Supplementary Material to "Tuning the Ca content of Ni-Ca-Al layered-double hydroxide catalysts for low-temperature CO_2 methanation"

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Table S1. Molar proportions of co-precipitated Ni-Ca-Al LDH catalysts.

Sample	Label	Ni (%M)	Ca (%M)	Al (%M)	M^{II}/M^{III} molar ratio	Ni/Ca molar ratio
Ni63Ca3Al33	Ca3	63	3	33	2	21
Ni60Ca6Al33	Ca6	60	6	33	2	10
Ni55Ca11Al33	Ca11	55	11	33	2	5
Ni44Ca22Al33	Ca22	44	22	33	2	2
Ni33Ca33Al33	Ca33	33	33	33	2	1

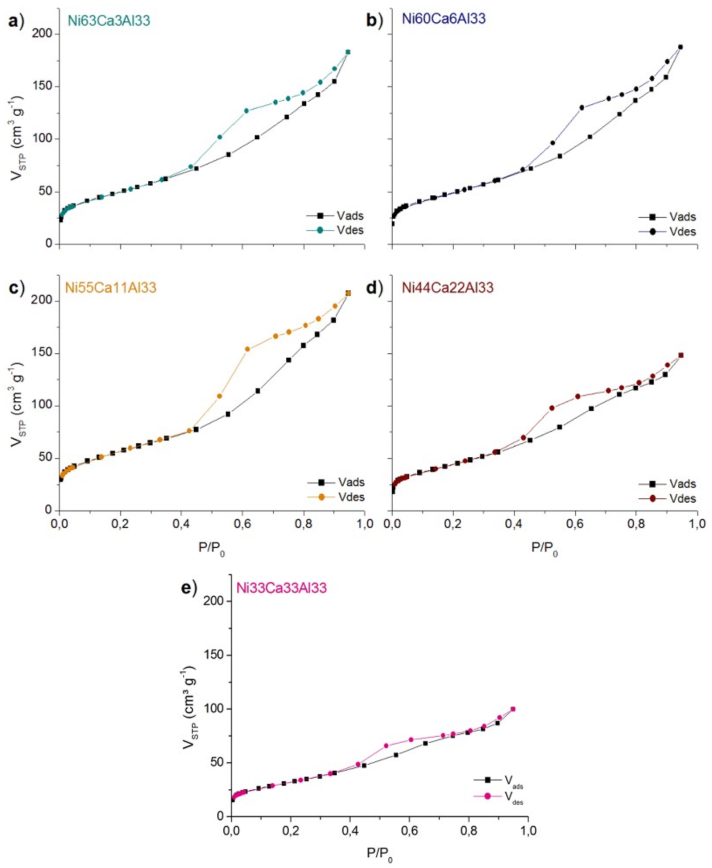

Figure S1. N_2 physisorption isotherms of Ni-Ca-Al samples calcined at 600 °C: (a) Ni63Ca3Al33, (b) Ni60Ca6Al33, (c) Ni55Ca11Al33, (d) Ni44Ca22Al33, and (e) Ni33Ca33Al33.

