Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Appendix A. Supplementary data

Coke-promoted Ni/CaO catal-sorbent in a cyclic CO and syngas production process

Seongbin Jo[a], Jong Heon Lee[b], Jin Hyeok Woo[b], Tae Young Kim[b], Ho-Jung Ryu[d], Byungwook Hwang[d], Jae Chang Kim[b,†], Soo Chool Lee[c,†] and Kandis Leslie Gilliard-AbdulAziz[a,e,†]

[a] *Department of Chemical and Environmental Engineering, University of California–Riverside, Riverside, California 92521, United States*

[b] *Department of Chemical Engineering, Kyungpook National University, Daegu, 41566, Republic of Korea*

[c] *Research Institute of Advanced Energy Technology, Kyungpook National University, Daegu, 41566, Republic of Korea*

[d] *Korea Institute of Energy Research, Daejeon 34129, Republic of Korea*

[e] *Department of Material Science and Engineering, University of California–Riverside, Riverside, California 92521, United States*

[†] To whom all correspondence should be addressed.

E-mail address: kjchang@knu.ac.kr (J.C. Kim), soochool@knu.ac.kr (S.C. Lee), klabdulaziz@engr.ucr.edu (K.L. Gilliard-AbdulAziz)

Table S1. Metal contents of the NiO/CaO catal-sorbent in fresh state

	Metal content (wt%)[a]
NiO/CaO	Ni : 9.3

[a] Obtained by ICP-OES

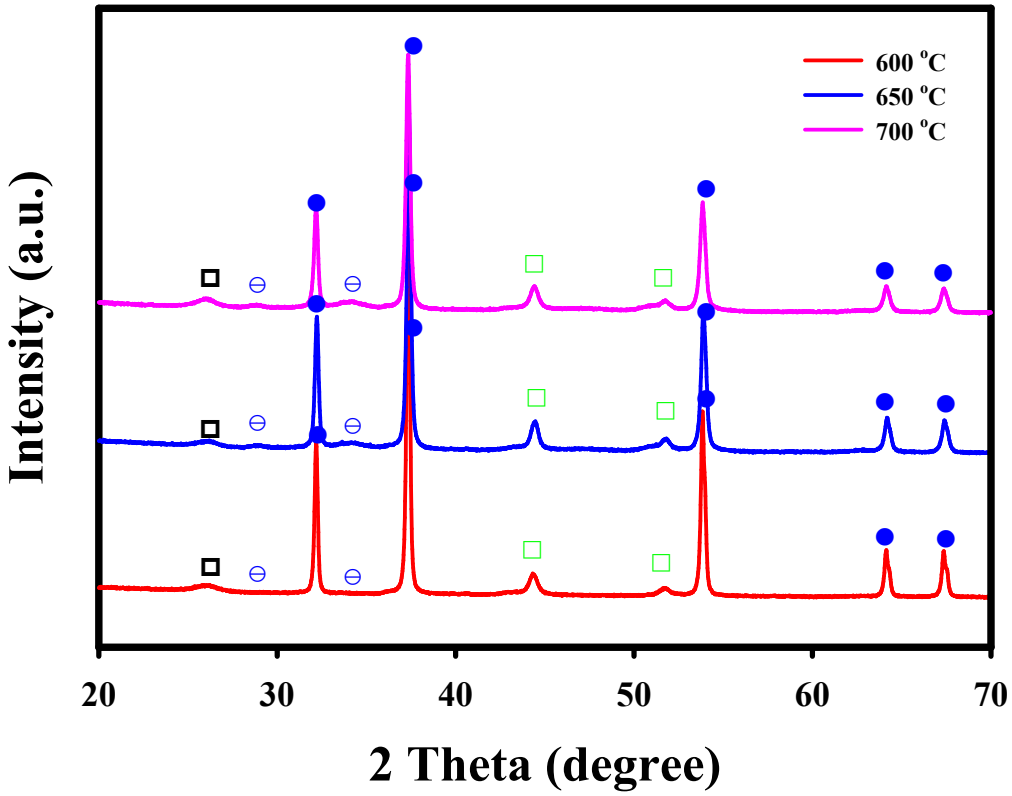

Figure S1 XRD patterns of coke-promoted Ni/CaO (C-Ni/CaO) catal-sorbents reduced under 10% CH_4 at different temperatures (600, 650 and 700 °C): (■) NiO, (□) Ni^0, (●) CaO, (⊖) $Ca(OH)_2$ and (▲) Coke.

