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[Supporting information]

Development of an effective bi-functional Ni-CaO catalyst-sorbent for the sorption-enhanced water gas shift reaction through structural optimization and the controlled deposition of a stabilizer by atomic layer deposition

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Table S1. Textural properties of cycled hollow and benchmark CaO-based CO_2 sorbents.[a]

Sorbent	Ca : Al (molar ratio)	Surface area [$m^2/g_{sorbent}$]	Pore volume [$cm^3/g_{sorbent}$]
Al (2 nm)-$CaCO_3$_hollow	90 : 10	13	0.132
Al (10 nm)-$CaCO_3$_limestone	89 : 11	5	0.051
Al (10 nm)-$CaCO_3$_bulk	88 : 12	4	0.072
Al (1 nm)-$CaCO_3$_NP	90 : 10	2	0.020

[a] Textural properties after 30 cycles of carbonation and calcination (in a calcined form)

Table S2. Textural properties of freshly calcined and cycled bifunctional Ni-CaO catalyst-sorbent

Materials	SE-WGS Cycles	Surface area [$m^2/g_{sorbent}$]	Pore volume [$cm^3/g_{sorbent}$]
Ni/Al (0 nm)-$CaCO_3$_hollow[a]	0	15	0.175
Ni/Al (0 nm)-$CaCO_3$_hollow	10	3	0.021
Ni/Al (2 nm)-$CaCO_3$_hollow[a]	0	18	0.190
Ni/Al (2 nm)-$CaCO_3$_hollow	10	13	0.120

[a] Freshly calcined materials.

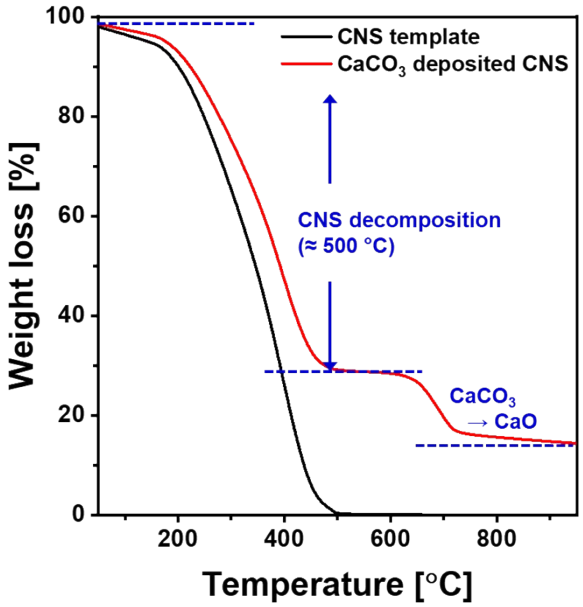

Figure S1. Thermal decomposition profile of the CNS template and $CaCO_3$ deposited onto CNS.

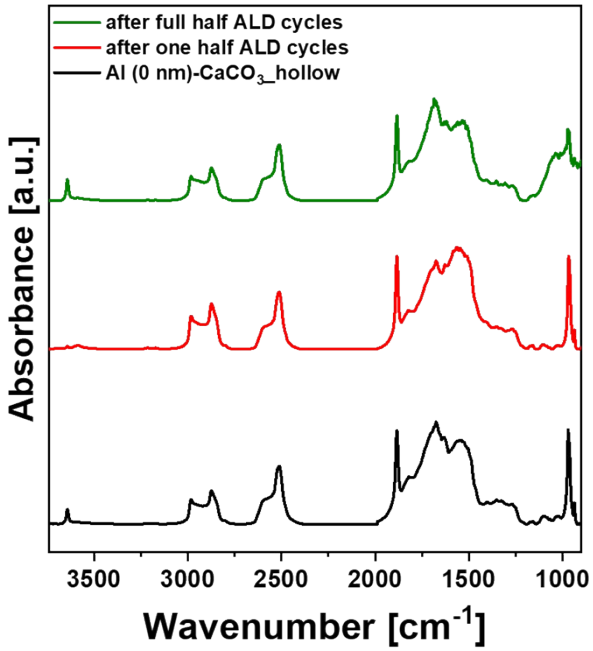

Figure S2. DRIFT spectra of Al (0 nm)-$CaCO_3$ hollow and hollow $CaCO_3$ after one half and one full ALD cycles.

