Electronic Supplementary Information

From the perspectives of DFT calculations, thermodynamic modeling, and kinetic Monte Carlo simulations: the interaction between hydrogen and Sc_2C monolayers

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S1. Optimized structures and energies at LDA level

S1.1. Free H_2

Energy (eV): -6.69

Simulation cell vectors (Å):

a =	15.0000000000000000	0.0000000000000000	0.0000000000000000
b =	0.0000000000000000	15.0000000000000000	0.0000000000000000
c =	0.0000000000000000	0.0000000000000000	15.0000000000000000

Fractional coordinates:

No.	Element	x	y	z
1	H	0.376608868	0.326601368	0.343045126
2	H	0.360891132	0.368198632	0.317954874

S1.2. Sc_2C (S)

Energy (eV): -213.72

Simulation cell vectors (Å):

a =	8.4200792804032201	4.8613350391388108	0.0000000000000000
b =	0.0000000000000000	9.7226700782775914	0.0000000000000000
c =	0.0000000000000000	0.0000000000000000	21.2637805938720987

Fractional coordinates:

No.	Element	x	y	z
1	C	0.330770671	0.001121333	0.056775000
2	C	0.664104005	0.001121333	0.056775000
3	C	0.997437338	0.001121333	0.056775000
4	C	0.330770671	0.334454667	0.056775000
5	C	0.664104005	0.334454667	0.056775000
6	C	0.997437338	0.334454667	0.056775000
7	C	0.330770671	0.667788000	0.056775000
8	C	0.664104005	0.667788000	0.056775000
9	C	0.997437338	0.667788000	0.056775000
10	Sc	0.219659666	0.223343670	0.113445997
11	Sc	0.108548333	0.112232337	0.000104000

12	Sc	0.552993000	0.223343670	0.113445997
13	Sc	0.441881667	0.112232337	0.000104000
14	Sc	0.886326333	0.223343670	0.113445997
15	Sc	0.775215000	0.112232337	0.000104000
16	Sc	0.219659666	0.556677004	0.113445997
17	Sc	0.108548333	0.445565671	0.000104000
18	Sc	0.552993000	0.556677004	0.113445997
19	Sc	0.441881667	0.445565671	0.000104000
20	Sc	0.886326333	0.556677004	0.113445997
21	Sc	0.775215000	0.445565671	0.000104000
22	Sc	0.219659666	0.890010337	0.113445997
23	Sc	0.108548333	0.778899004	0.000104000
24	Sc	0.552993000	0.890010337	0.113445997
25	Sc	0.441881667	0.778899004	0.000104000
26	Sc	0.886326333	0.890010337	0.113445997
27	Sc	0.775215000	0.778899004	-0.000601425

S1.3. Sc_2CH_2 (SH)

Energy (eV): -298.31

Simulation cell vectors (Å):

a =	8.4200792804032201	4.8613350391388108	0.0000000000000000
b =	0.0000000000000000	9.7226700782775914	0.0000000000000000
c =	0.0000000000000000	0.0000000000000000	21.2637805938720987

Fractional coordinates:

No.	Element	x	y	z
1	H	0.223277208	0.226092817	0.142716198
2	H	0.112094579	0.114800501	0.353078748
3	H	0.556610541	0.226092817	0.142716198
4	H	0.445427912	0.114800501	0.353078748
5	H	0.889943874	0.226092817	0.142716198
6	H	0.778761246	0.114800501	0.353078748
7	H	0.223277208	0.55942615	0.142716198
8	H	0.112094579	0.448133835	0.353078748
9	H	0.556610541	0.55942615	0.142716198
10	H	0.445427912	0.448133835	0.353078748
11	H	0.889943874	0.55942615	0.142716198
12	H	0.778761246	0.448133835	0.353078748
13	H	0.223277208	0.892759483	0.142716198

14	H	0.112094579	0.781467168	0.353078748
15	H	0.556610541	0.892759483	0.142716198
16	H	0.445427912	0.781467168	0.353078748
17	H	0.889943874	0.892759483	0.142716198
18	H	0.778761246	0.781467168	0.353078748
19	C	0.000883628	0.003900035	0.24783144
20	C	0.334216961	0.003900035	0.24783144
21	C	0.667550295	0.003900035	0.24783144
22	C	0.000883628	0.337233369	0.24783144
23	C	0.334216961	0.337233369	0.24783144
24	C	0.667550295	0.337233369	0.24783144
25	C	0.000883628	0.670566702	0.24783144
26	C	0.334216961	0.670566702	0.24783144
27	C	0.667550295	0.670566702	0.24783144
28	Sc	0.223115264	0.22604049	0.306283049
29	Sc	0.112074315	0.114996815	0.189416595
30	Sc	0.556448597	0.22604049	0.306283049
31	Sc	0.445407648	0.114996815	0.189416595
32	Sc	0.889781931	0.22604049	0.306283049
33	Sc	0.778740981	0.114996815	0.189416595
34	Sc	0.223115264	0.559373823	0.306283049
35	Sc	0.112074315	0.448330149	0.189416595
36	Sc	0.556448597	0.559373823	0.306283049
37	Sc	0.445407648	0.448330149	0.189416595
38	Sc	0.889781931	0.559373823	0.306283049
39	Sc	0.778740981	0.448330149	0.189416595
40	Sc	0.223115264	0.892707157	0.306283049
41	Sc	0.112074315	0.781663482	0.189416595
42	Sc	0.556448597	0.892707157	0.306283049
43	Sc	0.445407648	0.781663482	0.189416595
44	Sc	0.889781931	0.892707157	0.306283049
45	Sc	0.778740981	0.781663482	0.189416595

