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Mechanistic Understanding of CaO-based Sorbents for High-Temperature CO₂ Capture: Recent Advances by Advanced Characterization and Prospects

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Abstract: Carbon dioxide capture and storage technologies are short to mid-term solutions to reduce anthropogenic CO₂ emissions. CaO-based sorbents have emerged as a viable class of cost-efficient CO₂ sorbents for high temperature applications. Yet, CaO-based sorbents are prone to deactivation over repeated CO₂ capture and regeneration cycles. Various strategies have been proposed to improve their cyclic stability and rate of CO₂ uptake including the addition of promoters and stabilizers (e.g. alkali metal salts and metal oxides), as well as nano-structuring approaches. However, our fundamental understanding of the underlying mechanisms through which promoters or stabilizers affect the performance of the sorbents is limited. With the recent application of advanced characterization techniques, new insight into the structural and morphological changes that occur during CO₂ uptake and regeneration has been obtained. This review summarizes recent advances that have improved our mechanistic understanding of CaO-based CO₂ sorbents with and without the addition of stabilizers and/or promoters, with a specific emphasis on the application of advanced characterization techniques.

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Christoph Müller obtained a diploma in mechanical/process engineering from TU Munich in 2004 and a PhD in chemical engineering from the University of Cambridge in 2008, under the supervision of Prof. John Dennis. In 2010, he became assistant professor at the department of mechanical and process engineering at ETH Zürich. Since 2018, he is full professor at the same institution. His research group is active in the development of CO₂ sorbents and catalysts as well as studying single- and multiphase granular flows.
1. Introduction

Anthropogenic emissions of CO$_2$ have increased substantially since the industrial revolution.$^{[1]}$ As a result, the atmospheric CO$_2$ concentration has reached 410 ppm in 2019.$^{[1-3]}$ Reaching the goal of the Intergovernmental Panel on Climate Change of limiting global warming to 1.5°C until 2050 requires a significantly less CO$_2$ intensive society and industry than the ones we have now.$^{[1,4]}$ Besides the transition to renewable energy sources, the application of carbon dioxide capture and storage (CCS) is key to mitigate CO$_2$ emissions. The IPCC estimates that CCS can contribute up to 20% to the 2050 CO$_2$ reduction goals.$^{[1]}$

Combined with CO$_2$ utilization technologies, CCS provides also the means for a circular carbon-based economy, e.g. through the production of (close-to) carbon-neutral methanol.$^{[5-8]}$

Calcium oxide-based solid sorbents that undergo cyclic carbonation and calcination reactions during CO$_2$ capture and regeneration, viz.

$$\text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3$$

have emerged as a cost-efficient class of CO$_2$ sorbents.$^{[9-12]}$ On the process level, the use of CaO-based CO$_2$ sorbents is referred to as calcium looping (CL). Techno-economic analyses have provided evidence that the CL process for CO$_2$ capture is competitive to the established amine-scrubbing process. Mackenzie et al.$^{[13]}$ estimated the capture costs to be as low as 20 USD per tonne of CO$_2$ and identified the cyclic CO$_2$ uptake capacity of the sorbents as a key metric determining the capture costs. However, under realistic process and testing conditions, CaO-based sorbents (mostly limestone-derived) show rapid deactivation over repeated carbonation and calcination cycles, with a residual uptake of 0.05 g$_{\text{CO}_2}$/g$_{\text{CaO}}$ after 500 calcination-carbonation cycles.$^{[14]}$ The asymptotic value of the CO$_2$ uptake was found to be independent of the process conditions, although the rate of the decay in the CO$_2$ uptake does depend strongly on the calcination and carbonation conditions.$^{[14]}$

Initial research efforts on CL focused on natural limestone as the sorbent material. More recently, the development of synthetic CaO-based CO$_2$ sorbents has gained momentum.$^{[15-20]}$ A number of approaches have been proposed to improve the cyclic stability and residual CO$_2$ uptake capacity of CaO-based sorbents, including the addition of promoters or stabilizers as well as the micro- and nanostructuring of the sorbents.$^{[16-18,21-26]}$ Several reviews have summarized the engineering strategies to promote or stabilize the CO$_2$ uptake.$^{[9,12,27]}$ However, our fundamental knowledge of the underlying mechanisms that control the CO$_2$ uptake characteristics of CaO is limited. Indeed, even the different kinetic regimes in the carbonation reaction and the morphological changes occurring during the carbonation and calcination of bare CaO and CaCO$_3$ are not fully understood. Recently, the

![Figure 1: Key characterization techniques to determine the structure of CaO-based sorbents at different length scales providing insight required for the rational design of next generation CaO-based sorbents.](image-url)
introduction of advanced characterization techniques such as high-resolution transmission electron microscopy (HR-TEM) and HR scanning electron microscopy (SEM), electron-dispersive X-ray spectroscopy (EDX), in-situ X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance (NMR) spectroscopy has shed light on the functioning of CaO-based CO$_2$ sorbents during CO$_2$ uptake and regeneration. This review aims at summarizing recent advances in obtaining a fundamental understanding of structural and morphological changes that occur in CaO-based CO$_2$ sorbents over cyclic operation and in addressing the question to what extent specific structural and morphological features control their CO$_2$ uptake characteristics. In this respect, an in-depth understanding of the evolution of the sorbents at the Ångstrom to micrometer scale, depicted in Figure 1, is critical to advance the design of next generation CaO-based CO$_2$ sorbents.

