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Development of high-performance CaO-based CO₂ sorbents stabilized with Al₂O₃ or MgO

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Abstract

Two organic templating methods, viz., a Pechini and a resorcinol/formaldehyde (RF) carbon-gel approach were employed to prepare CaO-based, Al₂O₃- and MgO-stabilized CO₂ sorbents. Scanning electron microscopy confirmed the formation of micro- and nanostructured morphologies in the synthetic sorbents. The cyclic CO₂ uptake performance of the sorbents was assessed in a thermo-gravimetric analyzer and compared to the reference limestone. It was found that as little as 10 mol% Al³⁺ was required to obtain cyclically stable CO₂ sorbents independent of the synthesis method used. However, a sintering-induced capacity decay of MgO-supported CaO could only be overcome via RF carbon-gel templating approach using at least 20 mol% of Mg²⁺ for stabilization. X-ray diffraction revealed the formation of mayenite, whereas MgO did not form a solid solution with CaO. The CO₂ uptake of the best synthetic sorbent exceeded limestone by more than 300% (after 10 carbonation/calcination cycles).

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Keywords: CO₂ capture; calcium looping; carbon template; mayenite; sintering

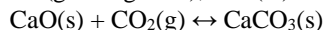
1. Introduction

To mitigate climate change, reduction of anthropogenic CO₂ emissions through carbon capture and storage (CCS) is a possible solution [1]. Among the solid CO₂ sorbents studied, calcium oxide (CaO) is arguably regarded as one of

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the most promising materials due to (i) the vast abundance of natural materials that can be utilized as CaO precursors (e.g., limestone, dolomite), (ii) being environmentally benign, (iii) having a high theoretical CO₂ uptake capacity of ~0.78 (g CO₂/g CaO), and (iv) the relatively fast absorption and release kinetics for CO₂, viz.:



However, the main disadvantage of CaO-based CO₂ sorbents derived from natural limestone (CaCO₃) is the rapid decay in their CO₂ uptake capacity over repeated carbonation (i.e., CO₂ capture) and calcination (i.e., regeneration of the sorbent) cycles. This decay in the CO₂ uptake capacity of the material has been attributed to sintering [2]. The operating temperature for CaO-based CO₂ sorbents is in the range of 600-700 °C for carbonation and 850-950 °C for calcination, i.e. significantly above the Tamman temperature of CaCO₃ (533 °C). Hence, sintering becomes inevitable for such materials. To mitigate sintering-induced deactivation, synthetic CaO-based CO₂ sorbents have been developed, whereby CaO is supported on a material with high Tamman temperature [3].

Herein, we report the synthesis and characterization of supported CaO-based CO₂ sorbents featuring a high and cyclically stable CO₂ uptake. Two different materials, i.e., magnesium oxide (MgO) and aluminum oxide (Al₂O₃), have been studied as support material. Apart from possessing a high Tamman temperature, these low-cost materials are cheap and environmentally benign.

2. Experimental

2.1. Materials and methods

Al₂O₃- and MgO-stabilized CaO-based CO₂ sorbents were synthesized by two methods, viz., a Pechini and a RF carbon-gel templating technique.

Pechini method

In a typical synthesis, calcium nitrate (Ca(NO₃)₂·4H₂O; Acros Organics) and the precursor for the support (Al(NO₃)₃·9H₂O for Al₂O₃ or Mg(NO₃)₂·6H₂O for MgO from Acros Organics) were mixed with an equimolar quantity of citric acid. Thereafter, a deionized water/ethanol solution (50 ml, volumetric ratio 4:1) was added and mixed until all chemicals were fully dissolved. The mixture was then, under stirring, placed in an oil bath (80 °C) to evaporate excess water and to obtain a wet gel. Subsequently, the wet gel was placed in an oven for further drying and foaming (130 °C for 24 h). Finally, the dried material was ground via a mortar and calcined at 800 °C (5 °C/min ramping-up rate) for 2 h.

