Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Na_2CO_3-modified CaO-based CO_2 Sorbents: The Effects of Structure and Morphology on CO_2 Uptake

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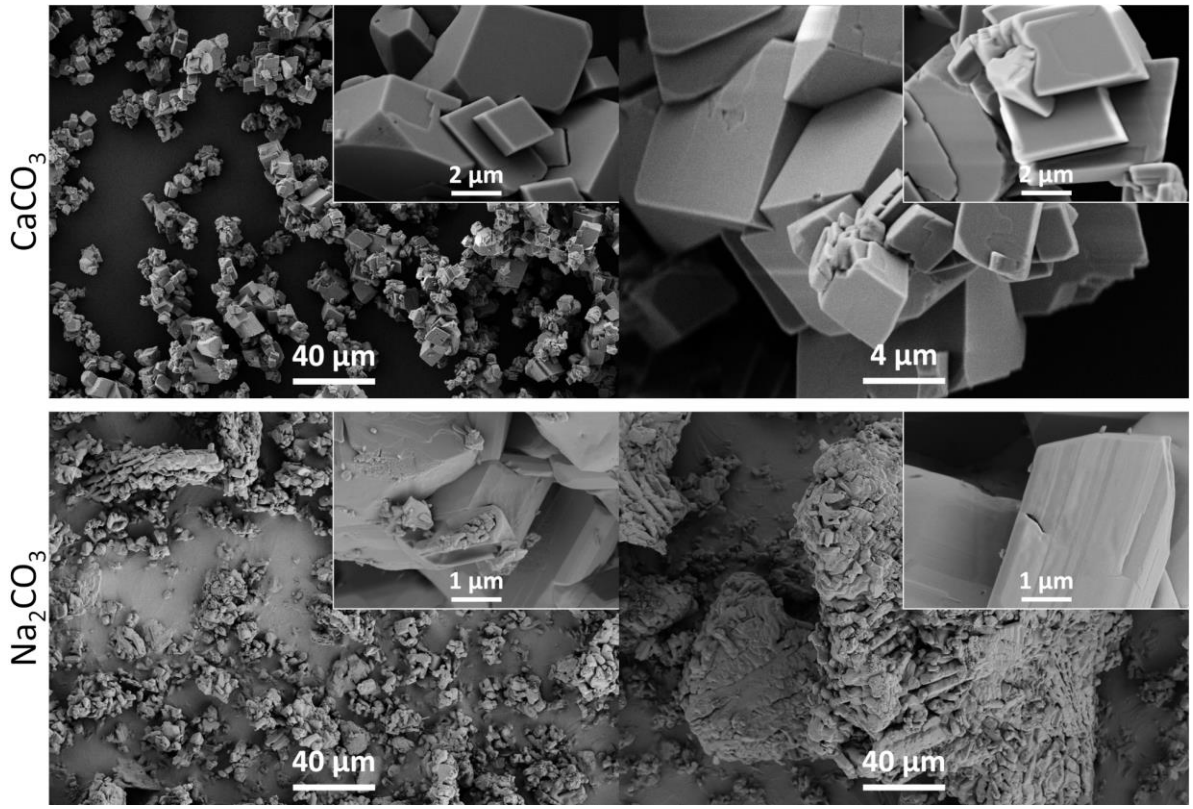

Figure S1. SEM images of the $CaCO_3$ and Na_2CO_3 precursors.

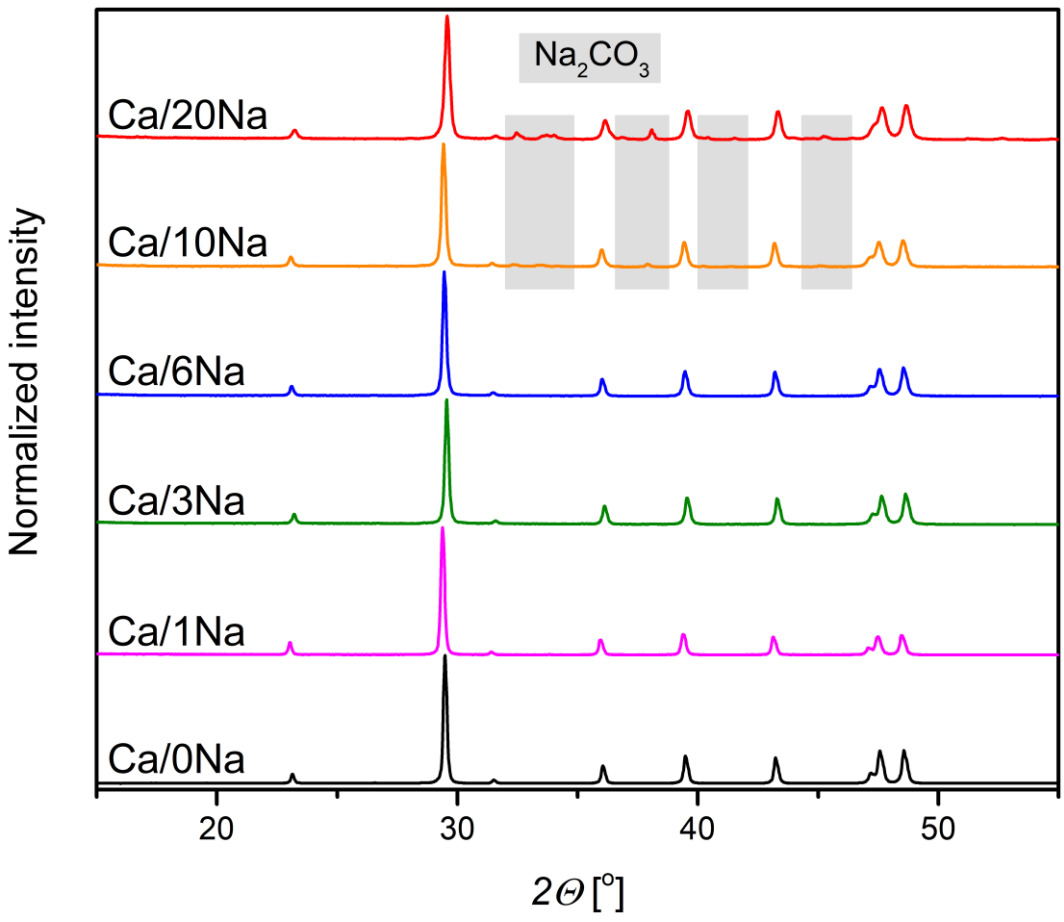

Figure S2. XRD patterns of as prepared CaO-based sorbents.

