

# Mechanical Activation of CaO-Based Adsorbents for CO<sub>2</sub> Capture

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The reversible cycling of CaO adsorbents to CaCO<sub>3</sub> for high-temperature CO<sub>2</sub> capture is substantially improved by mechanical treatment. The mechanical milling intensity and conditions of grinding (e.g., wet vs. dry, planetary vs. vibratory milling) were determined to be the main factors that control the effectiveness of the mechanochemical synthesis to enhance the recycling stability of the sorbents prepared. In addition, MgO

was used as an example of an inert binder to help mitigate CaCO<sub>3</sub> sintering. Wet planetary milling of MgO into CaCO<sub>3</sub> allowed efficient particle size reduction and the effective dispersion of MgO throughout the particles. Wet planetary milling yielded the most stable sorbents during 50 cycles of carbonation–calcination.

## Introduction

Fossil-fuel-burning power plants account for approximately one third of anthropogenic CO<sub>2</sub> emissions.<sup>[1,2]</sup> Carbon capture and storage (CCS) has received considerable attention as an option to reduce CO<sub>2</sub> emissions from such power plants.<sup>[3,4]</sup> Currently the only commercialized CO<sub>2</sub> separation technology is amine scrubbing.<sup>[5]</sup> This technique, however, has several disadvantages, including poor energy efficiency, low adsorption/desorption rates, solvent degradation, and equipment corrosion.<sup>[6]</sup> In recent years there have been many efforts to find less energy-intensive and more cost-effective ways for CO<sub>2</sub> capture, which accounts for 75% of the overall cost of CCS.<sup>[3]</sup> In principle, coal conversion to synthesis gas (i.e., H<sub>2</sub> plus CO) with additional H<sub>2</sub> and CO<sub>2</sub> from the reaction of CO with water by the water–gas–shift (WGS) reaction allows the capture of CO<sub>2</sub> prior to combustion; such pre-combustion capture is one of the most viable options in integrated gasification combined cycle (IGCC) plants.<sup>[7]</sup> Combining high-temperature CO<sub>2</sub> adsorption with the WGS reaction has several advantages over conventional IGCC, which presently uses solvent-based CO<sub>2</sub> capture at low temperature (e.g., Selexol): high-temperature sorption of CO<sub>2</sub> would eliminate the need for multiple catalytic WGS reactors and a separate low-temperature CO<sub>2</sub> capture unit and would avoid several gas cooling and reheating steps.<sup>[8]</sup>

Among high-temperature CO<sub>2</sub> adsorbents, CaO-based materials are considered the most promising candidates because of their relatively low cost, high capacity, and selectivity toward CO<sub>2</sub>. CaO, however, suffers from rapid performance degradation over multiple cycles of carbonation and calcination,<sup>[9]</sup> primarily because CaCO<sub>3</sub> sinters during the high temperatures of the regeneration step, which can dramatically slow the amount of CO<sub>2</sub> binding in subsequent cycles.<sup>[1]</sup> This drawback can be largely overcome by the incorporation of inert additives into CaO sorbents to prevent sintering.<sup>[1]</sup> Various metal oxides have been investigated to improve CaO stability (e.g., MgO, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>).<sup>[10–14]</sup> Previous synthetic methods

to incorporate the inert oxides include precipitation,<sup>[15]</sup> calcination of precursors mixture,<sup>[16,17]</sup> flame spray pyrolysis,<sup>[12]</sup> and sol–gel combustion.<sup>[13]</sup> We present here a mechanochemical synthesis as a simple, efficient, and inexpensive tool for the synthesis of highly stable CaO-containing sorbents for high-temperature CO<sub>2</sub> capture. Mechanochemical synthesis (e.g., mechanical activation) by using high-energy ball milling has a long history as a powder processing technique to make alloys, composites, and structural materials.<sup>[18]</sup> In this technique, materials undergo repeated deformation, fracturing, and cold welding,<sup>[19]</sup> and at the end of the process, a finely dispersed composite structure is recovered.<sup>[18]</sup>

No systematic study has been reported in the literature on the use of mechanically treated CaO-based adsorbents for CO<sub>2</sub> capture applications. We have examined two common high-energy ball milling techniques (vibratory and planetary) in wet

