000 Tambov, Russia; razlivalova8@yandex.ru

* Correspondence: rodaev1980@mail.ru; Tel.: +7-910-6522328; Fax: +7-4752-532680

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Abstract: We fabricated the Zr-doped CaO sorbent for high-temperature CO_2 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 CO_2 uptake capacity was determined using thermogravimetric analysis. After 50 carbonation–calcination cycles, the Zr-doped CaO sorbent characterized by a high enough CO_2 uptake capacity of 8.6 mmol/g and unchanged microstructure due to $CaZrO_3$ nanoparticles uniformly distributed in the CaO matrix to prevent $CaCO_3$ sintering under carbonation. The proposed easy-to-implement CaO-based sorbents fabrication technique is promising for industrial application.

Keywords: CaO; ZrO_2; high-energy milling; CO_2 capture; sorbent

1. Introduction

Carbon dioxide is among the major greenhouse gases promoting global warming leading to climate change. The main anthropogenic CO_2 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, CO_2 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 CO_2 capture: pre-combustion, post-combustion and oxy-combustion [3–5]. Post-combustion capture, used to capture CO_2 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 CO_2 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 $CaO+CO_2 \leftrightarrow CaCO_3$: 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, Al_2O_3, ZrO_2, Y_2O_3, CeO_2 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. ZrO_2 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%, Kovdorsky 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 we 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 $CuK\alpha1$ 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 CO_2 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 ZrO_2 resulted in a sorbent initial capacity reduction. The dopant was inactive for CO_2 capture which reduced the initial CO_2 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.
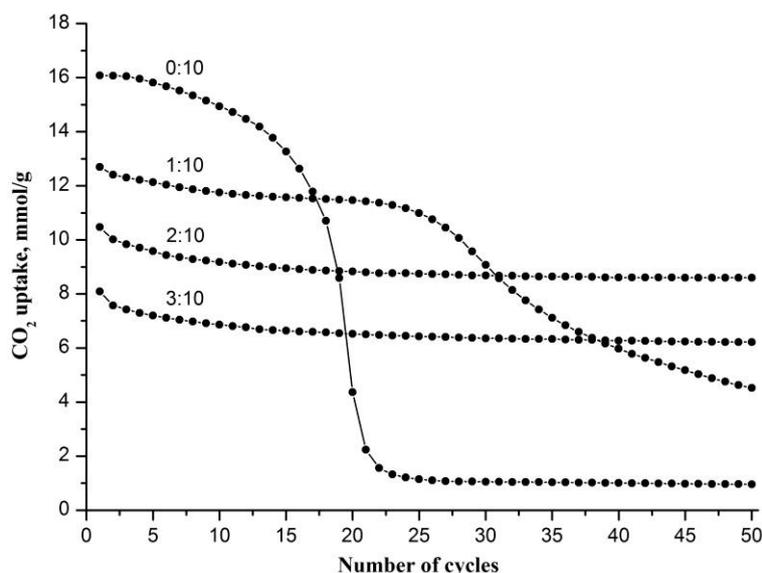

Figure 1. The dependencies of the CO_2 uptake capacity of the sorbents with different Zr/Ca molar ratios on the number of carbonation–calcination cycles.

During the multi-cycle carbonation–calcination process, the Zr-doped CaO sorbent prepared by wet high-energy milling showed the CO_2 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.
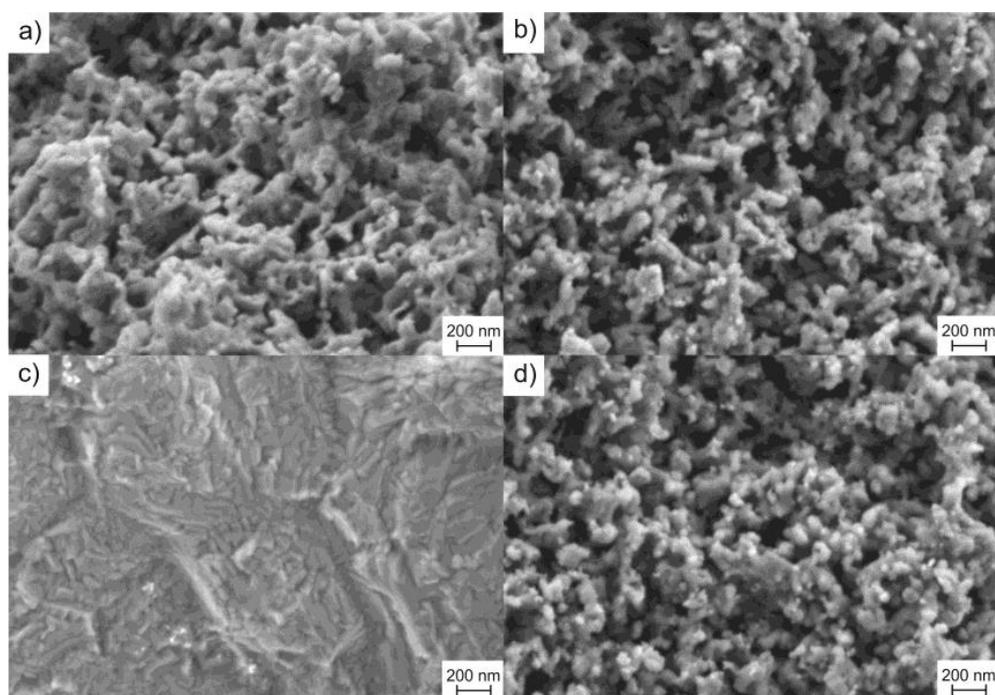

