Supplemental Information

Surface basicity controls C-C coupling rates during carbon dioxide-assisted oxidative coupling of methane over bifunctional Ca/ZnO catalysts

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Table S1. Summary of catalytic performance

Sample	CH_4 Conversion (%)	CO_2 Conversion (%)	C_2H_6 Yield (mmol/h)	C_2H_4 Yield (mmol/h)	CO Yield (mmol/h)
ZnO	6.7	7.3	0.01	0.005	0.60
0.4% Ca/ZnO	4.6	4.8	0.02	0.01	0.38
0.6% Ca/ZnO	2.9	1.9	0.05	0.03	0.11
2% Ca/ZnO	2.3	1.3	0.05	0.03	0.07
35% Ca/ZnO	1.7	0.9	0.04	0.02	0.05
45% Ca/ZnO	1.4	0.7	0.04	0.01	0.04
CaO	0.6	0.5	0.006	0.006	0.04

Reaction conditions: 850 °C; 100 mg catalyst; 13.3 mL/min total gas flow rate with P_{CH_4} = 0.25 atm, P_{CO_2} = 0.5 atm, P_{N_2} = 0.25 atm; 4 h on stream. All Ca loadings are reported in molar concentration of metal cations, as determined by ICP-MS (Table S2).

Table S2. Summary of physical properties of pure and binary metal oxides.

Sample	BET Surface Area[a] (m^2/g)	Ca Loading[b] (%)	Ca Surface Concentration[c] (%)
ZnO	2.7075 ± 0.0127		
0.4% Ca/ZnO	3.7840 ± 0.0193	0.41	6.9
0.6% Ca/ZnO	5.4405 ± 0.0418	0.62	12.1
2% Ca/ZnO	7.2562 ± 0.1101	2.04	10.2
35% Ca/ZnO	3.0918 ± 0.0095	34.94	62.1
45% Ca/ZnO	7.0391 ± 0.0375	44.55	71.8
CaO	39.6071 ± 0.0125		

[a]Determined by N_2 physisorption. [b]Determined by ICP-MS. [c]Determined by XPS