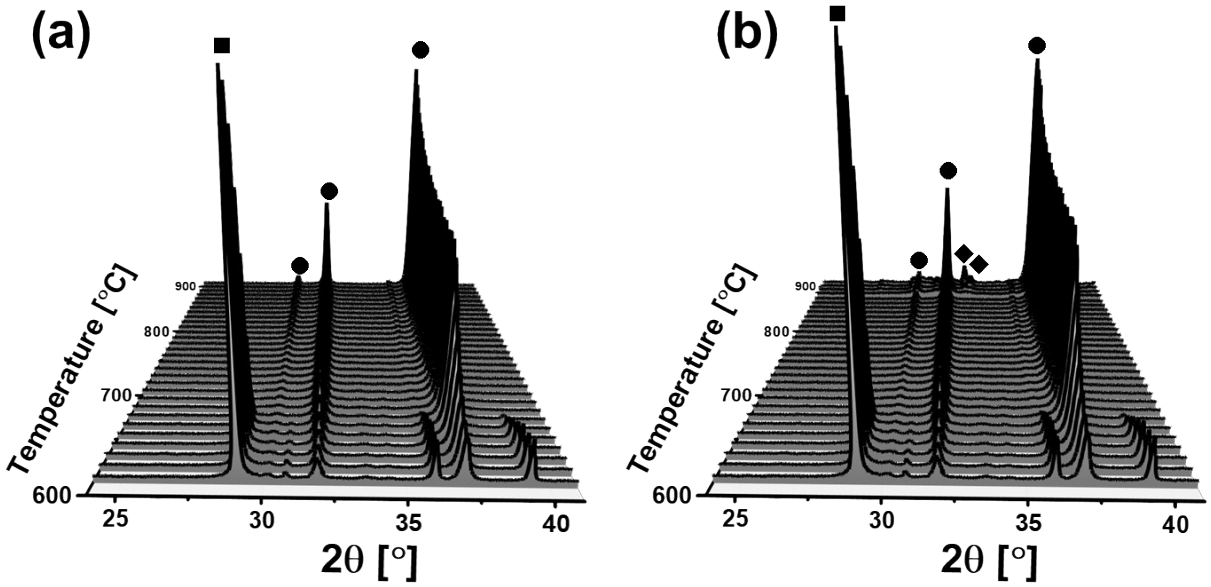

Figure S3. *In situ* XRD diffractograms of (a) Al (0 nm)- and (b) Al (2nm)-$CaCO_3$_hollow during calcination in the temperature range of 600–900 °C: (■) calcite ($CaCO_3$), (●) lime (CaO) and (◆) tricalciumaluminate ($Ca_3Al_2O_6$).

