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Effect of Support Material on Carbonation and Sulfation of Synthetic CaO-Based Sorbents in Calcium Looping Cycle

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ABSTRACT: Calcium looping cycle for post-combustion CO₂ capture has gained increasing attention worldwide. However, CaO-based sorbents derived from natural sources for calcium looping cycle experience rapid loss of capacity during high-temperature cyclic carbonation/calcination reactions. Synthesizing sintering-resistant CaO-based sorbents by adding a support material has been extensively studied as an effective method of combating the problem. The support material in the synthetic sorbents plays an important role in retaining the capacity, and various support materials have been tested in the literature. In practical reactors, sulfur is present and it has been reported that sulfation of sorbents will also reduce the CO₂ capture capacity. However, thus far, it is not clear whether/how support material would affect sulfation of sorbents and, thus, CO₂ capture. In this paper, four different support materials, such as Ca₂MnO₄, La₂O₃, Ca₁₂Al₁₄O₃₃, and MgO, were studied. The cyclic CO₂ capture performance of the synthetic sorbents made from CaO and the support materials were investigated in detail, in the presence of SO₂ and steam. The results showed that a mass ratio of 20–25% support material would be optimum for synthesizing sorbents with high cyclic CO₂ capture capacity, and Ca₁₂Al₁₄O₃₃ and MgO seem to be more effective than Ca₂MnO₄ and La₂O₃. The 80:20 wt % CaO/MgO synthetic sorbent achieved the highest CO₂ capture capacity under ideal conditions over 100 cycles. However, the CaO/MgO sorbent had a strong affinity to SO₂ capture during cyclic reactions, especially in the presence of steam. Under realistic conditions (i.e., both SO₂ and steam are present during carbonation), the CaO/MgO sorbent showed the highest cumulative SO₂ capture capacity, whereas the CaO/Ca₁₂Al₁₄O₃₃ sorbent obtained the highest CO₂ capture capacity after 10 cycles. The smaller average crystallite size of MgO in the sorbent was responsible for the strong SO₂ affinity of the CaO/MgO sorbent as well as its stable cyclic CO₂ capture abilities under ideal conditions.

1. INTRODUCTION

The reduction of greenhouse gas emissions particularly CO₂ emissions is gaining increased attention from governments and researchers worldwide.¹ One of the promising post-combustion CO₂ capture technologies for practical large-scale applications is calcium looping cycle, which uses the reversible gas–solid reaction between CaO and CO₂.^{2,3}



The reaction is carried out at high temperatures (for the carbonation reaction typically at about 650 °C, whereas for the reverse calcination reaction at >900 °C). Because the operating temperatures are much higher than the sintering temperature (or Tammann temperature, ~533 °C) of CaCO₃,⁴ sintering of CaCO₃ or CaO crystals occurs and leads to aggregation of crystals. Consequently, the surface area and pore volume decrease.⁵ As a result, common CaO-based sorbents experience rapid loss of capacity during cyclic carbonation/calcination reactions.^{6–8} For example, the carbonation conversion of natural limestone declines to <20% after 10 cycles under the aforementioned carbonation/calcination conditions.⁹

Synthesizing sintering-resistant sorbents, by adding support material into CaO to retain surface area and pore volume, has been proposed and studied extensively as an effective way of combating the loss-in-capacity problem. Aihara et al.¹⁰ applied the method of mixing CaCO₃ and CaTiO₃ precursor in ethanol followed by hydrolysis of alkoxide to produce durable synthetic

CaO-based sorbents for CO₂ capture. Afterward, a range of support materials, such as Ca₁₂Al₁₄O₃₃,^{11–14} MgO,^{15–17} La₂O₃,^{15,18} ZrO₂,^{4,19} and Cs₂O,²⁰ has been reported to be effective support materials for the manufacture of sintering-resistant synthetic CaO-based sorbents. The synthesis method has been discussed in detail in our recent review paper.²¹

It has been reported that the presence of SO₂ during carbonation (or sulfation) will significantly affect the CO₂ capture capacity of the synthetic CaO-based sorbents.²² However thus far, data are limited, and it is not clear whether and how support material would affect both sulfation and carbonation simultaneously in the presence of SO₂ and steam. Therefore, the objective of this paper is to clarify the effect of support material on carbonation in the presence of SO₂ and steam.

2. EXPERIMENTAL SECTION

Four types of metal nitrate, namely, manganese nitrate, lanthanum nitrate, aluminum nitrate, and magnesium nitrate, were selected as the precursors of support material. Predetermined amounts of these metal precursors were mixed with the CaO precursor of calcium nitrate at different mass ratios of support material before sorbent preparation. Synthetic sorbents were then produced by a standard sol–gel process as introduced in our previous work:⁹ predetermined amounts of analytical-

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reagent-grade metal nitrate tetrahydrate and citric acid monohydrate were added to distilled water at a water/metal ion molar ratio of 40:1 and a citric acid/metal ion molar ratio of 1:1. Then, the mixture was continuously stirred and kept at 80 °C in an electrically heated thermostatic water bath for 7 h to form a translucent sol. Subsequently, the sol was placed at room temperature for 18 h in a sealed container to form a wet gelatin before it was placed in a drying oven at 80 °C for 5 h and then dried at 110 °C for another 12 h until a dry gelatin was formed. At last, the dry gelatin was placed in a muffle furnace at 600 °C for a few seconds, and then the sample was calcined at 700 °C for 2 h.

