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Effect of Pelletization and Addition of Steam on the Cyclic Performance of Carbon-Templated, CaO-Based CO_2 Sorbents

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ABSTRACT: In this work, we report the development of a synthetic CO_2 sorbent that possesses a high cyclic CO_2 uptake capacity and, in addition, sufficient mechanical strength to allow it to be used in fluidized-bed reactors. To overcome the problem of elutriation of the original powdered material, the synthetic CO_2 sorbent was pelletized. An important aspect of this work was to assess the effect of steam on the cyclic CO_2 capture capacity of the original, powdered CO_2 sorbent and the pelletized material. After 30 cycles of repeated calcination and carbonation reactions conducted in a fluidized bed, the CO_2 uptake of the pellets was 0.29 g of CO_2/g of sorbent, a value that is 45% higher than that measured for the reference limestone. For the case that carbonation/calcination cycles were conducted in a thermogravimetric analyzer under steam-free carbonation conditions, the CO_2 uptake of the best sorbent was 0.33 g of CO_2/g of sorbent (after 10 cycles). Importantly, it should be noted that, after 10 cycles using wet carbonation conditions, the CO_2 uptake of this material increased by 55% when compared to dry conditions. This observation was attributed to enhanced solid-state diffusion in the $CaCO_3$ product layer under wet conditions. However, independent of the reaction conditions, the pelletized material showed a lower cyclic CO_2 uptake when compared to the original powder. A detailed morphological characterization of the pellets indicated that the destruction of the primary, hollow micrometer-sized spheres during pelletization was responsible for the lower cyclic CO_2 uptake of the pellets.
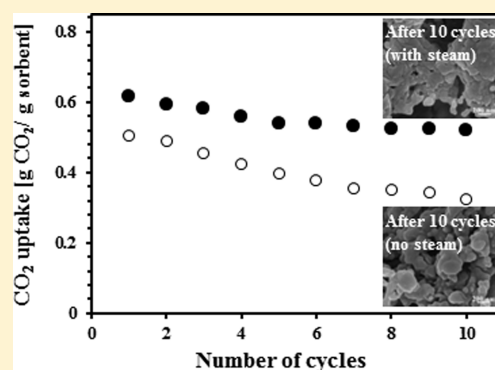
INTRODUCTION

The anthropogenic emissions of greenhouse gases, in particular, carbon dioxide, appear to be the main contributors to global warming and the climate change associated with it.[1] In 2010, the generation of electricity and heat were the industrial sectors that contributed most to the global anthropogenic CO_2 emissions, i.e., emitting 12.4 Gt, corresponding to ~41% of the total, global, anthropogenic CO_2 emissions.[2] Both industrial sectors rely on large-scale installations. Thus, the implementation of CO_2 capture and storage (CCS) technologies at large-scale CO_2 point sources has be proposed as a possibility to effectively reduce CO_2 emissions. However, the only CO_2 capture process that is currently available at large scale, i.e., amine scrubbing, comes with a large penalty for plant efficiency.[3] Thus, significant research efforts are currently directed toward the development of novel, less energy intensive CO_2 capture processes. Promising alternatives to amine scrubbing can be a process using solid CO_2 sorbents, such as zeolites, hydrotalcite-like compounds, metal oxides, or carbon-based materials.[4] Because of its low price and high availability in naturally occurring minerals (limestone or dolomite), theoretically high CO_2 uptake capacity, and fast CO_2 uptake kinetics, CaO is arguably the most promising CO_2 capture material

among the wide range of potential solid CO_2 sorbents.[5−9] Using CaO as a CO_2 sorbent, the CO_2 capture and sorbent regeneration occurs via the reversible reaction.

$$CaO(s) + CO_2(g) \leftrightarrow CaCO_3(s) \tag{1}$$
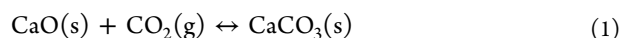
The carbonation reaction is characterized by an initial rapid, kinetically controlled reaction stage, in which pores of diameter $d_{pore} < 100$ nm are filled with the $CaCO_3$ product.[10] Once the pores have been filled or blocked, a rapid transition to a significantly slower reaction stage occurs. In this reaction stage, $CaCO_3$ is deposited on the outside of CaO grains.[10] Alvarez and Abanades[11] estimated the critical $CaCO_3$ layer thickness, at which the transition from the fast to the diffusion-limited reaction stage occurs, to be approximately ~50 nm. CaO derived from natural sorbents has, however, another serious drawback, viz., a rapid decay in its CO_2 capture capacity with cycle number.[12] The rapid decrease in its CO_2 uptake capacity has been attributed previously to thermal sintering, resulting in

a loss of volume in small pores.[11] In the past, various methods have been proposed to reactivate or stabilize the CO_2 uptake of limestone, with steam activation probably being the most promising approach.[13−15] The presence of steam during the carbonation and calcination reaction also effects the cyclic CO_2 capture capacity of CaO-based sorbents.[13−16] There seems to be a general agreement that the presence of steam during the calcination step significantly enhances the rate of the calcination reaction, even at a relatively low partial pressure of steam (∼0.0077 atm).[16] On the other hand, contradictory results have been reported concerning the influence of steam on the carbonation reaction. For example, Manovic and Anthony[17] reported an improved cyclic CO_2 uptake of limestone under wet carbonation conditions, which was explained by an enhancement of the solid-state diffusion in the $CaCO_3$ product layer. In contrast, Linden et al.,[18] who investigated the effect of steam on the carbonation of limestone in the temperature range of 450−550 °C, found that steam had a negligible impact for reaction temperatures of >500 °C. A major drawback of the reactivation by the hydration approach is reduced mechanical stability of the CO_2 sorbent, leading to enhanced attrition rates and, consequently, the elutriation of fines from fluidized-bed reactors.[19] This negative effect of steam reactivation on the mechanical properties of CaO-based sorbents can be reduced or even avoided by a subsequent superheating step.[20]