RF carbon-gel templating method

A detailed description of the RF carbon-gel templating technique can be found in our previous works [4, 5]. In short, the carbon template was prepared via the poly-condensation of resorcinol (R) (Fisher Scientific) with an aqueous formaldehyde (F) solution (37 wt.%, Sigma Aldrich). Firstly, an appropriate amount of resorcinol (R) was completely dissolved in reverse osmosis water (15 MΩ cm) at room temperature. In the next step, an aqueous formaldehyde solution was added to the resorcinol solution (solution A). The calcium precursor (Ca(NO₃)₂·4H₂O; Acros Organics) and the respective nitrate salt of the support material (Al(NO₃)₃·9H₂O for Al₂O₃ and Mg(NO₃)₂·6H₂O for MgO) were dissolved in the appropriate quantities of reverse osmosis water to obtain a 1.5 M solution (solution B). The solutions A and B were mixed together under vigorous stirring for 5 min and subsequently transferred to a sealed glass bottle that was placed in an oven at 80 °C for 24 h. After aging, the solidified gel was collected through filtration and dried at room temperature for 24 h. Following the drying process, the collected material was first pyrolyzed in a N₂ flow (400 mL/min) at 500 °C (2 °C/min ramping-up rate) for 2 h. Finally, the calcination was performed in a muffle furnace at 800 °C (2 °C/min ramping-up rate) for 2 h.

Throughout this paper, the abbreviations CaXAlY-Z and CaXMgY-Z, where X and Y represent the molar percentage of the respective elements and Z represents the synthesis method used, will be used to refer to the different materials prepared. For example, the materials Ca90Al10-P and Ca90Al10-RF contain a Ca²⁺:Al³⁺ mole ratio of 90:10 and were synthesized by a Pechini (P) and RF carbon-gel templating technique, respectively.

2.2. Physicochemical characterization

A Bruker D8 Advance diffractometer equipped with a Lynxeye super-speed detector was utilized to investigate the crystallinity and the chemical composition of the synthesized materials. The diffractometer was operated at 40 mA and 40 kV using Cu K α radiation. The scanning was performed within the 2θ range of 10° to 90° with a step size of 0.025 and a step duration of 0.8 s.

A scanning electron microscope (Zeiss ULTRA 55 plus) was used to characterize the surface morphology of the fresh and cycled CO₂ sorbents. Prior to imaging, the samples were carefully placed onto aluminum stubs with the help of a conductive carbon tape, followed by a short (90 s) gold/palladium (Au/Pd) sputtering (BAL-TEC SCD-050) in order to improve the conductivity of the samples.

2.3. Performance evaluation

To evaluate the cyclic CO₂ uptake of the synthesized CO₂ sorbents, a thermogravimetric analyser (TGA, Mettler Toledo TGA/DSC 1) was used. In a typical experiment a sample of approximately 5 mg was placed in an alumina crucible with a volume of 70 μ L. Prior to the cyclic calcination and carbonation tests, the sample was calcined at 900 $^\circ$ C (50 $^\circ$ C/min ramping) in a N₂ flow of 125 mL/min. The sample was maintained at the calcination temperature for 10 min. Subsequently, the sample was cooled down to 650 $^\circ$ C (-50 $^\circ$ C/min ramping) and the carbonation reaction was performed in 24 vol% CO₂ in N₂ for 20 min. After carbonation, the temperature was increased to 900 $^\circ$ C (50 $^\circ$ C/min) and the CO₂ sorbent was regenerated in a pure CO₂ atmosphere for 10 min. In total, 10 calcination/carbonation cycles were performed for all sorbents.