S1.4. $Sc_2CH_2\_(H_2)_2$ ($SH\_(H_2)$)

Energy (eV): -421.60

Simulation cell vectors (Å):

a =	8.4200792804032201	4.8613350391388108	0.0000000000000000
b =	0.0000000000000000	9.7226700782775914	0.0000000000000000
c =	0.0000000000000000	0.0000000000000000	21.2637805938720987

Fractional coordinates:

No.	Element	x	y	z
1	H	0.145003185	0.096653394	0.111601137
2	H	0.145003185	0.429986715	0.111601137
3	H	0.145003185	0.763320088	0.111601137
4	H	0.478336513	0.096653394	0.111601137
5	H	0.478336513	0.429986715	0.111601137
6	H	0.478336513	0.763320088	0.111601137
7	H	0.811669827	0.096653394	0.111601137
8	H	0.811669827	0.429986715	0.111601137
9	H	0.811669827	0.763320088	0.111601137
10	H	0.054021060	0.144603238	0.119179934
11	H	0.054021060	0.477936566	0.119179934
12	H	0.054021060	0.811269879	0.119179934
13	H	0.387354404	0.144603238	0.119179934
14	H	0.387354404	0.477936566	0.119179934
15	H	0.387354404	0.811269879	0.119179934
16	H	0.720687747	0.144603238	0.119179934
17	H	0.720687747	0.477936566	0.119179934
18	H	0.720687747	0.811269879	0.119179934
19	H	0.243668213	0.197135732	0.466449112
20	H	0.243668213	0.530469060	0.466449112
21	H	0.243668213	0.863802373	0.466449112
22	H	0.577001572	0.197135732	0.466449112
23	H	0.577001572	0.530469060	0.466449112
24	H	0.577001572	0.863802373	0.466449112
25	H	0.910334885	0.197135732	0.466449112
26	H	0.910334885	0.530469060	0.466449112
27	H	0.910334885	0.863802373	0.466449112
28	H	0.199511245	0.288378745	0.459326237
29	H	0.199511245	0.621712089	0.459326237
30	H	0.199511245	0.955045402	0.459326237
31	H	0.532844603	0.288378745	0.459326237
32	H	0.532844603	0.621712089	0.459326237
33	H	0.532844603	0.955045402	0.459326237
34	H	0.866177917	0.288378745	0.459326237
35	H	0.866177917	0.621712089	0.459326237
36	H	0.866177917	0.955045402	0.459326237
37	H	0.231575921	0.223347306	0.186524674
38	H	0.231575921	0.556680620	0.186524674
39	H	0.231575921	0.890013993	0.186524674
40	H	0.564909279	0.223347306	0.186524674
41	H	0.564909279	0.556680620	0.186524674
42	H	0.564909279	0.890013993	0.186524674
43	H	0.898242593	0.223347306	0.186524674
44	H	0.898242593	0.556680620	0.186524674