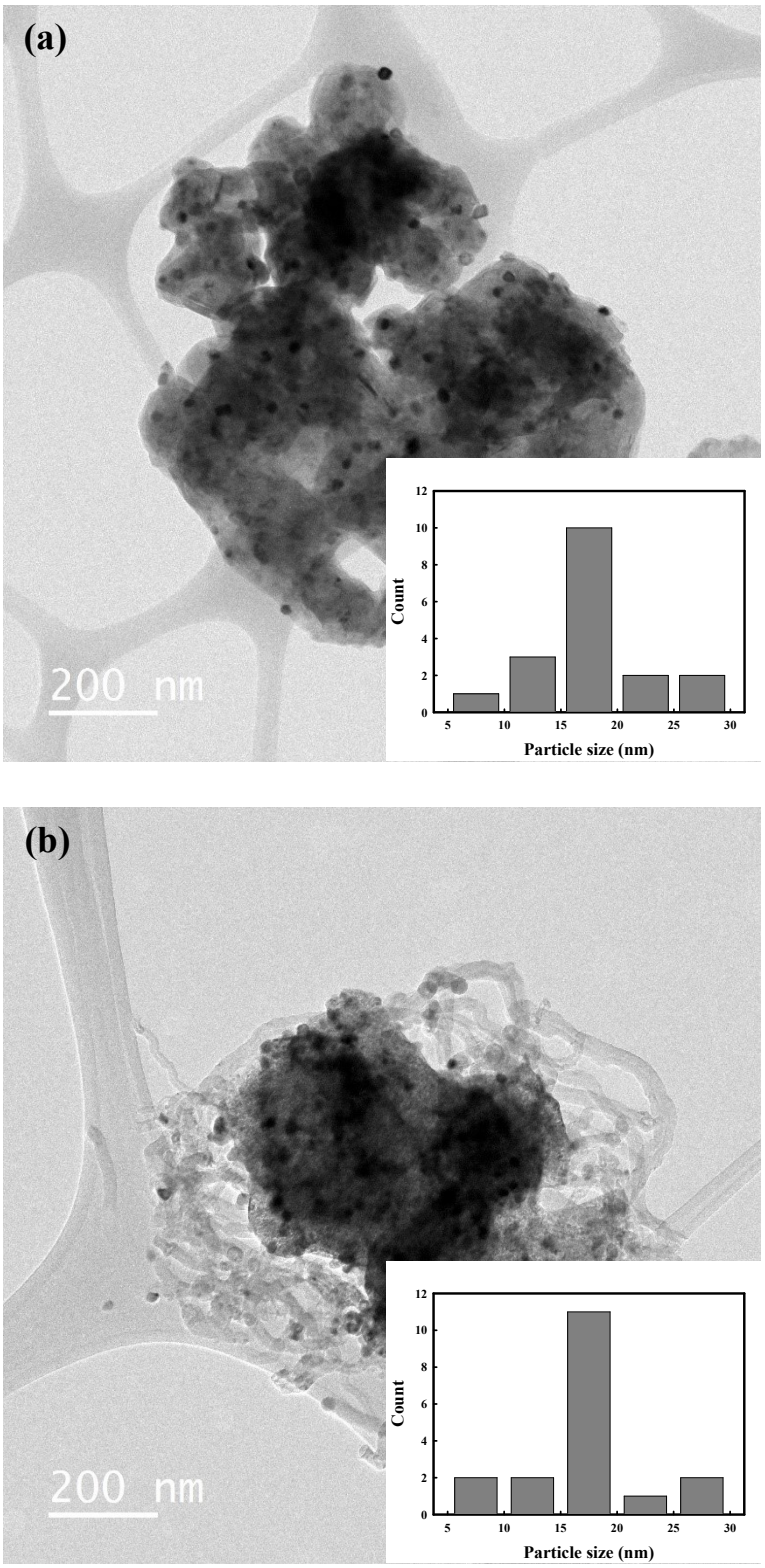

Figure S2 TEM images and particle size distribution of (a) NiO/CaO and (b) C-Ni/CaO that were reduced at 650°C