2. Morphological and structural evolution of the CaO-CaCO$_3$ sorbents during operation

The carbonation reaction of CaO occurs in two stages (Figure 2a): I) A fast, kinetically-controlled regime, that is followed by II) a significantly slower, diffusion-limited regime.$^{28,29}$ The transition between the two regimes has been linked to a critical product layer thickness.$^{29}$ Most works report a calculated critical product layer thickness in the range of 20 – 50 nm, although these values are obtained through estimations using simple (bulk) morphological models, in which a product layer is assumed to be a homogenous, continuous and flat layer.$^{29-31}$ Furthermore, the total pore volume and surface area of the sorbent rapidly decrease in the kinetically-controlled regime due to the large difference in molar volume between CaO (16.7 cm$^3$/g) and the product CaCO$_3$ (36.9 cm$^3$/g). Hence, it has been argued that the initial pore volume critically influences the CO$_2$ capacity of the sorbent.$^{26,32,33}$ For a given "family" of a CaO-based sorbent, a larger initial pore volume (in pores with $d_{pore} < 100$ nm) often results in higher CO$_2$ uptakes (e.g. for CaO-based sorbents with an inverse opal type morphology.$^{26}$ see Figure 2b). Nevertheless, when plotting the initial pore volume ($d_{pore} < 100$ nm) versus the CO$_2$ uptake in the first cycle for a range of different CaO-based sorbents no obvious correlation between the CO$_2$ uptake and the initial pore volume of the sorbent can be found (Figure 2b). The same finding can be made when plotting the same data over the BET surface area, determined before the first carbonation step, see Figure 2c. Therefore, recent studies have introduced advanced characterization techniques, including in-situ X-ray techniques and atomic force microscopy (AFM), in an attempt to identify the structural and morphological features that exhibit a direct relationship to the CO$_2$ uptake and, in general, to obtain a more fundamental understanding of the processes occurring on the atomic scale during the carbonation and calcination reaction.$^{34-37}$

2.1. The relationship between the CO$_2$ uptake of CaO and its microstructure

Advanced characterization tools have proven to be instrumental to understand the relationship between the microstructure and the CO$_2$ uptake performance of CaO-based sorbents. For instance, synchrotron-based studies under reaction conditions (in-situ) or after having exposed the materials to reaction conditions (ex-situ)
have been carried out with the aim to identify relationships between the porosity, crystallite size and the CO₂ uptake performance of CaO-based sorbents. For example, Benedetti et al. applied ex-situ synchrotron small angle X-ray scattering (SAXS), ultra small angle X-ray scattering (USAXS) and wide angle X-ray scattering (WAXS) on CaO-based sorbents to study their microstructural features (Figure 3a). Specifically, SAXS and USAXS probed the sorbents’ microstructural properties such as pore size distribution, specific surface area and pore radius of gyration. (U)SAXS can be performed simultaneously with WAXS, from which the crystalline phases of a given material can be identified. The ex-situ investigation of the micro-textural properties in a series of CaO samples with different degrees of carbonation showed that the surface area decreases linearly with increasing CaO conversion, confirming the important role of the CaO surface area on the overall CO₂ capacity of a sorbent. However, the relevance of larger (> 100 nm) pores for the CO₂ uptake performance was not elucidated. Furthermore, studying the morphological and structural changes using in-situ methods, i.e. during the reaction of CaO with CO₂ and during the release of CO₂ from CaCO₃, can provide time-resolved insight into the structural evolution of the sorbents.

Dunstan et al. investigated the morphological changes in the macro-porous range during CaO carbonation by in-situ synchrotron X-ray tomography. Owing to the different densities of CaO and CaCO₃ a phase contrast is visible. The macro-porous network in CaO particles before and after carbonation is visualized in Figure 3b. This experiment clearly evidenced that also the volume in macro-pores reduces after 50 min of carbonation at 650°C in 100% CO₂. It has also been argued that apart from the porosity and the surface area, the CaO/CaCO₃ crystallite size can influence the carbonation kinetics. The effect of the crystallite size of CaO/CaCO₃ on their reactivity was investigated by Biasin et al. utilizing in-situ time resolved (0.2 s acquisition time) synchrotron XRD allowing to determine the rates of CaCO₃ formation. Here, the carbonation kinetics of CaO-based sorbents of varying initial crystallite sizes were investigated and the degree of CaO conversion was determined by Rietveld refinement. The authors reported an inverse proportionality between the conversion of CaO in the first cycle and the initial crystallite size of CaO. It was hypothesized that smaller CaO crystallites increase the total length of crystallite boundaries when normalized by the surface area; and that the number of “reactive” sites for the CaO–CO₂ reaction depend not only on the surface area, but also on the length of crystallite boundaries. An interpretation of this observation is that grain boundary diffusion of CO₂ controls to some extent the rate of CaO conversion.

Figure 3: (a) Illustration of the methodology used to quantify changes in pore size distribution during carbonation of CaO by USAXS-SAXS. Reprinted with permission from [35]; copyright Elsevier, 2019. (b) Visualization of the macro-pores in a CaO particle prior to and after carbonation. Adapted with permission from [36]; copyright Royal Society of Chemistry, 2016.

However, this hypothesis needs further investigation.