The cyclic calcination/carbonation performance and the effect of SO₂ and steam were investigated by thermogravimetric analysis (TGA) using a Cahn 121 instrument. The synthetic sorbents were placed in a quartz sample pan with an inner diameter of 13 mm. To minimize mass-transfer limitations, five holes with a diameter of 2.5 mm were drilled on the bottom of the sample pan. Preliminary experiments demonstrated that, when the sample mass was below 5 mg at a total gas flow rate of 100 mL/min, there was no effect of the sample mass on the sulfation rate of CaO-based sorbents in TGA. Therefore, about 4–5 mg of the sorbent was selected for every test. Before the cyclic experiment, the sample was heated from room temperature to 950 °C and maintained at 950 °C for 10 min in a N₂ atmosphere to fully decompose CaCO₃. Subsequently, the sample was cooled to 650 °C in a N₂ flow of 100 mL/min, and then cyclic tests were performed. The cyclic testing conditions were as follows: carbonation was performed at 650 °C for 2.5 min in 15 vol % CO₂, 0–0.2 vol % SO₂, 0–5 vol % O₂, and 0–10 vol % H₂O balanced by N₂ with a total flow rate of 100 mL/min. Calcination was performed at 950 °C for 2.5 min in 100% CO₂ with a total flow rate of 100 mL/min. Both cooling and heating processes of TGA were conducted in a N₂ flow of 100 mL/min at a heating or cooling rate of 20 °C/min. It should be noted that the calcination actually occurred during the heating process in N₂ and completed before the temperature reached 950 °C. The reason for an additional 2.5 min calcination in the CO₂ atmosphere was to simulate a practical calcination condition in calcium looping cycle. The initial experiment indicated that the sorbents derived from the sol–gel process had a high CO₂ sorption rate, and the carbonation reaction in the fast chemical-controlled reaction regime completed within 2.5 min. Water vapor was introduced by passing a dry N₂ gas mixture through a gas-washing bottle filled with deionized water. Then, the mixed N₂ and water vapor were mixed with the other reaction gases at the inlet of the TGA furnace. The temperature of the water was controlled by an electrical heater, and the amount of water vapor carried out by N₂ was calculated from the saturation pressure of the vapor.

The pore structure parameters of the calcined samples were determined by N₂ adsorption and desorption isotherms, which were measured at the temperature of liquid N₂ (Micromeritics ASAP 2020-M). The surface area was calculated using the Brunauer–Emmett–Teller (BET) equation. The microstructure of the calcined samples was investigated using a field-emission scanning electron microscopy (SEM) system (SIRION200, FEI, Inc.) with 10 kV of accelerating voltage. The phase composition of the samples was determined by X-ray diffraction (XRD, PANalytical B.V.) with Cu K α radiation ($\lambda = 0.1542$ nm) within the 2θ range of 20–70° and a scanning speed of 0.05°/s.

3. RESULTS AND DISCUSSION

3.1. XRD Analysis. The as-prepared samples were first characterized by powder XRD to identify the phase composition of the synthetic CaO-based sorbents supported with four different materials. Manganese, lanthanum, aluminum, and magnesium oxide were chosen as supporting materials because previous studies have shown that these materials are effective in reducing the sintering of CaO-based sorbents.^{22–25} Figure 1 shows the XRD patterns of the sorbents at 80:20 mass ratio of CaO/support material after 2 h of calcination in a muffle furnace. The final phase compositions of calcium nitrate were CaO and CaCO₃. The existence of CaCO₃ in the sample was due to the reaction of CaO with CO₂ induced by the combustion of citric acid during preparation. Generated CaCO₃ would be decom-

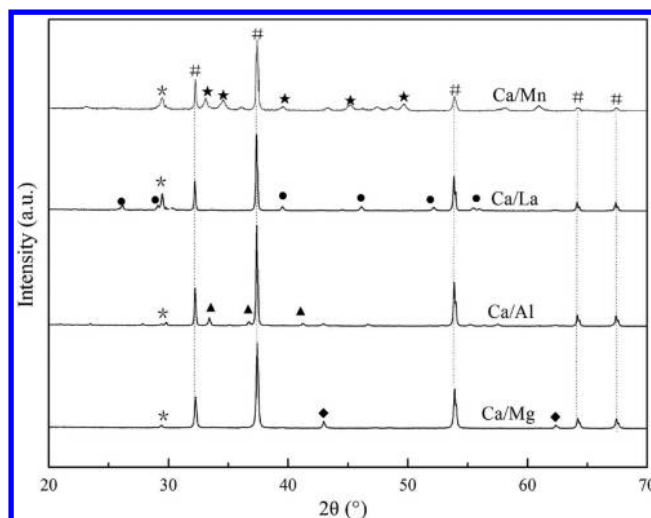


Figure 1. XRD patterns of synthetic CaO-based sorbents after calcination in the muffle furnace at 700 °C for 2 h in air (#, CaO, PDF 37-1497; ★, Ca₂MnO₄, PDF 82-0351; ●, La₂O₃, PDF 74-1144; ▲, Ca₁₂Al₁₄O₃₃, PDF 48-1882; ◆, MgO, PDF 77-2364; and *, CaCO₃, PDF 13-0192).

posed into CaO during the initial calcination prior to cyclic CO₂ capture tests. The final phase compositions of the four supported precursors (manganese nitrate, lanthanum nitrate, aluminum nitrate, and magnesium nitrate) were Ca₂MnO₄, La₂O₃, Ca₁₂Al₁₄O₃₃, and MgO, respectively. The results for the latter three support materials were consistent with those reported in previous studies.^{11,15,16} The support material Ca₂MnO₄ differed from that used in the study by Lu and Smirniotis,²⁶ who obtained Mn₂O₃ as a final product. This difference could be due to the different preparation methods used. The co-precipitation method used by Lu and Smirniotis²⁶ is based on wet chemistry, whereas our new method was based on the intense combustion of a well-dispersed gel that contributed to the transformation of manganese ion from the transient phase Mn₂O₃ to the phase of MnO₂. Then, MnO₂ reacted with CaO and formed Ca₂MnO₄.