An alternative strategy to circumvent the rapid decay in the CO_2 capture capacity of naturally derived CaO is the development of synthetic CO_2 sorbents, in which CaO is stabilized by a high melting point support, e.g., Al_2O_3,[21,22] MgO,[23,24] or ZrO_2.[25,26] Thus far, many different techniques have been employed to manufacture synthetic CO_2 materials, such as (i) sol−gel,[21] (ii) co-precipitation,[23] or (iii) flame spray pyrolysis.[26] However, to date, most synthetic CaO-based CO_2 sorbents were produced in the form of powders, thus making them of very little practical relevance. Furthermore, their cyclic CO_2 capture capacity has often been assessed under unrealistic conditions, i.e., ignoring the effect of steam or in situations where calcination was performed at low temperatures.

Thus, this work is concerned with the development of a synthetic CO_2 sorbent that possesses favorable CO_2 uptake characteristics and, at the same time, sufficient mechanical strength to allow for its use in fluidized-bed reactors. To overcome the problem of friability and elutriation of the original powder, the synthetic material was first pelletized. The effect of pelletization on the morphology and, in turn, the CO_2 uptake characteristics of the material was studied in detail. An important facet of this work has been the assessment of the effect of steam on the CO_2 uptake of the original powder and the pelletized material.

2. EXPERIMENTAL SECTION

2.1. Preparation of CaO-Based Pellets. The CaO-based, Al_2O_3-stabilized powder was prepared according to the protocol recently reported by Broda and Müller.[27] Here, an appropriate amount of resorcinol was dissolved in reverse-osmosis water (15 MΩ·cm). After complete dissolution, formaldehyde was added to the aqueous solution of resorcinol to obtain a molar ratio of resorcinol/formaldehyde of 1:2. Subsequently, $Ca(NO_3)_2·4H_2O$ (Acros Organics) and Al-$(NO_3)_3·9H_2O$ (Acros Organics) were dissolved in water (1.5 M solution) and added to the aqueous solution of resorcinol and formaldehyde to obtain a molar ratio of $C/(Ca^{2+} + Al^{3+})$ of

80:20. The mixture was stirred for 5 min at room temperature. Gelation was performed in a water bath at 80 °C for 3 days. The gel obtained was pyrolyzed for 2 h at 500 °C in a tubular, horizontal furnace under a nitrogen flow of 0.5 L/min and then calcined at 800 °C for 2 h in a muffle furnace. Subsequently, a mechanical pelletizer (Glatt GmbH) was used to prepare the pellets (batch mode). During pelletization, water was sprayed intermittently through a nozzle that dispersed water into micrometer-sized droplets (<300 μm at ∼25 mL/min water and a total pressure of 800 kPa). The final size of the pellets is predominantly affected by the droplet size and the total amount of water added. The pellet size was also controlled by the speed of a pair of rotor blades attached to the vessel, i.e., one agitator (operated at 500 rpm) located on the bottom and one chopper (operated at 2500 rpm) on the side. Typically, it took 20−30 min to produce one batch of pellets. After pelletization, the pellets were sieved (1.18−2 mm) and air-dried.

For comparison, the CaO-based powder was pressed into pellets using a manual hydraulic press (Specac) without the addition of water (denoted as dry pellets). The dry pellets were sieved to size of 1.18−2 mm.

2.2. CO_2 Capture Test. The cyclic carbonation tests were performed using a PerkinElmer TGA-7 thermogravimetric analyzer (TGA). The sorbent sample (5−10 mg) was placed in a platinum pan (5 mm inner diameter) suspended in a quartz tube (20 mm inner diameter). The gas flow rate, controlled by a flowmeter, was 40 mL/min. The sample mass during the experiments was recorded, and the degree of carbonation was calculated on the basis of the recorded mass change, assuming that the observed mass change was exclusively due to the formation and decomposition of $CaCO_3$. A gas mixture containing 20% CO_2 (balance N_2) was used during both the calcination and carbonation reactions. The pellets were carbonated and calcined at 600 and 900 °C, respectively. During the cooling step, the gas atmosphere was switched to N_2 to avoid carbonation before the actually desired carbonation temperature was reached. The heating and cooling rates were set to 50 °C/min. To stabilize the carbonation temperature, the gas mixture (20% CO_2 in nitrogen) for the carbonation step was introduced 10 min after the carbonation temperature was reached. The carbonation reaction was performed for 10 min. In the experiments, which assessed the effect of steam, steam was introduced via a syringe pump fed steam generator such that the carbonation reaction was performed in an atmosphere containing 20 vol % CO_2, 20 vol % H_2O, and 60 vol % N_2. To avoid any condensation, the steam feeding lines were electrically heated (150 °C).