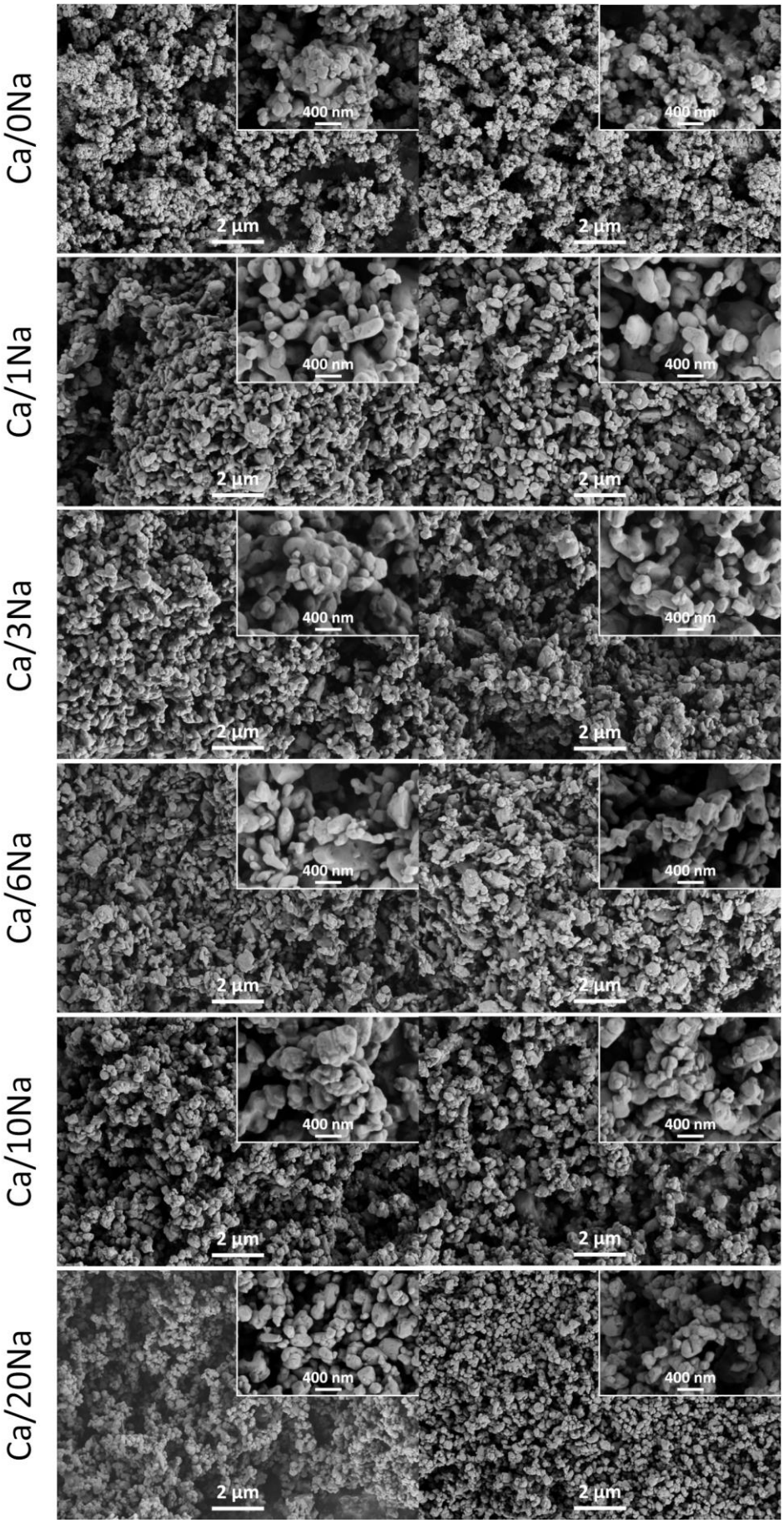

Figure S3. SEM images of the as prepared sorbents, i.e. Ca/0Na, Ca/1Na, Ca/3Na, Ca/6Na, Ca/10Na, and Ca/20Na.