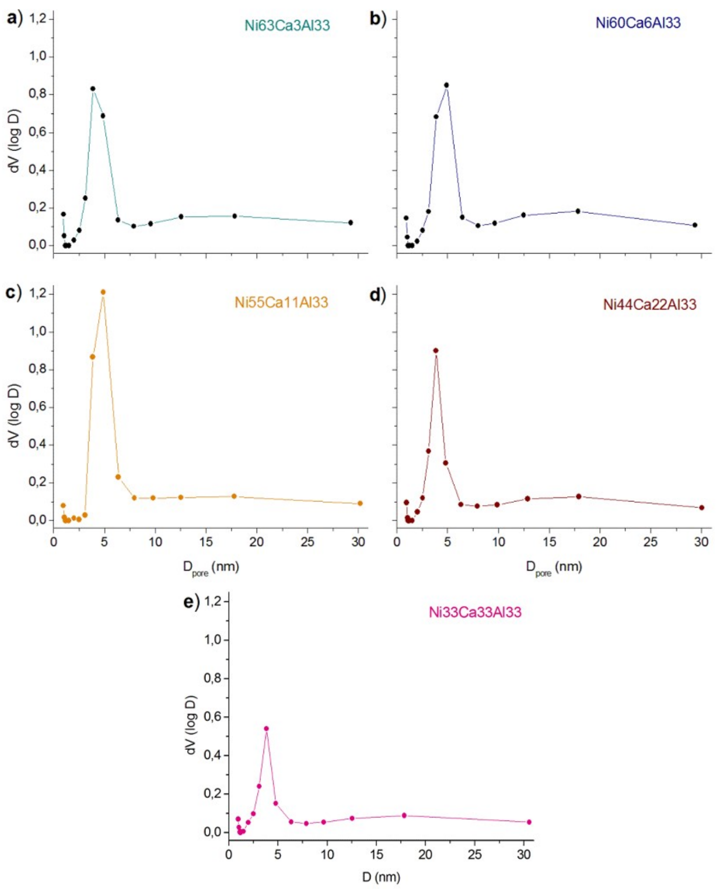

Figure S2. Pore diameter distributions from N_2 physisorption data of Ni-Ca-Al samples calcined at 600 °C: (a) Ni63Ca3Al33, (b) Ni60Ca6Al33, (c) Ni55Ca11Al33, (d) Ni44Ca22Al33, and (e) Ni33Ca33Al33.

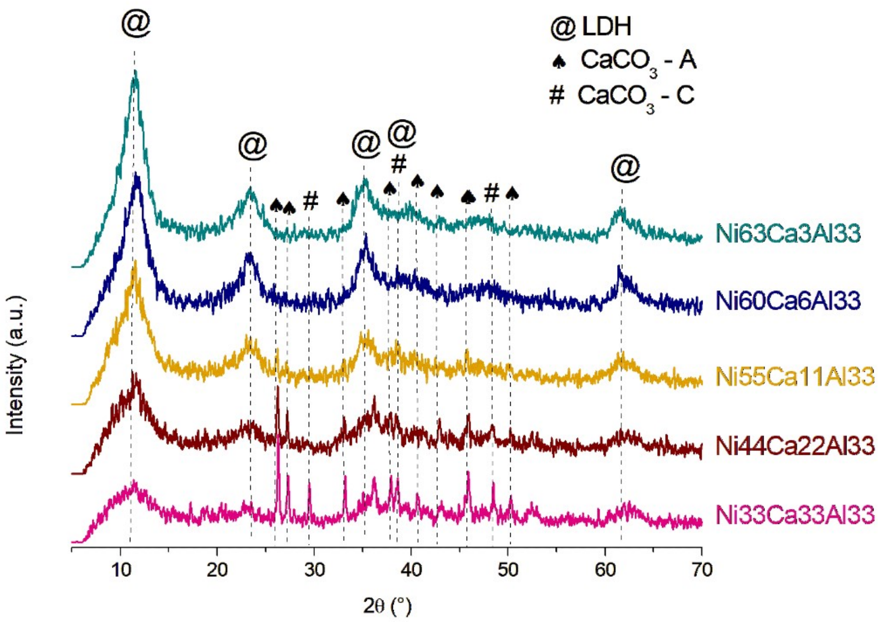

Figure S3. XRD patterns of as-prepared (LDH) Ni-Ca-Al samples.

Table S2. Quantified data from H_2-TPR profile deconvolutions of Ni-Ca-Al samples.