3.2. Optimization of the Mass Ratio of Different Supports. To compare the cyclic performance of CaO-based sorbents supported with different mass ratios of materials, all synthetic sorbents (CaO/Ca₂MnO₄, CaO/La₂O₃, CaO/Ca₁₂Al₁₄O₃₃, and CaO/MgO) were prepared at 5, 10, 15, 20, 25, and 30% mass ratio of support material (assuming that the support material in the sorbent was only Ca₂MnO₄, La₂O₃, Ca₁₂Al₁₄O₃₃, and MgO, respectively). Figure 2 shows the CO₂ capture capacity of CaO-based sorbents supported with four types of material as a function of the mass ratio of the support material. Generally, the cyclic stability of all synthetic CaO-based sorbents was enhanced by increasing the mass ratio of support material. The support material could act as a metal skeleton in the sorbent to reduce the sintering tendency of CaCO₃ grains; thus, a large amount of support contributes to the enhanced stability of the sorbent during cyclic high-temperature reactions. However, too large amount of support in a sorbent decreased the CO₂ capture capacity. As shown in Figure 2, all of the curves of CO₂ capture capacity after 20 cycles reached maximum values at a mass ratio of 20–25 wt % support material. This result was consistent with a previous study that a mass ratio of 14–20 wt % resulted in a high CO₂ capture capacity of the synthetic sorbents.²⁷ The peak value should be owing to a trade-off between the positive effect of a decreasing rate of sintering of the

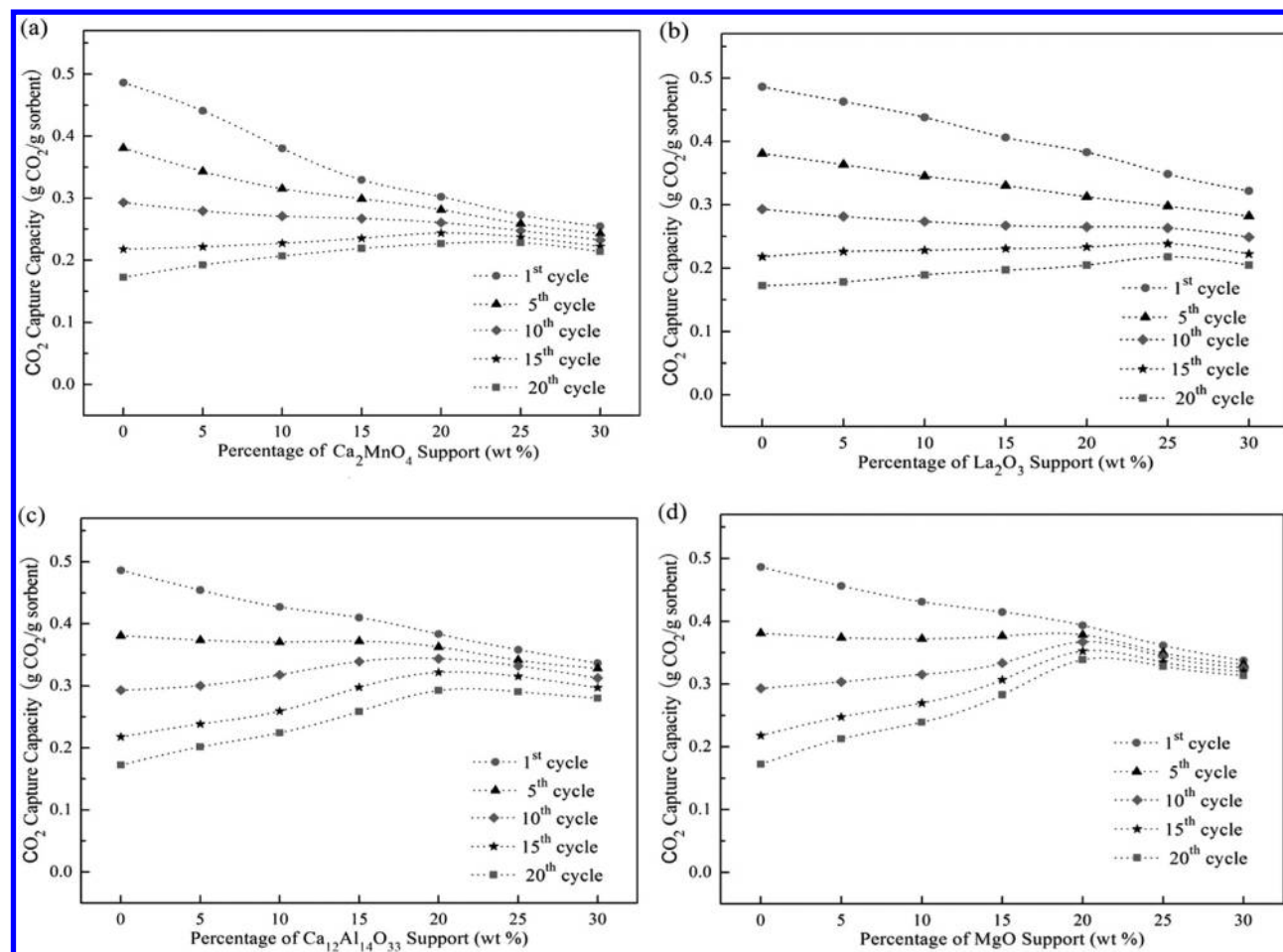


Figure 2. CO₂ capture capacities of synthetic sorbents with different amounts of support materials: (a) CaO/Ca₂MnO₄, (b) CaO/La₂O₃, (c) CaO/Ca₁₂Al₁₄O₃₃, and (d) CaO/MgO (carbonated at 650 °C for 2.5 min in 15% CO₂ balanced by N₂ and calcined at 950 °C for 2.5 min in 100% CO₂).

sorbents with the increase of the support material and the negative effect of reducing the total amount of reactive CaO.