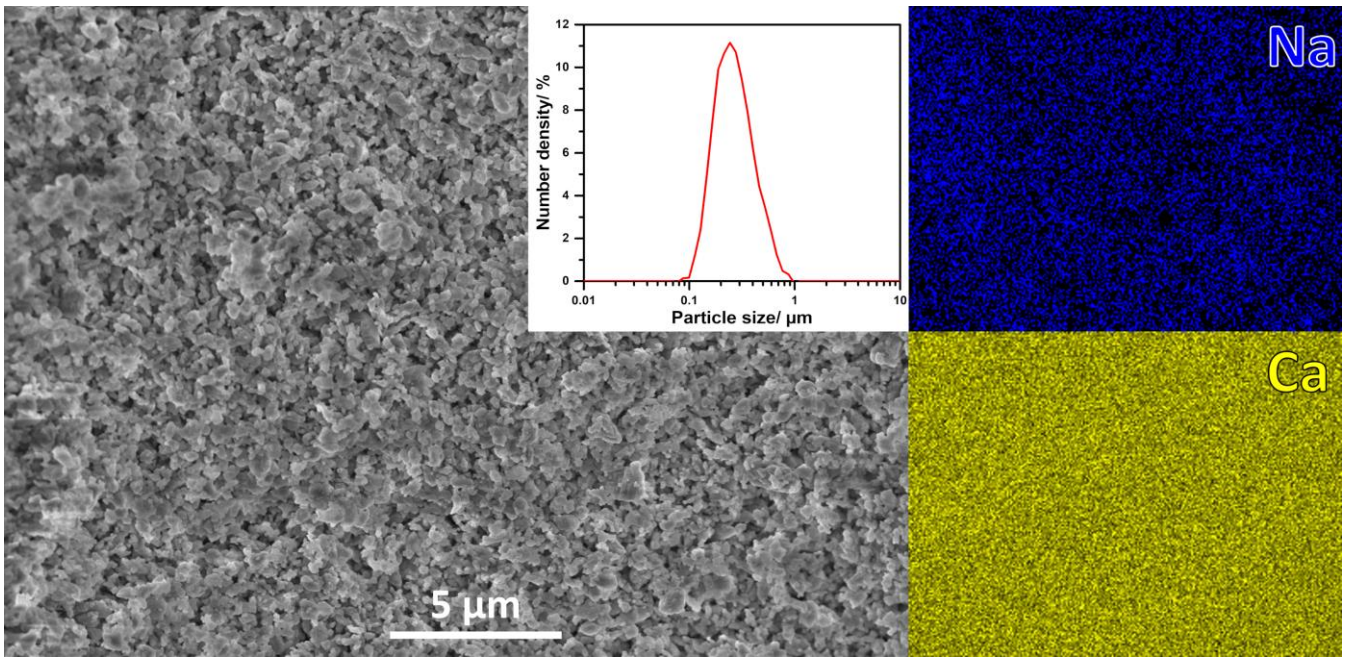

Figure S4. SEM/EDX elemental mapping of Ca/3Na.

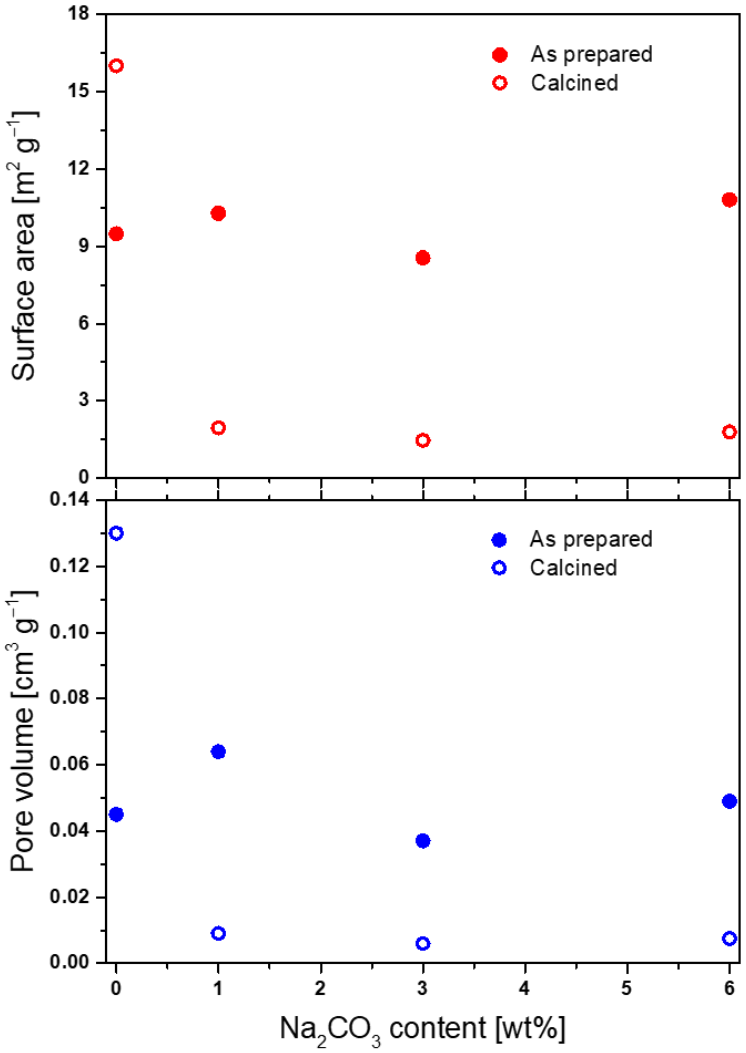

Figure S5. BET surface area and BJH pore volume of CaO-based sorbents in the as-prepared (prior to the initial calcination) and calcined states as a function of the Na_2CO_3 content.