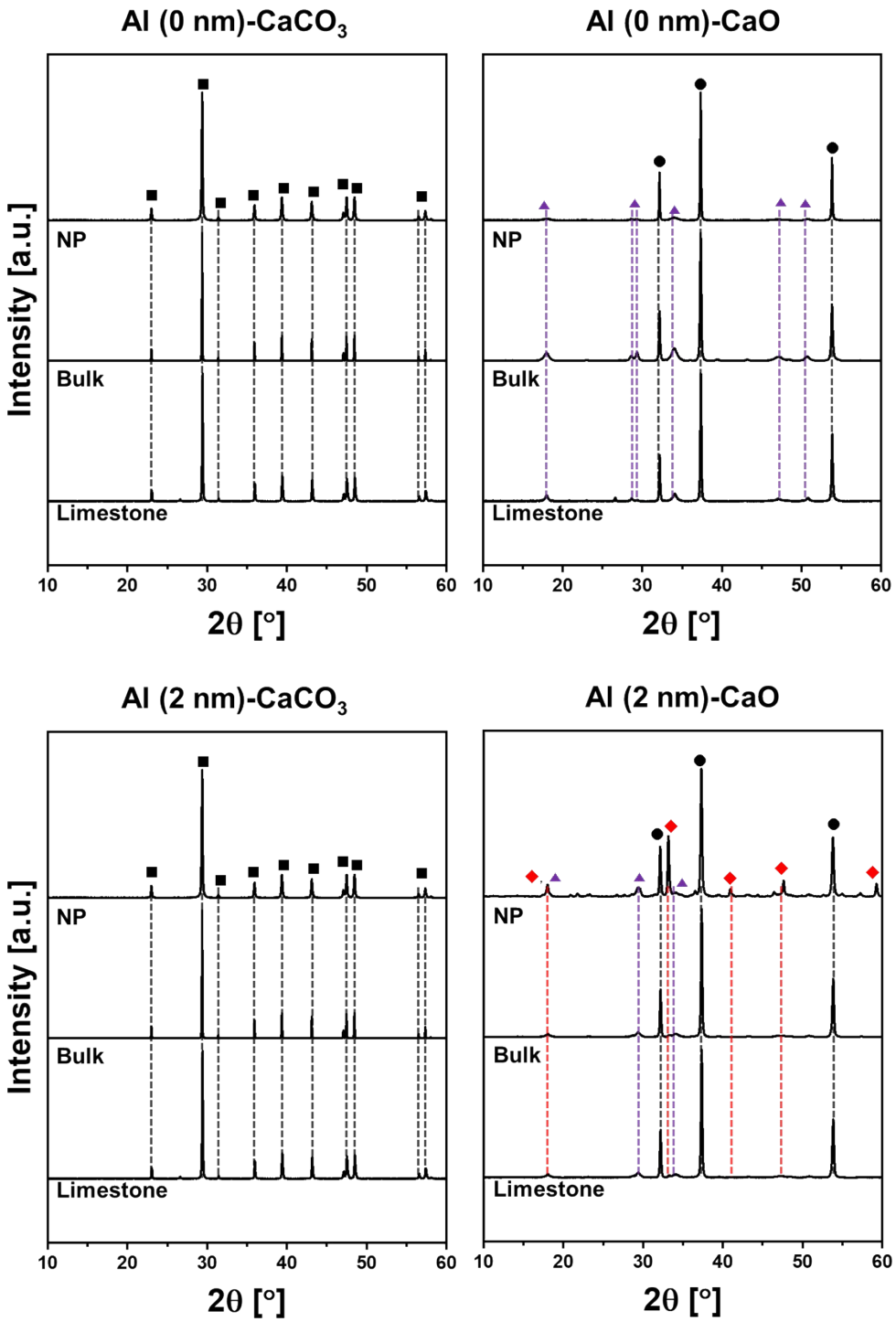

Figure S4. XRD diffractograms of benchmark materials and calcined materials at 900 °C in the presence or absence of an Al_2O_3 coating: (■) calcite ($CaCO_3$), (●) lime (CaO), (▲) portlandite ($Ca(OH)_2$), and (◆) tricalciumaluminate ($Ca_3Al_2O_6$).

