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CaO-based CO₂ Sorbents with a Hierarchical Porous Structure made *via* Microfluidic Droplet Templating

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Abstract

Calcium looping, a CO₂ capture technique based on the cyclic carbonation and calcination of CaO, is a promising short- to mid-term solution to reduce CO₂ emissions. However, CaO suffers from sintering under industrially relevant operating conditions, which reduces rapidly its cyclic CO₂ uptake capacity. Here, we report the design and manufacture of a hierarchical, porous (HP) CaO-based CO₂ sorbent. The hierarchically porous sorbent is created through the assembly of calcium carbonate nanoparticles and monodisperse oil droplets generated via microfluidic emulsification. The structure of the sorbent is stabilized by an Al₂O₃ coating via atomic layer deposition (ALD). The sorbent outperformed the CO₂ uptake of the reference limestone by ca. 140 %. The improved CO₂ uptake capacity is attributed to: i) the stabilization of the micro- and mesoporous structure of the material by the formation of Ca-Al mixed oxides, i.e. Ca₁₂Al₁₄O₃₃ and Ca₃Al₂O₆, and ii) an improved mass transport within the sorbent particles owing to the HP structure of the material.

Introduction

CO₂ capture and storage (CCS) is expected to contribute appreciably to the reduction of anthropogenic CO₂ emissions that are linked directly to global warming.¹⁻⁴ One of the most promising carbon capture technologies is calcium looping that relies on CaO for CO₂ capture, forming CaCO₃ in a reversible, cyclic fashion. Sorbents based on CaO are relatively cheap, naturally abundant and pure CaO has a high theoretical CO₂ uptake capacity (0.78 g_{CO₂} g_{sorbent}⁻¹).⁵⁻⁸ However, CaO-based sorbents undergo a rapid decay in their CO₂ uptake upon repeated carbonation-calcination cycles, which has been attributed largely to the sintering of the CaCO₃ phase.⁹⁻¹¹ That is because the operational temperatures of the calcium looping process range between 650-950 °C, which is considerably higher than the Tammann temperature of CaCO₃ (T_T = 533 °C).⁵ To mitigate the sintering-induced deactivation of CaO-based sorbents, several concepts have been implemented such as high temperature activation,¹²⁻¹³ steam treatment¹⁴⁻¹⁵ and the stabilization of CaO with high-T_T materials such as Al₂O₃, MgO, TiO₂, or ZrO₂.^{5,16-21} Among these approaches, the introduction of a thermal stabilizer tends to improve significantly the cyclic CO₂ uptake stability of CaO. Besides sintering, breakage and attrition of sorbent particles are further challenges encountered in the calcium looping process. When operated in a (circulating) fluidized bed, fine particles can entrain from the bed and leave the reactor system. As a consequence, an additional make-up stream of fresh material is required, increasing the operational cost of the process.²²⁻²⁴ If the calcium looping process is employed for CO₂ capture, the most likely reactor will be (circulating) fluidized beds to handle the large volumetric flow rates of gas.²⁵⁻²⁶ Synthetic sorbents with a high surface area and large pore volume will most likely not be suitable for such reactor systems, owing to their lack of mechanical strength.

Calcium looping has been used also for sorption-enhanced reaction schemes, e.g. the sorption-enhanced reforming of CH_4 to produce high purity H_2 .²⁷ For sorbent-enhanced reactions, fixed bed reactors are employed commonly, thus reducing the requirements on the mechanical stability of the sorbent to some extent.²⁸⁻³⁰ Previous works have demonstrated the general feasibility of the processes using a mixture of a dry reforming catalyst, e.g. Ni supported in Al_2O_3 and a CaO-based sorbent.³¹⁻³² In these sorption-enhanced processes the deactivation of the CaO-based sorbent is also a key limitation, as it reduces process performance, i.e. the time during which H_2 of high purity can be generated.³¹ The stability of the reforming catalyst has been less of a concern. When used in a packed bed configuration, (internal) mass transfer limitations in a material have to be considered, in addition to resistance to sintering. One strategy to reduce mass transfer limitations is the design of materials of high porosity. In this context, materials that contain a hierarchical porosity (HP), allowing fast mass transfer even if sintering occurs, are an attractive choice.³³⁻³⁴ Such HP materials have been applied in a variety of applications including catalysis,^{33,35} and, particularly, sorption-based techniques.^{21,36} Commonly adopted protocols to prepare HP structures include sacrificial templating,³⁷⁻³⁹ freeze drying,⁴⁰ and sol-gel techniques.⁴¹

In this work, we report on a microfluidic approach to prepare HP- CaCO_3 structures using an oil-in-water emulsion as sacrificial template (Figure 1).⁴²⁻⁴³ To stabilize the HP structure of the sorbent at high temperatures, the CaCO_3 particles are covered with a uniform coating of Al_2O_3 through atomic layer deposition (ALD). We first study the effect of the Al_2O_3 layer thickness on the stability and on the CO_2 capture efficiency of the structure by performing cyclic carbonation-regeneration experiments. Electron microscopy and X-ray diffraction are used to characterize the sorbents and shed light on the mechanisms underlying the stability and performance of the hierarchical porous structures.