Sintering induced deactivation is a major drawback in CaO-based sorbents; and the underlying sintering process and identification...
of the key parameters controlling its rate remain under investigation. Sintering can be assessed by following the CaO crystallite size, e.g., under realistic calcination conditions under high partial pressures of CO₂.[14,24,39] For example, Valverde et al.[40,41] studied the calcination of limestone in CO₂ partial pressures (0.05–0.9 bar) and temperature conditions near equilibrium (P/P₀ ≲ 1) by in-situ XRD. They found that at low conversions, an intermediate metastable CaO* phase is present, which forms during the desorption of CO₂ and is characterized by a preferred orientation of CaO in the [110] direction.[42] The proposed exothermicity of the CaO* to CaO transformation and the high CO₂ partial pressure were suggested to delay the nucleation of CaO. As the calcination temperature is well below the Tamman-temperature (Tₐ; an indication for the onset of sintering) of CaO (Tₐ = 1310 °C),[12] the authors concluded that the observed CaO crystallite growth during calcination in CO₂ is mainly a consequence of the sintering of the metastable CaO* phase rather than that of the final CaO.

2.2. CaCO₃ product layer formation

A crucial aspect of the kinetics of the carbonation reaction is the growth mechanism of the CaCO₃ product on the CaO surface. Hypothetically, CaCO₃ can grow on CaO as a uniform layer, in the form of islands or in a combination of both modes.[34,43] A study by Li et al.[34], in which CaO single crystals were carbonated at different temperatures and subsequently analyzed by AFM, tentatively indicates that CaCO₃ starts to grow in the form of islands, which eventually merge. As displayed in Figure 4a, the size and distribution of the CaCO₃ islands depend on the carbonation temperature. Higher carbonation temperatures result in larger islands and lower island densities. At high conversions, the islands have merged into a CaCO₃ layer with a thickness of about 90 nm. A visualization of the morphology of the product layer at the end of the kinetically-controlled reaction regime has not been reported yet, due to the difficulty to ‘freeze’ the reaction exactly at the transition from the kinetically-controlled to the diffusion-limited reaction regime.

In the diffusion-limited regime, a number of diffusion processes, including grain boundary and bulk diffusion govern the rate of the carbonation reaction.[28,45–47] Concerning bulk diffusion, which includes vacancy and interstitial diffusion,[43,48] and becomes dominating for longer reaction times, the most likely diffusing species are CO₂, Ca²⁺, CO₃²⁻ and O²⁻. Considering that charge balance must be maintained, three diffusion mechanisms can be envisioned, i.e. an inward diffusion of CO₂, a counter diffusion of O²⁻ and CO₃²⁻ or an outward diffusion of both Ca²⁺ and O²⁻ (Figure 5a).[46,48,49] To elucidate the prevailing diffusion mechanism, Sun et al.[49] performed an inert platinum marker experiment by placing a platinum marker on top of a sintered CaO pellet. The pellet was carbonated for 4 months at 650°C in pure CO₂. SEM-EDX analysis of the reacted pellet shows that the platinum marker is on top of the partially carbonated CaO layer (Figure 5b). From this observation the authors concluded that there is an inward diffusion of CO₃²⁻ and an outward diffusion of O²⁻. However, the carbonation time of 4 months is unrealistic (a typical carbonation time in a TGA is 20 minutes, and even shorter in a fluidized bed).

![Figure 4: AFM graphs of CaO single crystals after treatment in CO₂ at (a) 500°C and (b) 600°C. Adapted with permission from [34]; copyright American Chemical Society, 2012 (c) FIB-TEM image showing the CaCO₃ product layer. Adapted with permission from [44]; copyright Royal Society of Chemistry, 2019](image_url)
for the CaO/CaCO$_3$-system and the implications of this experiment for practical CL applications are unclear. In addition, the diffusion of CO$_2$ by a sequential decomposition of neighboring carbonate ions in the product layer was not considered, which could be very effective as the carbonation is performed at temperatures above the T$_T$ of CaCO$_3$ (T$_T$ = 553 °C).

Generally, it is very challenging to distinguish experimentally between the three diffusion mechanisms outlined in Figure 5a. However, ab initio, atomic-scale simulations of diffusion processes in calcite can provide valuable insights. Besson et al.$^{[48]}$ simulated the diffusion of oxygen and the relevant carbon containing species (including CO, CO$_2$ and CO$_3^{2-}$) in calcite at 527 °C by means of ab-initio calculations. Based on the calculated migration energies for different diffusion pathways of oxygen they found that the transport of oxygen ions in calcite occurs easily (migration energy ~ 0.5 eV) and is mediated by either an interstitial or an oxygen vacancy mechanism, depending on the thermodynamic conditions. In contrast, the diffusion of carbon containing species requires complex point defects (CPDs; defects in the crystal structure that involve 2 or more sites). At the investigated temperature (527 °C), the diffusion of CO$_2$ can be ruled out due to the very high formation energy of the CO$_2$ CPD (> 2.2 eV). Similarly, the diffusion of CO$_3^{2-}$ via a CPD is associated with a migration energy barrier of 5 eV, which is too high to occur at the given temperature. The authors could not identify an energetically favorable diffusion pathway for carbon containing species in calcite. Note that the outcome of the calculations at the actual carbonation temperature in the CL process (> 600°C) could be profoundly different. Thus far, no evidence for any of the three diffusion mechanisms sketched in Figure 5a has been reported. Therefore, further theoretical calculations in combination with diffusion experiments on (partially) carbonated CaO model systems under realistic conditions are needed.

