Effect of surface morphology on the CH_4 interaction with $CaCO_3$: A DFT study

Supporting Information

Table S1. Parameters used in deriving the surface energies.

Surface	E_{slab} (eV)	N_{slab}	A (Å)	B (Å)	Area (Å^2)	E surf (eV)	Surface Energy(γ) J/m2
104	-892.672	24	16.192	9.980	161.592	0.036	0.57
105	-1540.759	41.5	27.644	9.980	275.885	0.041	0.66
103	-1182.880	32	21.572	9.980	215.289	0.053	0.85
001_CO_3	-854.408	23	9.980	9.980	99.600	0.061	0.97
110	-587.006	16	8.096	12.750	103.223	0.076	1.23
100	-1477.822	40	9.980	17.060	170.259	0.086	1.37
101_Ca	-879.664	24	12.750	9.980	127.247	0.096	1.54
101_CO_3	-850.098	24	9.980	17.060	170.259	0.104	1.66
001_Ca	-881.359	24	9.980	9.980	99.600	0.115	1.84

$$\gamma = \frac{\left(E_{slab} - N_{slab}E_{bulk}\right)}{2A_{slab}} \quad (1)$$

Energy of the calcite bulk = -226.049 eV

Table S2. The various adsorption positions and energies of the calcite surfaces studied (the highlighted rows have the highest adsorption energy for that surface)

$$E_{ads} = E_{surface+CH_4} - E_{surface} - E_{CH_4} \quad (2)$$

	Position	$E_{surface}$	E_{CH_4}	$E_{surface+CH_4}$	$E_{ads}\,(eV)$
104	**Atop_Ca (3 layers)**	**-892.672**	**-24.265**	**-917.022**	**-0.085**
	Atop_O (3 layers)	-892.672	-24.265	-916.957	-0.019

	Atop_C (3 layers)	-892.672	-24.265	-916.893	-0.050
	Atop_Ca (4 layers)	-1192.029	-24.265	-1216.384	-0.089
$001CO_3$	**Atop_C**	**-854.4078**	**-24.265**	**-878.776**	**-0.103**
	Atop_Ca	-854.4078	-24.265	-878.773	-0.100
	Atop_O	-854.4078	-24.265	-878.767	-0.094
001Ca	**Atop_Ca**	**-881.35943**	**-24.265**	**-905.940**	**-0.316**
	Atop_C	-881.35943	-24.265	-905.937	-0.312
	Atop_O	-881.35943	-24.265	-905.927	-0.303
100	**Atop_Ca**	**-1477.822**	**-24.265**	**-1502.630**	**-0.543**
	Atop_O_top	-1477.822	-24.265	-1502.411	-0.324
	Atop_C	-1477.822	-24.265	-1502.406	-0.319
	Atop_O_below	-1477.822	-24.265	-1502.371	-0.284
101Ca	**Atop_Ca**	**-879.664**	**-24.265**	**-904.335**	**-0.406**
	Atop_O_below	-879.664	-24.265	-904.300	-0.371
	Atop_C	-879.664	-24.265	-904.269	-0.340
	Atop_O_top	-879.664	-24.265	-904.257	-0.328
101CO3	**Atop_O**	**-850.0984**	**-24.265**	**-874.424**	**-0.061**
	Atop_Ca	-850.0984	-24.265	-874.423	-0.059
	Atop_C	-850.0984	-24.265	-874.421	-0.058
103	**Atop_C_lower(O)**	**-1182.880**	**-24.265**	**-1207.452**	**-0.307**
	Atop_O_lower	-1182.880	-24.265	-1207.445	-0.301
	Atop_Ca_upper	-1182.880	-24.265	-1207.390	-0.245
	Atop_O_upper	-1182.880	-24.265	-1207.341	-0.196
	Atop_C_Upper	-1182.880	-24.265	-1207.282	-0.137
	Atop_Ca_Lower	-1182.880	-24.265	-1207.246	-0.101
105	**Atop_Ca_upper**	**-1540.759**	**-24.265**	**-1565.215**	**-0.191**
	Atop_C_Upper	-1540.759	-24.265	-1565.126	-0.102
	Atop_O_upper	-1540.759	-24.265	-1565.110	-0.086
	Atop_C_lower	-1540.759	-24.265	-1565.079	-0.055
	Atop_O_lower	-1540.759	-24.265	-1565.076	-0.051
	Atop_Ca_Lower	-1540.759	-24.265	-1565.071	-0.046
110	**Atop_O1**	**-587.006**	**-24.265**	**-613.18**	**-1.910**
	Atop_Ca	-587.006	-24.265	-612.31	-1.036
	Atop_O3	-587.006	-24.265	-611.94	-0.666
	Atop_O2_top	-587.006	-24.265	-611.47	-0.198

	Atop_O1 (5 layers)	-739.269	-24.265	-765.453	-1.919

Table S3. The parameters used in deriving the adsorption capacity for the 110 surface

$$E_{ads.cap} = \frac{E_{ads}}{nA_{slab}} \quad (3)$$

N	N* $E_{methane}$ (eV)	$E_{surface+methane}$ (eV)	Ads.capacity (eV)	Ads. capacity/Area ($eV/Å^2$)
1	-24.265	-613.180	-1.910	-0.018
2	-48.530	-637.589	-1.027	-0.010
3	-72.795	-662.003	-0.734	-0.007
4	-97.060	-686.366	-0.575	-0.006
5	-121.325	-710.806	-0.495	-0.005
6	-145.591	-735.255	-0.443	-0.004
7	-169.856	-759.655	-0.399	-0.004
8	-194.121	-784.004	-0.360	-0.003
9	-218.386	-808.394	-0.334	-0.003
10	-242.651	-832.855	-0.320	-0.003
11	-266.916	-857.456	-0.321	-0.003
12	-291.181	-881.803	-0.301	-0.003
13	-315.446	-906.255	-0.293	-0.003
14	-339.711	-930.703	-0.285	-0.003
15	-363.976	-955.248	-0.284	-0.003
16	-388.241	-978.819	-0.223	-0.002
17	-412.506	-1003.175	-0.215	-0.002
18	-436.772	-1027.544	-0.209	-0.002
19	-461.037	-1051.870	-0.201	-0.002
20	-485.302	-1076.198	-0.195	-0.002
21	-509.567	-1100.542	-0.189	-0.002
22	-533.832	-1124.885	-0.184	-0.002
23	-558.097	-1149.259	-0.181	-0.002
24	-582.362	-1149.265	0.838	0.008

The E_{slab} and Area for the 110 surface can be found in Table S1.

Table S4. The parameters used in deriving the adsorption capacity for the 104surface

N	N* $E_{methane}$ (eV)	$E_{surface+methane}$ (eV)	Ads.capacity (eV)	Ads. capacity/Area ($eV/Å^2$)
1	-24.265	-917.022	-0.085	-0.0005
2	-48.530	-941.443	-0.120	-0.0007
3	-72.795	-965.849	-0.127	-0.0008
4	-97.060	-989.664	0.017	0.0001

The E_{slab} and Area for the 104 surface can be found in Table S1