Sample	Peak temperature (°C)					Peak area (%)					Total area (a.u.)	Total H_2 consumption ($\mu mol\ g_{cat}^{-1}$)
	T1	T2	T3	T4	T5	A1	A2	A3	A4	A5		
Ni63Ca3Al33	508	613	690	-	-	8.4	67.7	23.9	-	-	4068.7	1522.2
Ni60Ca6Al33	502	622	701	-	-	11.8	62.5	25.7	-	-	3991.7	1481.6
Ni55Ca11Al33	518	631	704	-	-	11.5	57.2	31.2	-	-	3950.9	1470.8
Ni44Ca22Al33	479	578	662	702	-	5.6	38.7	50.4	5.3	-	3552.4	1306.9
Ni33Ca33Al33	491	561	659	719	741	6.4	17.3	57.8	13.1	5.4	3192.6	1182.7

Table S3. Quantified data from CO_2-TPD profile deconvolutions of reduced Ni-Ca-Al samples.

Sample	Peak temperature (°C)				Peak area (%)				Total area (a.u.)	CO_2 desorption ($\mu mol\ g_{cat}^{-1}$)	
	T1	T2	T3	T4	A1	A2	A3	A4		Weak-medium sites	Total sites
Ni63Ca3Al33	224	312	496	-	33.9	43.6	22.5	-	212.0	153.6	198.2
Ni60Ca6Al33	222	301	567	-	26.8	49.9	23.3	-	231.5	165.5	215.7
Ni55Ca11Al33	229	342	625	-	51.8	9.1	39.1	-	223.7	127.1	208.7
Ni44Ca22Al33	212	261	623	-	21.7	15.5	62.8	-	232.1	80.8	217.0
Ni33Ca33Al33	206	-	661	732	14.8	-	62.1	23.1	429.9	59.4	309.5

Table S4. Quantified data from H_2-TPD profile deconvolutions of reduced Ni-Ca-Al samples.

Sample	Peak temperature (°C)				Peak area (%)				Total area (a.u.)	Total H_2 desorption (μmol g_{cat}^{-1})
	T1	T2	T3	T4	A1	A2	A3	A4		
Ni63Ca3Al33	141	192	308	524	8.8	19.9	37.3	34.0	529.9	195.1b
Ni60Ca6Al33	143	195	327	554	6.5	24.7	41.3	27.5	820.2	301.2
Ni55Ca11Al33	148	211	364	545	10.5	31.6	32.9	25.0	720.1	265.8
Ni44Ca22Al33	165	245	374	474	16.5	20.1	15.7	47.8	670.0	247.8
Ni33Ca33Al33	176	299	427	540	24.5	25.7	38.7	26.5	339.6	133.9

Table S5. Turnover frequency (TOF) on stepwise catalytic tests at 200 °C over Ni-Ca-Al samples.

Sample	Turnover frequency, TOF (min^{-1})
Ni63Ca3Al33	3.8
Ni60Ca6Al33	2.9
Ni55Ca11Al33	3.1
Ni44Ca22Al33	3.1
Ni33Ca33Al33	3.2