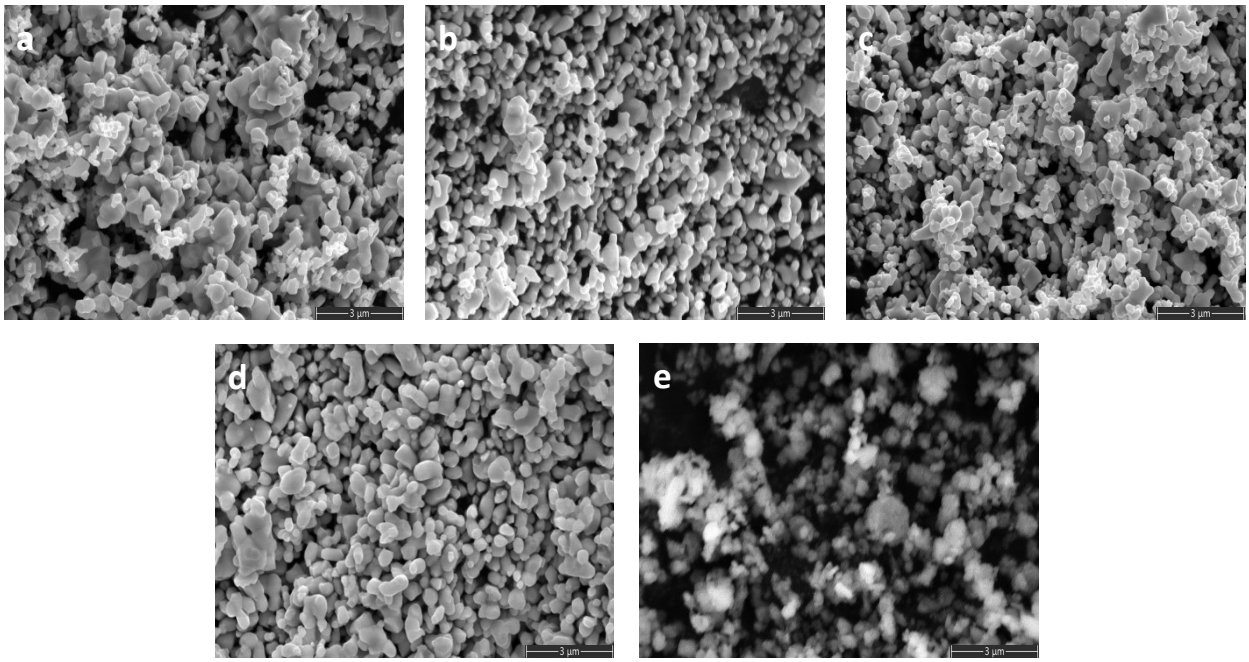

Figure S1. SEM images of calcined (a) ZnO, (b) 0.4% Ca/ZnO, (c) 0.6% Ca/ZnO, (d) 2% Ca/ZnO, (e) CaO.

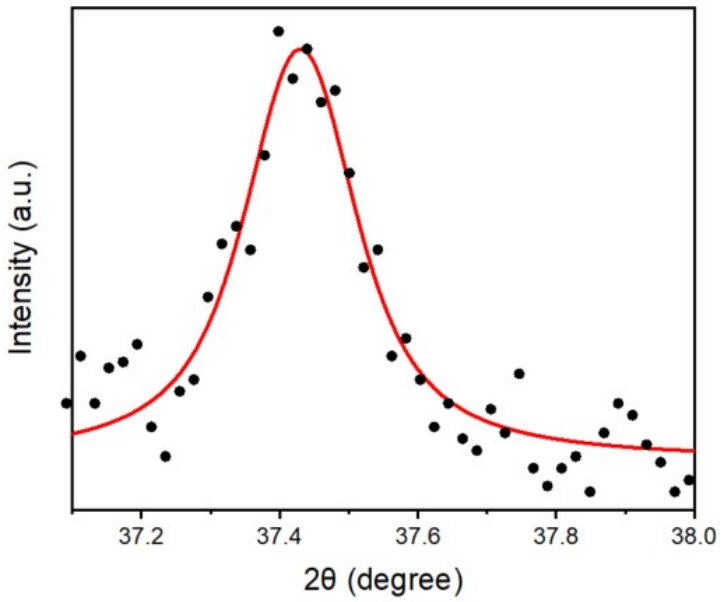

Figure S2. Magnification of CaO (200) peak in X-ray diffractogram characterizing the 2% Ca/ZnO sample.

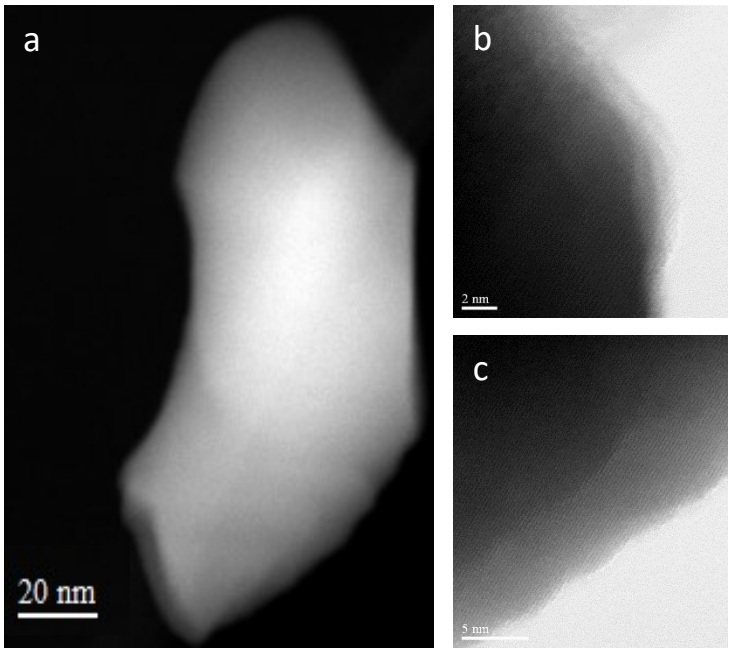

Figure S3. HAADF-STEM images of (a) a representative particle of 0.6% Ca/ZnO and (b-c) magnification of ZnO lattice fringes.