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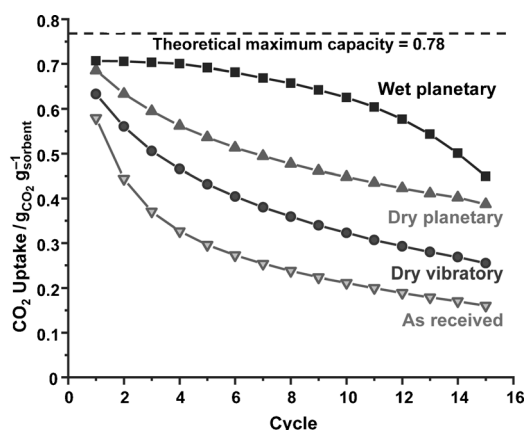
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or dry milling conditions and then studied the performance of the treated materials for CO<sub>2</sub> capture in a cyclic operation. MgO was chosen as an example of an inert additive material for this study because it possesses the highest melting temperature<sup>[20]</sup> (2826 °C) among refractory metal oxides and can provide structural stability to the CaO sorbent while resisting excessive CaO grain growth.<sup>[10]</sup>

## Results and Discussion

As a control, we first compared the recycling stability of milled pure CaCO<sub>3</sub> sorbents (as described in the Experimental Section) to that of as-received non-milled CaCO<sub>3</sub> from Sigma–Aldrich during 15 cycles of calcination–carbonation. As shown in Figure 1, the milled CaCO<sub>3</sub> samples show a higher CO<sub>2</sub> uptake



**Figure 1.** CO<sub>2</sub> uptake by CaO after calcination of pure CaCO<sub>3</sub> samples prepared under different milling conditions; carbonation at 650 °C for 30 min under 100% CO<sub>2</sub> and calcination at 900 °C for 5 min under 100% N<sub>2</sub>. Wet-milled CaCO<sub>3</sub> in planetary ball mill maintains the highest CO<sub>2</sub> uptake during 15 cycles of operation.

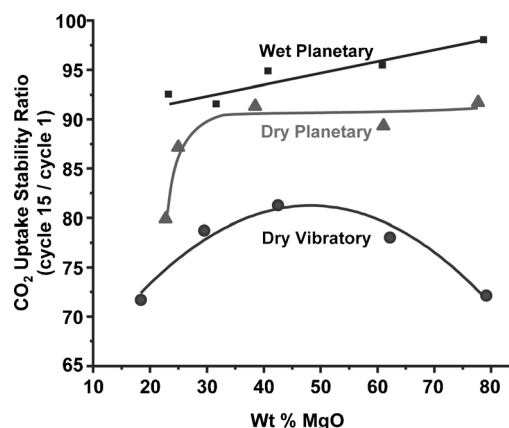
than the non-milled sample for 30 min carbonation at 650 °C. The rapid formation of a CaCO<sub>3</sub> layer on the outer surface of the CaO particles is followed by slow reactive diffusion of CO<sub>2</sub>.<sup>[1,9]</sup> It must be emphasized that the cycling between calcination and CO<sub>2</sub> re-uptake is a kinetically controlled process: in general, cycling experiments are not performed slowly enough for full equilibration to occur. Therefore, the CO<sub>2</sub> sorption rate is influenced both by particle size and by surface texture and porosity [as determined from the N<sub>2</sub> Brunauer–Emmett–Teller (BET) surface area]. Consistent with the observed behavior in Figure 1, the specific surface areas (N<sub>2</sub> BET) of the milled samples are significantly higher than that of the non-milled sample (Table 1).