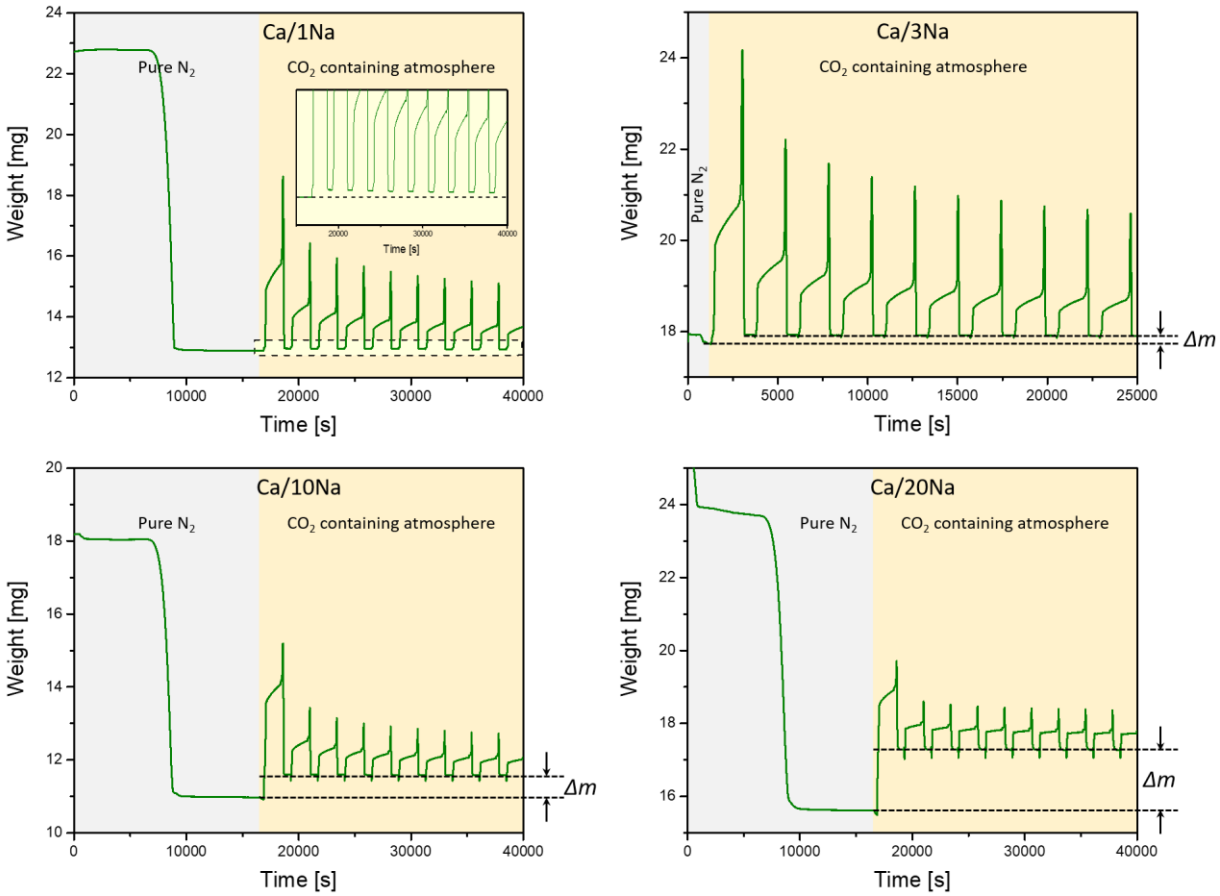

Figure S6. CO_2 uptake profile of Ca/1Na, Ca/3Na, Ca/10Na, and Ca/20Na revealing a weight difference, Δ*m,* when the sorbent is calcined in pure N_2 or a CO_2-rich atmosphere.

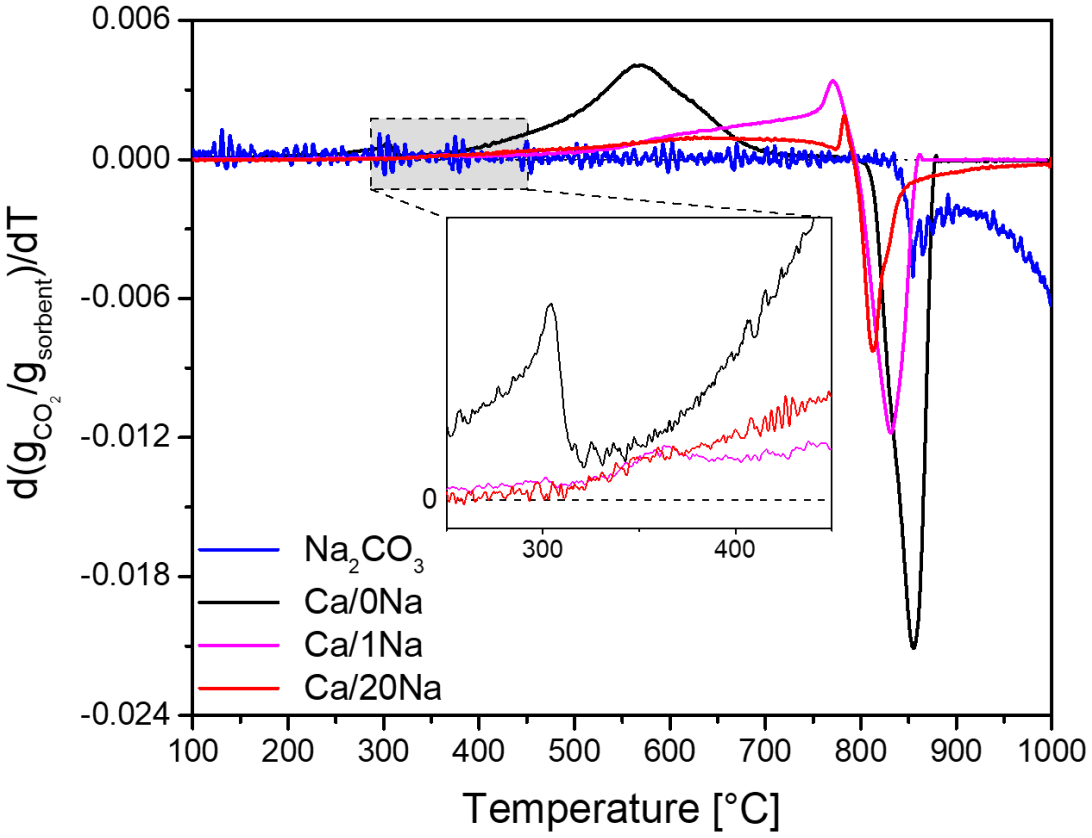

Figure S7. TPC profiles of $CaCO_3$, Na_2CO_3, Ca/1Na and Ca/20Na.