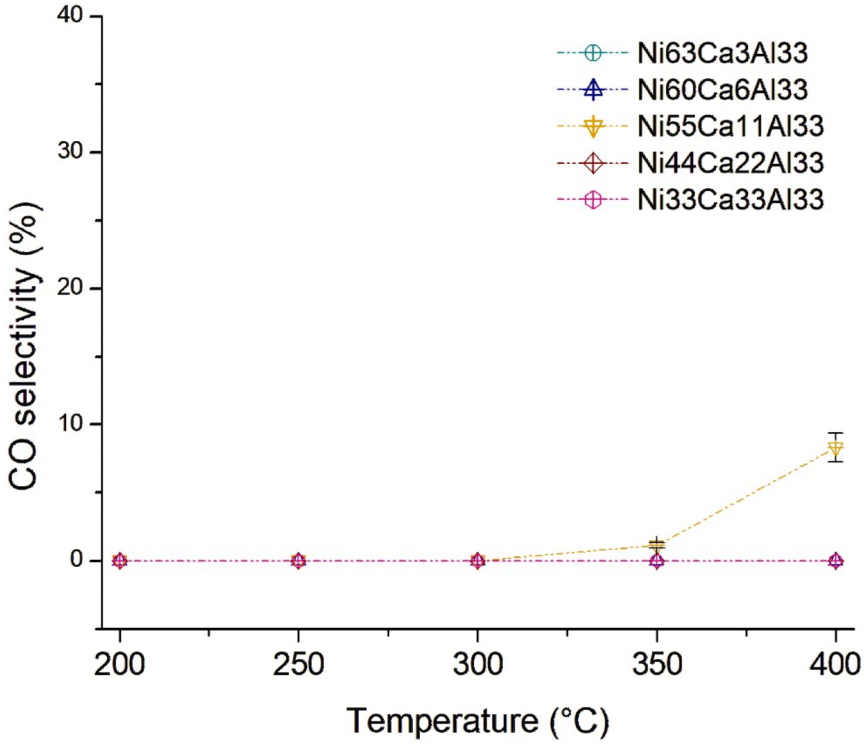

Figure S4. CO selectivity as a function of reactional temperature for CO_2 methanation over Ni-Ca-Al samples (GHSV = 60000 mL (g_{cat} h)$^{-1}$, H_2:CO_2:N_2 = 4:1:15, P = 1 atm).

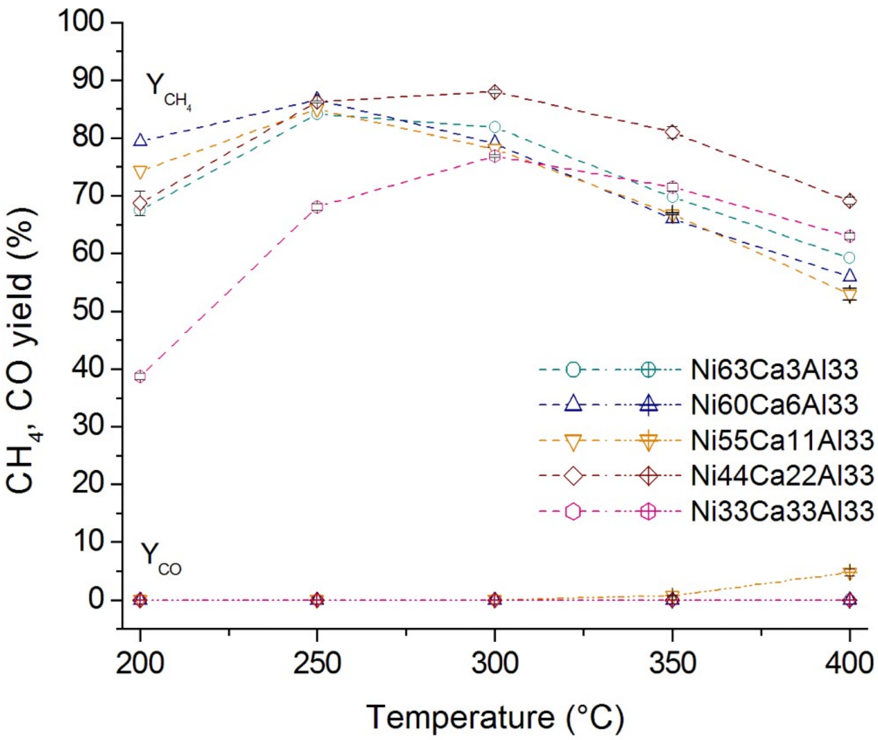

Figure S5. CH_4 and CO yield as a function of reactional temperature for CO_2 methanation over Ni-Ca-Al samples (GHSV = 60000 mL (g_{cat} h)$^{-1}$, H_2:CO_2:N_2 = 4:1:15, P = 1 atm).