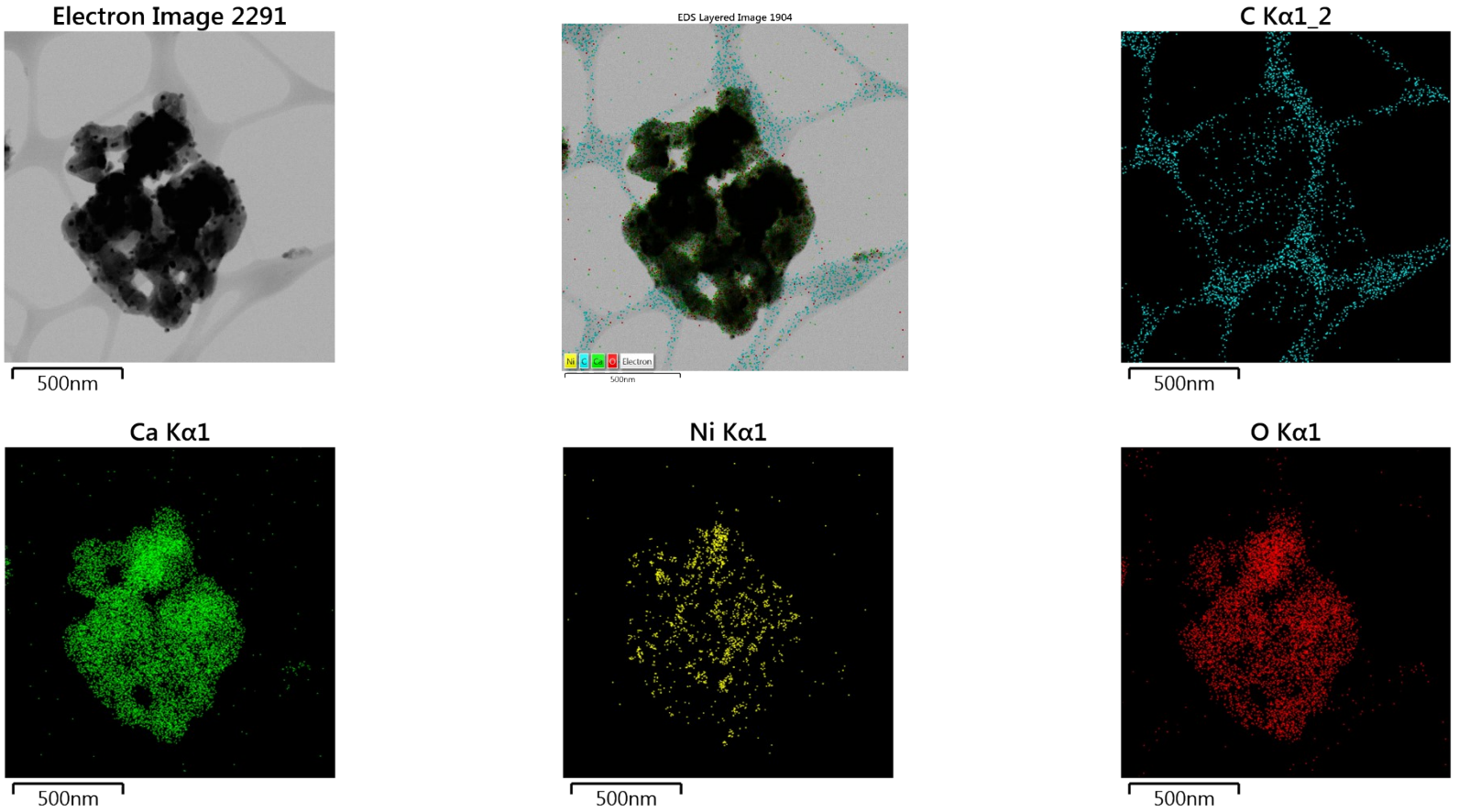

Figure S3 TEM-EDS analysis of NiO/CaO catal-sorbent

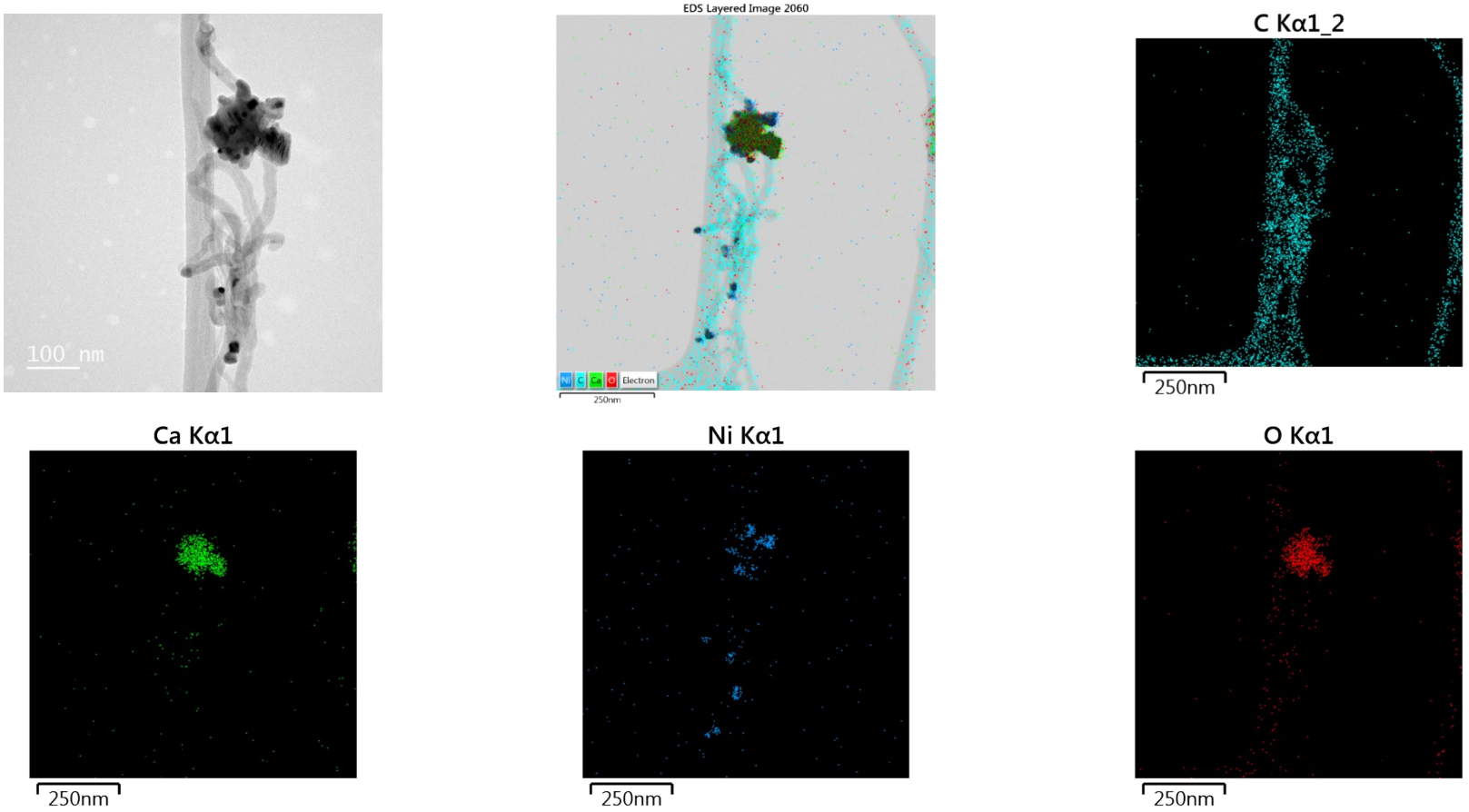