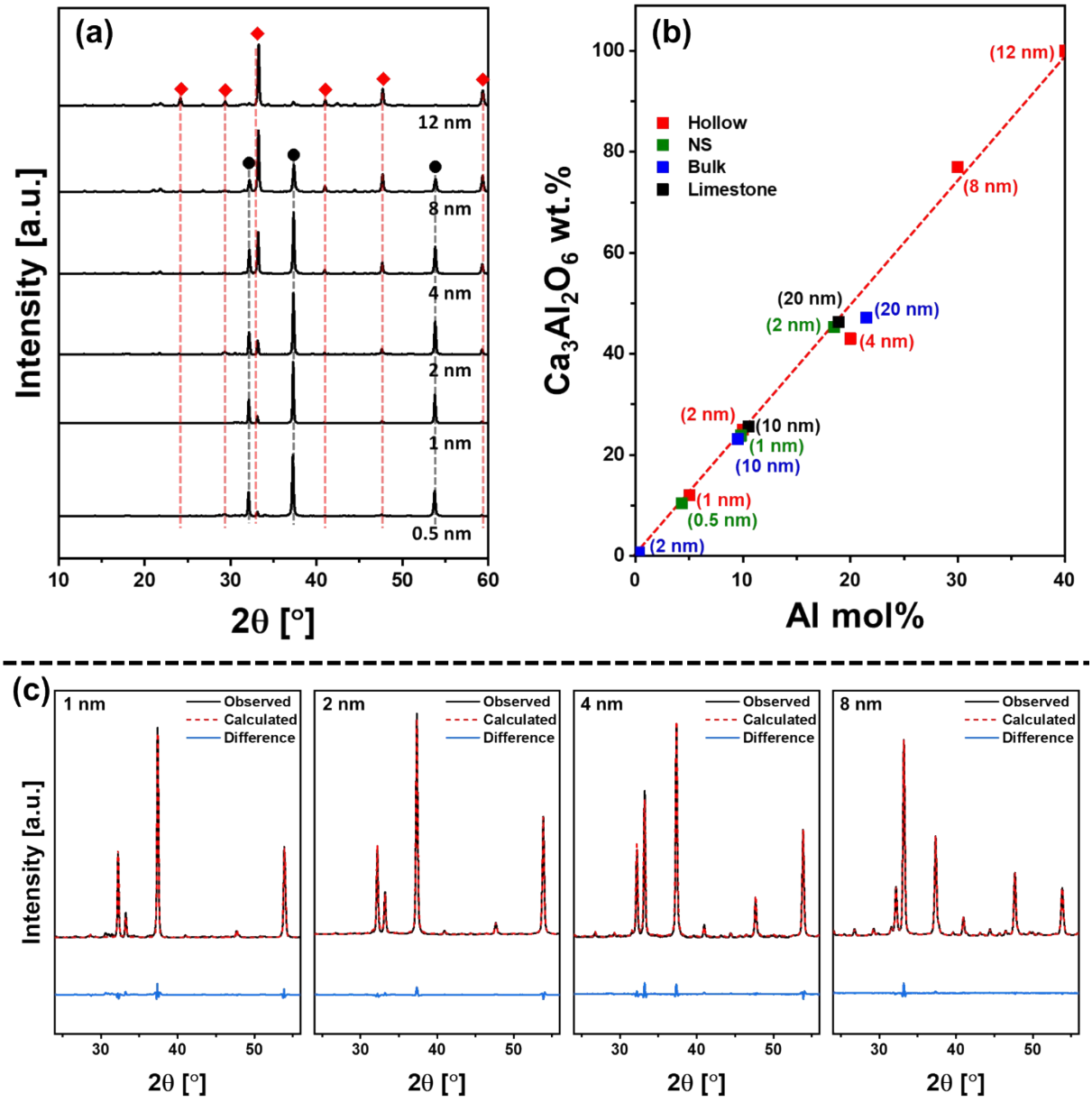

Figure S5. (a) XRD diffractograms of Al_2O_3-coated, hollow CaO with different thicknesses of an ALD-grown Al_2O_3 coating: (■) Lime (CaO), and (◆) tricalcium aluminate ($Ca_3Al_2O_6$). (b) Calculated weight fractions of $Ca_3Al_2O_6$ in the calcined sorbents as a function of Al mol% determined by ICP-OES. (c) Rietveld analysis of selected, Al_2O_3-coated, hollow CaO sorbents with different thicknesses of an ALD-grown Al_2O_3 layer. The number in brackets refers to the thickness of the ALD-grown Al_2O_3 coating. The dashed line in (b) represents the theoretical $Ca_3Al_2O_6$ content in the sorbent depending on the molar ratio of Ca^{2+} to Al^{3+}.