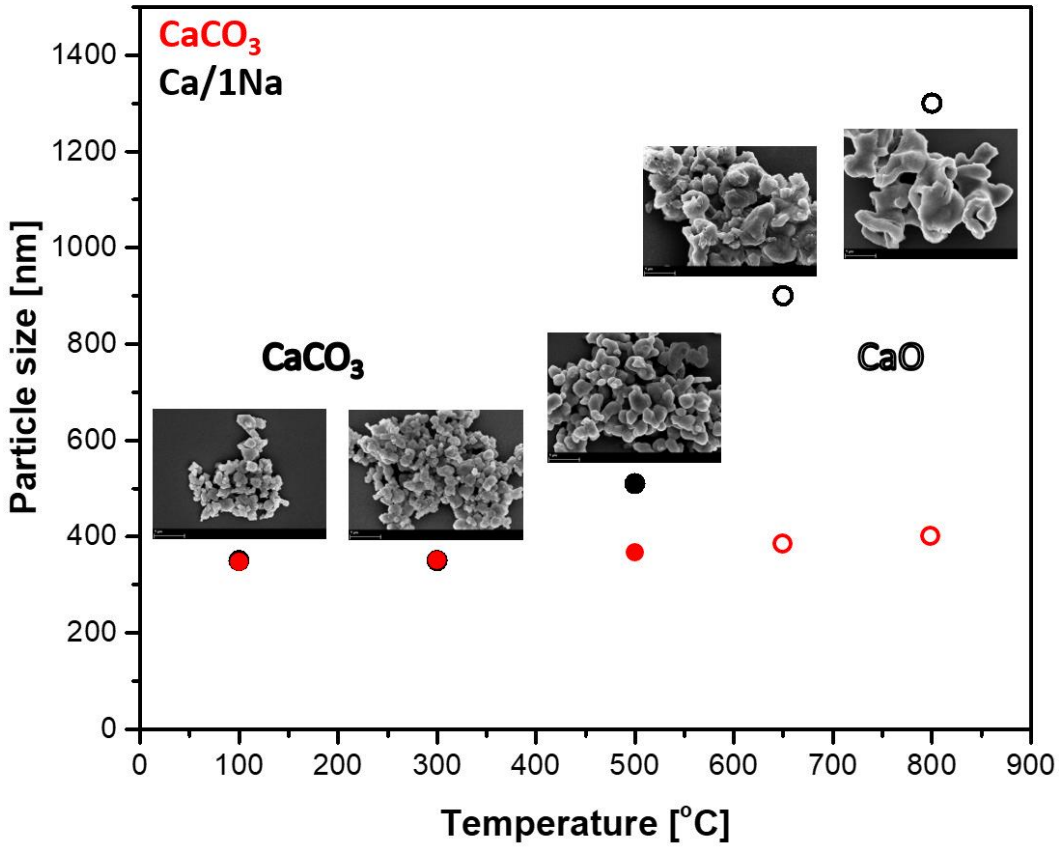

Figure S8. Increase in particle size of $CaCO_3$ (red) and Ca/1Na (black) during the initial calcination step in N_2 as a function of the calcination temperature.

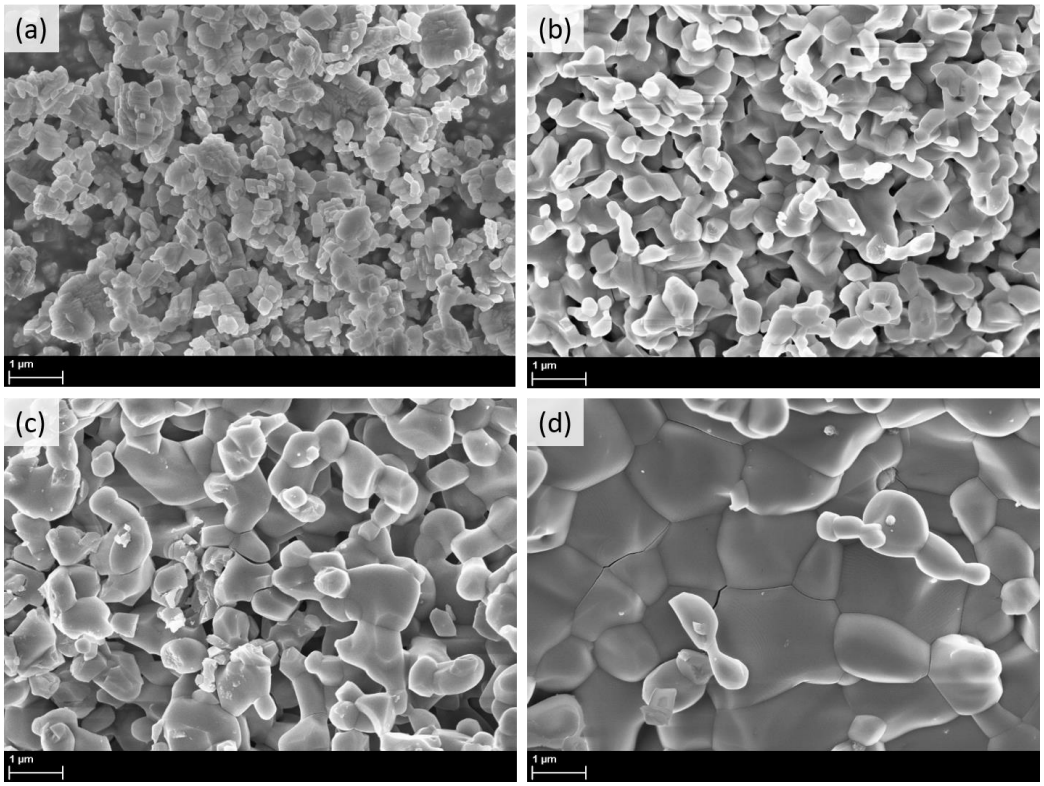

Figure S9. SEM images of $CaCO_3$ annealed at 750 °C in CO_2 for a) 0 h, b) 1 h, c) 5 h and d) 12 h.

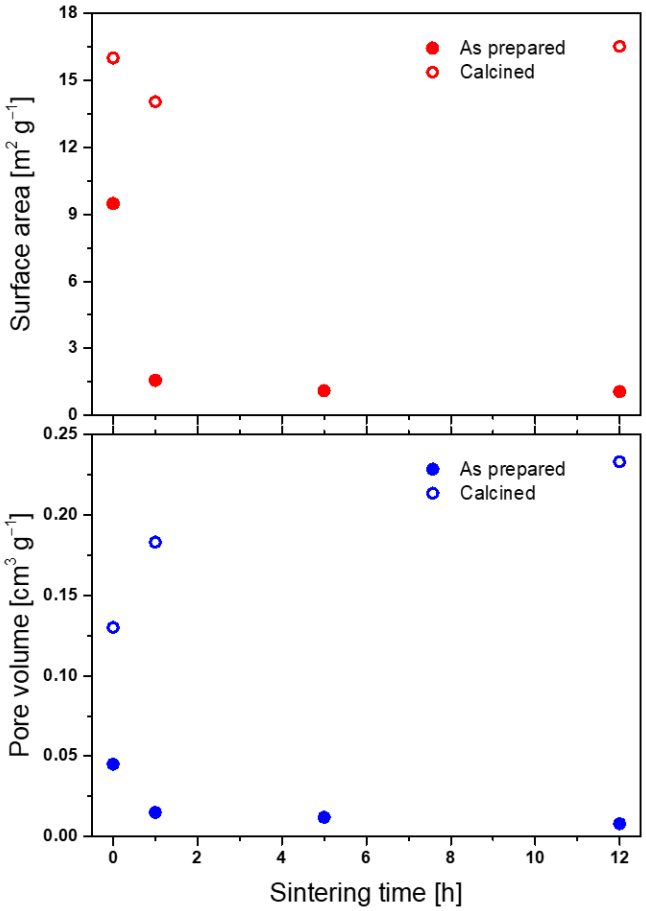

Figure S10. Surface area and pore volume of $CaCO_3$ in the as-prepared (prior to the initial calcination) and calcined states as a function of sintering time.