3. Results and discussion

The X-ray diffraction patterns of the freshly calcined, Al₂O₃- and MgO-stabilized CaO-based CO₂ sorbents are presented in Figure 1 and 2, respectively. For Al₂O₃-stabilized CaO (Fig. 1), four main crystalline phases, viz., lime (CaO), portlandite (Ca(OH)₂), calcite (CaCO₃) and mayenite (Ca₁₂Al₁₄O₃₃) were identified independent of the synthesis method. The diffraction peaks detected at $2\theta = 18.2^\circ$, 23.5° , and 33.4° are ascribed to mayenite (PDF: 09 0413), while other high intensity peaks observed at $2\theta = 32.2^\circ$, 37.3° , 53.9° , 64.2° , 67.7° and 79.7° are indicative of CaO (PDF: 37-1497). The presence of Al₂O₃ could not be identified by XRD. This could be due to its presence (at least partially) in an amorphous phase or all of the Al₂O₃ formed a solid solution with CaO, i.e. mayenite. It is important to note that mayenite is inert with respect to the calcination and carbonation reactions, i.e. it does not take part in the capture of CO₂.

As in the case of Al₂O₃-supported CaO, irrespective of the synthesis method, four crystalline phases were detected in MgO-stabilized CaO (Fig. 2), viz., CaO, Ca(OH)₂, CaCO₃ and MgO. However, unlike in Al₂O₃-supported CaO, we did not observe a solid solution between CaO and MgO, independent of the Ca to Mg ratio in the material. Again it is important to note, that at the carbonation temperature studied here MgO does not participate in the capture of CO₂ and can be considered as inert [6].

From the diffractograms plotted in Figures 1 and 2 we also observed the presence of CaCO₃, yet its presence is more pronounced in the samples synthesized via an RF carbon-gel templating technique. The formation of CaCO₃ in the RF carbon-gel templated samples is attributed to the formation of CO₂ during removal of the carbon template.

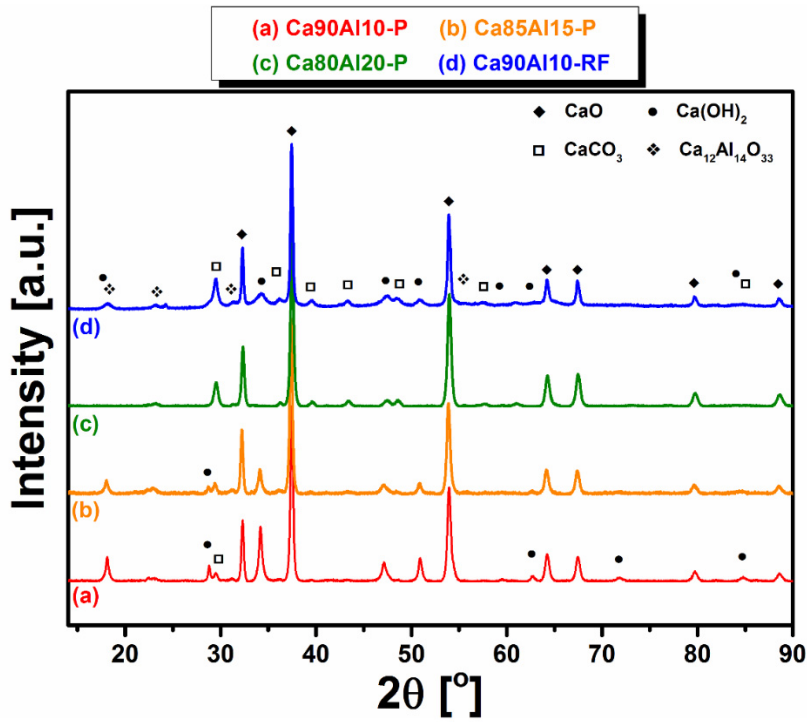


Fig. 1. XRD diffractograms of Al₂O₃-stabilized CaO.