Figure S4 TEM-EDS analysis of C-Ni/CaO catal-sorbent

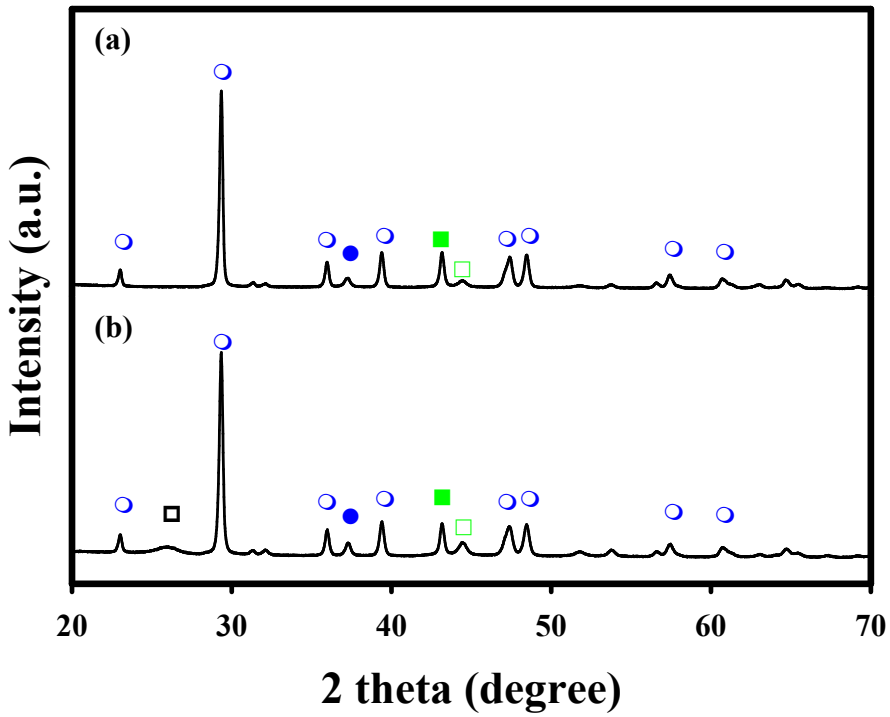

Figure S5 XRD patterns of (a) Ni/CaO and (b) C-Ni/CaO catal-sorbents after CO_2 conversion step under 10 vol% CO_2 at 650 °C: (■) NiO, (□) Ni^0, (●) CaO, and (▲) coke.