To compare the performance of the four types of synthetic sorbent under different reaction conditions, sorbents with an 80:20 mass ratio of CaO/support were used. Figure 3 shows the

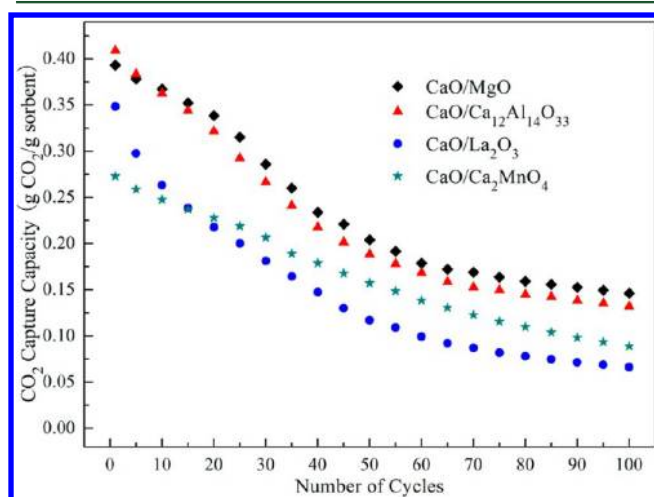
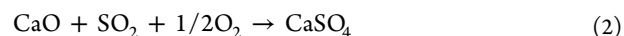


Figure 3. CO₂ capture capacities of synthetic sorbents with extended cycles (carbonated at 650 °C for 2.5 min in 15% CO₂ balanced by N₂ and calcined at 950 °C for 2.5 min in 100% CO₂).

CO₂ capture capacities of the synthetic sorbents with extended cycles. The rate of capacity loss of CaO/MgO was slightly lower than that of CaO/Ca₁₂Al₁₄O₃₃, whereas the rate of capacity loss of CaO/Ca₂MnO₄ was much lower than that of CaO/La₂O₃. After 100 cycles, the cyclic performance of the synthetic sorbents followed the order CaO/MgO > CaO/Ca₁₂Al₁₄O₃₃ > CaO/Ca₂MnO₄ > CaO/La₂O₃. The CO₂ capture capacity of the CaO/MgO sorbent achieved 0.15 g of CO₂/g of sorbent within 2.5 min of carbonation after 100 cycles, which was more than twice that of the CaO/La₂O₃ sorbent. Because the sorbents with Mg and Al supports are much cheaper than the sorbents with Mn and La supports, MgO- and Ca₁₂Al₁₄O₃₃-supported sorbents are more promising for CO₂ capture.

3.3. Effect of SO₂ and H₂O on the Cyclic CO₂ Capture Performance. Given that fossil fuels almost always contain some sulfur, SO₂ is present with CO₂ in flue gas. Initially, the synthetic sorbents were subjected to sulfation tests in the presence of 0.2 vol % SO₂ and 5 vol % O₂ balanced by N₂ for 60 min based on the following reaction:



As shown in Figure 4, CaO/Ca₁₂Al₁₄O₃₃, CaO/Ca₂MnO₄, and CaO/La₂O₃ showed similar sulfation behaviors, whereas the CaO/MgO sorbent exhibited the fastest sulfation rate within 60 min and showed the highest weight increase after 60 min. Thermodynamically, MgO could also absorb SO₂ at 650 °C in 0.2% SO₂ and form MgSO₄. Therefore, the higher mass increase

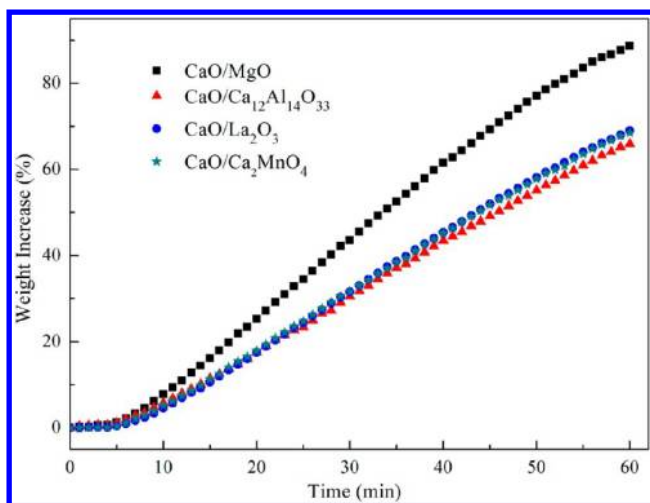


Figure 4. Sulfation behaviors of synthetic CaO-based sorbents (sulfated at 650 °C in 0.2% SO₂ and 5% O₂ balanced by N₂ for 60 min).

of the CaO/MgO sorbent was caused by sulfation of both CaO and MgO, while for the other three sorbents, the higher mass increase was caused by sulfation of CaO only. Because the sulfation reaction was normally diffusion-controlled, MgO and CaO were assumed to have a similar reaction rate, despite the fact that CaO has stronger alkalinity than MgO. The CaO sulfation degree of the CaO/MgO sorbent was calculated as follows:

$$X_{\text{sulf}}' = \frac{\left(\frac{m' - m_{\text{cal}(0)}}{m_{\text{cal}(0)} M_{\text{SO}_3}} \right)}{\left(\frac{b}{M_{\text{CaO}}} + \frac{1-b}{M_{\text{MgO}}} \right)} \times 100\% \quad (3)$$

The CaO sulfation degree of the other three sorbents (CaO/Ca₁₂Al₁₄O₃₃, CaO/Ca₂MnO₄, and CaO/La₂O₃) was calculated as follows:

$$X_{\text{sulf}} = \frac{\left(\frac{m' - m_{\text{cal}(0)}}{m_{\text{cal}(0)} M_{\text{SO}_3}} \right)}{\left(\frac{b}{M_{\text{CaO}}} \right)} \times 100\% \quad (4)$$

The result of the CaO sulfation degree after 60 min revealed that the conversion of MgO and CaO to sulfates was 57%, which agreed well with the CaO conversion (about 58%) of the other three sorbents.