Figure 2. SEM images of the virgin sorbents and the same sorbents after the 50 cycle: (**a,c**) the pure CaO sorbent; (**b,d**) the Zr-doped CaO sorbent.

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.

Table 1. The specific surface area and pore volume of the virgin sorbents and the same sorbents after carbonation–calcination cycling.

Sorbent	Before the 1st Cycle		After the 50th Cycle	
	S_{BET}, m^2/g	V_{sp}, cm^3/g	S_{BET}, m^2/g	V_{sp}, cm^3/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° 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°, 56.7 and 65.8°, 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°, 30.2 and 31.5°) 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).
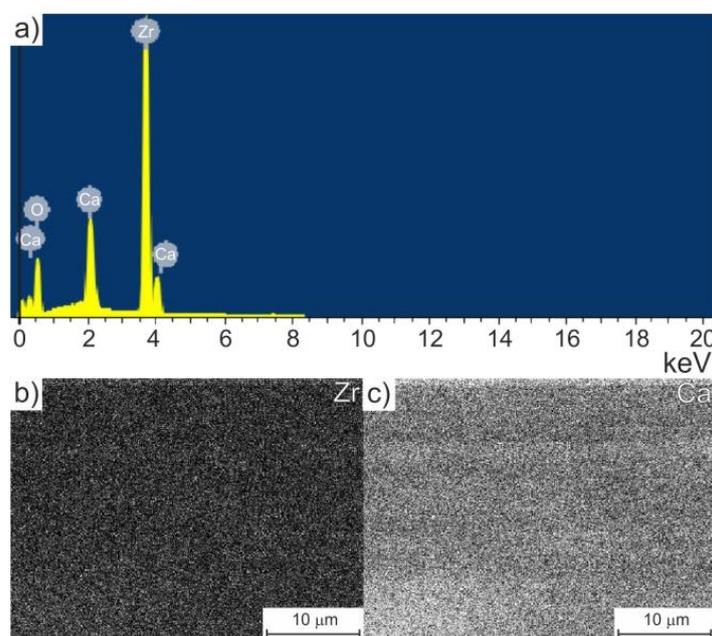

Figure 3. The results of (**a**) energy-dispersive X-ray spectrometer (EDS) analysis of the virgin Zr-doped CaO sorbent; (**b**,**c**) EDS mapping of Zr and Ca in the virgin Zr-doped CaO sorbent.

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.
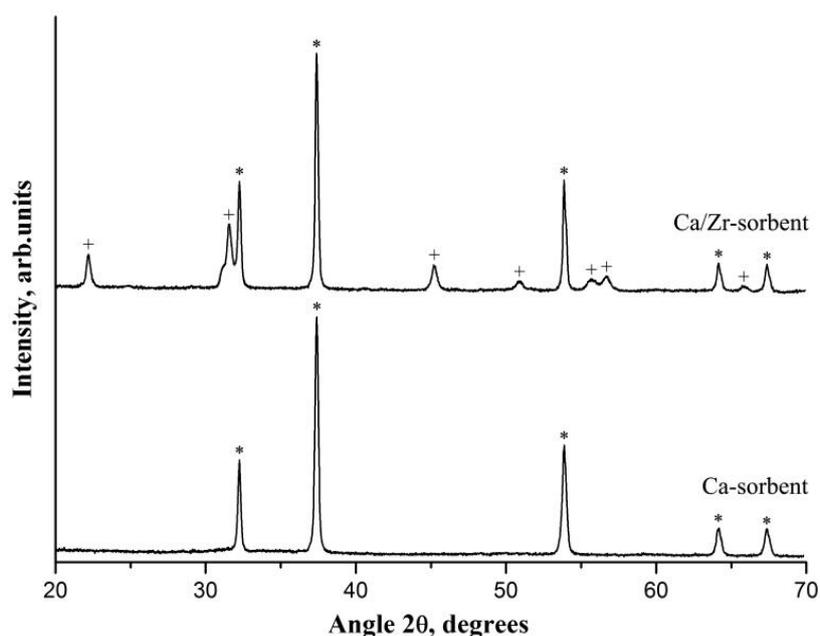
Figure 4. XRD patterns of the pure CaO sorbent and the Zr-doped CaO sorbent. The following compounds were identified: (*)–CaO; (+)–CaZrO$_3$.

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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Conflicts of Interest: The authors declare no conflict of interest.

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