The wet-planetary-milled CaCO<sub>3</sub> sample maintains the highest amount of CO<sub>2</sub> uptake (and thus the largest effective capacity for CO<sub>2</sub> binding over a finite time) with the least decay over 15 cycles of all samples. The wet-planetary-milled sample possesses the highest surface area and also the smallest median particle size (1 μm, based on particle mass), as shown in Table 1. In contrast, the dry-vibratory-milled CaCO<sub>3</sub> sample shows a substantial increase in mean particle size after milling

| Sample             | $A_{\text{BET}}$ [m <sup>2</sup> g <sup>-1</sup> ] | $D_{\text{m50}}$ [μm] |
|--------------------|--|-----------------------|
| as-received        | < 1  | 40                    |
| dry vibratory mill | 4  | 810                   |
| dry planetary mill | 5  | 10                    |
| wet planetary mill | 17   | 1                     |

and a modest increase in total surface area. This apparent paradox is easily explained: the increase in particle size is a result of cold welding and particle agglomeration that are often observed during dry milling,<sup>[18,21]</sup> which we too observe in both the particle-size histogram and SEM image (Figures S1 and S3). The increase in BET surface area, in contrast, is a result of the production of fines (50% of the number of particles are less than 50 μm, from the particle-size histogram shown in Figure S1) and to added surface texture (Figure S3). All milling techniques improved the CO<sub>2</sub> cycling of pure CaCO<sub>3</sub>, and wet planetary milling provided the greatest improvement.

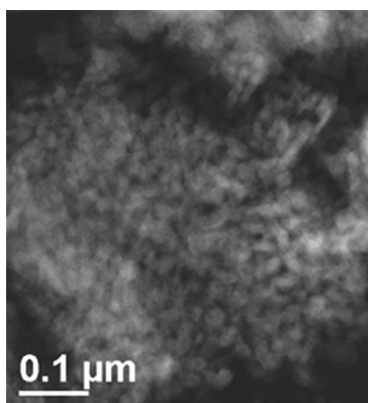
To further improve sorbent recyclability, we explored the mechanochemical preparation of mixed CaCO<sub>3</sub>/MgO materials. CaCO<sub>3</sub>/MgO mixtures were milled in different weight ratios for 2 h using the milling conditions discussed earlier. Figure 2 illus-



**Figure 2.** Stability of CO<sub>2</sub> uptake by MgO-doped adsorbents (as a function of MgO/CaO content) prepared using three different grinding conditions: wet-planetary, dry-planetary, and dry-vibratory milling. The amount of CO<sub>2</sub> binding is compared after the 15th cycle vs. the first cycle. Wet planetary milling is shown to be the most effective in terms of recycling stability. The solid lines are meant only as a guide to the eye and do not represent any meaningful fit to the data.

trates the ratio of CO<sub>2</sub> sorption uptake after the 15th cycle compared to the first cycle as a function of MgO content for three different grinding conditions: wet planetary, dry planetary, and dry vibratory milling. Mechanochemically synthesized MgO-doped sorbents retained a CO<sub>2</sub> uptake of > 70% after 15 cycles over the range of 20–80 wt% MgO. Three different trends were observed for the stability of the synthesized sorbents with varying MgO content. Stability for the dry-vibratory-

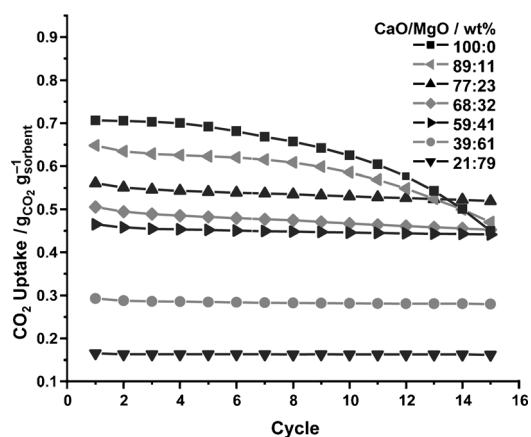
milled samples reached a maximum at 45 wt% MgO and then decreased (bottom line). As discussed above, dry-vibratory-milled samples agglomerate during processing, which limits the accessibility of CO<sub>2</sub> to the interior, unreacted CaO. The stability of dry-planetary-milled samples (middle line) increased until it reached a plateau at approximately 40 wt% MgO; this suggests that beyond this MgO concentration, dry planetary milling reaches a steady state between further particle size reduction and particle reagglomeration. Wet grinding in the planetary ball mill yielded the most stable sorbents (top line). Wet-milled MgO-doped CaCO<sub>3</sub> samples retained more than 90% of the initial uptake at cycle 15, and the stability increases linearly with increasing MgO content. Consistent with the cycling stability of the wet-milled MgO-doped CaCO<sub>3</sub>, the particle microstructure heterogeneity is quite low, roughly 10 nm scale after milling, as can be seen from the scanning transmission electron microscopy (STEM) image shown in Figure 3.