Figure 5 showed the sulfation–desulfation behavior of analytical reagent MgO in 0.2% SO₂ at different temperatures. The sulfation of MgO contained a rapid chemical reaction-controlled period, followed by a slower diffusion-controlled period. However, with the elevating reaction temperature, formed MgSO₄ can be decomposed to MgO again in 0.2% SO₂. At 950 °C, the mass weight of the sample was the same as that of its initial stage.

To investigate the effect of SO₂ on cyclic CO₂ capture, further tests on CO₂/SO₂ co-capture were performed. The cumulative SO₂ capture capacity of the synthetic sorbents was based on the sulfation of CaO in the sorbents, because formed MgSO₄ of the CaO/MgO sorbent during the carbonation stage could be fully decomposed in the calcination stage of the calcium looping cycle, while the other three sorbents experienced sulfation of CaO only.

The cumulative SO₂ capture capacity of the CaO/Ca₁₂Al₁₄O₃₃, CaO/Ca₂MnO₄, and CaO/La₂O₃ sorbents in the *n*th cycle was calculated as follows:

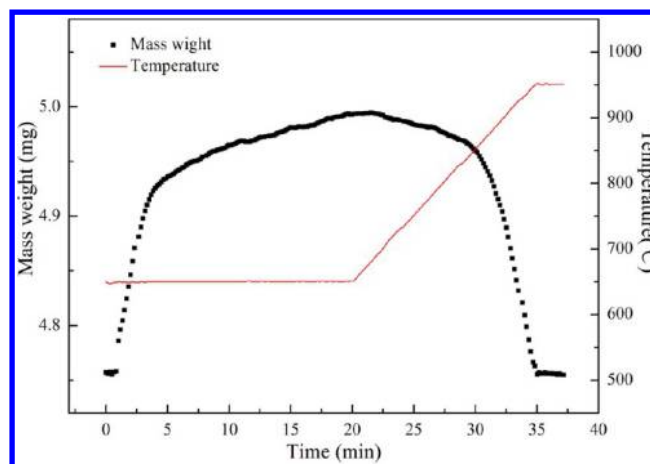


Figure 5. Sulfation–desulfation behavior of analytical reagent MgO (atmosphere: 0.2% SO₂ and 5% O₂ balanced by N₂).

$$C_{\text{SO}_2(n)} = \frac{m_{\text{cal}(n)} - m_{\text{cal}(0)}}{m_{\text{cal}(0)}} \frac{M_{\text{SO}_2}}{M_{\text{SO}_3}} \quad (n = 1, 2, 3, \dots) \quad (5)$$

The cyclic CO₂ capture capacity of the CaO/Ca₁₂Al₁₄O₃₃, CaO/Ca₂MnO₄, and CaO/La₂O₃ sorbents in the *n*th cycle was calculated as follows:

$$C_{\text{CO}_2(n)} = \frac{m_{\text{carb}(n)} - m_{\text{cal}(n-1)}}{m_{\text{cal}(n-1)}} \quad (n = 1, 2, 3, \dots) \quad (6)$$

Because MgO could also absorb SO₂ during carbonation, if we assumed that MgO and CaO absorbed the same amount of SO₂ according to their mass ratio in the sorbent, then the cyclic CO₂ capture capacity of the CaO/MgO sorbent in the *n*th cycle was calculated as follows:

$$C_{\text{CO}_2(n)}' = \frac{m_{\text{carb}(n)} - m_{\text{cal}(n-1)} - (1-b)(m_{\text{cal}(n)} - m_{\text{cal}(n-1)})}{m_{\text{cal}(n-1)}} \quad (n = 1, 2, 3, \dots) \quad (7)$$

As shown in Figure 6, the cumulative SO₂ capture capacity of the CaO/MgO sorbent was the highest, whereas the other three sorbents showed similar cumulative SO₂ capture capacities. This indicates that the CaO/MgO sorbent has a stronger affinity to SO₂ than any other sorbents during cyclic reactions. Because the formed CaSO₄ could not be decomposed at the cyclic reactions, the amount of CaO available for CO₂ capture decreased with the number of cycles. Thus, the rate of loss in capacity of the CaO/MgO sorbent was a little faster than that of the CaO/Ca₁₂Al₁₄O₃₃ sorbent during cyclic reactions and led to a lower value of the CO₂ capture capacity of the CaO/MgO sorbent after 20 cycles in the presence of SO₂ during the carbonation stage. However, the CO₂ capture capacity of the CaO/MgO sorbent was still much higher than those of the CaO/Ca₂MnO₄ and CaO/La₂O₃ sorbents.