3. Recent advances in the characterization and engineering of CaO-based sorbents

The engineering of CaO-based sorbents by nanostructuring and the addition of stabilizers or promoters has led to substantial improvements in their CO$_2$ uptake performance.$^{[9,12]}$ These strategies and our current mechanistic understanding thereof will be discussed in the following sections.

3.1. Nanostructured CaO: towards fast and full conversion

Since CaO-based sorbents derived from naturally occurring precursors such as limestone do not reach full CaO conversion within reasonable timescales and experience rapid deactivation with increasing cycle numbers, intensive efforts are undertaken to design more effective sorbent materials. An ideal CaO-based CO$_2$ sorbent displays a rapid and (close to) full conversion over many carbonation-calcination cycles.$^{[12,14,50,51]}$ Since a drop in the CO$_2$ uptake is observed, an improved design of the sorbent is required to ensure long-term sorption capacities.
uptake capacity is associated largely with pore blockage due to the large difference in the molar volume between CaO and CaCO$_3$ and diffusion limitations with increasing thicknesses of the carbonate layer, an ideal sorbent should contain a largely mesoporous (≤ 100 nm particle sizes) morphology.[14,18,21,39,52,53] To this end, template-assisted synthesis approaches have proven to be very useful.[18,24,39,53] For example, Wang et al.[54] used a sacrificial N-doped carbon nanosheet template to synthesize highly macroporous CaO nanosheets (CaN), see Figure 6a. Furthermore, Naeem et al.[24] developed hollow CaO microspheres utilizing spherical, carbonaceous templates (Figure 6b) and Kim et al.[26] obtained inverse opal-type CaO (Figure 6c) relying on carbon nanospheres as templates. These CaO-based materials show an enhanced CO$_2$ sorption capacity as compared to limestone, with CO$_2$ uptakes of up to 0.7 g$_{CO_2}$/g$_{sorbent}$ (Figure 6 d - e). Nevertheless, all three nanostructured materials suffered from sintering-induced deactivation (owing to the lack of a structural stabilizer), which led to a gradual destruction of the structured morphology (and it turn the CO$_2$ uptake) with cycling.

3.2. Stabilization and deactivation mechanisms of metal oxide-stabilized CaO-based sorbents

The currently dominating approach to mitigate sintering induced deactivation of CaO is the introduction of high Tamman-temperature metal oxide stabilizers.[9,12,55] It is believed that stabilizers act as physical barriers between otherwise adjacent CaO grains, hence reducing the rate of sintering and stabilizing the pore network and surface area of the sorbent.[23,56,57] Various metal oxides have been explored as stabilizers including Al$_2$O$_3$[20,23,26,58-60] (and the respective mixed calcium aluminate Ca$_x$Al$_y$O$_z$ that form during calcination[23,25,61]), MgO[17,18,24,54,62,63], SiO$_2$[64-67], TiO$_2$[68] or ZrO$_2$[57,69-72] Stabilizers are commonly added in quantities ranging between 5 - 20 wt.%, with the optimal quantity being a trade-off between the degree of morphological stabilization and the quantity of CO$_2$ capture-inert material added.
The addition of stabilizers has often resulted in significant improvements, in particular during the first few cycles (see Figure 6 e), achieving CO₂ uptakes that exceeded the values of the limestone-benchmark by 300 - 500% after 30 carbonation-calcination cycles (calcination performed in CO₂ at 900°C).[23,24]

According to sintering theory, a delay (or even prevention) of the coalescence of adjacent grains requires a deceleration of thermally induced diffusion processes (i.e., surface, grain boundary and volume diffusion).[73,74] Therefore, there are at least three factors that influence the ability of a stabilizer to prevent sintering: (i) the morphology of the stabilizer phase, e.g. as a coating on top of grains or as (nano)particles between grains, (ii) the thickness of the coating/the size of the particles of the stabilizer phase and (iii) the diffusivity of Ca in the stabilizer phase and on its surface and grain boundaries.

The physical separation of two adjacent CaO (or CaCO₃) grains increases the length of the diffusional paths, hence increasing the timescale of sintering. Zhang et al.[80] investigated the sintering of two separated spherical sorbent nanoparticles (CaO-CaO or CaO-MgO) during CO₂ sorption conditions and in an inert atmosphere via molecular dynamics simulations. The authors show that the carbonation of previously separated CaO nanoparticles leads to the formation of a handle-like, strongly sintered particle as shown in Figure 7 a - b, indicating that the volume expansion during carbonation is the main contributor to sintering of CaO-based sorbents. Simulations with varying radial distances between the CaO nanoparticles revealed that an increase in the radial distance significantly reduced sintering and in turn increased the CO₂ uptake during carbonation. Indeed, simulations of a stabilized nanoparticle system (CaO-MgO) showed that the presence of a metal oxide stabilizer significantly reduced the degree of inter-particle sintering, resulting in a substantially higher CO₂ uptake of the individual CaO nanoparticles, see Figure 7c.

The critical volume fraction of a stabilizer required to achieve a stabilization effect in a large system with many particles has been estimated by percolation theory, which is a mathematical approach to investigate random packings of materials and their connectivity.[81] For example, Jagota et al.[82] investigated a general system of three-dimensional packings of soft and hard spheres via percolation theory to study the influence of the latter on the sintering process. It was shown that the volume fraction of the second, i.e. the stabilizing, phase is a key parameter to control the effective sintering rate. Yet, it is unclear what the most effective distribution of a stabilizer would be, owing to a lack of in-situ observations of both the morphology and stability of the stabilizer and CaO/CaCO₃ phases during cyclic operation.