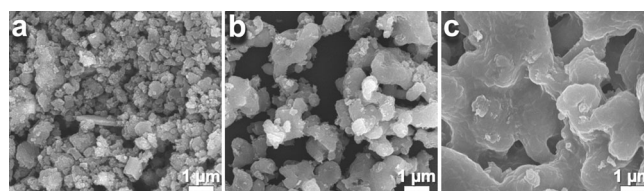
**Figure 3.** STEM image of the wet-milled sample (MgO/CaO 23:77 wt%) after 2 h processing time in a planetary ball mill (Pulverisette 7). The contrast between Mg-rich (dark) and Ca-rich (light) regions shows that the microstructure heterogeneity is roughly 10 nm after milling.

Recyclability is critical to any potential sorbent for CO<sub>2</sub> capture. The incorporation of inert additives, however, imposes energy penalties owing to the heating and cooling of the additives; for example, MgO does not sequester CO<sub>2</sub> under high-temperature WGS reaction conditions. Sorbent composition, therefore, needs to be optimized to obtain a high CO<sub>2</sub> capture uptake per unit mass of a sorbent while maintaining high reversibility during calcination. CO<sub>2</sub> uptake of wet-milled MgO-doped sorbents were compared for various sorbent compositions during 15 cycles (Figure 4). Initial CO<sub>2</sub> uptake decreased as a result of the addition of inert MgO, whereas the recycling stability showed a significant improvement with a minimum of 23 wt% MgO addition.

The sample with 23 wt% MgO was further characterized by SEM and XRD before (as synthesized) and after 15 cycles of CO<sub>2</sub> uptake and calcination. The SEM images in Figure 5 show a noticeable increase in particle size after 15 cycles (and even greater agglomeration after 50 cycles), which indicates particle sintering and the loss of microporosity after multiple CO<sub>2</sub> binding and calcination. The Debye–Sherrer formula was used to

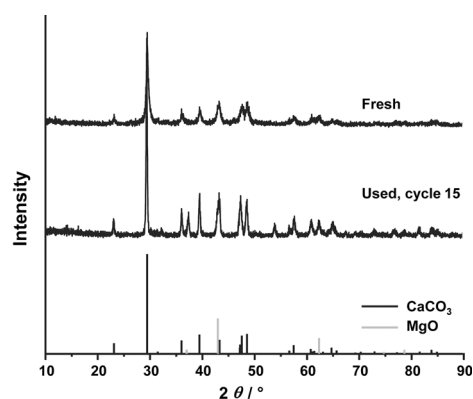


**Figure 4.** CO<sub>2</sub> uptake by wet-milled MgO-doped CaCO<sub>3</sub> samples during 15 cycles of operation; carbonation at 650 °C for 30 min under 100% CO<sub>2</sub> and calcination at 900 °C for 5 min under 100% N<sub>2</sub>. Adding a minimum of 23 wt% MgO significantly improves the cycling stability over 15 cycles.



**Figure 5.** SEM images of the wet-milled sample with the composition of MgO/CaO 23:77 wt%, a) fresh sample, b) after 15 cycles, and c) after 50 cycles. The images are at the same magnification; sintering of the particles is evident from the size increases observed.

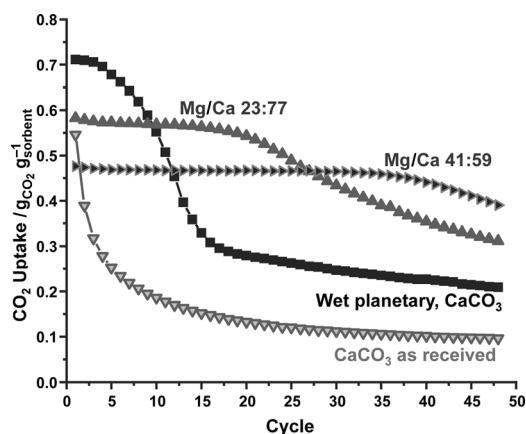
calculate the CaCO<sub>3</sub> crystallite size from the XRD characterization in Figure 6. The crystallite size increases from 19 to 46 nm after 15 cycles. Based on these results, it is evident that 23 wt% MgO content does not sufficiently resist crystallite growth during multicycle operation. Therefore, it may not