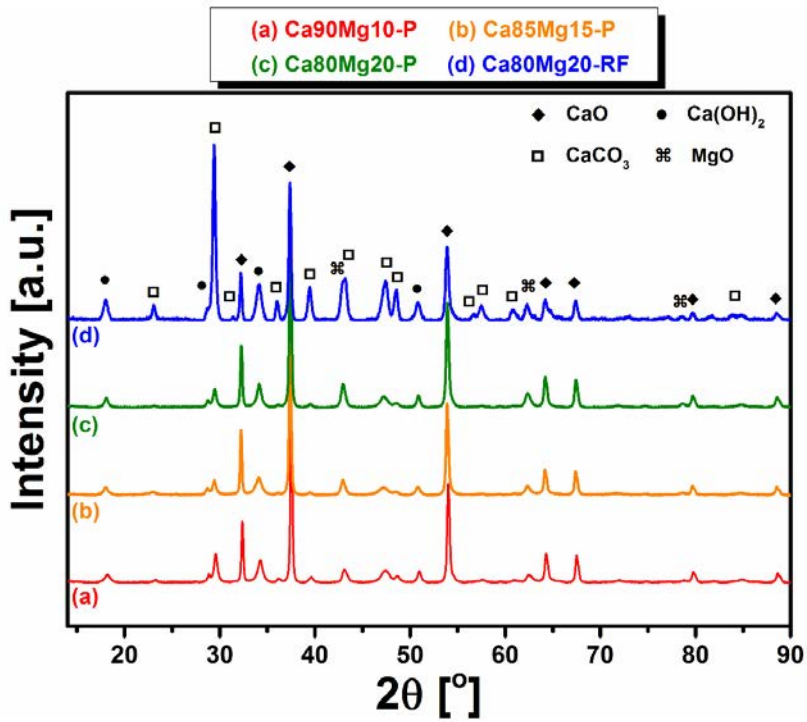


Fig. 2. XRD diffractograms of MgO-stabilized CaO.

The cyclic CO₂ capture performance of the Al₂O₃- and MgO-stabilized CO₂ sorbents was assessed in a TGA and compared to the CO₂ capture characteristics of limestone (Fig. 3 and 4). In both figures, the horizontal dashed lines mark the maximum theoretical CO₂ uptake capacity of pure CaO (i.e., 0.78 g CO₂/g CaO). As expected, limestone deactivates rapidly owing to severe thermal sintering. This is in agreement with previous studies [3]. The initial CO₂ uptake of limestone was 0.54 g CO₂/g CaO which is only ~70% of the theoretical CO₂ uptake of pure CaO. The reason for the rather low CO₂ uptake of limestone already in the first cycle may be explained by: (i) the initial calcination step already caused significant sintering in the material, and (ii) the carbonation process proceeds mainly in the diffusion-controlled regime due to the lack of sufficient meso- and/or micro-porosity.

In the case of Al₂O₃-stabilized CaO, independent of the synthesis method, all of the CO₂ sorbents showed stable CO₂ uptakes (Fig. 3). This stable performance can be attributed to the homogenous distribution and mixing of Al³⁺ species with Ca²⁺ species potentially on a molecular level via the formation of mayenite [4]. For the materials reported here, a content of 10 mol% of Al³⁺ (i.e., ~9 wt.% Al₂O₃) seemed to be sufficient to stabilize the CO₂ uptake over several carbonation/calcination cycles. Indeed, for samples Ca85Al15-P and Ca80Al20-P a small increase in the CO₂ uptake was observed after the first few cycles. This might be explained by some structural changes the materials undergo during cyclic operations [7, 8]. Figure 3 also reveals that there is a linear relationship between the molar ratio of Ca²⁺ to Al³⁺ and the CO₂ uptake capacity of the material synthesized.

In contrast to Al₂O₃-stabilized CaO, MgO-stabilized CaO showed a poorer cyclic stability, except for Ca80Mg20-RF. Our data seems to indicate that using MgO as a support with a content of at least 20 mol% of Mg²⁺ (i.e., ~16 wt% MgO) is required to stabilize the CO₂ uptake of the material. However, when using a Pechini method for synthesis, even 20 mol% Mg²⁺ was not sufficient to yield a cyclically stable CO₂ uptake. This might indicate that the RF carbon-gel templating method is more effective in providing a homogeneous distribution between the support material and CaO.