### Table 1: Typical metal oxide stabilizers

| Metal oxide | Structural characterization techniques | Mixed phases reported | Thermodynamically favorable mixed phase at CL conditions (600 – 900°C, 10wt.% stabilizer) | References |
|-------------|----------------------------------------|-----------------------|----------------------------------------------------------------------------------|-----------|
| ZrO₂        | (in-situ) XRD, DNP, SENS, XPS, XRD,    | Ca₂ZrO₄, Ca₃ZrO₆     | Ca₂ZrO₄                                                                          | [23,58,76]|
| MgO         | XRD                                   | -                     | -                                                                                | [83,76,77]|
| MnO₂        | XRD                                   | Ca₃MnO₄               | -                                                                                | [78]      |
| NdO₂        | -                                     | -                     | -                                                                                | [78]      |
| SiO₂        | XRD                                   | Ca₂SiO₃, α-Ca₂SiO₃, γ-Ca₂SiO₃ | α-Ca₂SiO₃ (carb.), γ-Ca₂SiO₃ (calc.)                                                                                   | [85,78]   |
| TiO₂        | XRD                                   | Ca₂TiO₃               | -                                                                                | [78]      |
| Y₂O₃        | -                                     | -                     | -                                                                                | [78]      |
| ZrO₂        | XRD, XPS                              | Ca₂ZrO₃               | Ca₂ZrO₃                                                                         | [70–73]   |

In solids, the speed of volume diffusion becomes significant at elevated temperatures.[83] Most studies argue that the Tammann
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The temperature of the stabilizing phase, which is an indicator for the temperature at which volume diffusion becomes relevant, is a good measure for the stabilizer’s ability to prevent CaO and CaCO$_3$ grains from sintering. At least two cases must be distinguished here: (i) a stabilizing phase that contains Ca ions and (ii) a stabilizing phase that does not contain Ca ions. For case (i), the diffusion of Ca in the stabilizing phase and on its surface may be directly related to the Tammann temperature of the phase. The Tammann temperature is an indicator for the diffusion of stabilizer ions within the stabilizing phase, and hence can only be an indirect and qualitative measure to evaluate the diffusion of Ca ions. However, the performance of a stabilized CaO-based sorbent is also affected by the sorbent morphology, phase distribution and other factors, as discussed above. Therefore, the Tammann temperature can at best be one, but not necessarily the most important, indicator for the performance of the complex stabilizer-CaO system.

Generally, metal oxide stabilizers can be classified into reactive metal oxides and inert metal oxides, whereby the latter do not form mixed oxides with CaO (such as MgO) under CL conditions. The formation of mixed oxides has been reported for a variety of stabilizers including Al$_2$O$_3$, ZrO$_2$ and SiO$_2$, see Table 1, and has in some cases been linked to the deactivation of the sorbent. In many cases metal oxide stabilizers have been added in comparatively high quantities (5-20 wt.%), the formation of CO$_2$-capture-inactive mixed oxides can reduce significantly the maximal theoretical CO$_2$ uptake of the material. For example, Al$_2$O$_3$-stabilized CaO can form at least two Ca-Al mixed oxides under reactive conditions, viz. tricalcium aluminate (Ca$_3$Al$_2$O$_6$) and mayenite (Ca$_{12}$Al$_{14}$O$_{33}$). These high-Tammann temperature (T$_T$(Ca$_3$Al$_2$O$_6$) = 1280°C; T$_T$(Ca$_{12}$Al$_{14}$O$_{33}$) = 770°C);
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The phase composition of sorbents stabilized by reactive metal oxides can change with cycle number if (i) several mixed Ca-stabilizer phases exist, (ii) the transformation to the thermodynamically most favorable phase is slow compared to the process timescale (minutes) and (iii) the phase stability is affected by the temperature and atmosphere changes during calcination and carbonation.\(^{[8,52]}\) The formation of mixed phases between CaO and a reactive stabilizer has been studied extensively using ex-situ XRD by taking samples after the respective heat and gas treatment steps.\(^{[9,12,52]}\) Yet, the dynamics (and intermediate phases) of the respective transformations can only be understood in full detail when utilizing in-situ XRD combined with further structure sensitive techniques.\(^{[12,23]}\) For example, Kim et al.\(^{[23]}\) studied the phase transformations of Ca\(_2\)Al\(_2\)O\(_6\)-stabilized CaO during cyclic operation using a combination of in-situ XRD, \(^{27}\)Al-NMR and EDX-TEM, see Figure 8 and 9. While the as-prepared (calcined) sorbent was composed of CaO, Ca\(_2\)Al\(_2\)O\(_6\) and Ca\(_{12}\)Al\(_{14}\)O\(_{33}\) phases (Figure 8 c - e), in-situ XRD during cyclic operation revealed a complex phase evolution. In the first 10 cycles the fraction of Ca\(_2\)Al\(_2\)O\(_6\) continuously decreased, ultimately disappearing, while the content of the Ca\(_{12}\)Al\(_{14}\)O\(_{33}\) phase increased together with a slight increase in CaO. Between cycles 20 and 30, the phases evolved further, showing a decrease in the fraction of Ca\(_{12}\)Al\(_{14}\)O\(_{33}\) and an increase in CaO, suggesting a segregation of an Al\(_2\)O\(_3\) phase. However, since no Al\(_2\)O\(_3\) phases could be detected by XRD, an element specific technique, i.e. \(^{27}\)Al-NMR, was applied. Between cycle number 10 and 30, conventional \(^{27}\)Al-NMR shows Al\(^{IV}\) coordination, in agreement with the expected Al coordination in Ca\(_2\)Al\(_2\)O\(_6\) and Ca\(_{12}\)Al\(_{14}\)O\(_{33}\). On the other hand, after 30 cycles dynamic nuclear polarization surface-enhanced (DNP-SENS) \(^{27}\)Al-NMR revealed signatures due to an Al\(^{III}\) coordination owing to α-Al\(_2\)O\(_3\) (Figure 8c). However, according to the CaO-Al\(_2\)O\(_3\) equilibrium phase diagram,\(^{[85]}\) between 650 - 900°C and with a Al : Ca ratio of 1 : 9, CaO and Ca\(_2\)Al\(_2\)O\(_6\) are the thermodynamically stable phases while Al\(_2\)O\(_3\) is not expected to be present under these conditions.