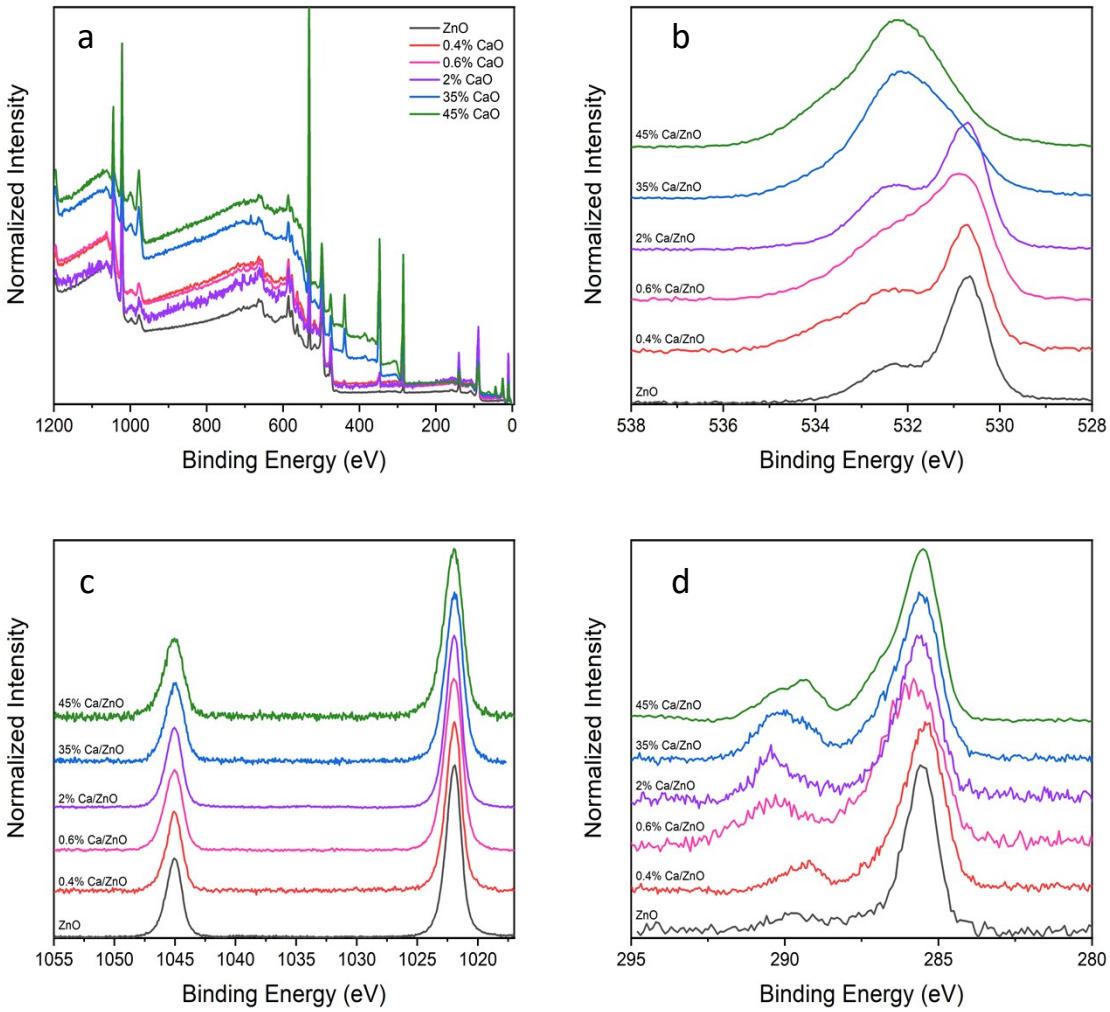

Figure S4. XPS spectra: (a) survey scan, and (b) O 1s, (c) Zn 2p, and (d) C 1s regions.