The effect of steam during carbonation on the cyclic performance of the synthetic sorbents was also examined. Figure 7 shows that the CO₂ capture capacity improved to different extents with different support materials. These results were consistent with those by Donat et al.,²⁸ who found that the presence of steam during carbonation reduced diffusion resistance of CO₂ gas through the carbonate layer to the unreacted CaO grains. In particular, the CO₂ capture capacity of the CaO/MgO sorbent improved slightly better than those of the other three sorbents in the presence of 10% H₂O during

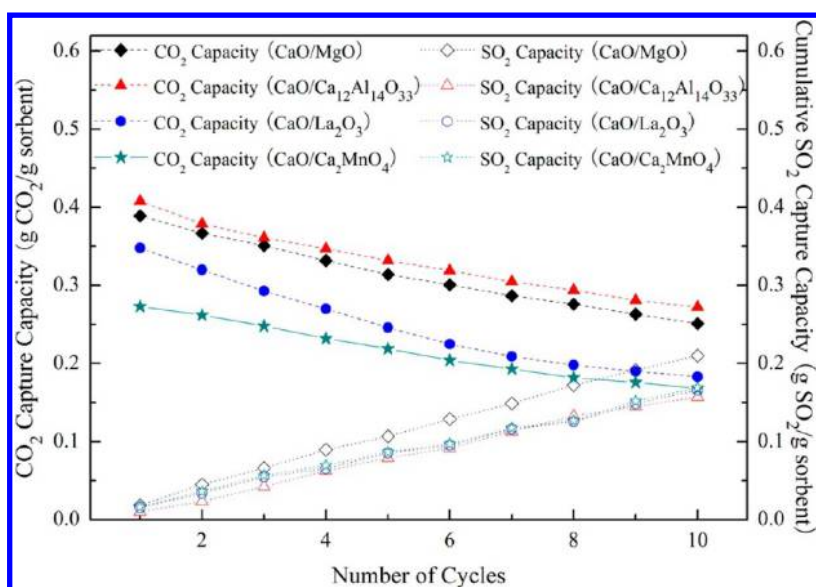


Figure 6. Cyclic performance of synthetic CaO-based sorbents in the presence of SO_2 (carbonated at 650°C for 2.5 min in 15% CO_2 , 0.2% SO_2 , and 5% O_2 balanced by N_2 and calcined at 950°C for 2.5 min in 100% CO_2).

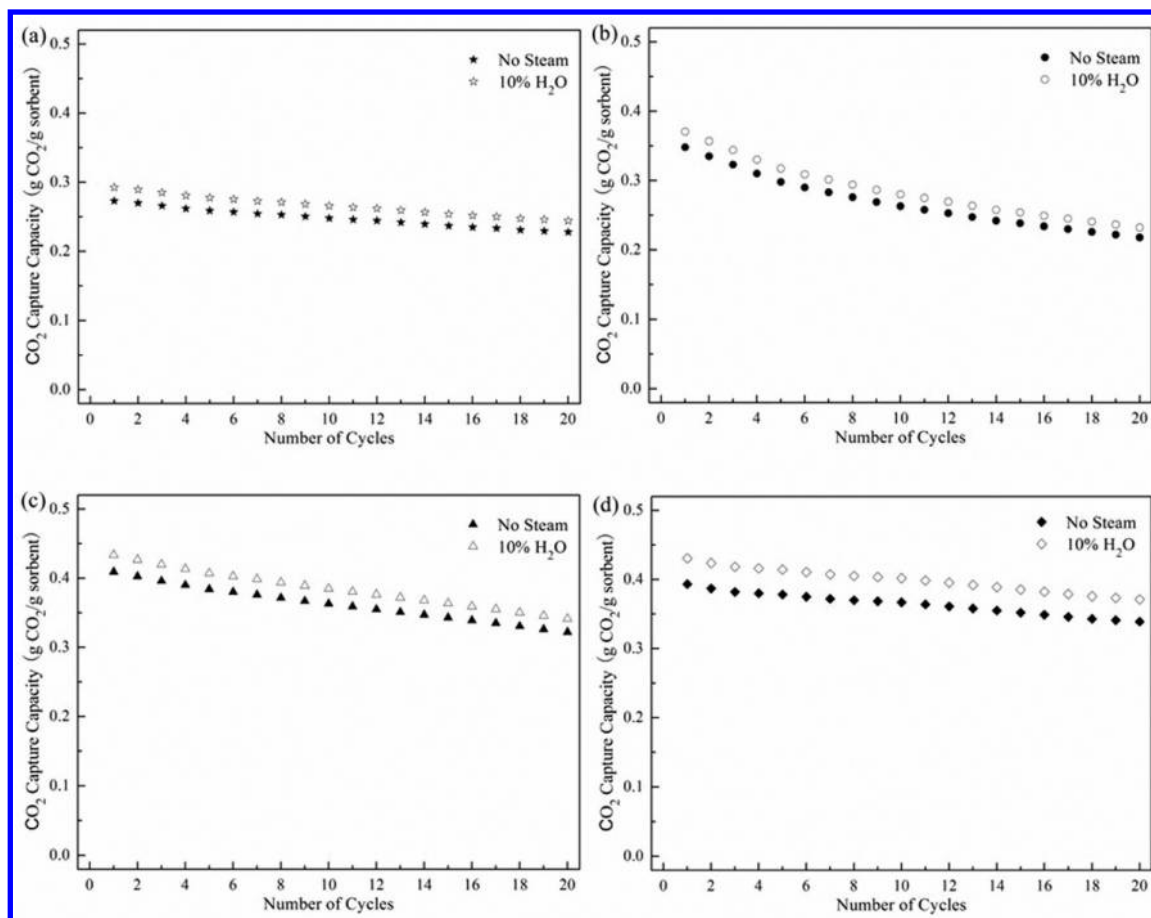


Figure 7. Cyclic performance of synthetic CaO-based sorbents in the presence of steam: (a) $\text{CaO}/\text{Ca}_2\text{MnO}_4$, (b) $\text{CaO}/\text{La}_2\text{O}_3$, (c) $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, and (d) CaO/MgO (carbonated at 650°C for 2.5 min in 15% CO_2 and 10% H_2O balanced by N_2 and calcined at 950°C for 2.5 min in 100% CO_2).

carbonation. The CO_2 capture capacity of the CaO/MgO sorbent was almost equal to that of the $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ sorbent in the first few cycles. However, after 20 cycles, the CO_2 capture capacity of the CaO/MgO sorbent was about 10% higher than that of the $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ sorbent, indicating that

the CaO/MgO sorbent was more affected by steam during carbonation.