At the surface of the CaO particles, the nanoparticles of the stabilizing phase tend to agglomerate, reducing their effectiveness to act as a physical barrier against sintering, leading in turn to a reduced CO\(_2\) uptake of the material. For example in the study of Kim et al., alumina-rich phases are well distributed after the initial calcination step but segregate towards the particle surface to form large agglomerates over cycling, which is confirmed via EDX-TEM, see Figure 9a. TEM analysis clearly shows the segregation of an Al-rich phase in the form of nanoparticles of 200 nm in size and their migration to the surface. Interestingly, this surface-enrichment of Al\(_2\)O\(_3\) through phase-segregation from the Ca-Al mixed oxides was identified to trigger the deactivation of the sorbents (and material sintering). Yet, the nature of this phase transformation remains unclear.

Indeed, for a variety of stabilizers the segregation of (nano)particles of the stabilizing phase from bulk CaO to the
surface (with or without phase change) has been observed during heat treatment and over cycling.\textsuperscript{[23,57,65]} Yoon et al. investigated CaZrO$_3$- and ZrO$_2$-stabilized CaO, synthesized via a sol-gel method and observed the segregation of Ca-Zr mixed phases to the particle surface after cyclic operation. After cycling, segregated Zr-rich particles with a diameter of several hundred nm were observed via back-scattered electron microscopy. However, the authors did not identify the surface segregated phases via surface-sensitive techniques. Koirala et al.\textsuperscript{[69]} investigated CaZrO$_3$-stabilized CaO, see Figure 10 a–b, with XPS to identify changes in the phase composition near the particle surface. Based on the Ca2p XPS spectrum shown in Figure 10 c–f, the authors concluded that the quantity of CaZrO$_3$ nanoparticles on the surface of CaO particles increased after heat treatment with the amount of zirconia added until a saturated value was achieved. The best performing sorbent had a bulk ratio of Ca : Zr = 5.$^6$\textsuperscript{[69]} High-resolution TEM studies revealed that sorbents containing Zr : Ca ratios of 4 : 10 and 5 : 10 show an increase in sorbent particle size from 4 – 6 nm and 4 – 5 nm, respectively, to 24 – 58 nm and 12 – 32 nm after 250 isothermal cycles (i.e., calcination in N$_2$ and carbonation in 15 vol.% CO$_2$ at 700°C$^6$). Hence, the growth of particle size was correlated with the amount of stabilizer added, with increasing amounts of stabilizer leading to smaller sorbent particle sizes after cycling.

Turning to SiO$_2$-stabilized CaO-based sorbents, several mixed oxide phases and polymorphs exist in the Ca-Si-O system, depending on the Ca : Si ratio and the respective pre-treatment and operating temperatures. Wang et al.\textsuperscript{[79]} showed that the calcination temperature and time influence the formation of mixed Ca-Si oxides for a given sorbent composition, i.e. the solid-state reaction to the thermodynamically favorable mixed oxide is slow. For example, after calcination at 900°C for 1h four Si-containing phases were detected: Ca$_2$SiO$_4$, CaSiO$_3$ (calcium silicate and wollastonite polymorphs) and SiO$_2$. However, based on the CaO-SiO$_2$ phase diagram, only Ca$_2$SiO$_4$ should be observed (8 wt.% SiO$_2$, i.e. Ca : Si = 12, 900°C), indicating that the transformation to the thermodynamically favorable phase was not completed. In addition, both α- and γ-phases of Ca$_2$SiO$_4$ exist, and the transition between these two polymorphs is observed at around 700°C. Therefore, the stabilizing phase in SiO$_2$-CaO sorbents may transform between different phases owing to the temperature swing between calcination (typically around 900°C) and carbonation (typically around 650°C) as well as the incomplete transformation to the thermodynamically most favorable phase during the first heat treatment. Yet, the influence of these phase transformations during cycling has not been investigated in detail. Inert metal oxide stabilizers such as MgO do not form mixed phases with CaO and do not form carbonates at typical CL
conditions (i.e., T > 600 °C). However, a similar tendency for agglomeration of the stabilizer phases as observed in reactive stabilizers (e.g., A12O3 or ZrO2), is observed for inert stabilizers. In an early study, Liu et al. used a wet-mixing method to synthesize MgO-stabilized CaO with an almost constant CO2 uptake of 0.59 gCO2/gSorbent over the course of 24 cycles (25 wt.% MgO, carbonation at 650°C and calcination at 900°C in N2). The authors showed via EDX-TEM that MgO forms agglomerates on the surface of CaO particles. It was argued that these agglomerates act as barriers against sintering of CaO. In a more recent study, Kurlov et al. investigated the distribution of MgO and changes thereof over cycling in MgO-stabilized CaO-based sorbents using EDX-TEM see Figure 9b. Initially, nanoparticles of MgO of diameters up to 50 nm, were evenly distributed on the surface of CaO grains in the as-prepared sorbent. After 30 cycles, the MgO nanoparticles agglomerated leading to an increase in particle size (100 – 200 nm). It was argued that larger MgO nanoparticles were less effective in mitigating sintering and hence led to a decrease in the CO2 uptake. Naeem et al., who synthesized hollow microspheres of CaO stabilized by MgO24, also observed an increase in the size of the MgO nanoparticles over cycling. The shell of these microspheres consists of CaO and MgO nanoparticles. Over cycling, the size of the MgO nanoparticles increased from 15 - 35 nm in the as-prepared sorbents to about 80 - 100 nm after 10 cycles under realistic conditions (i.e., calcination under CO2 at 900°C). However, the authors observed a homogeneous distribution of the MgO nanoparticles in the sorbent even after cycling and no significant segregation of larger MgO aggregates from CaO.