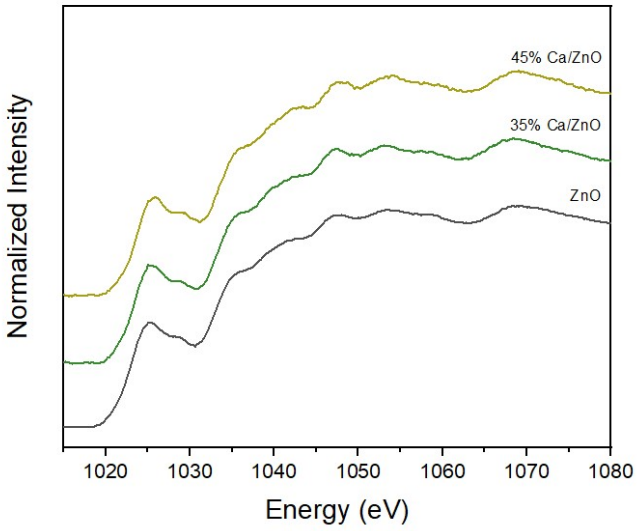

Figure S5. XANES spectra of Zn L_{23} region: high Ca loading samples compared to pure ZnO.

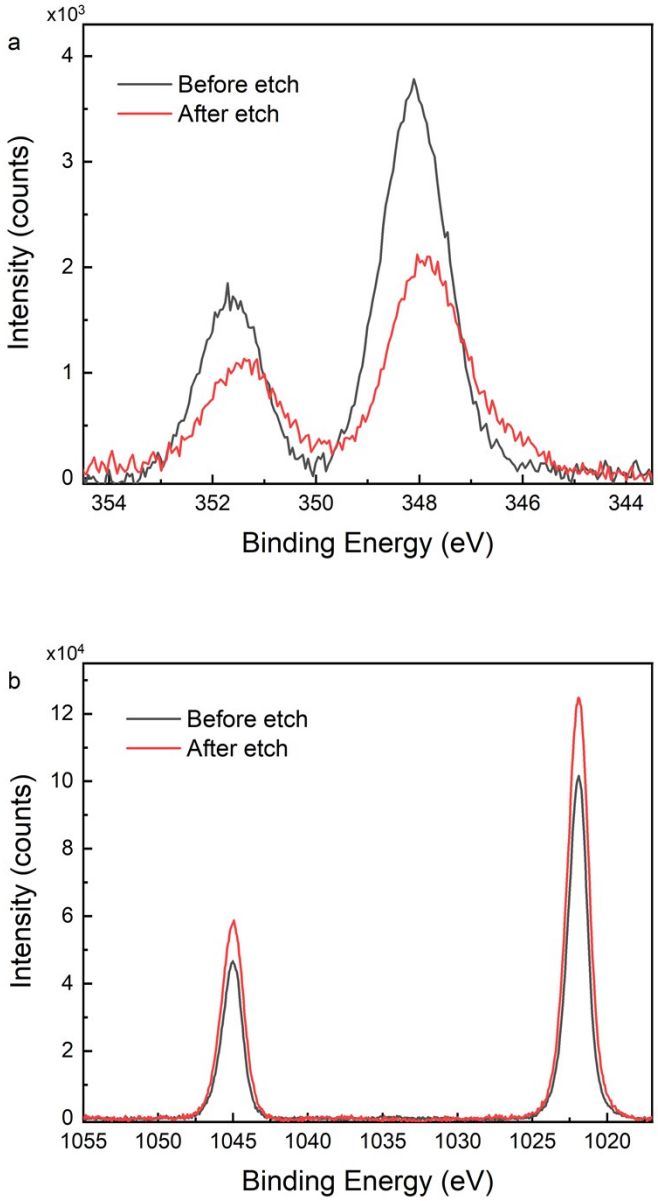

Figure S6. XPS scans of (a) Ca 2p and (b) Zn 2p regions characterizing 2% Ca/ZnO before and after an argon etch of the surface.