**Figure 6.** XRD characterization of the wet-milled sample with the composition of MgO/CaO 23:77 wt% before and after 15 cycles of adsorption and regeneration cycles. The Debye–Sherrer formula was used to calculate the crystallite size; the crystallite size for the fresh sample is 19 nm and for the recycled sample is 46 nm after 15 cycles. The XRD patterns of pure CaCO<sub>3</sub> and MgO shown in the bottom panel are from ICDD PDF cards 04-007-8659 and 04-012-3469, respectively.

prove as effective for CO<sub>2</sub> capture after extended cyclic operation (e.g., > 15 cycles).

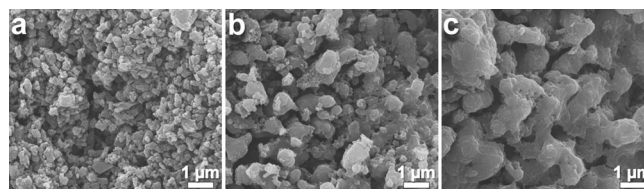
To examine the longer term stability of our sorbents, we extended the recycling to 50 cycles of carbonation–calcination (Figure 7) for 1) as-received non-milled CaCO<sub>3</sub>, 2) wet-planeta-



**Figure 7.** CO<sub>2</sub> capture performance during 50 cycles of carbonation–calcination for four sorbents: 1) non-milled as-received CaCO<sub>3</sub>, 2) wet-planetary-milled pure CaCO<sub>3</sub>, and 3,4) two MgO-doped wet-milled samples (MgO/CaO 23:77 and 41:59 wt%). The cycling conditions were carbonation at 650 °C for 30 min under 100% CO<sub>2</sub> and calcination at 900 °C for 5 min under 100% N<sub>2</sub>. Wet milling along with the addition of an inert additive (e.g., MgO) improves the sorbent stability in extended operating cycles.

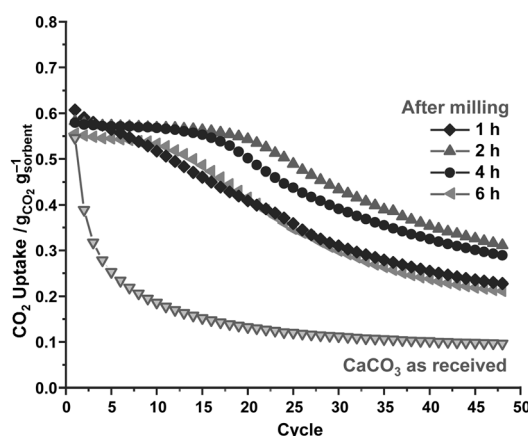
ry-milled pure CaCO<sub>3</sub>, and 3,4) two MgO-doped wet-planetary-milled samples (23 and 41 wt% MgO). Comparing the performance of the pure CaCO<sub>3</sub> samples reveals the positive effect of wet milling alone on the sorbent stability. As discussed earlier, wet milling produces finer particles with a higher surface area. The observed higher stability may be partly because of the use of ethanol in the wet-milling preparation; it has been suggested that ethanol can create more hydrophilic and consequently larger pores in CaO, which provides greater stability over multiple recycling.<sup>[22]</sup> The addition of 23 wt% MgO significantly improves the CO<sub>2</sub> uptake stability especially during the first 20 cycles. As the amount of MgO was increased to 41 wt%, the material retained its stability up to approximately cycle 35 before it began to show a decay in the uptake performance. These results show that wet milling along with the addition of an inert additive (e.g., MgO) improve the sorbent stability in extended operating cycles.