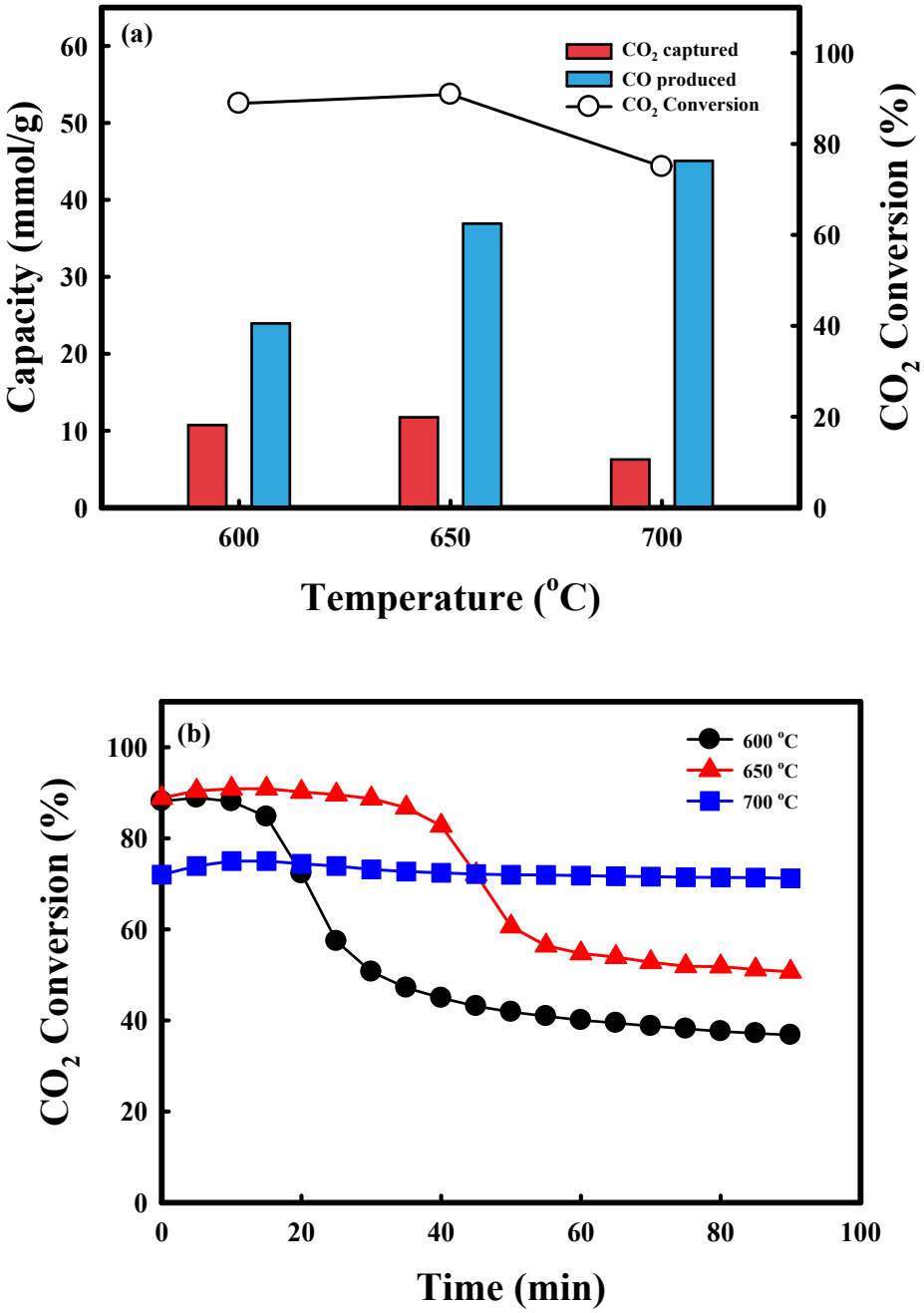

Figure S6 (a) CO_2 consumption and CO production capacity and (b) CO_2 conversion over C-Ni/CaO catal-sorbent under 10 vol% CO_2 condition at different temperatures (600, 650 and 700 °C)