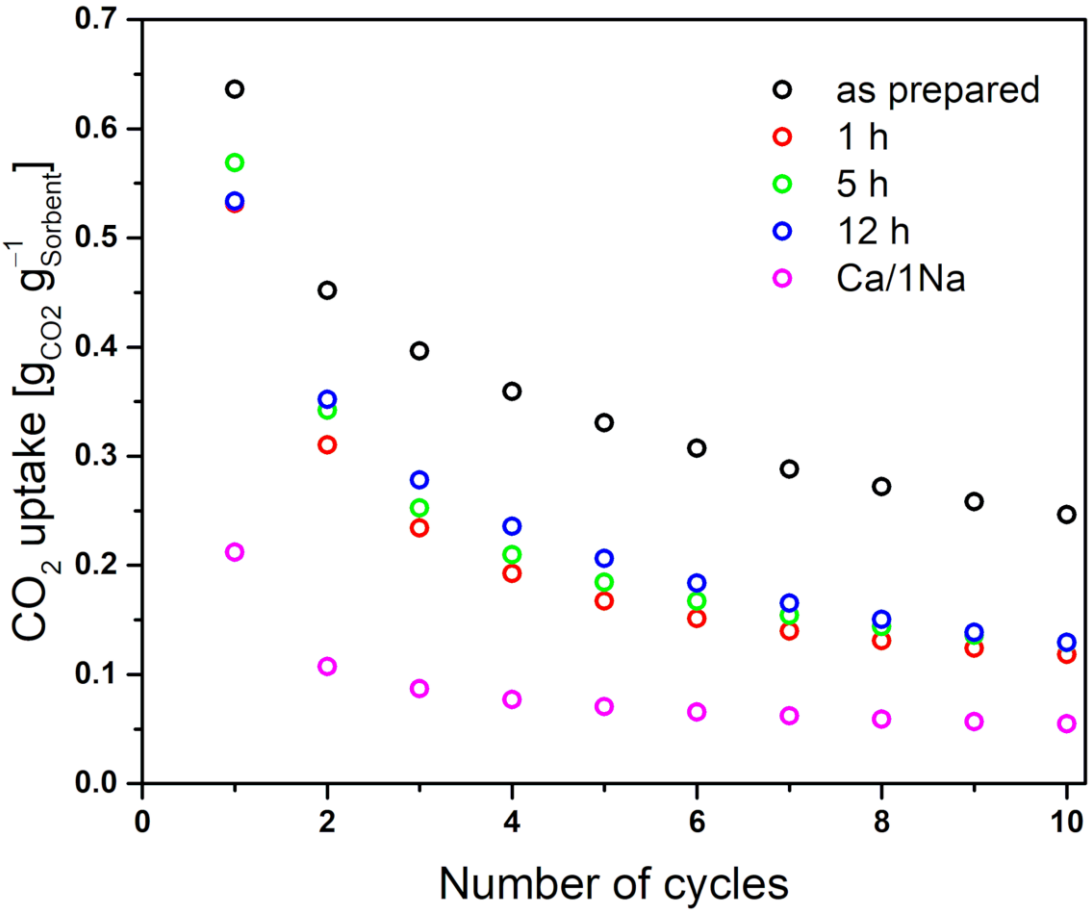

Figure S11. Cyclic CO_2 uptake of ball-milled $CaCO_3$ that has been exposed prior to CO_2 uptake test to sintering conditions for varying durations (sintering temperature 750 °C in pure CO_2 atmosphere) under realistic CO_2 capture conditions (calcination at 900 °C in a CO_2-rich atmosphere; carbonation at 650 °C in 20 vol.% CO_2/N_2). Abbreviations 1 h, 5 h and 12 h in the legend correspond to the samples which have been annealed at 750 °C in CO_2 for 1 h, 5 h and 12 h, respectively (as described in Figures S9 and S10).

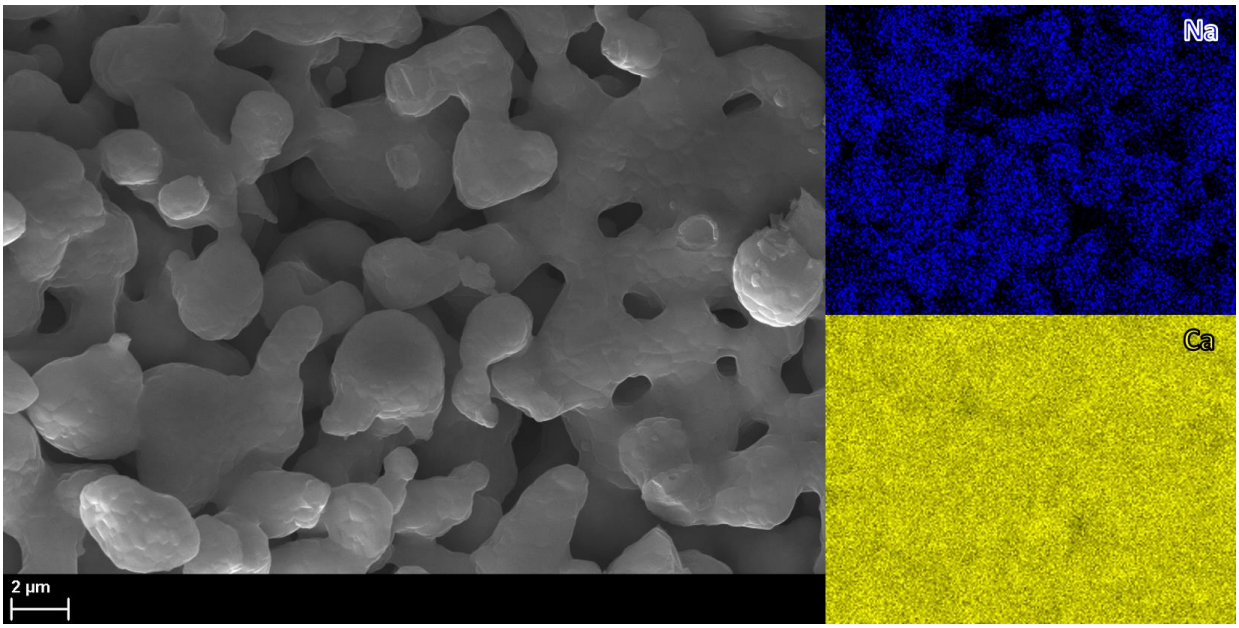

Figure S12. SEM images and EDX elemental mapping of Ca/3Na after the 10th carbonation step.