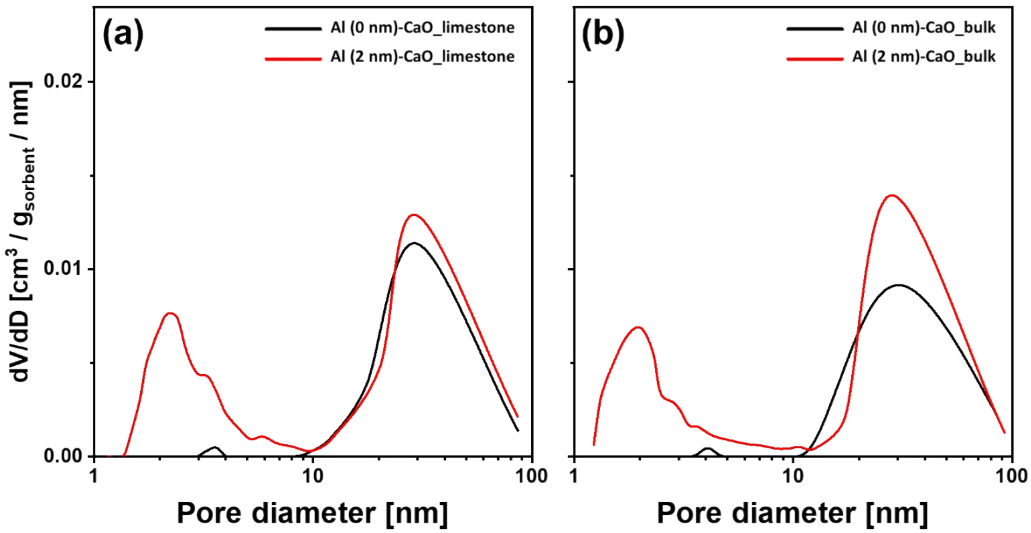

Figure S6. BJH pore distribution of the calcined benchmarks: (a) limestone and (b) bulk $CaCO_3$ in the absence (i.e., Al (0 nm)) and presence of a 2 nm-thick Al_2O_3 overcoat.

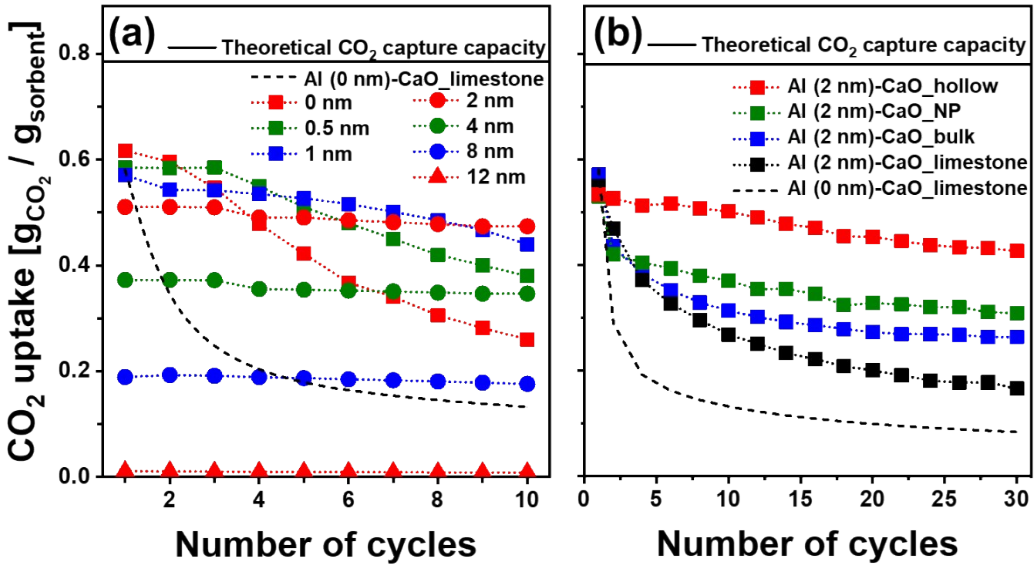

Figure S7. CO_2 capture performance of (a) Al_2O_3-coated, hollow CaO with different thicknesses of an ALD-grown Al_2O_3 layer, and (b) Al (2 nm)-CaO. The dashed line (-----) represents the cyclic CO_2 capture performance of limestone-derived CaO, i.e., Al (0 nm)-CaO limestone, and the solid line (——) gives the maximum theoretical CO_2 uptake of pure CaO. Carbonation was performed at 650 °C for 20 min in 20 vol.% CO_2/N_2 (150 ml/min) and calcination was performed at 900 °C for 15 min in pure CO_2 stream (30 ml/min).