Experimental

Materials preparation: Commercial CaCO_3 (Fischer Chemicals, analytical reagent grade, $10\pm 5\ \mu\text{m}$ particle size, Figure S1) was modified through ball-milling (48 h milling at 500 rpm) to decrease its particle size following a reported method.¹⁹ The calcite nanoparticles obtained had a monomodal particle size distribution with an average size of 350 nm (Figure S2) and BET surface area and BJH pore volume values of $16\ \text{m}^2\ \text{g}^{-1}$ and $0.13\ \text{cm}^3\ \text{g}^{-1}$, respectively. Hierarchical porous structures were prepared by a sacrificial template method. A sacrificial emulsion template was produced *via* a microfluidic technique in a microcapillary reactor (Figures 1a,b). Here, a 2 wt.% PVA (Sigma-Aldrich, MW = 31000-50000) aqueous solution was used as the outer phase and 1,2-dichlorobenzene (DCB) (Sigma-Aldrich, 99 %) as the inner oil phase. The flow rates of the water and oil phase were controlled by syringe pumps (PHD 2000, Harvard Apparatus). Once a desired volume of DCB oil droplets had been collected (Figure 1c), the oil droplets were mixed with the freshly sonicated suspension of 40 vol.% CaCO_3 in a 2 wt.% PVA aqueous solution and left to settle to the bottom of a beaker. Once all oil droplets had settled, excess water was removed and the emulsion was left to dry at room temperature for 48 h. To remove the PVA coating of the CaCO_3 particles, the material was calcined in air at $500\ ^\circ\text{C}$ for 2 h. The calcined material was sieved to 300-1180 μm for assessing the cyclic performance. Commercial limestone (*Rheinkalk limestone* pit, Germany), was used as a reference material.

Atomic layer deposition (ALD) of Al_2O_3 : A commercial ALD system (Sunale R-150B, Picosun) was used to deposit Al_2O_3 films onto HP- CaCO_3 porous structures. Prior to deposition, the ALD chamber was flushed three times with nitrogen. Nitrogen served as both the purge and carrier gas for the precursors. Throughout the deposition process, the temperature of the reaction chamber was maintained at $300\ ^\circ\text{C}$, and the sample therein was exposed to pulse injections of electronic grade trimethylaluminium (TMA, Pegasus Chemicals) and deionized (DI) water in an alternating fashion. In a

typical synthesis, the pulse and purge times of the precursors were set to 1 s and 10 s, respectively. According to reference experiments performed on Si wafers, the deposition rate of Al₂O₃ was ca. 0.9 nm/cycle as determined by spectroscopic ellipsometry (Sentech SE850 Ellipsometer).

X-ray diffraction (XRD): The crystallinity and phase composition of the sorbents was analyzed by XRD (Bruker, AXS D8 Advance). The X-ray diffractometer was equipped with a Lynxeye superspeed detector and operated at 40 mA and 40 kV. All samples were scanned within the 2θ range of 5 – 90° using a step size of 0.025°. A qualitative phase analysis was performed using the Eva software package (Bruker Corporation).

Electron microscopy: Scanning electron microscopy (SEM) was performed on a LEO Gemini 1530 (Zeiss, Germany). Prior to imaging all samples were sputtered with a thin (ca. 3 nm) layer of Pt. Scanning micrographs were obtained at 5 kV while cross sectional back scattered electron micrographs and EDX mapping were obtained at 20 kV. Prior to cross sectional imaging the sample was embedded into a matrix of an acrylic resin (SpeciFast, Struers) and polished first using sandpaper (from 300 to 1200 grade) and, finally, a 1 µm diamond paste (M106, Reishauer). Scanning transmission electron microscopy (STEM) was performed on a FEI Talos F200X operated at 200 kV and equipped with a SuperX EDX consisting of four SDD detectors. The probe size for STEM was approximately 0.8 nm × 0.8 nm. A 3-pixel smoothing filter was applied for visualization purposes.