3.3. Alkali metal salt modified CaO-based sorbents

An actively debated question is whether the addition of alkali metal salts such as Na2CO3, K2CO3, Li2CO3, NaCl or KCl can improve the cyclic CO2 uptake of CaO-based CO2 sorbents. Most alkali metal salts (here only considering chlorides and carbonates) melt at similar temperatures as CaCO3 (Tm(AcI, AC2CO3) = 600 - 900 °C with A = Li, Na, K, Rb, Cs; Tm(CaCO3) = 825 °C) and have significantly lower Tamman-temperatures than CaO (Tf(AcI, AC2CO3) = 300 - 450 °C; Tf(CaCO3) = 1313 °C). Hence, most studies argue that alkali metal salts may act as promoters of the CO2 uptake, e.g., via kinetic effects, in contrast to metal oxides, which act as stabilizers against sintering.

Figure 11: (a) In-situ XRD of Na2CO3-wet-impregnated CaO between 25°C and 800°C (b) Proposed formation mechanism of Na2Ca(CO3)2. Adapted with permission from [22]; copyright Elsevier, 2018.

The cyclic CO2 uptake performance of alkali-metal promoted CaO varies strongly depending on the nature of the alkali metal (i.e., Li, Na, K, Rb and Cs), the precursors used for synthesis (e.g., Na2CO3 vs. NaCl) and the content of alkali metal salt added. However, a general trend of a decreased CO2 uptake with increasing alkali metal content seems to hold for most studies. For high contents of Na and K (i.e., several mol. %), independent of the precursor used, various authors have shown that the CO2 uptake performance is decreased, possibly due to enhanced sintering effects. In such cases, the addition of alkali metals leads to an inferior performance over cycling showing CO2 uptakes as low as 0.05 gCO2/gSorbent (e.g., 20 wt.% NaOH, wet-impregnated) already during the first carbonation step (40% CO2, 600°C, 5 hours).
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For low alkali metal contents, some studies have observed a strong promotional effect of alkali metal salts such as NaCl\[^{[86]}\] (2 wt.% wet impregnation, uptake 10\(^{th}\) cycle 0.48 g\(_{CO_2}/g_{\text{sorbent}}\)), KCl (2 wt.% wet impregnation, uptake 10\(^{th}\) cycle 0.50 g\(_{CO_2}/g_{\text{sorbent}}\)) and Na from sea salt (~ 0.13 wt.% NaCl, wet impregnation, uptake 10\(^{th}\) cycle 0.33 g\(_{CO_2}/g_{\text{sorbent}}\)). It has been proposed that there is an appreciable effect of alkali metals on the kinetics of the carbonation and calcination reactions which may enhance the CO\(_2\) uptake performance\[^{[89]}\]. For example, Wieczorek-Ciurowa et al.\[^{[89]}\] have shown that the decomposition temperature of calcite is reduced by about 10°C by the addition of NaCl, i.e. alkali metals can shift the CaO/CaCO\(_3\) equilibrium. A similar shift of the decomposition temperature by about 10°C has been reported by Xu et al. for the addition of KCl and KOH.\[^{[86]}\] Other authors have reported that alkali metals may also positively affect the diffusion process of CO\(_2\) in the product layer of CaCO\(_3\). For example, Gonzalez et al.\[^{[90]}\] reported that for wet-impregnated limestone (0.05 – 0.5M KCl/K\(_2\)CO\(_3\) aqueous solution) the conversion rate of CaO in the diffusion-limited carbonation regime was enhanced by the addition of either KCl or K\(_2\)CO\(_3\) compared to the pristine limestone benchmark. The authors concluded that the incorporation of potassium impurities in the sorbent promotes the diffusional processes during carbonation, the diffusion of CO\(_2\) through the CaCO\(_3\) product layer. However, there is limited fundamental understanding of how low alkali metals may affect diffusional processes or promote the performance of CaO-based sorbents. Therefore, this area deserves further research using advanced characterization techniques to understand the underlying mechanisms of promotion.