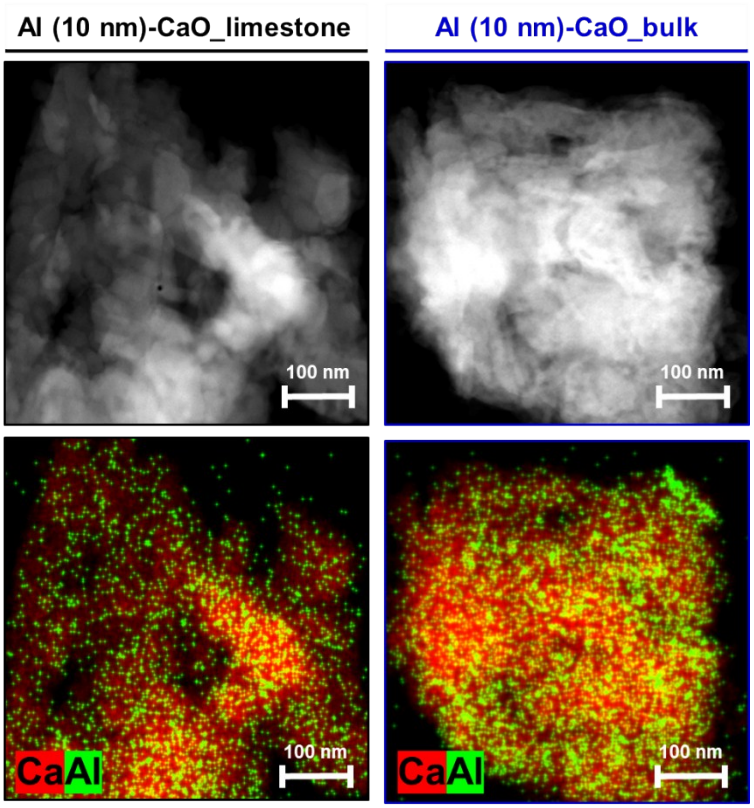

Figure S8. HAADF-STEM with EDX analysis of calcined Al (10 nm)-Ca_limestone and Al (10 nm)-CaO_bulk.

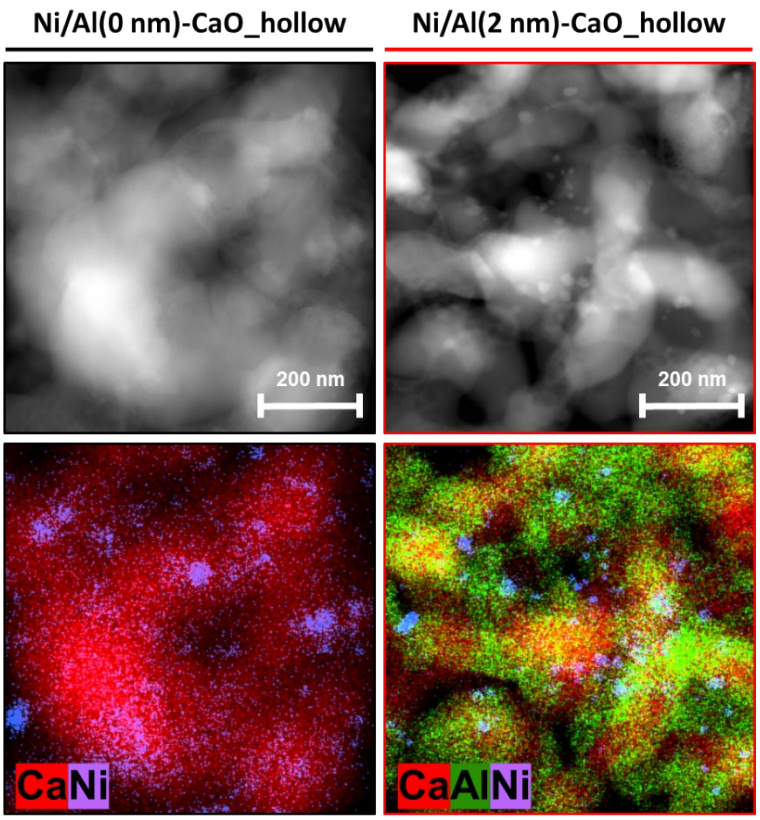

Figure S9. HAADF STEM with EDX analysis of Ni/Al (0 nm)-CaO_hollow and Ni/Al (2 nm)-CaO_hollow after 10 cycles of SE-WGS.