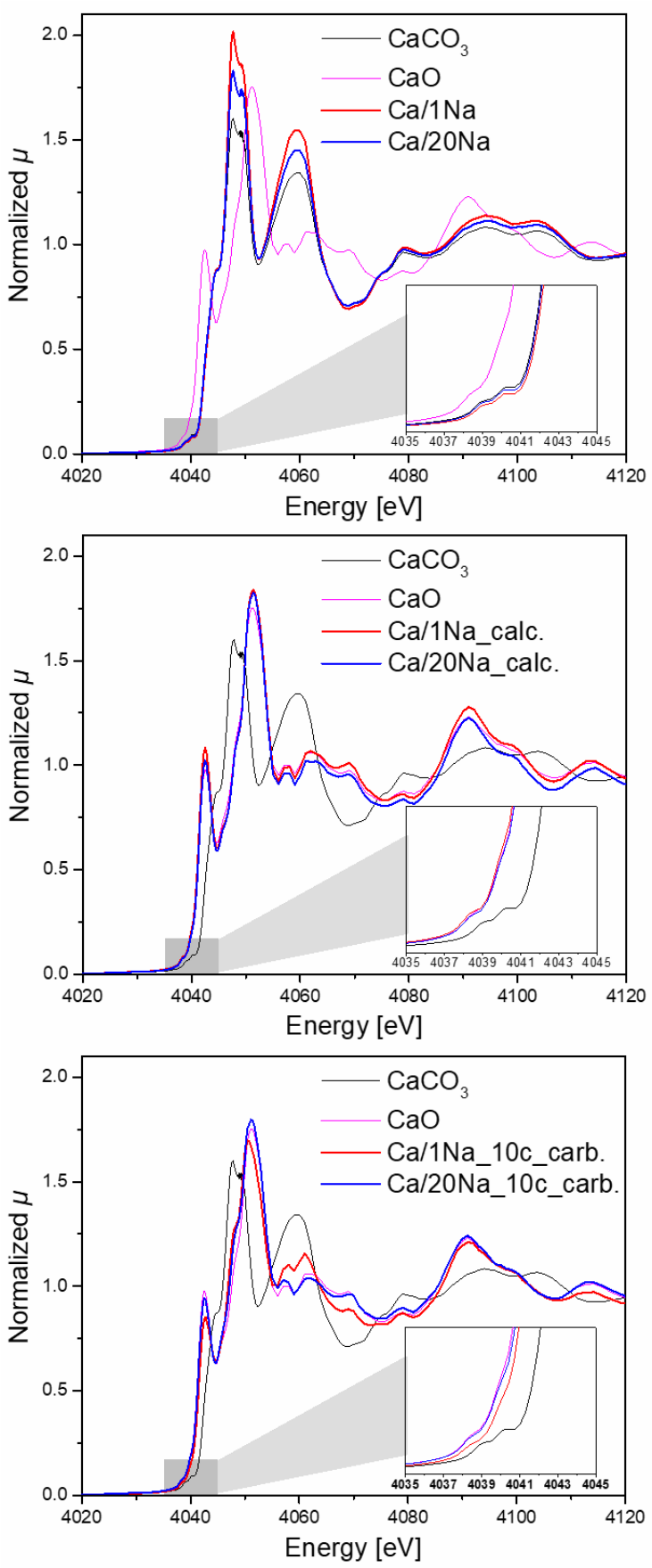

Figure S13. Ca K-edge spectra of Ca/1Na and Ca/20Na at different states, i.e. as prepared, after the initial calcination (_calc.) and after the 10th carbonation step (_10c_carb.) compared to the reference spectra of CaO and $CaCO_3$.

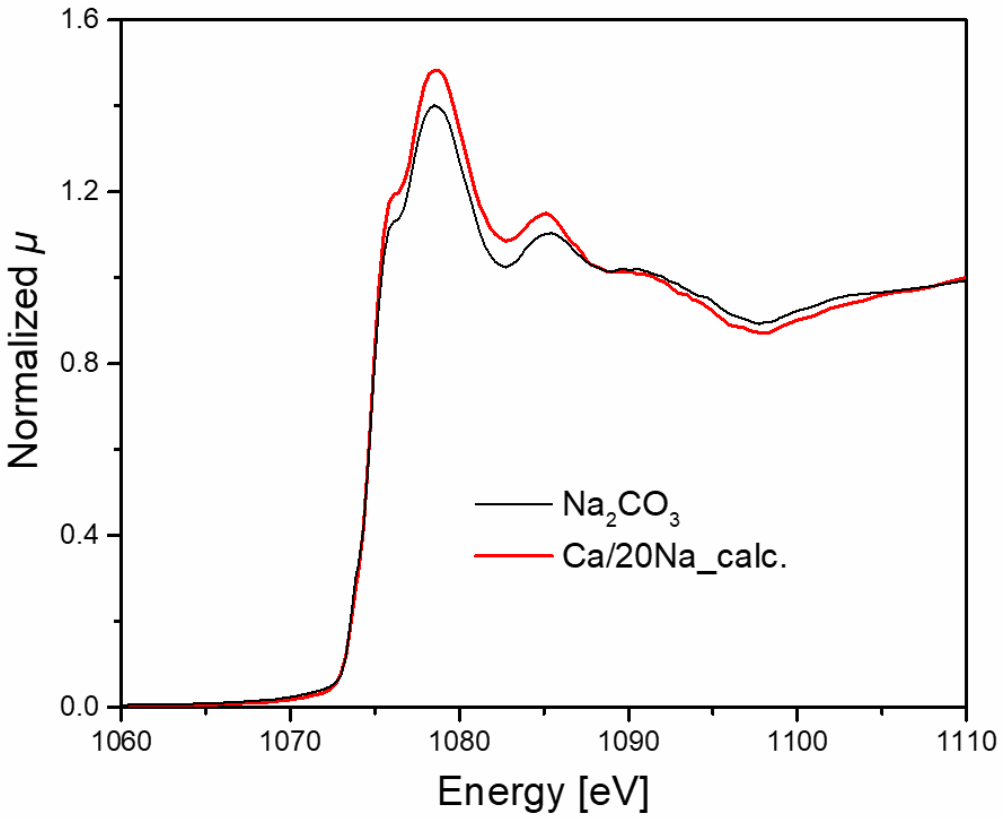

Figure S14. Na K-edge spectra of Na_2CO_3-modifed CaO after initial calcination (800 °C, N_2) compared to the reference spectra of $NaCO_3$.