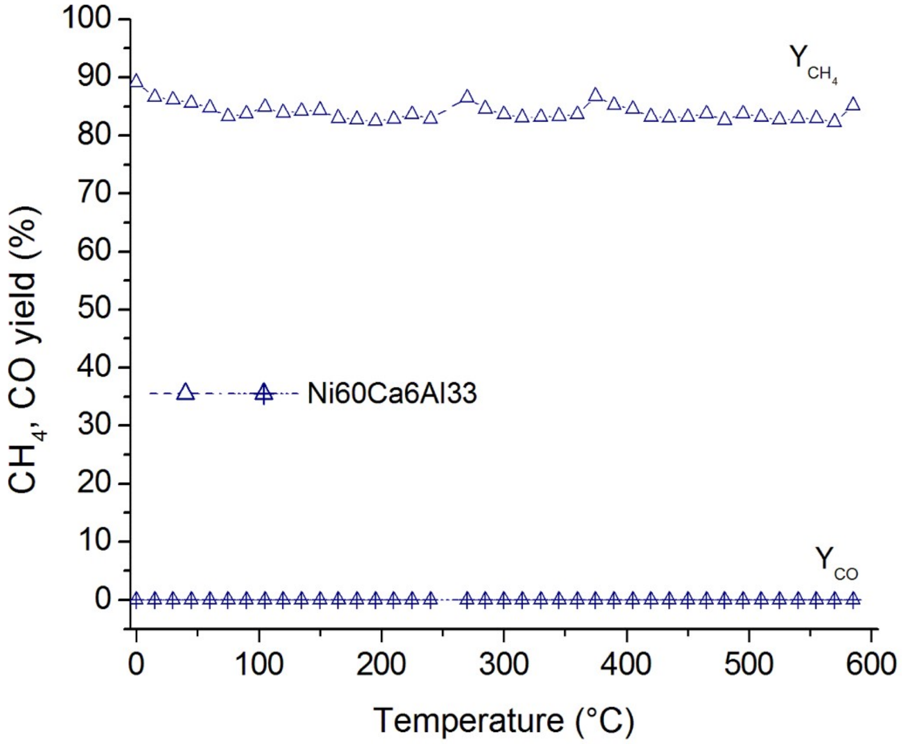

Figure S6. CH_4 and CO yield as a function of time-on-stream at 250 °C for CO_2 methanation over Ni60Ca6Al33 sample (GHSV = 60000 mL (g_{cat} h)$^{-1}$, H_2:CO_2:N_2 = 4:1:5, P = 1 atm).

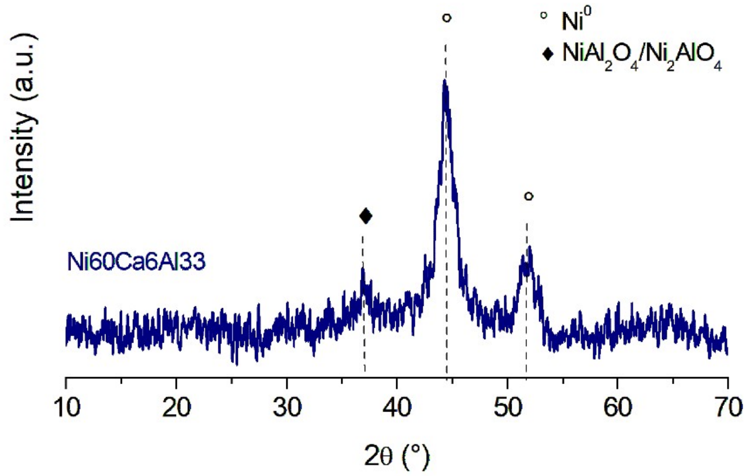

Figure S7. XRD pattern of Ni60Ca6Al33 sample spent on a 10 h stability test at 250 °C.