In addition, to assess the performance of the pellets under fluid-dynamic conditions that mimic practical reactors, the cyclic calcination and carbonation reactions were conducted in a fluidized-bed reactor. The fluidized-bed reactor was constructed of a quartz tube (length of 500 mm and inner diameter of 25 mm). A sintered quartz frit, positioned 250 mm above the bottom of the reactor, was used as the gas distributor. The reactor was placed in an electrically heated, tubular, vertical furnace (Carbolite MTF 12/38/250). The temperature of the bed (20 mL of Al_2O_3 sieved to a size of 300−425 μm, which corresponds to ∼36.5 g of Al_2O_3) was controlled via an N-type thermocouple. The flow rates of N_2 and CO_2 were controlled using calibrated flow-meters (Honeywell AWM5101N) and a computer-controlled solenoid valve setup. A stream (1 L/min) of the effluent gas of the reactor was sampled via a quartz tube and subsequently dried via an anhydrous $CaCl_2$ trap. The CO_2

concentration of the dehydrated sample gas was continuously monitored using a non-dispersive infrared analyzer (ABB Uras26). In a typical experiment, the bed was heated to 750 °C under a flow of 3 L/min N_2. Once the reaction temperature was reached, 0.5 g of the calcined and sieved pellets (sieved to a size of 1.18−2 mm) was added to the fluidized bed. Once the reaction temperature was stabilized, a CO_2 flow of 0.75 L/min was added to the N_2 flow such that the carbonation reaction was performed in an atmosphere containing 20 vol % CO_2. At 750 °C, the ratio U/U_{mf} was ∼5.6. After carbonation (360 s), the CO_2 flow was turned off, allowing the sorbent to recalcine in a pure N_2 atmosphere. In total, 30 cycles of the repeated carbonation and calcination reactions were performed.

2.3. Structural Characterization. The surface structure of the CaO-based materials was characterized using scanning electron microscopy (Zeiss Gemini 1530 FEG and Hitachi S3400). A double-sided carbon tape was used to attach the material onto a 12.5 × 10 mm aluminum holder. Prior to imaging, the sample was sputter-coated (MED 010) with an approximately 8 nm thick layer of platinum.

An N_2 adsorption analyzer (Quantachrome NOVA 4000e) was used to determine the surface area and pore volume of the CO_2 sorbents. The surface area was calculated using the Brunauer−Emmett−Teller (BET) model,[28] whereas the volume of pores with diameters d_{pore} < 100 nm was estimated using the Barrett−Joyner−Halenda (BJH) model.[29] Prior to the acquisition of the N_2 isotherms, each sample was degassed at 300 °C for at least 3 h.

3. RESULTS AND DISCUSSION

First, the structural changes during hydration/pelletization of the powdered material as determined by high-resolution scanning electron microscopy (HR-SEM) are presented. Figure 1a confirms that the original, carbon-templated CO_2 sorbent
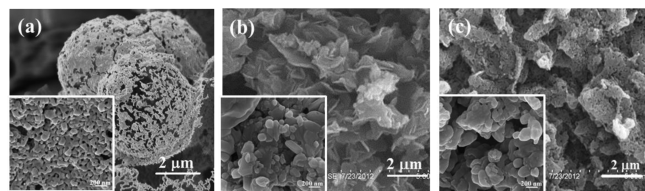

Figure 1. SEM images of unreacted CaO-based CO_2 sorbents: (a) original carbon-templated CO_2 material, (b) freshly pelletized material, and (c) calcined pellets.

(CaO-based, Al_2O_3-stabilized material in which a resorcinol−formaldehyde gel was used as a hard template to generate extra porosity[27]) is composed of hollow spheres, which formed after the removal of the template via calcination in air. Furthermore, an inset of Figure 1a shows that the shell of the hollow sphere is composed of spherical grains with a size of 135 ± 32 nm. However, after pelletization (Figure 1b), the morphology of the CO_2 sorbent substantially changed. In Figure 1b, hollow spheres cannot be observed anymore. Indeed, hydration, i.e., the transformation of CaO into $Ca(OH)_2$, densified the material. Nonetheless, the primary grains comprising the pellets were only slightly larger than the grains that comprised the shell of the hollow spheres, i.e., 226 ± 74 nm. Furthermore, after calcination, the pelletized material maintained its morphology; i.e., the size of the grains was 187 ± 42 nm. Thus, pelletization and subsequent calcination did not seem to negatively affect the grain size of the material.