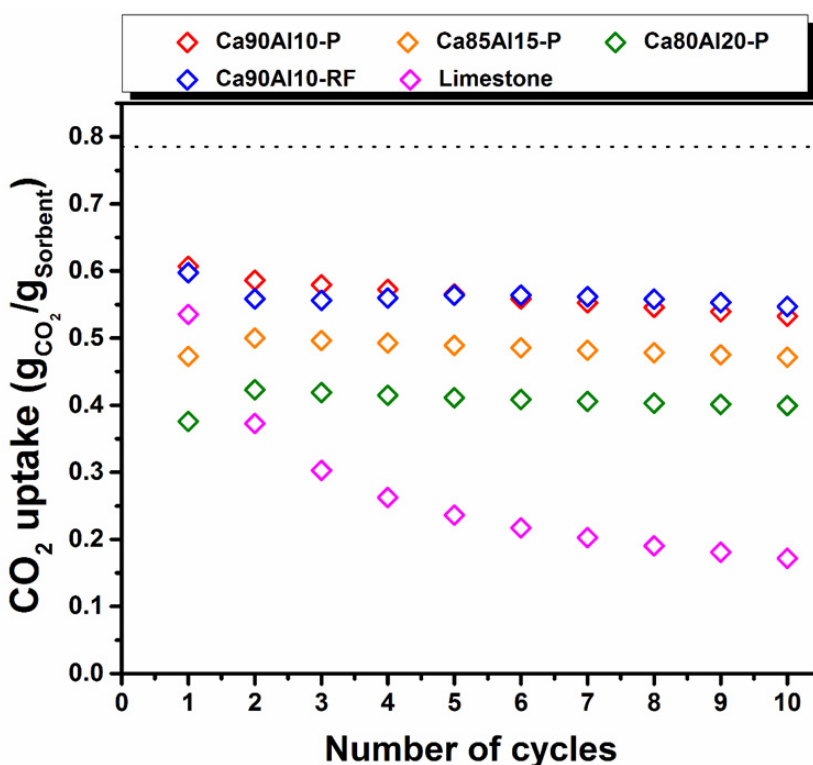


Fig. 3. Cyclic CO₂ uptake of Al₂O₃-stabilized CaO using limestone as reference.

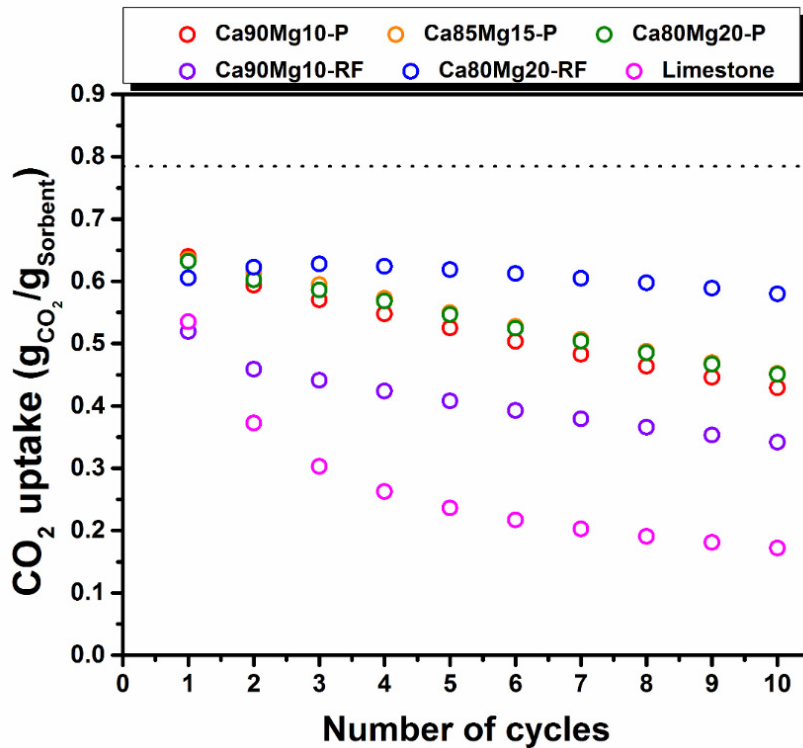


Fig. 4. Cyclic CO₂ capture of MgO-stabilized CaO using limestone as reference.