CO₂ capture test: The materials synthesized were investigated under realistic capture conditions using a thermogravimetric analyzer (TGA, Mettler Toledo TGA/DSC 3). The calcination reaction was performed in a CO₂-rich atmosphere at 900°C. Prior to the cyclic CO₂ uptake experiments, all samples were calcined at 800 °C for 2 h in air. In a typical TGA experiment 2.5-3 mg of sample was placed in a 70 µL alumina crucible. The carbonation reaction was performed for 20 min in 20 vol.% CO₂ in N₂ (total flow rate: 150 cm³ min⁻¹, measured at ambient temperature and pressure) at 650 °C. Subsequently, the materials were calcined for 10 min in a CO₂-rich atmosphere at 900 °C (total flow rate: 55 cm³ min⁻¹). Flow rates include a N₂ purge flow of 25 cm³ min⁻¹ over the microbalance. All heating and cooling steps were performed at a rate of 50 °C min⁻¹ in pure CO₂ and 20 vol.% CO₂, respectively. The cyclic carbonation-calcination experiments were repeated 10 times. The cyclic CO₂ uptake, expressed in g_{CO2} g_{sorbent}⁻¹, was calculated from the measured weight change as:

$$CO_2 \text{ uptake} = \frac{m_{carb} - m_{calc}}{m_{calc}}$$

where m_{carb} is the sample mass measured at the end of the carbonation stage and m_{calc} is the sample mass measured at the end of the calcination stage. Replacing m_{carb} with $m(t)$, the sample mass measured during the carbonation reaction, gives the CO₂ uptake as a function of time.

Results and discussion

Sorbent synthesis

Electron micrographs of the HP-CaCO₃ structure obtained by the microfluidic approach capture the unique hierarchical architecture of the sorbent (Figure 1d). The low magnification image reveals the formation of an open, macroporous structure with a macropore size of ca. 150-200 µm. This open porosity ensures a rapid access of the gaseous reactants to the sorbent particles. The image at a higher magnification (inset of Figure 1d) depicts the predominantly submicron-sized grains that serve as the building blocks of the backbone of the hierarchical structure. The open windows between the macropores in the dried structure correspond to the contact points between the oil droplets of the

initial emulsion template. As observed in earlier work,⁴² particles present in the aqueous continuous phase of the emulsion are depleted from the contact point between droplets during the assembly process. This occurs when the particles are well wetted by the continuous phase and thus do not adsorb at the oil-water interface of the templating emulsions. It is worth mentioning that while the microfluidic device utilized in this study delivers emulsion quantities that are sufficient for preparing lab-scale samples, the fabrication of larger porous structures would require a higher emulsification throughput. Recent developments in microfluidic emulsification technologies have shown that the production of monodisperse droplets at high throughput rates is possible by combining a step emulsification mechanism with extensive parallelization of droplet-making fluidic channels.⁴⁴

Figure 1. a) Schematic illustration of the preparation of the templating emulsion in a double microcapillary device, b) high-magnification light microscopy image of the microfluidic device, and c) example image of the droplets of 1,2-dichlorobenzene formed in the microcapillary device. SEM images of the hierarchical, porous CaCO_3 structure (d) as-prepared and (e) after 100 Al_2O_3 ALD cycles. f) Cross-sectional SEM image of as-prepared HP- CaCO_3 after exposure to 100 Al_2O_3 ALD cycles. The inset shows EDX map the distribution of aluminium in the structure. g) STEM-EDX maps of the CaCO_3 particles comprising the backbone of the HP- CaCO_3 structure after exposure to 100 Al_2O_3 ALD cycles.

Coating of the material with Al_2O_3 via ALD, shown in Figure 1e, did not cause a notable change in the material's macrostructure, suggesting that the operating conditions of the ALD process have no detrimental impact on the morphology. In the given example, 100 ALD cycles were employed to generate an Al_2O_3 layer of 9 nm thickness. The high-magnification SEM image, shown in Figure 1e, reveals that the surface morphology of the building blocks became smoother after ALD coating. XRD analysis of the ALD-coated materials (Figure 2a) shows the presence of CaCO_3 (calcite) only, indicating that the as-synthesized Al_2O_3 coating was amorphous.

To probe the homogeneity of the ALD-grown Al_2O_3 film within the CaCO_3 structure, EDX was performed on cross-sections. An EDX mapping confirms the homogeneous distribution of aluminium within the sorbent structure (Figure 1f). Furthermore, STEM/EDX maps of Ca and Al (in blue and green, respectively in Figure 1g) indicate a conformal coating of Al_2O_3 onto the submicron-sized CaCO_3 particles comprising the backbone of the HP structure.