Scanning electron micrographs of the original powder and the pellets after being exposed to 10 cycles of the repeated carbonation and calcination reactions are shown in Figure 2.
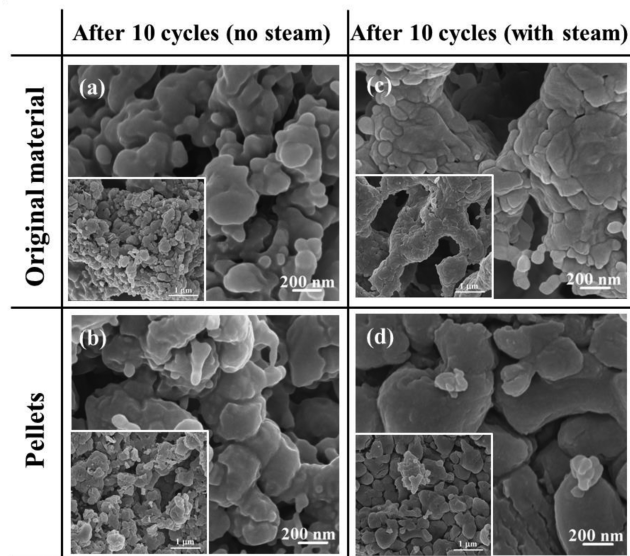

Figure 2. SEM images of CaO-based CO_2 sorbents after 10 cycles: (a and c) original carbon-templated CO_2 sorbent and (b and d) pellets.

The HR-SEM images given in panels a and b of Figure 2 demonstrate that, under a dry carbonation reaction, the initial morphology of the synthetic CO_2 sorbents (panels a and c of Figure 1) did not change significantly over 10 cycles. On the basis of the analysis of 30 grains, the average grain size of the powdered material and the pellets was determined as 175 ± 83 and 191 ± 86 nm, respectively. This observation is in agreement with Broda and Müller,[27] who reported that the carbon-templated material maintained its nanostructured morphology over 30 cycles using calcination temperatures of 750 °C. However, for the case that steam was added during the carbonation reaction, both synthetic CO_2 sorbents lost their nanostructured morphology, resulting in the formation of large grains separated by micrometer-size voids (panels c and d of Figure 2).

Turning now to the N_2 adsorption measurements of the calcined CO_2 sorbents, BET surface area and BJH pore volume of 15 m^2/g and 0.12 cm^3/g, respectively, were determined for the original powder. After pelletization and calcination, the surface area and pore volume of the material decreased to 12 m^2/g and 0.05 cm^3/g, respectively; i.e., the decrease in pore volume is more pronounced than the drop in surface area.

The CO_2 uptake, defined as grams of CO_2 captured per gram of sorbent, was used to characterize the CO_2 capture performance of the CO_2 sorbents synthesized here. First, the pellets were subjected to multiple carbonation/calcination cycles in a fluidized bed, allowing us to assess their mechanical stability. The fluidized bed was operated in the bubbling regime (U/U_{mf} ∼ 5.6). The cyclic CO_2 uptake of the pellets, as obtained from the fluidized-bed experiments, is plotted in Figure 3. For comparison, the performance of Cadomin limestone is also included in Figure 3. In the fluidized-bed experiments, the CO_2 uptake of limestone decreased from 0.50 g of CO_2/g of sorbent in the first cycle to 0.20 g of CO_2/g of sorbent in the 30th cycles. On the other hand, the pellets developed here possessed a CO_2 uptake of 0.43 g of CO_2/g of
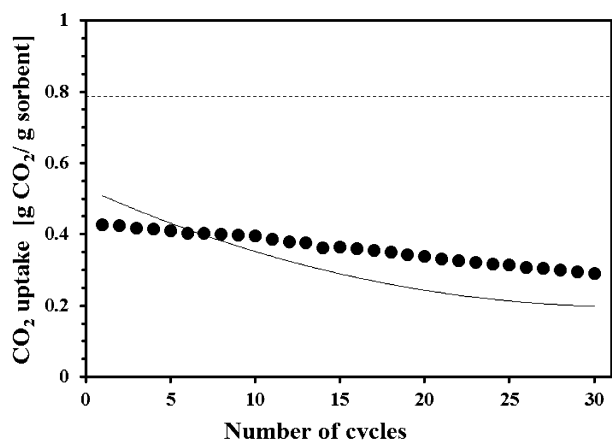
Figure 3. CO_2 uptake of (●) CaO-based pellets and (—) Cadomin limestone, as determined in a fluidized-bed reactor. The experiments were performed isothermally at 750 °C using a carbonation atmosphere of 20 vol % CO_2 in N_2. The dashed line gives the theoretical CO_2 uptake of pure CaO.

sorbent in the first cycle reducing to 0.29 g of CO_2/g of sorbent in the 30th cycle. Thus, after 30 cycles, the CO_2 uptake of the pellets was 45% higher than that of the reference limestone.

Subsequently, the influence of steam during carbonation was studied for both the original powder and the pellets in a thermogravimetric analyzer (TGA). Figure 4a shows that, even under severe calcination conditions, i.e., $T = 900$ °C, and the addition of steam during carbonation (20 vol %), the original CO_2 sorbent (powder) possessed a very high cyclic CO_2 capture capacity; i.e., the average CO_2 uptake over 10 cycles was 0.55 g of CO_2/g of sorbent. Interestingly, a significantly lower CO_2 capture capacity was measured for the original CO_2 sorbent (powder) under dry carbonation conditions. Here, the CO_2 uptake in the first and 10th cycles was 0.50 and 0.33 g of CO_2/g of sorbent, respectively. However, after 10 cycles and using dry carbonation conditions, the CO_2 uptake of the powder was still 50% higher than that of the reference limestone. Turning now to the pelletized material (Figure 4b), it can be seen that independent of the carbonation conditions, the pellets (prepared via the addition of water) showed a lower cyclic CO_2 uptake when compared to the original, powdered CO_2 sorbent. Under dry conditions, the pellets possessed a

CO_2 uptake of 0.20 g of CO_2/g of sorbent after 10 cycles, slightly under-performing limestone. This value increased to 0.31 g of CO_2/g of sorbent under wet conditions, a value that is ~10% higher than that of the reference limestone.