The cyclic CO_2 capture performances of the synthetic sorbents in the presence of both SO_2 and steam during carbonation were also tested, and the results are shown in Figure 8. The loss of CO_2

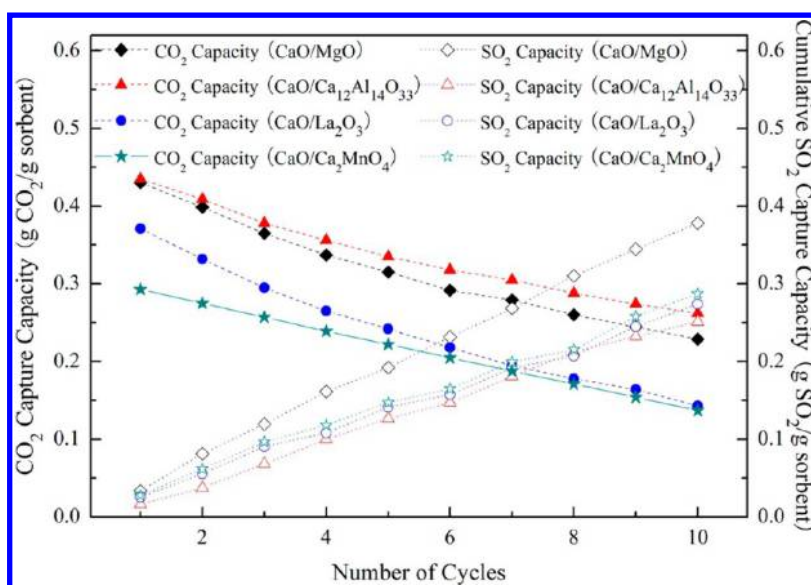


Figure 8. Cyclic performance of synthetic CaO-based sorbents in the presence of both SO₂ and steam (carbonated at 650 °C for 2.5 min in 15% CO₂, 0.2% SO₂, 5% O₂, and 10% H₂O balanced by N₂ and calcined at 950 °C for 2.5 min in 100% CO₂).

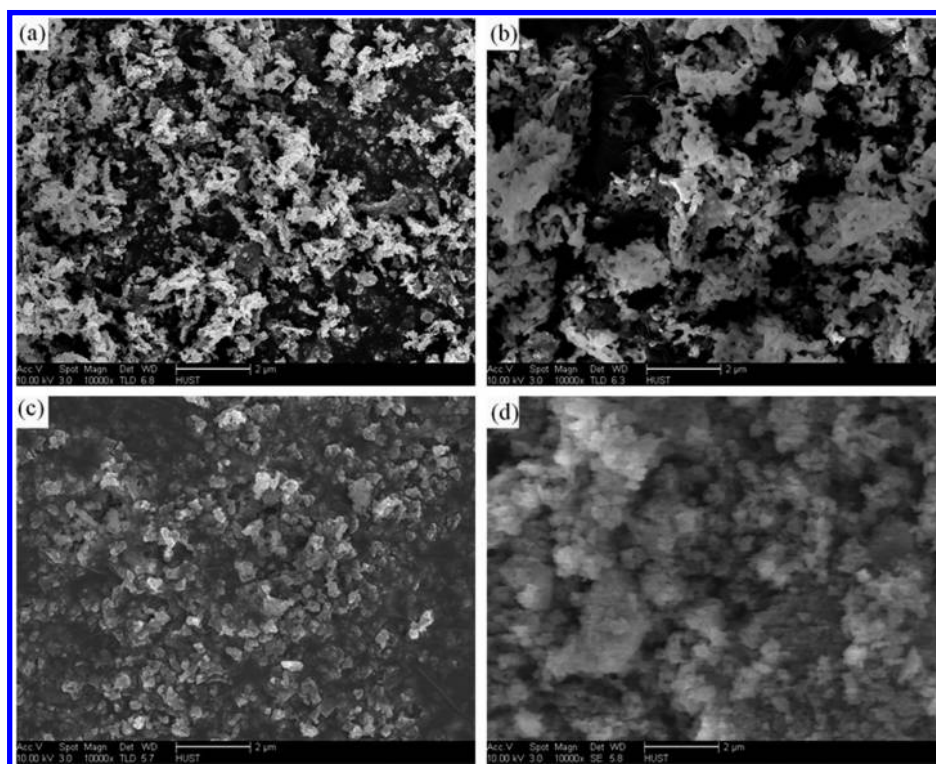


Figure 9. SEM images of synthetic CaO-based sorbents after initial calcination: (a) CaO/Ca₂MnO₄, (b) CaO/La₂O₃, (c) CaO/Ca₁₂Al₁₄O₃₃, and (d) CaO/MgO.

capture capacity of the CaO/MgO sorbent was faster than that of the CaO/Ca₁₂Al₁₄O₃₃ sorbent, and the CaO/MgO sorbent still showed the highest cumulative SO₂ capture capacity after 10 cycles among all sorbents tested. This result can be due to the strong affinity of the CaO/MgO sorbent to SO₂, as shown in Figure 5. Another reason was that the steam present during carbonation not only promoted the carbonation reaction but also enhanced the sulfation reaction.²⁹ Moreover, a comparison of Figures 6 and 8 in the 10th cycle revealed that the CO₂ capture capacities of all synthetic sorbents in the presence of both SO₂ and steam were slightly lower than those in the presence of SO₂

alone. This indicates that the presence of steam enhanced the sulfation rate slightly more than the carbonation rate.