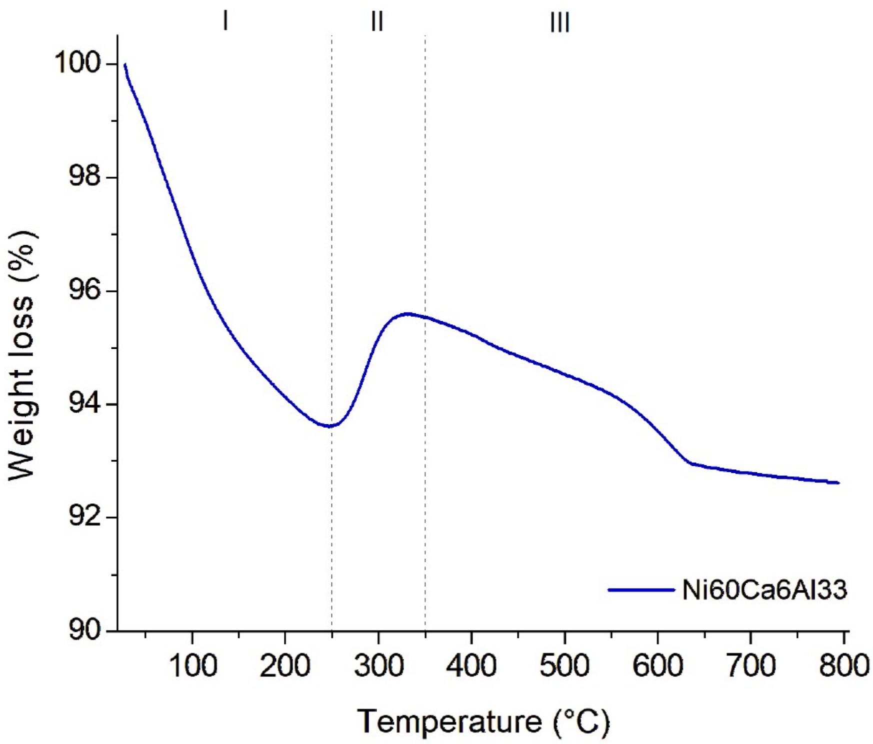

Figure S8. TPO profile of Ni60Ca6Al33 sample spent on a 10 h stability test at 250 °C.

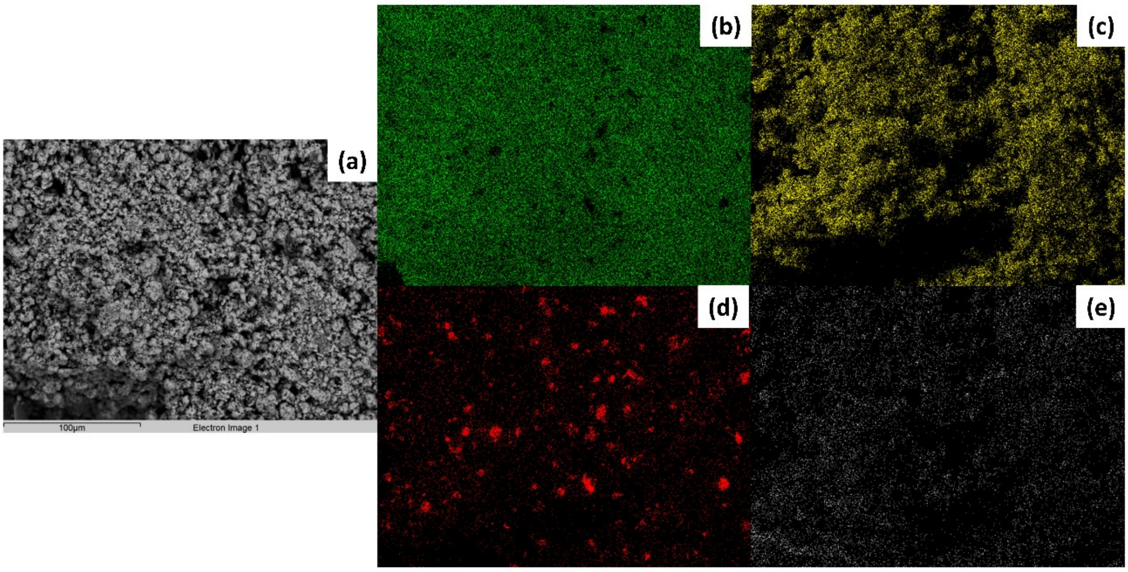

Figure S9. (a) Elemental distribution through EDS of Ni60Ca6Al33 sample spent on a 10 h stability test at 250 °C, where (b) Ni, (c) Al, (d) Ca, and (e) C.