Previous work by Broda and Müller[27] demonstrated that the high cyclic CO_2 capture capacity of carbon-templated, CaO-based, and Al_2O_3-stabilized CO_2 sorbents was due to its nanostructure, i.e., being composed of grains with an average size of 170 nm, and the homogeneous dispersion of the high melting point mayenite, $Ca_{12}Al_{14}O_{33}$, which effectively stabilized the nanostructured morphology over repeated carbonation/calcination cycles. Mayenite is a mixed oxide of CaO and Al_2O_3 and is inert; i.e., it cannot be carbonated under the conditions studied here.[30] For CaO-based CO_2 sorbents, it is well-documented that the carbonation reaction can be split into two reaction regimes, i.e., an initial, very rapid, kinetically controlled reaction rate, characterized by a linear functionality between the sample mass and reaction time.[10] This is followed by a significantly slower reaction regime, in which newly formed $CaCO_3$ is deposited on the outside of the CaO grains.[10] Because the critical product layer of $CaCO_3$ is estimated as ~50 nm,[11] nanostructuring of the material would minimize the extent of the slow, diffusion-limited reaction regime of the carbonation reaction. Thus, with regard to excellent CO_2 capture characteristics, it is critical that the nanosized structure of the original material is not destroyed during the pelletization process and subsequent carbonation/calcination cycles. Figure 1c seems to confirm that, during pelletization, the nano-structured character of the material is maintained; i.e., the particle size of the nanometer-sized building blocks of the CO_2 sorbent only increased from 135 ± 32 nm in the original powder to 187 ± 42 nm in the pelletized material. However, in comparison of panels a and c of Figure 1, the pelletization process and subsequent calcination have seemingly "densified" the material; i.e., the central voids of the hollow spheres and the large voids between individual spheres were destroyed. The dramatic morphological changes of the pellets as imaged by electron microscopy are accompanied by a sharp reduction in the volume in pores with $d_{pore} < 100$ nm. Figure 5, which plots the BJH pore size distribution of the CO_2 sorbents as a function of the pore diameter, revealed a bimodal pore size distribution with peaks located at $d_p \sim 4$ and ~20 nm for the original powder. On the other hand, after pelletization, the pore size
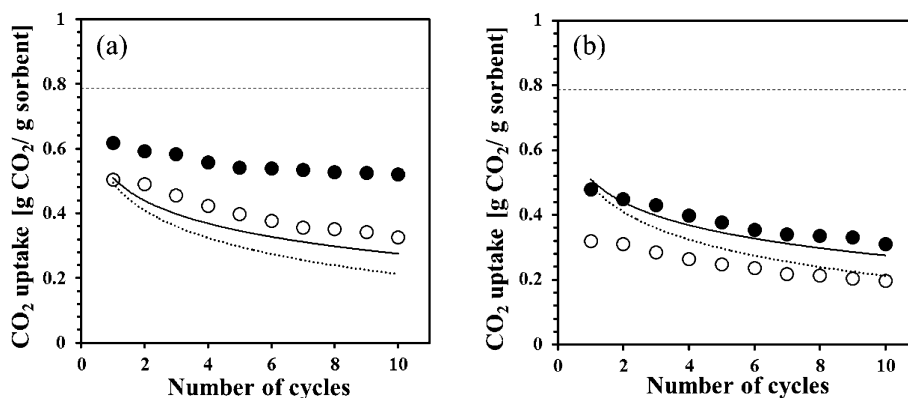

Figure 4. CO_2 capture performance of (a) the original carbon-templated CO_2 sorbent (powder form) and (b) the pelletized material, as determined in a TGA. Experiments were performed (●) with and (○) without the addition of steam during the carbonation reaction. The cyclic CO_2 capture capacity of limestone under wet (—) and dry (···) conditions is plotted for comparison. The dashed line gives the theoretical CO_2 uptake of pure CaO.
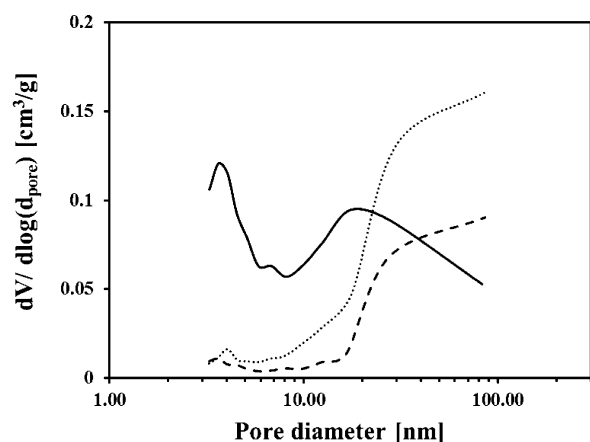
Figure 5. BJH pore size distribution of CaO-based CO_2 materials in their calcined stage: (—) original powder, (⋯) pellets, and (- - -) dry pellets.