Figure 2. a) XRD patterns of HP- CaCO_3 -based, Al_2O_3 -coated CO_2 sorbents at different reaction stages, i.e. as-prepared (ALD100), calcined (ALD100-calc) and after 10 carbonation-calcination cycles (carbonated state, ALD100-10c and ALD240-10c). Samples ALD100-10c and ALD240-10c were previously prepared using 100 and 240 Al_2O_3 deposition cycles during the ALD coating process. Crystalline ($\square$) calcite, CaCO_3 ; ($\circ$) lime, CaO ; ($\blacklozenge$) mayenite, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$; ($\bullet$) tricalcium aluminate, $\text{Ca}_3\text{Al}_2\text{O}_6$ phase are indicated directly in the XRD pattern. b) Cyclic CO_2 uptake of HP-based CO_2 sorbents as a function of cycle number and number of ALD cycles. The benchmark limestone is also included.

CO_2 capture performance

The cyclic CO_2 uptake performance of the HP-based sorbents was assessed in a TGA and compared to that of the benchmark limestone (Figure 2b). The HP-structured material without Al_2O_3 showed only a marginal improvement over the benchmark sorbent limestone. The minor improvement can be

explained by the introduction of extra macroporosity as well as the smaller initial grain size in HP-CaCO₃ compared to the limestone. Calcite nanoparticles in the HP-CaCO₃ structure have a diameter of ca. 350 nm, whereas those in the reference limestone exhibit ca. 2 μ m (Figure S3). Nonetheless, both sorbents were prone to sintering under the harsh operating conditions, as visualized by SEM (Figures 3a and S4).

Al₂O₃-stabilized sorbents with a film thickness as low as 1 nm (10 ALD cycles, Ca:Al $\sim$ 50) outperformed their counterparts from the second calcination/carbonation cycle onward and exhibited a remarkable cyclic stability. The incorporation of higher amounts of Al₂O₃ to reach coating thicknesses of 2.7 and 9 nm (30 and 100 ALD cycles and Ca:Al atomic ratios of 5 and 3, respectively) resulted in a further improvement in the cyclic stability of the sorbents, albeit at the cost of an overall reduced CO₂ uptake. The decrease in the overall CO₂ uptake can be explained by the formation of mixed oxides in the CaO - Al₂O₃ system (i.e. mayenite and/or tricalcium aluminate),⁴⁵⁻⁴⁶ which is not active for CO₂ uptake at the conditions studied. After 10 carbonation-calcination cycles, the CO₂ uptake of the sorbents that had been stabilized with Al₂O₃ coatings of a thickness of 2.7 or 9 nm, was 0.41 and 0.36 g_{CO2} g_{sorbent}⁻¹, respectively. These values exceeded the performance of the reference limestone by ca. 110 % and 140 %, respectively. A substantial further increase of the thickness of the Al₂O₃ coating to ca. 20 nm (240 ALD cycles, Ca:Al atomic ratio of ca. 1.6) reduced the CO₂ uptake capacity of the sorbent to negligible quantities, i.e. 0.04 g_{CO2} g_{sorbent}⁻¹ after 10 carbonation-calcination cycles.

The carbonation profiles shown in Figure S5 revealed a much slower carbonation rate in the first carbonation for the Al₂O₃ coated (i.e. HP-CaCO₃ coated with 30 ALD cycles) sorbent compared to pure HP-CaCO₃, which was probably due the amorphous Al₂O₃ layer hampering CO₂ access to CaO. For higher cycle numbers, i.e. 5 and 10, the carbonation rates of both pure and Al₂O₃ coated HP-CaCO₃ were very similar. As is also evident from the XRD pattern in Figure 2a, the amorphous Al₂O₃ transformed into crystalline calcium aluminate during cycling and thus impaired the integrity of the Al₂O₃ coating, providing a better access of CO₂ to unreacted CaO and stabilizing the structure.

Characterization of reacted sorbents

XRD analysis of the sorbents after 10 carbonation-calcination cycles (carbonated state) was performed to probe the interaction between Al₂O₃ and CaO and link this interaction to material stabilization or deactivation. HP-CaCO₃ containing a 1 nm thick coating of alumina showed no reflections due to aluminium-containing phases (Figure S6), probably because the relative quantity of the Ca-Al mixed oxide was too small (the atomic ratio Ca:Al in this material was 50:1). XRD analysis of the sorbents that contained an Al₂O₃ coating of thickness 2.7 or 9 nm revealed the presence of a mayenite (Ca₁₂Al₁₄O₃₃) phase (Figure 2a), which has been associated with the stabilization of CaO-based sorbents against sintering.^{17,45} In addition, XRD analysis of the sorbent with a 9nm-thick alumina coating shows ca. 8 wt% of the Ca-rich tri-calcium-aluminate (Ca₃Al₂O₆) phase.