The morphology of Al₂O₃- and MgO-stabilized CaO was characterized by SEM and given in Figure 5 and 6, respectively. As shown in Figure 5, Al₂O₃-stabilized CaO, prepared using the Pechini method resulted in the formation of porous sheet-like structures. On the other hand, an inverse-opal-like morphology was obtained when using the RF carbon-gel templating technique for synthesis. A close-up view of the macrostructures is provided in the insets of Figure 5 (Fig. 5a and 5c). The structures of Ca90Al10-P and Ca80Al20-P are composed of an assembly of nanoparticles with a particle size in the range of 30–200 nm, providing a highly porous nanostructured backbone. A porous, nanostructured CaO-based CO₂ sorbent is highly advantageous for CO₂ capture as the diffusion path length for CO₂ is reduced, and in turn, the rate of CO₂ uptake is improved. SEM also confirms that the macrostructure of Ca90Al10-RF did not collapse with cycle number, and its porous morphology was maintained over 10 successive carbonation and calcination cycles.

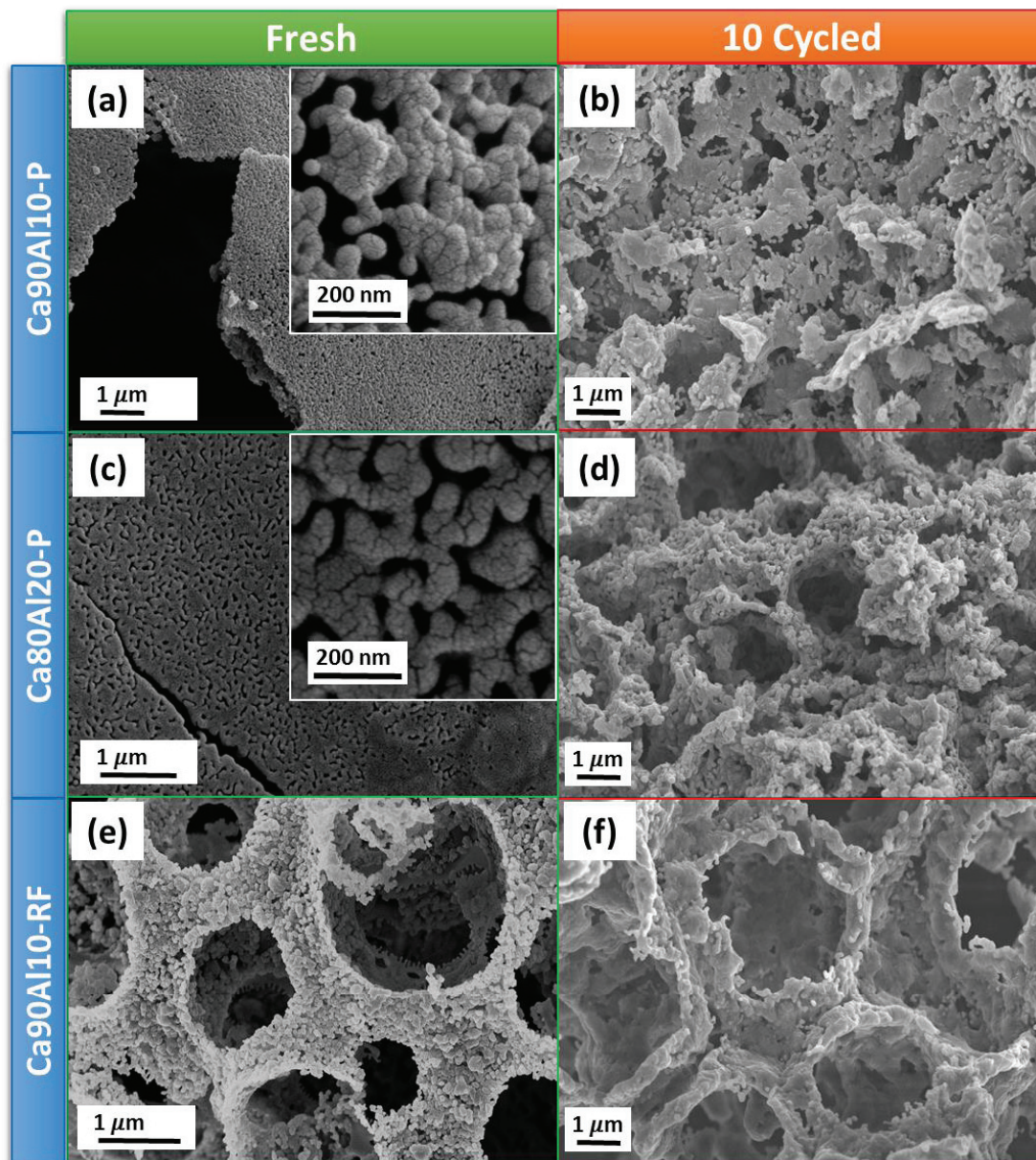


Fig. 5. SEM images of fresh and cycled Al_2O_3 -stabilized CaO.