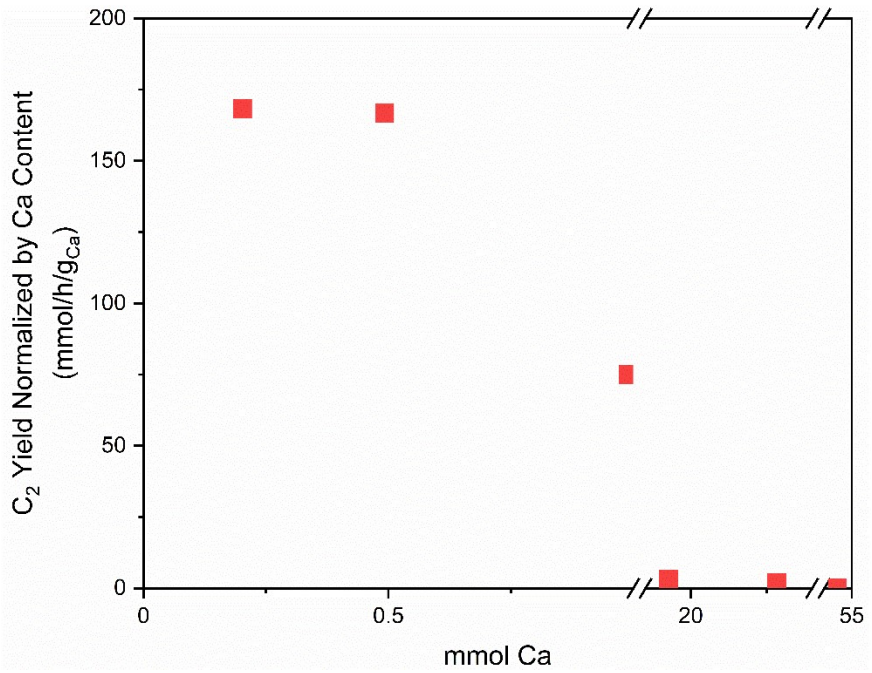

Figure S7. Methane coupling activity per calcium site demonstrates effectiveness of each calcium atom for different calcium loadings.

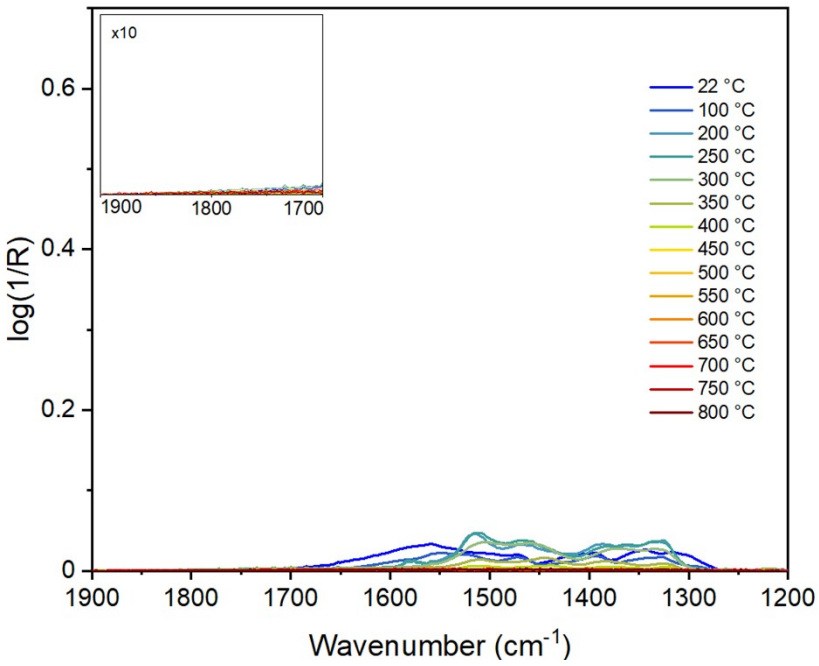

Figure S8. DRIFTS temperature programmed desorption of carbonate on ZnO in nitrogen ramping 1 °C/min. Spectra have been subtracted from sample at corresponding temperature prior to carbonate adsorption. Data are shown with the same axis scales as in main text Figure 4, for comparison.