The results suggest that SO₂ should be separated from flue gas if CO₂ was to be captured with steam. Otherwise, the synthetic sorbents would experience severe deactivation with a significant loss of CO₂ capture capacity after only a few cycles.

3.4. Characteristics of CaO-Based Sorbents with Different Supports. SEM images were obtained and analyzed to compare the morphologies of the synthetic sorbents. As shown in Figure 9, no obvious morphological differences existed among CaO-based sorbents with different supports. All sorbents

showed well-dispersed, hollow structures with similar particle sizes and grain shapes. The BET test results, as shown in Table 1,

Table 1. BET Surface Area and Grain Size of CaO and Its Support of Different Sorbents after Initial Calcination

	BET surface area (m ² /g)	average crystallite size of CaO (nm)	average crystallite size of support (nm)
CaO/Ca ₂ MnO ₄	17.4	82	97
CaO/La ₂ O ₃	16.2	91	88
CaO/Ca ₁₂ Al ₁₄ O ₃₃	16.5	85	109
CaO/MgO	16.9	78	38

further confirmed that the surface areas of all synthetic sorbents were similar and corresponded to their morphological structures. Therefore, the particle size and morphology of the sorbents cannot explain the strong SO₂ affinity of the CaO/MgO sorbent especially in the presence of steam. The crystallite sizes of CaO and supports were determined on the basis of their XRD peaks, as shown in Figure 1, using Scherrer's equation.

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (8)$$

As shown in Table 1, the average crystallite size of CaO was similar regardless of the type of support material. However, the average crystallite size of the MgO support was much smaller than that of the other three supports. It is reasonable that a smaller crystallite size of support material led to better sintering resistance of the sorbent because more support crystallites can work as separating media between adjacent CaO grains. Therefore, the sorbent with MgO support exhibited strong SO₂ affinity as well as stable cyclic CO₂ capture ability. As for the other three sorbents, the average crystallite size of Ca₁₂Al₁₄O₃₃ was similar to that of Ca₂MnO₄ and La₂O₃; accordingly, the SO₂ capture capacity of the three sorbents was similar. However, the average crystallite size of the supports cannot explain the much higher CO₂ capture capacity of the CaO/Ca₁₂Al₁₄O₃₃ sorbent than the CaO/Ca₂MnO₄ and CaO/La₂O₃ sorbents. Further work is needed to clarify it.

4. CONCLUSION

The precursors of manganese, lanthanum, aluminum, and magnesium nitrate were transformed into Ca₂MnO₄, La₂O₃, Ca₁₂Al₁₄O₃₃, and MgO, respectively, during the sol–gel process of CaO-based sorbent synthesis. The cyclic stability of all synthetic CaO-based sorbents was improved by increasing the mass ratio of support material. It appears that an optimum mass ratio of support material exists, which was found to be around 20–25%, consistent with literature data. The 80:20 wt % CaO/MgO sorbent achieved the highest CO₂ capture capacity at 0.15 g of CO₂/g of sorbent within 2.5 min of carbonation time after 100 cycles. However, CaO/MgO had the strongest affinity to SO₂ during cyclic reactions, especially in the presence of steam, whereas the other three synthetic sorbents showed similar sulfation behaviors. In the presence of both SO₂ and steam during carbonation, steam promoted the carbonation reaction and in the meantime promoted the sulfation reaction even more. The CaO/MgO sorbent showed the highest cumulative SO₂ capture capacity, whereas the CaO/Ca₁₂Al₁₄O₃₃ sorbent had the highest CO₂ capture capacity after multiple cycles. The smaller average crystallite size of the MgO support in the sorbents would be the cause of the strong SO₂ affinity of the CaO/MgO sorbent

as well as its stable cyclic CO₂ capture ability. The results in the paper suggest that SO₂ should be removed before CO₂ capture using CaO-based synthetic sorbents. Otherwise, the synthetic sorbents would experience severe deactivation with significant loss in CO₂ capture capacity after only a few cycles.

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Notes

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NOMENCLATURE

- X_{sulf} = sulfation degree of CaO (with Al, Mn, and La supports) (%)
- X_{sulf}' = sulfation degree of CaO (with Mg support) (%)
- m' = mass of the sample during reaction recorded by TGA (g)
- $m_{\text{cal}}^{(0)}$ = mass of the sample after the initial calcinations in TGA (g)
- M_{CaO} = mole mass of CaO (g/mol)
- M_{SO_3} = mole mass of SO₃ (g/mol)
- M_{SO_2} = mole mass of SO₂ (g/mol)
- M_{MgO} = mole mass of MgO (g/mol)
- b = content of CaO in the initial calcined sample (%)
- n = cycle number
- $C_{\text{CO}_2}^{(n)}$ = CO₂ capture capacity in n th cycle (with Al, Mn, and La supports) (g of CO₂/g of sorbent)
- $C_{\text{CO}_2}^{(n)'}$ = CO₂ capture capacity in n th cycle (with MgO support) (g of CO₂/g of sorbent)
- $C_{\text{SO}_2}^{(n)}$ = cumulative SO₂ capture capacity after n cycle(s) (g of SO₂/g of sorbent)
- $m_{\text{carb}}^{(n)}$ = mass of the sample after the n th carbonation (g)
- $m_{\text{cal}}^{(n)}$ = mass of the sample after the n th calcination (g)
- D = average crystallite size (nm)
- B = main peak breadth in the XRD spectra
- λ = X-ray wavelength (nm)
- θ = Bragg angle (deg)
- k = Scherrer constant

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