The sample with 41 wt% MgO was characterized by using SEM (Figure 8). Although the sintering of the particles is evident from the size increases observed, the degree of particle growth is less than that in samples with less MgO (Figure 5). According to XRD patterns, the CaCO<sub>3</sub> crystallite size shows an increase from 15 to 37 nm after 15 cycles. The stability through 35 cycles for the 41 wt% compared to the 23 wt%-MgO-containing sample (Figure 7) is also attributed to the inclusion of more MgO, which physically separates CaO grains and facilitates the diffusion of CO<sub>2</sub> through the grain boundaries.



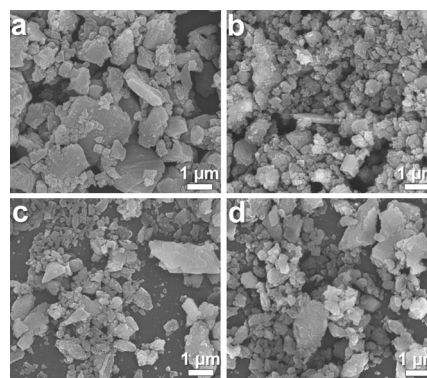
**Figure 8.** SEM images of the wet-milled sample with the composition of MgO/CaO 41:59 wt%, a) fresh sample, b) after 15 cycles, and c) after 50 cycles. The images are at the same magnification. The extent of particle growth is less than that seen with 23 wt% MgO (Figure 5).

Moreover, we examined the effect of milling processing time for the wet-planetary-milled sample (MgO/CaO 23:77 wt%) on its CO<sub>2</sub> uptake performance during 50 cycles. The sample was milled for 1, 2, 4, and 6 h before CO<sub>2</sub> uptake cycling. As illustrated in Figure 9, 2 h processing time proved to be the opti-



**Figure 9.** Effect of milling time (1–6 h) on the CO<sub>2</sub> capture performance of the wet-planetary-milled sample (MgO/CaO 23:77 wt%) during 50 cycles of carbonation–calcination compared to non-milled, as-received CaCO<sub>3</sub>. A milling time of 2 h led to the most stable performance.

mal treatment, which led to the most stable performance over the course of 50 cycles. As shown in Figure 10, the minimum particle size is achieved with 2 h of milling: shorter milling



**Figure 10.** SEM images of the wet-planetary-milled sample (MgO/CaO 23:77 wt%) after a) 1, b) 2, c) 4, and d) 6 h milling. The minimum particle size is achieved with 2 h of milling.

times do not sufficiently grind the material and longer milling times lead to particle agglomeration. The rate of CO<sub>2</sub> capture and release depends on particle size, which explains the optimal milling time observed.

## Conclusions

We have shown for the first time that mechanical activation provides an efficient route to the synthesis of stabilized sorbents for high-temperature CO<sub>2</sub> capture. Wet-planetary-milled samples produced the most stable and most efficient CO<sub>2</sub> sorbents; the incorporation of 41 wt% of MgO led to a CO<sub>2</sub> uptake of approximately 0.4 g<sub>CO<sub>2</sub></sub> g<sub>sorbent</sub><sup>-1</sup> after 50 cycles of carbonation–calcination, much higher than 0.1 g<sub>CO<sub>2</sub></sub> g<sub>sorbent</sub><sup>-1</sup> for as-received CaCO<sub>3</sub>. The recyclability of calcination–CO<sub>2</sub> sorption is a kinetic process and strongly dependent on both the surface porosity and the particle size of the solid sorbent: mechanical milling of CaCO<sub>3</sub>/MgO provides a facile means for the production of more stable CO<sub>2</sub> sorbents through efficient particle size reduction and the effective dispersion of an inert binder (in this case MgO).

## Experimental Section

A vibratory ball mill (SPEX 8000M) and a planetary ball mill (Pulverisette 7) were used to synthesize mixtures of CaCO<sub>3</sub> and MgO. In general, more intense milling is generated with a vibratory ball mill,<sup>[23]</sup> but the experimental parameters (ball-to-material mass ratio, rpm, solid powder vs. liquid slurry) can be more easily controlled with a planetary ball mill. We note that CaCO<sub>3</sub> nanoparticles have been prepared previously by dry-planetary-ball milling of CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> with NaCl as a solid diluent.<sup>[24]</sup> MgO and CaCO<sub>3</sub> were purchased from Sigma–Aldrich. Dry milling by using the SPEX 8000M apparatus was performed in a tungsten vial set. The ball-to-powder ratio was kept at the optimal value (5 g g<sup>-1</sup>) for this apparatus.<sup>[18c]</sup> The SPEX 8000M was operated at a fixed 1000 rpm; it was paused for 1 min every 30 min to avoid overheating. Total processing time was 2 h of milling.