distribution shifts dramatically to larger pore diameters. For pellets, pores with d_p > 20 nm dominate. For comparison, the pore size distribution of the dry pellets is also plotted in Figure 5. From Figure 5, it is evident that, independent of the pelletization method used, the pore volume in pores with d_{pore} < 20 nm in pellets is significantly reduced. The destruction of the highly porous structure of the original powder during the pelletization process results in a denser and more sintering susceptible material. This dramatic change in morphology may explain the substantial difference in the CO_2 uptake between the pellets and the original powder (Figure 4). A higher susceptibility to sintering of the pellets when compared to the original powder is in agreement with an earlier report by Borgwardt,[31] who investigated the rate of sintering of CaO derived from both limestone and $Ca(OH)_2$. He observed a significantly higher sintering rate for CaO prepared from $Ca(OH)_2$.[31] Borgwardt explained this observation on the basis of the lower porosity of CaO derived from $Ca(OH)_2$. This implied a closer contact between grains and a greater propensity for neck formation.

Turning now to the reacted CO_2 sorbents, the HR-SEM images given in panels a and b of Figure 2 demonstrate that, under dry carbonation conditions, the initial morphology of the synthetic CO_2 sorbents (panels a and c of Figure 1) did not change significantly over 10 cycles. On the other hand, after the

addition of steam, both synthetic CO_2 sorbents lost their nanostructured morphology, resulting in the formation of large grains and voids (panels c and d of Figure 2). The substantial difference in the morphology of materials exposed to either dry or wet carbonation conditions can be attributed to an acceleration of sintering under wet carbonation conditions because of the surface interaction between H_2O and unreacted CaO, i.e., possibly forming short-lived hydroxyl groups at the surface, which, in turn, enhance the mobility of O^{2-} along the surface.[32] However, these observations are, at first sight, inconsistent with the results of the CO_2 capture experiments that show a significantly increased CO_2 uptake capacity of the sorbents under wet carbonation conditions (Figure 4). To better understand the effect of steam during carbonation, the CO_2 uptake as a function of time is plotted in Figure 6. It can be seen that, in the 10th cycle and under dry conditions, the contribution of the fast reaction stage to the overall CO_2 uptake was 48 and 40% for the original powder and pellets, respectively. In contrast, these values decreased to 37 and 32% under wet conditions, respectively. Figure 6 shows that the addition of steam has a very positive effect on the diffusion-limited stage of the carbonation reaction. According to Manovic and Anthony,[17] the higher cyclic CO_2 uptake under wet carbonation conditions may be due to an enhancement of solid-state diffusion in the $CaCO_3$ product layer. This is in agreement with the work by Bhatia and Perlmutter,[33] who proposed a reaction mechanism that is controlled by the effective diffusion of CO_2 through a sequential decomposition of carbonate ions in the $CaCO_3$ product layer for temperatures exceeding 515 °C. A different reaction mechanism was introduced by Sun et al.,[34] who investigated the carbonation reaction of CaO using an inert marker technique and proposed that the carbonation reaction was controlled by the counter-current diffusion of CO_3^{2-} (diffusing inward from the $CaCO_3$/gas interface to the $CaCO_3$/CaO interface) and O^{2-} (diffusion outward from the $CaCO_3$/CaO interface to the $CaCO_3$/gas interface). Upon the addition of steam, H^+ interacted with O^{2-}, forming OH^-.[35] Because OH^- diffuses faster from the $CaCO_3$/CaO interface to the $CaCO_3$/gas interface than O^{2-}, steam enhances the overall rate of the carbonation reaction.

In this work, we investigated the cyclic CO_2 uptake of carbon-templated, CaO-based sorbents, in either powdered or pelletized form, in a TGA and fluidized-bed reactor, which mimics practical reaction conditions. However, pelletization has
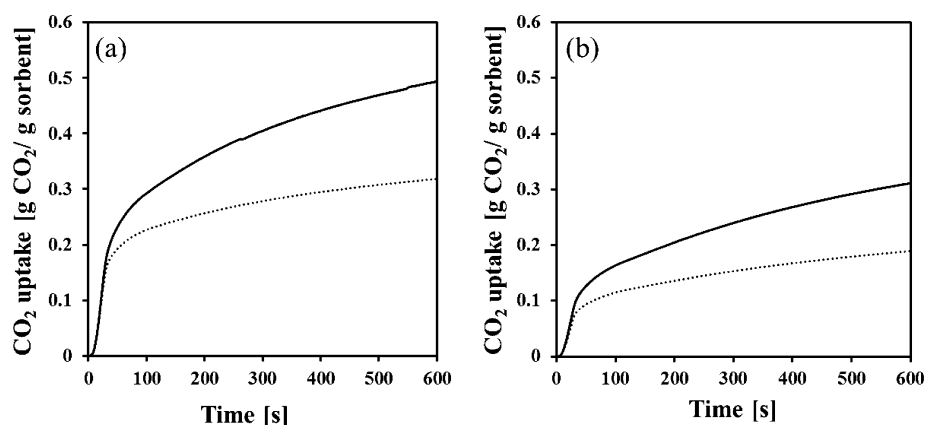