Figure 6 compares the morphology of different MgO-stabilized CO_2 sorbents synthesized. Similar to Al_2O_3 -stabilized CaO, porous structures were obtained. For the CO_2 sorbents that were prepared via the Pechini method, MgO was heterogeneously distributed in the CaO matrix species, and MgO nanoparticles (light color particles in Fig. 6a, 6c, and 6d) mostly agglomerated on the surface of the material. This was not observed for Al_2O_3 -supported CaO (Fig. 5). As a result of this heterogeneous distribution of MgO, all of the CO_2 sorbents synthesized by Pechini method underwent severe sintering over multiple carbonation/calcination cycles as confirmed by SEM (Fig. 6). This observation is in line with the cyclic CO_2 uptake of Ca90Mg10-P, Ca85Mg15-P, and Ca80Mg20-P (Fig. 4). None of

the CO₂ sorbents that were synthesized via the Pechini method showed a cyclically stable performance. Interestingly, the structures synthesized via RF carbon-gel templating technique featured both spherical (Fig. 6e) and inverse-opal-like morphologies (inset of Fig. 6e). In comparison to materials prepared using the Pechini method, Ca80Mg20-RF showed a better morphological stability over repeated carbonation and calcination cycles (Fig. 6f), which was also reflected by its CO₂ uptake performance as shown in Figure 4.