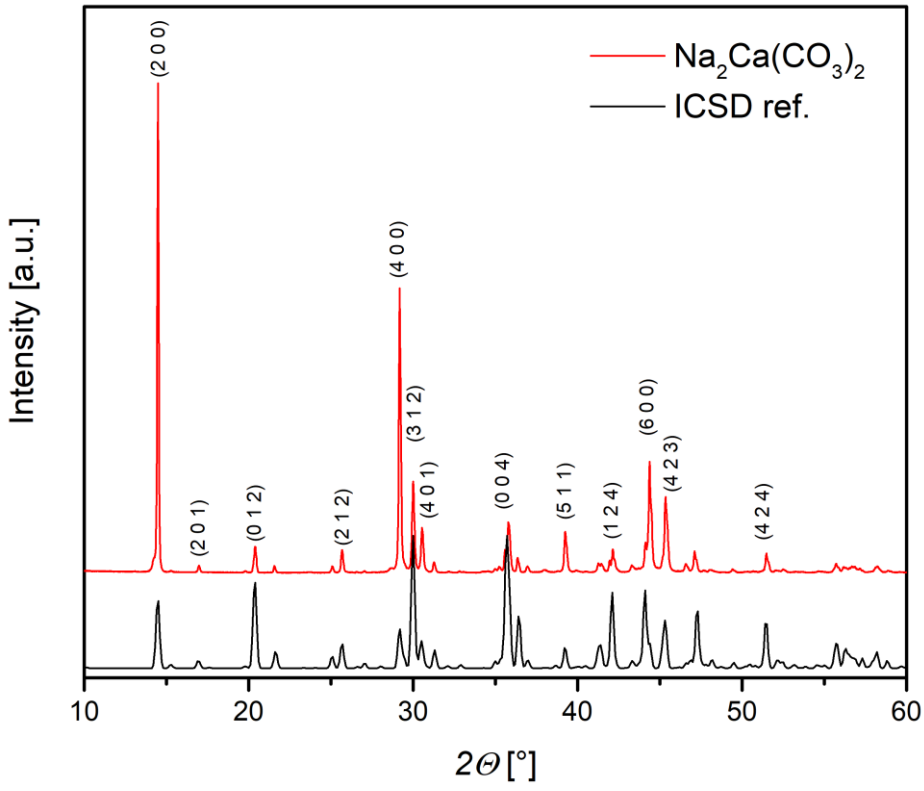

Figure S15. XRD pattern of the $Na_2Ca(CO_3)_2$ reference and the simulated pattern according to the ICSD database, crystal structure reported in *Cryst. Growth Des.* **2016**, 16, 1893–1902 ($P2_1ca$, a = 10.0713 Å, b = 8.7220 Å, c = 12.2460 Å).

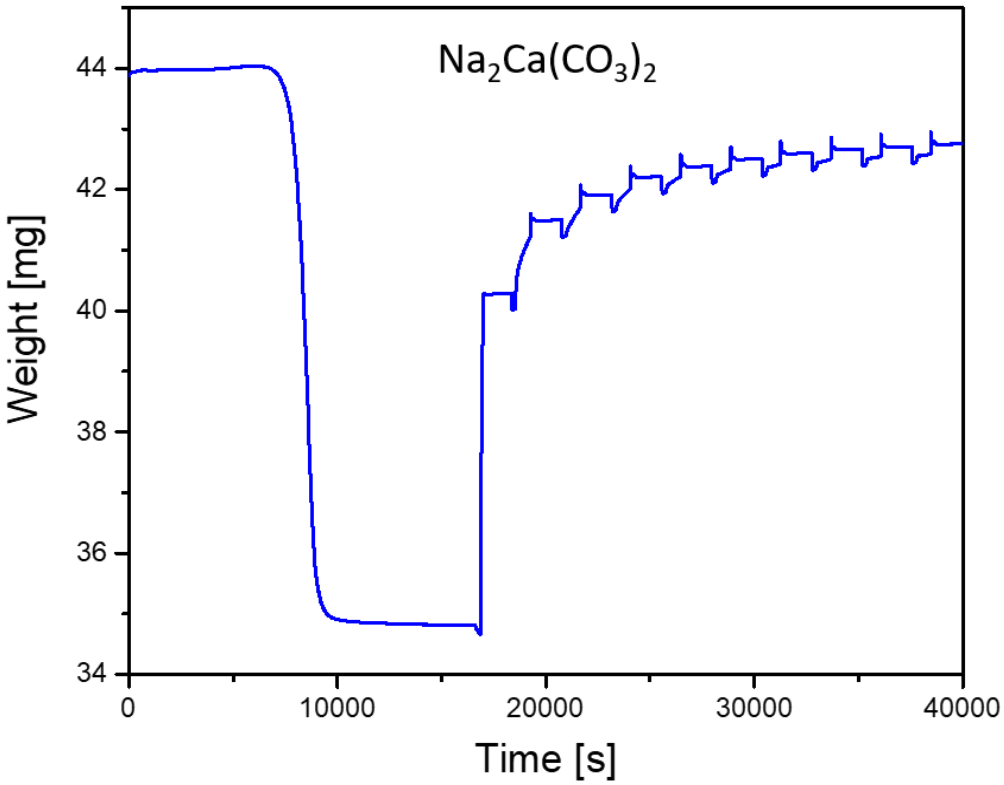

Figure S16. TGA data when the reference $Na_2Ca(CO_3)_2$ is exposed to cyclic carbonation calcination conditions. $Na_2Ca(CO_3)_2$ does not decompose under the carbonation and calcination conditions studied (CO_2, 650–900 °C).

Table S1. Theoretical and ICP-determined Na_2CO_3 contents in the prepared sorbents.

Sample	Nominal Na_2CO_3 content wt.%	Na/Ca ratio	Determined Na_2CO_3 content wt.%
Ca/1Na	1	0.009	0.8
Ca/3Na	3	0.057	5
Ca/10Na	10	0.130	10.7
Ca/20Na	20	0.301	21.7