On the contrary, the sorbent with the thickest Al₂O₃ coating, i.e. ca. 20 nm (240 ALD cycles), is almost phase pure Ca₃Al₂O₆, containing only small quantities of mayenite (2 wt.%), calcite (5 wt.%) and lime (<1 wt.%) (Figure 2a). This observation explains the dramatically reduced CO₂ uptake capacity of this sorbent (Figure 2b). The very low amount of active CaO in this sample is insufficient for effective CO₂ capture. The predominant presence of Ca₃Al₂O₆ in the HP-CaCO₃ sample coated with a 20 nm thick layer of alumina is also in agreement with the atomic ratio of Ca:Al $\sim$ 1.6 in this material as determined by EDX. Interestingly, only the Al₂O₃-stabilized sorbents showed some activation during the initial cycles. Such a behaviour has been observed previously in Al₂O₃-stabilized CaO-based sorbents²⁰ and was explained by phase changes in the Ca-Al mixed oxides.⁴⁶

Figure 3. SEM micrographs of HP- CaCO_3 after 10 calcination-carbonation cycles in the (a) absence and (b) presence of an ALD-grown Al_2O_3 coating (c) HAADF and STEM-EDX maps of agglomerates of CaCO_3 backbone particles in HP- CaCO_3 exposed to 100 Al_2O_3 ALD cycles after 10 calcination-carbonation cycles.

Finally, we probed the morphology of the cycled sorbents by electron microscopy (Figure 3a,b) aiming to link changes in the sorbents' morphology to changes in the carbonation profile of the materials (Figure S5). Although pure HP- CaCO_3 lacked a structural stabilizer (Al_2O_3), the sorbent maintained its HP macro-structure over the cyclic experiments. Only at the micro- and meso-porosity level, a significant degree of sintering was observed (Figure 3a). The loss in micro- and meso-porosity caused the appreciable reduction in the CO_2 uptake of the material (Figure 2b). Owing to the large volumetric expansion of the material during carbonation (the ratio of the molar volume of CaCO_3 to CaO is ca. 2:1) and the low diffusion coefficient of CO_2 in CaCO_3 (ca. 100 times lower than the diffusion coefficient of CO_2 in CaO), a high micro- and meso-porosity is required to yield high CO_2 uptakes.⁴⁷ The carbonation profile of HP- CaCO_3 (Figure S5) shows a very rapid transition from the kinetically-controlled to the diffusion-controlled regime, suggesting the blockage of micro- and small meso-pores such that some pore volume was inaccessible for carbonation. By contrast, Al_2O_3 -stabilized sorbents

did not only maintain their macro-structure but also preserved the porosity on the meso- and, most probably, micro-level to a large extent (Figure 3b). This structural stability was reflected by a relatively stable cyclic CO₂ uptake of these sorbents. Indeed, comparing the carbonation profiles of unstabilized HP-CaCO₃ and HP-CaCO₃ coated with 30 ALD cycles of Al₂O₃ reveals a major difference in the diffusion-limited regime. The smooth transition from the kinetically- to the diffusion-controlled regime for alumina-stabilized sorbents indicates that mesoporosity was largely preserved over 10 carbonation/calcination cycles. Additional high-resolution SEM images reveal the formation of dispersed nanoparticles upon cycling. Probing these areas by STEM/EDX (Figure 3c) confirmed that these nanoparticles were composed of Al-containing phases, i.e. mayenite and/or Ca₃Al₂O₆, acting as spacers between neighbouring grains of CaCO₃ and thus, providing stability to the sorbent against thermal sintering.

Conclusions

In summary, hierarchical porous CaO-based CO₂ sorbents were prepared *via* a sacrificial templating method and stabilized by an ALD-derived Al₂O₃ coating. The macrostructure of the sorbents was preserved throughout cyclic CO₂ capture and release reactions. Sorbents that were stabilized by an ALD-grown coating of Al₂O₃ showed also a high stability of the meso- and micro-scale structural features due to a significant reduction of sintering. Cyclic CO₂ uptake experiments revealed that after 10 carbonation-calcination cycles the best sorbent possessed a CO₂ uptake capacity of 0.41 g_{CO2} g_{sorbent}⁻¹, exceeding the capacity of the benchmark limestone by ca. 140 %.

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Supporting information

Supplementary SEM images, carbonation profiles and XRD data.

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