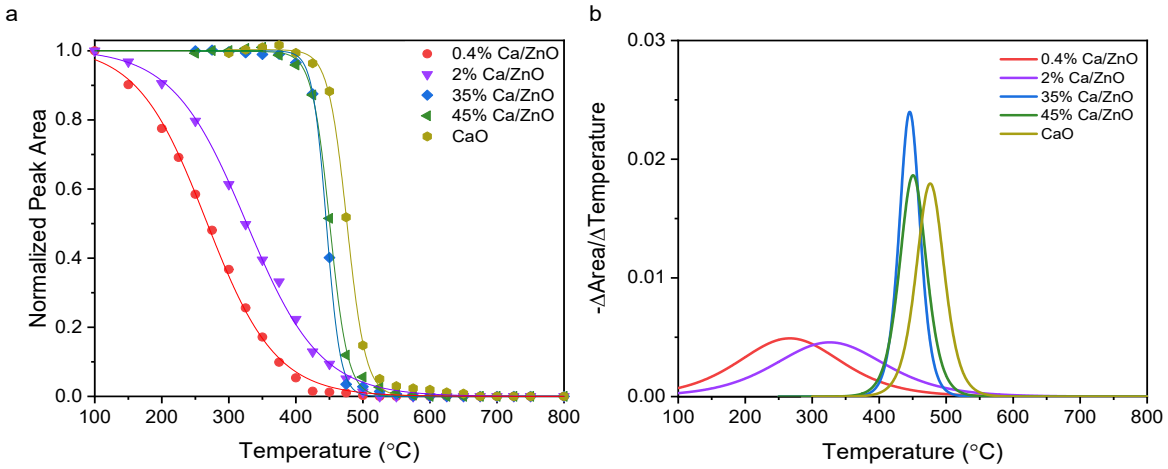

Figure S9. (a) DRIFTS-TPD profiles of integrated carbonate region and sigmoidal fit, (b) derivative of sigmoidal fits.

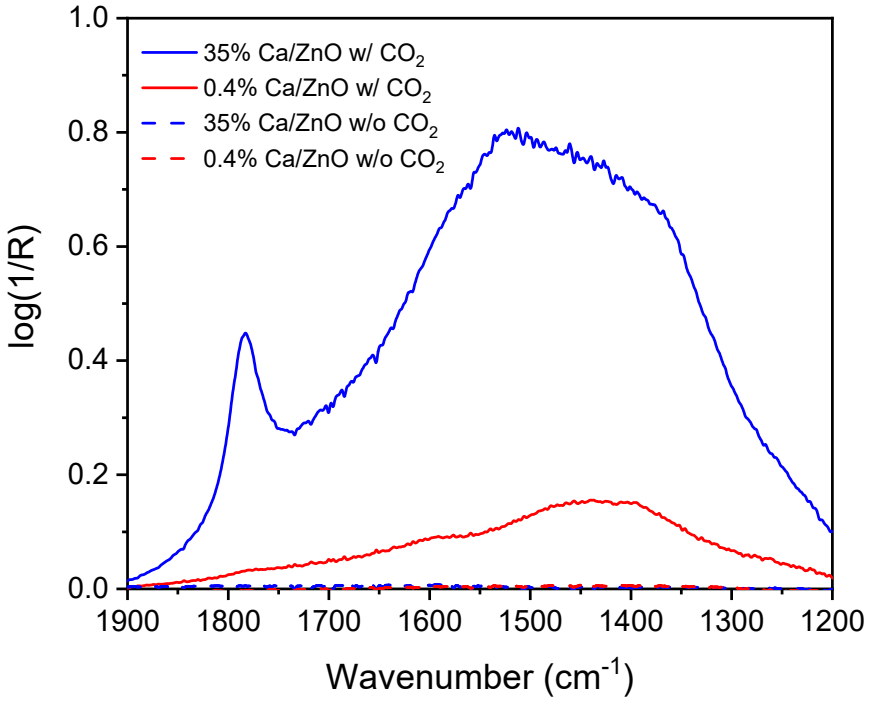

Figure S10. DRIFTS spectra characterizing the carbonate region at 850 °C in the absence and presence of 10% CO_2 during the temperature ramp.