Deciphering atomic and nanoscale dynamics of CaO under CO_2 capture by combining in situ SAXS/WAXS and environmental STEM

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Solid CaO-based CO_2 sorbents are promising for decarbonising the cement industry because they reversibly absorb CO_2 at high temperatures and are abundant, non-toxic, and cost-effective. Although many trial-and-error and engineering approaches have introduced promoters and stabilisers to improve the CO_2 uptake and cyclic stability of CaO-based sorbents, the parameters governing the performance of bare CaO-based sorbents remain poorly understood. Hence, a detailed understanding of sorbent transformations during CO_2 capture and regeneration is essential for designing more efficient sorbents. These transformations are complex because CO_2 sorption-regeneration cycles involve a simultaneous chemical, crystallographic (CaO/$CaCO_3$ phase transition), and morphological evolution, including changes in pore structure and particle sintering. To probe the evolution and entangle the interplay between these processes during CO_2 capture, we performed time-resolved studies that simultaneously probe pore structure, phase composition, crystallite size, and CaO/$CaCO_3$ interfaces. This was achieved by combining sample-averaging techniques (Small-angle X-ray scattering, SAXS/Wide-angle X-ray scattering, WAXS) with spatially resolved microscopy (environmental scanning transmission electron microscopy, STEM) and ex situ 4D-STEM mapping of CaO and $CaCO_3$ (Figure 1). Our multimodal approach reveals correlations between the porous structure and $CaCO_3$ growth/decomposition, providing new insights into the processes responsible for the deactivation of CaO-based sorbents.

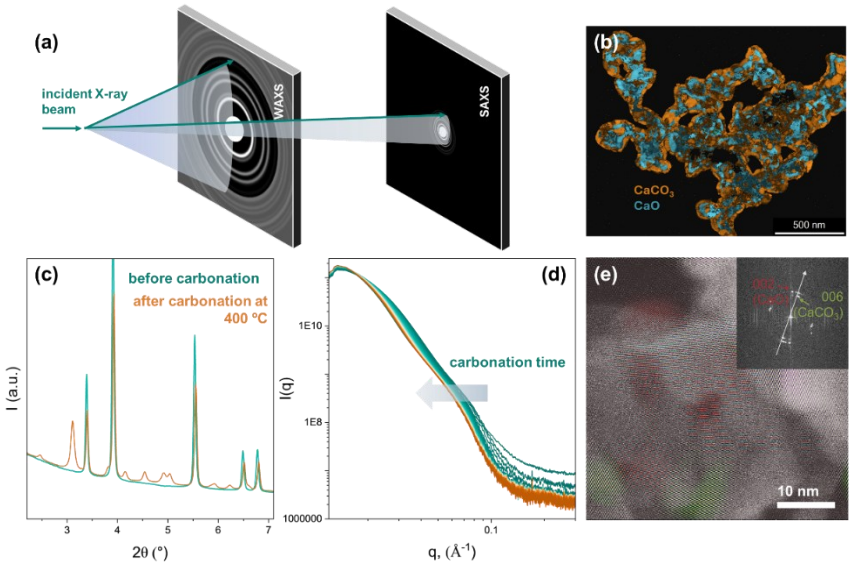


Figure 1. *(a) Schematic of the experimental setup for simultaneous SAXS and WAXS acquisition at the ESRF ID3 beamline. (b) 4D-STEM phase map of a partially carbonated sample, showing particles with CaO-rich cores and $CaCO_3$-rich shells. (c) WAXS patterns recorded before and after carbonation at 400 °C. (d) Time-resolved SAXS profiles collected during carbonation. (e) High-angle annular dark-field image of partially carbonated CaO nanoparticles acquired during an environmental STEM experiment. The inset FFT shows reflections from CaO and $CaCO_3$ grown on CaO, indicating a preferential orientation relationship, as marked by the arrow.*

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