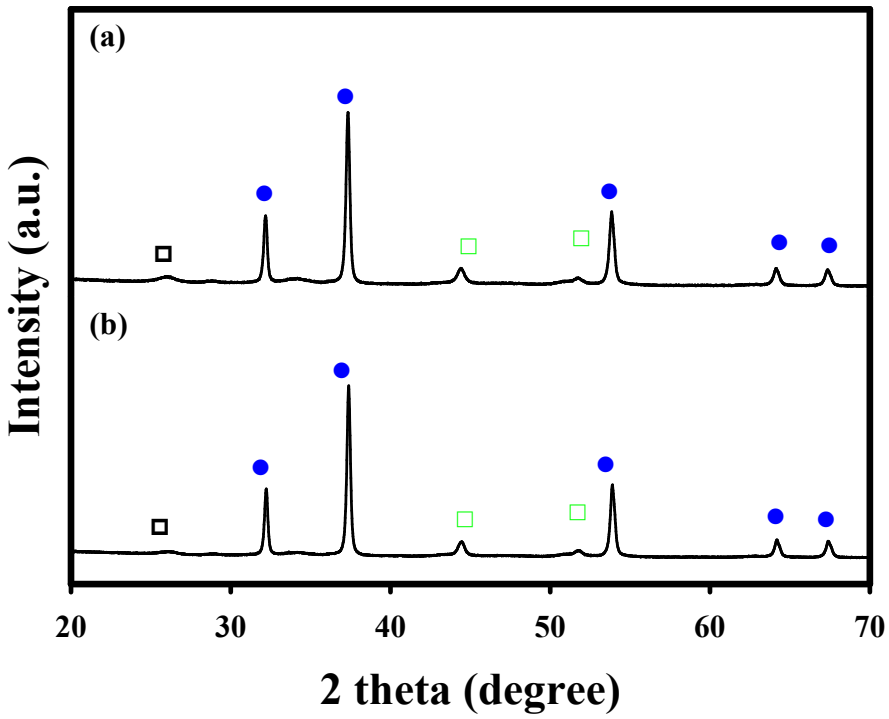

Figure S7 XRD patterns of (a) NiO/CaO and (b) NiO/$CaCO_3$ catal-sorbents after CH_4 conversion step under 10 vol% CH_4 at 650 °C: (■) NiO, (□) Ni^0, (●) CaO, and (▲) coke.