Alkali metals can react with CO\(_2\) to form carbonates of the form A\(_2\)CO\(_3\) (A = Na, K, Li, Cs). If present in a CaO environment, some alkali metals may form mixed bicarbonates of the structural formula A\(_2\)Ca(CO\(_3\))\(_2\) during carbonation. Similar to other alkali metal salts, these mixed bicarbonates have a low melting point (e.g. T\(_m\)(Na\(_2\)Ca(CO\(_3\))\(_2\)) = 810°C). Recently, using in-situ XRD, Lee et al.\[^{[82]}\] have shown that the mixed bicarbonate Na\(_2\)Ca(CO\(_3\))\(_2\) forms in Na\(_2\)CO\(_3\)-impregnated CaO (i.e., Figure 11a) during carbonation (i.e., 600-700°C in 15 vol.% CO\(_2\)). The authors provide a formation mechanism for the mixed bicarbonate and propose that it forms during the initial carbonation step, see Figure 11b. Hence, the study concludes that the mixed bicarbonate may form at the surface of the CaO particles and proposes the formation mechanism shown in Figure 11b. Currently, we have no in-depth understanding of how these mixed phases may affect the performance of alkali-metal promoted CaO.

Figure 12: TGA measurements of CO\(_2\) sorption on alkali-metal doped CaO at (a) 50°C and (b) at 500°C; (c) XPS spectra of sorbents before and after reaction with CO\(_2\); and (d) atomic ratios of Cs to Ca at the surface over the course of one carbonation-calcination cycle for Cs\(_2\)CO\(_3\)-promoted CaO. Adapted with permission from [87]; Copyright American Chemical Society, 2004.

In a study aiming to obtain a comprehensive description of the effect of different alkali metal salts on the CO\(_2\) uptake of CaO, Reddy et al. probed the influence of different alkali metals and precursors (ACl, AOH, and A\(_2\)CO\(_3\) with A = Li, Na, K, Rb, Cs) via the wet impregnation of CaO using loadings of 10 wt.% and 20 wt.% \[^{[87]}\]. The authors studied the CO\(_2\) uptake in the first carbonation cycle at temperatures between 50°C and 750°C, showing that the CO\(_2\) uptake in the first carbonation cycle increases with the electropositivity and ionic radii of the alkali metal (Cs > Rb > K > Na > Li), as shown in Figure 12. The authors hypothesize that alkali metals influence the affinity of CaO towards acidic CO\(_2\), resulting in a reduced CO\(_2\) uptake compared to CaO, even at low temperatures (i.e., 50°C). XPS analysis of Cs\(_2\)CO\(_3\)-promoted CaO indicates that CO\(_2\) preferentially reacts with CsO\(_2\), which forms during calcination. Yet, we currently lack a mechanistic explanation of how the electropositivity of the ion or the ionic radii may affect the affinity of the sorbent towards CO\(_2\). Indeed, morphological parameters such as the pore size distribution, pore volume and BET surface area have not been investigated in this study except for Cs/CaO and the CaO benchmark. Therefore, the results might as well be related to varying effects of the different alkali metals and precursors on the morphological characteristics of the sorbents rather than a change in their affinity towards CO\(_2\), as has been reported before.\[^{[70,91]}\] To conclude, a better understanding of the effect of alkali metals on the textural properties of CaO during
cycling will be pivotal to elucidate the effect of alkali metals on the CO$_2$ uptake of CaO.

4. Summary and Outlook

In the last decade, advanced characterization techniques have been applied increasingly to the field of CaO-based CO$_2$ sorbents and have provided novel insights into the structural and textural changes that occur during the carbonation and calcination reaction on the nanoscale. For example, AFM revealed an island-type growth mode of CaCO$_3$ on CaO in the early stage of carbonation. Furthermore, a better understanding of the morphological changes that occur at different stages during the carbonation step has been obtained by in-situ XRD, (U)SAXS and X-ray tomography. In the future, a combination of atomic scale simulations and in-situ visualization of the product layer formation should improve our understanding of the kinetics of the carbonation reaction in both the reaction- and the diffusion-limited regimes. In the case of stabilized and/or promoted CaO, some insights into the sintering mechanism have been obtained, with molecular dynamics simulations indicating that the volume expansion during carbonation is the main cause for sintering and that the effect of a stabilizer is to increase the length of the (diffusional) pathways between the individual CaO (CaCO$_3$) grains. In addition, the application of in-situ XRD, NMR and EDX-TEM characterization has provided insight into the stabilization and deactivation mechanisms of stabilized CaO during repeated cycling. However, studies on alkali metal-promoted CaO-based sorbents have largely lacked results from advanced characterization techniques, such that our current fundamental understanding of the promotion and deactivation mechanisms is very limited. In the future, studying the nanoscale interaction of stabilizers and promoters with CaO/CaCO$_3$ will be critical to guide the rational design of the next generation of CaO-based CO$_2$ sorbents.

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CaO-based sorbents for CO₂ capture are cost-efficient and readily available. Yet, these materials suffer from rapid deactivation due to sintering. Stabilizers and promoters are used to enhance the performance of such sorbents, but we lack a fundamental understanding of the underlying processes. Recently, advanced characterization techniques helped to advance our understanding of CaO-based sorbents. We review these recent advances and paint a vision for the design of next-generation CaO-based CO₂ sorbents.

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