Figure 6. CO_2 uptake as a function of the reaction time for the 10th carbonation and calcination cycle: (a) original powder and (b) pellets, as determined in a TGA. The following carbonation conditions are plotted: (—) wet condition and (⋯) dry condition.

a serious drawback, i.e., the destruction of the original morphology of the hollow micrometer-sized spheres and a sharp reduction of the volume in pores with d_{pore} < 100 nm. The pelletized materials are, thus, more susceptible to sintering. This morphological modification of the material was reflected by a lower cyclic CO_2 uptake when compared to the original, powdered CO_2 sorbent. It was also found that both CaO-based sorbents exhibited a significantly higher cyclic CO_2 uptake under wet carbonation conditions. However, under these conditions, the materials lost their nanostructured morphology, resulting in micrometer-sized grains separated by large voids. The increased CO_2 uptake under humid carbonation conditions implies, however, that the reduction in pore volume and porosity was more than offset by the enhanced solid-state diffusion in the $CaCO_3$ product layer. After 10 carbonation/calcination cycles, the CO_2 uptake of the best sorbent (powder) was 0.52 g of CO_2/g of sorbent, exceeding the performance of the reference limestone by 85%. However, independent of the carbonation condition used, the pelletized material showed a lower cyclic CO_2 uptake when compared to the original, powdered CO_2 sorbent. Under dry carbonation conditions and after 10 cycles, the pellets possessed a CO_2 uptake of 0.20 g of CO_2/g of sorbent, slightly under-performing limestone. This value increased to 0.31 g of CO_2/g of sorbent under wet carbonation conditions, a value that is ∼10% higher than that of the reference limestone. For the case that the carbonation and calcination reactions were performed in a fluidized bed, the CO_2 uptake of the pelletized material was 0.29 g of CO_2/g of sorbent after 30 cycles, outperforming the reference limestone by 45%.

An important requirement for potential CO_2 sorbents is a sufficient mechanical strength to allow them to be used in fluidized beds. Our fluidized-bed experiments demonstrate that the pelletized material is of sufficient mechanical strength for such a process. Assessing their CO_2 uptake in a fluidized bed showed that the pellets exceed the CO_2 uptake of the reference limestone by 45%. On the basis of these observations, we believe that pelletization has considerable potential to manufacture efficient CO_2 sorbents that can be used in practical installations. However, to assess in detail the attrition resistance of the material reported here, further measurements would be required.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Manabe, S.; Wetherald, R. T. On the distribution of climate change resulting from an increase in CO_2 content of the atmosphere. *J. Atmos. Sci.* **1980**, *37*, 99−118.

(2) International Energy Agency (IEA). *World Energy Outlook*; IEA: Paris, France, 2012.

(3) Bailey, D. W.; Feron, P. H. M. Post-combustion decarbonisation processes. *Oil Gas Sci. Technol.* **2005**, *60*, 461−474.

(4) Choi, S.; Drese, J. H.; Jones, C. R. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. *ChemSusChem* **2009**, *2*, 796−854.

(5) Kierzkowska, A. M.; Pacciani, R.; Müller, C. R. CaO-based CO_2 sorbents: From fundamentals to the development of new, highly effective materials. *ChemSusChem* **2013**, *6*, 1130−1148.

(6) Broda, M.; Kierzkowska, A. M.; Baudouin, D.; Imtiaz, Q.; Copéret, C.; Müller, C. R. Sorbent enhanced methane reforming over a Ni−Ca-based, bi-functional catalyst sorbent. *ACS Catal.* **2012**, *2*, 1635−1646.

(7) Kierzkowska, A. M.; Poulikakos, L. V.; Broda, M.; Müller, C. R. Synthesis of calcium-based, Al_2O_3-stabilized sorbents for CO_2 capture using a co-precipitation technique. *Int. J. Greenhouse Gas Control* **2013**, *15*, 48−54.

(8) Broda, M.; Manovic, V.; Imtiaz, Q.; Kierzkowska, A. M.; Anthony, E. J.; Müller, C. R. High-purity hydrogen via the sorption-enhanced steam methane reforming reaction over a synthetic CaO-based sorbent and a Ni catalyst. *Environ. Sci. Technol.* **2013**, *47*, 6007−6014.

(9) Anthony, E. J. Ca looping technology: Current status, developments and future directions. *Greenhouse Gas Sci. Technol.* **2011**, *1*, 36−47.

(10) Dennis, J. S.; Pacciani, R. The rate and extent of uptake of CO_2 by a synthetic, CaO-containing sorbent. *Chem. Eng. Sci.* **2009**, *64*, 2147−2157.

(11) Alvarez, D.; Abanades, J. C. Determination of the critical product layer thickness in the reaction of CaO with CO_2. *Ind. Eng. Chem. Res.* **2005**, *44*, 5608−5615.

(12) Grasa, G. S.; Abanades, J. C. CO_2 capture capacity of CaO in long series of carbonation/calcination cycles. *Ind. Eng. Chem. Res.* **2006**, *45*, 8846−8851.