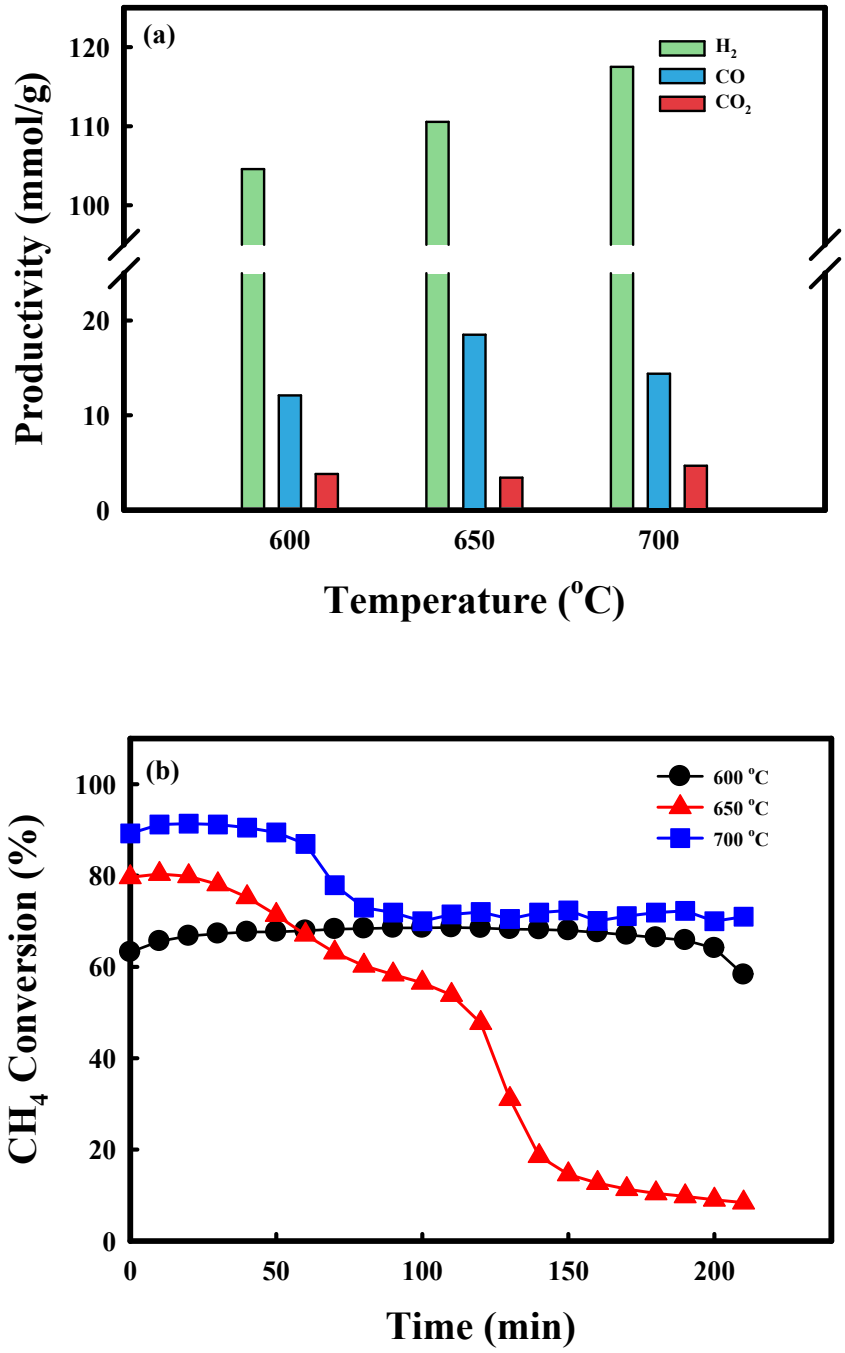

Figure S8 (a) Syngas (H_2 and CO) productivity and desorbed CO_2 capacity and (b) CH_4 conversion over Ni/$CaCO_3$ catal-sorbent under 10 vol% CH_4 condition at different temperatures (600, 650 and 700 °C)

Table S2 Amount of CO_2 captured, CO produced at CO_2 conversion step and CO produced, H_2 produced and coke accumulated at CH_4 conversion step in a consecutive 10 cycles

Cycle	CO_2 conversion step		CH_4 conversion step		
	CO_2 captured (mmol/g)	CO produced (mmol/g)	CO produced (mmol/g)	H_2 produced (mmol/g)	Coke accumulated (mmol/g)
1	10.5	35.9	15.5	75.7	58.2
2	11.2	34.4	16.8	66.0	65.6
3	11.3	34.2	17.6	63.7	71.6
4	11.9	34.0	16.3	60.3	76.6
5	11.1	33.9	17.5	62.8	82.3
6	10.7	34.7	14.7	56.5	85.8
7	8.1	34.3	14.1	48.3	85.8
8	9.1	33.5	15.4	46.7	84.7
9	9.5	33.0	15.2	46.7	84.0
10	9.5	33.9	15.2	47.6	83.2

Coke deposited in CH_4 treatment step: ~ 46.0 mmol/g

Table S3 crystallite size of C-Ni/CaO catal-sorbents in a consecutive 10 cycles of CO_2 and CH_4 conversion steps.

	Crystallite size (nm)[a]		
	Ni^0	CaO	$CaCO_3$
As prepared C-Ni/CaO	19.6	37.7	
After CO_2 conversion	20.1	27.1	34.9
After 1st CH_4 conversion	17.3	30.3	
After 5th CH_4 conversion	17.5	32.4	
After 10th CH_4 conversion	22.0	27.3	45.0

[a] Calculated by Scherrer equation