Wet and dry milling with the planetary ball mill was performed in an agate vial set with 5 mm diameter 3Y-TZP balls with the ball-to-powder ratio fixed at 40 g g<sup>-1</sup>. Ethanol was used as the process control agent for wet milling; 10 mL ethanol was added to 1 g of powder. After wet milling, the resulting sorbents were dried by using a rotary evaporator. The planetary ball mill operated at 500 rpm and was paused for 1 min every 15 min to avoid overheating. Total processing time was 2 h of milling.

The BET surface area of samples was determined from N<sub>2</sub> physisorption data by using a Quantachrome 2200e instrument; each sample was degassed under vacuum at 300 °C for 3 h prior to N<sub>2</sub> adsorption measurements. The median particle size of samples (*D*<sub>50</sub> in Table 1) was obtained by using a Horiba Partica LA-950 laser diffraction particle size analyzer. The CO<sub>2</sub> capture performance of the synthesized sorbents was examined by using a ThermoScientific VersaTherm thermogravimetric analyzer (TGA). Approximately 20 mg of sample was loaded into a quartz sample boat; carbonation and calcination cycles were performed at 650 °C for 30 min under 100% CO<sub>2</sub> and 900 °C for 5 min under 100% N<sub>2</sub>, respectively. For 15 cycle runs before and after each carbonation segment, the chamber was purged with N<sub>2</sub> for 5 min at the carbonation temperature. The purge segments were omitted in the 50 cycle runs

owing to the limitation of TGA software in the number of method segments. The flow rates of CO<sub>2</sub> and N<sub>2</sub> were kept at 35 SCCM for all experiments.

STEM, SEM, and XRD characterization were performed for the wet-planetary-milled sample (MgO/CaO 23:77 and 41:59 wt%). STEM images were collected by using a JEOL 2010F instrument with an accelerating voltage of 200 keV. SEM images were collected by using Hitachi S4700 instruments operating at 15 keV. Samples were sputter-coated with a Au/Pd alloy before SEM analysis. Powder X-ray diffraction patterns were collected by using CuK<sub>α</sub> radiation ( $\lambda = 1.5418 \text{ \AA}$ ) by using a Siemens–Bruker D5000 instrument operating at 40 kV and 30 mA and scanning  $2\theta = 10\text{--}90^\circ$  at a rate of  $1.0^\circ \text{ min}^{-1}$ .

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**Keywords:** ball milling · CO<sub>2</sub> sorption · calcium · carbon storage · microporous materials

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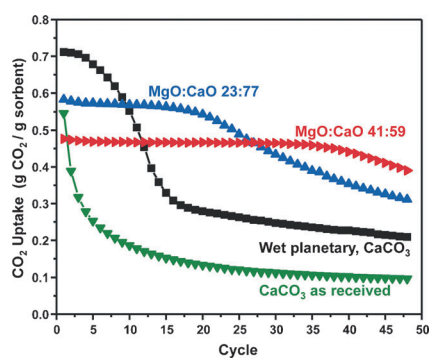
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## FULL PAPERS

**Having a ball with milling:** The reversible cycling of CaO adsorbents to CaCO<sub>3</sub> for high-temperature CO<sub>2</sub> capture is substantially improved by a mechanochemical approach. MgO has been used as an inert binder to help mitigate CaCO<sub>3</sub> sintering. Wet planetary milling of MgO into CaCO<sub>3</sub> allows for efficient particle size reduction and effective dispersion of MgO throughout the particles, yielding the most stable sorbents during several cycles of carbonation–calcination.



M. Sayyah, Y. Lu, R. I. Masel, K. S. Suslick\*



**Mechanical Activation of CaO-Based Adsorbents for CO<sub>2</sub> Capture**