(13) Symonds, R. T.; Lu, D. Y.; Hughes, R. W.; Anthony, E. J.; Macchi, A. CO_2 capture from simulated syngas via cyclic carbonation/calcination for a naturally occurring limestone: Pilot-plant testing. *Ind. Eng. Chem. Res.* **2009**, *48*, 8431−8440.

(14) Manovic, V.; Anthony, E. J. Steam reactivation of spent CaO-based sorbent for multiple CO_2 capture cycles. *Environ. Sci. Technol.* **2007**, *41*, 1420−1425.

(15) Donat, F.; Florin, N. H.; Anthony, E. J.; Fennell, P. S. Influence of high-temperature steam on the reactivity of CaO sorbent for CO_2 capture. *Environ. Sci. Technol.* **2012**, *46*, 1262−1269.

(16) Wang, Y.; Thomson, W. J. The effects of steam and carbon dioxide on calcite decomposition using dynamic X-ray diffraction. *Chem. Eng. Sci.* **1995**, *50*, 1373−1382.

(17) Manovic, V.; Anthony, E. J. Carbonation of CaO-based sorbents enhanced by steam addition. *Ind. Eng. Chem. Res.* **2010**, *49*, 9105−9110.

(18) Linden, I.; Backman, P.; Brink, A.; Hupa, M. Influence of water vapor on carbonation of CaO in the temperature range 400−550 °C. *Ind. Eng. Chem. Res.* **2011**, *50*, 14115−14120.

(19) Mess, D.; Sarofim, A. F.; Longwell, J. P. Product layer diffusion during the reaction of calcium oxide with carbon dioxide. *Energy Fuels* **1999**, *13*, 999−1005.

(20) Yin, J.; Qin, C.; An, H.; Veeraragavan, A.; Feng, B. Influence of hydration by steam/superheating on the CO_2 capture performance and physical properties of CaO-based particles. *Ind. Eng. Chem. Res.* **2013**, *52*, 18215−18224.

(21) Broda, M.; Kierzkowska, A. M.; Müller, C. R. Application of the sol−gel technique to develop novel, synthetic Ca-based sorbents that possess excellent CO_2 capture characteristics. *ChemSusChem* **2012**, *5*, 411−418.

(22) Broda, M.; Kierzkowska, A. M.; Müller, C. R. The influence of the calcination and carbonation conditions on the CO_2 uptake of synthetic Ca-based CO_2 sorbents. *Environ. Sci. Technol.* **2012**, *46*, 10849−10856.

(23) Filitz, R.; Kierzkowska, A. M.; Broda, M.; Müller, C. R. Highly efficient CO_2 sorbents: Development of synthetic, calcium-rich dolomites. *Environ. Sci. Technol.* **2012**, *46*, 559−565.

(24) Sultan, D. S.; Müller, C. R.; Dennis, J. S. The capture of CO_2 using sorbents of calcium magnesium acetate (CMA). *Energy Fuels* **2010**, *24*, 3687−3697.

(25) Broda, M.; Müller, C. R. Sol−gel-derived, CaO-based, ZrO_2-stabilized CO_2 sorbents. *Fuel* **2014**, *127*, 94−100.

(26) Koirala, R.; Gunugunuri, K. R.; Pratsinis, S. E.; Smirniotis, P. G. Effect of zirconia doping on the structure and stability of CaO-based sorbents for CO_2 capture during extended operating cycles. *J. Phys. Chem. C* **2011**, *115*, 24804−24812.

(27) Broda, M.; Müller, C. R. Synthesis of highly efficient, Ca-based, Al_2O_3 stabilized, carbon gel templated CO_2 sorbents. *Adv. Mater.* **2012**, *24*, 3059−3064.

(28) Brunauer, S.; Emmett, P. H.; Teller, E. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **1938**, *60*, 309−319.

(29) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. The determination of pore volume and area distribution in porous substances. I. Computation from nitrogen isotherms. *J. Am. Chem. Soc.* **1951**, *73*, 373−380.

(30) Li, Z. S.; Cai, N. S.; Huang, Y. Y.; Han, H. J. Synthesis, experimental studies and analysis of a new calcium-based carbon dioxide absorbent. *Energy Fuels* **2005**, *19*, 1447−1452.

(31) Borgwardt, R. H. Sintering of nascent calcium oxide. *Chem. Eng. Sci.* **1989**, *44*, 53−60.

(32) Borgwardt, R. H. Calcium oxide sintering in atmospheres containing water and carbon dioxide. *Ind. Eng. Chem. Res.* **1989**, *28*, 493−500.

(33) Bhatia, S. K.; Perlmutter, D. D. Effect of the product layer on the kinetics of the CO_2−lime reaction. *AIChE J.* **1983**, *29*, 79−86.

(34) Sun, Z. C.; Luo, S. W.; Qi, P. P.; Fan, L. S. Ionic diffusion through calcite ($CaCO_3$) layer during the reaction of CaO and CO_2. *Chem. Eng. Sci.* **2012**, *81*, 164−168.

(35) Li, Z. S.; Liu, Y.; Cai, N. S. Understanding the enhancement effect of high-temperature steam on the carbonation reaction of CaO with CO_2. *Fuel* **2014**, *127*, 88−93.