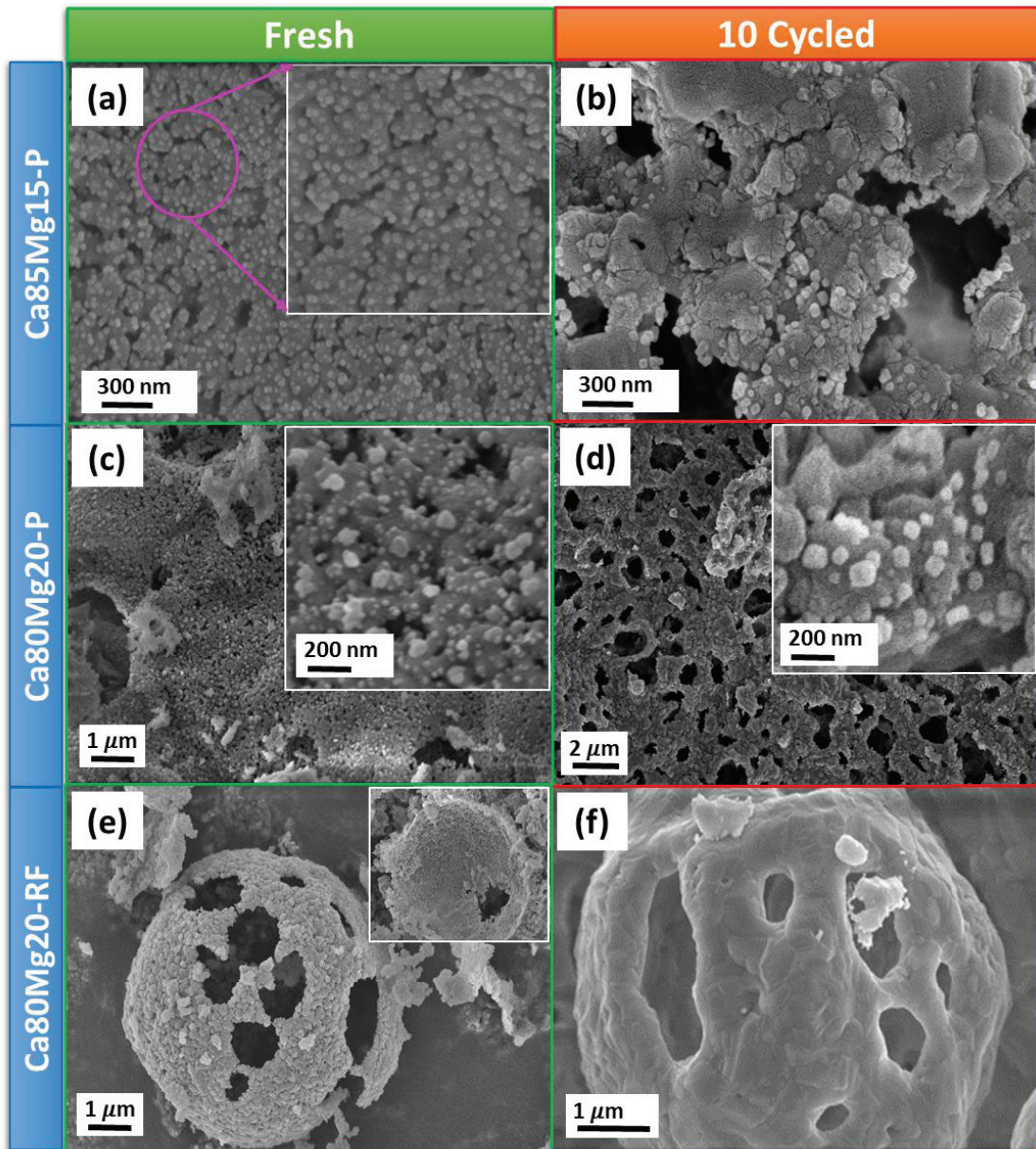


Fig. 6. SEM images of the fresh and cycled MgO-stabilized CaO.

Conclusions

CaO-based CO₂ sorbents supported with Al₂O₃ or MgO were synthesized by two different methods, viz., Pechini and RF carbon-gel templating. Both methods enabled the synthesis of sorbents featuring micro- and nanostructured morphologies. However, while Al₂O₃-supported CaO exhibited a high CO₂ uptake in combination with a remarkable cyclic stability independent of the synthesis technique and Al³⁺ content introduced, the synthesis method was found to play an important role for MgO-supported CaO. In the case of MgO-supported CaO, RF carbon-gel templating was more effective than Pechini in realizing cyclically stable materials; yet, when compared to Al₂O₃-supported CaO, a higher quantity of Mg²⁺ was required for a decent cyclic stabilization. This difference might stem from the fact that for Al₂O₃-supported CaO, a solid solution, i.e., mayenite, was formed between the support and active material, whereas this was not the case for MgO-supported CaO.

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