45	H	0.898242593	0.890013993	0.186524674
46	H	0.120593630	0.111646406	0.391682595
47	H	0.120593630	0.444979727	0.391682595
48	H	0.120593630	0.778313100	0.391682595
49	H	0.453926951	0.111646406	0.391682595
50	H	0.453926951	0.444979727	0.391682595
51	H	0.453926951	0.778313100	0.391682595
52	H	0.787260294	0.111646406	0.391682595
53	H	0.787260294	0.444979727	0.391682595
54	H	0.787260294	0.778313100	0.391682595
55	C	0.008979550	0.001294274	0.289110303
56	C	0.008979550	0.334627599	0.289110303
57	C	0.008979550	0.667960942	0.289110303
58	C	0.342312872	0.001294274	0.289110303
59	C	0.342312872	0.334627599	0.289110303
60	C	0.342312872	0.667960942	0.289110303
61	C	0.675646245	0.001294274	0.289110303
62	C	0.675646245	0.334627599	0.289110303
63	C	0.675646245	0.667960942	0.289110303
64	Sc	0.231085479	0.223694444	0.347717047
65	Sc	0.231085479	0.557027757	0.347717047
66	Sc	0.231085479	0.890361130	0.347717047
67	Sc	0.564418793	0.223694444	0.347717047
68	Sc	0.564418793	0.557027757	0.347717047
69	Sc	0.564418793	0.890361130	0.347717047
70	Sc	0.897752166	0.223694444	0.347717047
71	Sc	0.897752166	0.557027757	0.347717047
72	Sc	0.897752166	0.890361130	0.347717047
73	Sc	0.119640507	0.112577163	0.230503127
74	Sc	0.119640507	0.445910484	0.230503127
75	Sc	0.119640507	0.779243827	0.230503127
76	Sc	0.452973843	0.112577163	0.230503127
77	Sc	0.452973843	0.445910484	0.230503127
78	Sc	0.452973843	0.779243827	0.230503127
79	Sc	0.786307156	0.112577163	0.230503127
80	Sc	0.786307156	0.445910484	0.230503127
81	Sc	0.786307156	0.779243827	0.230503127

S1.5. $Sc_2CH_2\_(H_2)_4$ ($SH\_(H_2)_2$)

Energy (eV): -543.85

Simulation cell vectors (Å):

a = 8.4200792804032201 4.8613350391388108 0.0000000000000000

b = 0.0000000000000000 9.7226700782775914 0.0000000000000000
c = 0.0000000000000000 0.0000000000000000 21.2637805938720987

Fractional coordinates:

No.	Element	x	y	z
1	H	0.028702566	0.323874059	0.020834385
2	H	0.028702566	0.657207402	0.020834385
3	H	0.028702566	0.990540715	0.020834385
4	H	0.362035895	0.323874059	0.020834385
5	H	0.362035895	0.657207402	0.020834385
6	H	0.362035895	0.990540715	0.020834385
7	H	0.695369208	0.323874059	0.020834385
8	H	0.695369208	0.657207402	0.020834385
9	H	0.695369208	0.990540715	0.020834385
10	H	0.286476182	0.027488973	0.000430692
11	H	0.286476182	0.360822307	0.000430692
12	H	0.286476182	0.694155621	0.000430692
13	H	0.619809525	0.027488973	0.000430692
14	H	0.619809525	0.360822307	0.000430692
15	H	0.619809525	0.694155621	0.000430692
16	H	0.953142839	0.027488973	0.000430692
17	H	0.953142839	0.360822307	0.000430692
18	H	0.953142839	0.694155621	0.000430692
19	H	0.020715555	0.313061930	0.533923235
20	H	0.020715555	0.646395273	0.533923235
21	H	0.020715555	0.979728587	0.533923235
22	H	0.354048874	0.313061930	0.533923235
23	H	0.354048874	0.646395273	0.533923235
24	H	0.354048874	0.979728587	0.533923235
25	H	0.687382218	0.313061930	0.533923235
26	H	0.687382218	0.646395273	0.533923235
27	H	0.687382218	0.979728587	0.533923235
28	H	0.318413920	0.053028397	0.555565276
29	H	0.318413920	0.386361725	0.555565276
30	H	0.318413920	0.719695039	0.555565276
31	H	0.651747264	0.053028397	0.555565276
32	H	0.651747264	0.386361725	0.555565276
33	H	0.651747264	0.719695039	0.555565276
34	H	0.985080577	0.053028397	0.555565276
35	H	0.985080577	0.386361725	0.555565276
36	H	0.985080577	0.719695039	0.555565276
37	H	0.152073128	0.093746859	0.103517139
38	H	0.152073128	0.427080203	0.103517139
39	H	0.152073128	0.760413516	0.103517139
40	H	0.485406457	0.093746859	0.103517139

41	H	0.485406457	0.427080203	0.103517139
42	H	0.485406457	0.760413516	0.103517139
43	H	0.818739800	0.093746859	0.103517139
44	H	0.818739800	0.427080203	0.103517139
45	H	0.818739800	0.760413516	0.103517139
46	H	0.060719740	0.139146706	0.111000045
47	H	0.060719740	0.472480049	0.111000045
48	H	0.060719740	0.805813362	0.111000045
49	H	0.394053080	0.139146706	0.111000045
50	H	0.394053080	0.472480049	0.111000045
51	H	0.394053080	0.805813362	0.111000045
52	H	0.727386423	0.139146706	0.111000045
53	H	0.727386423	0.472480049	0.111000045
54	H	0.727386423	0.805813362	0.111000045
55	H	0.250334959	0.191603209	0.453260311
56	H	0.250334959	0.524936523	0.453260311
57	H	0.250334959	0.858269896	0.453260311
58	H	0.583668272	0.191603209	0.453260311
59	H	0.583668272	0.524936523	0.453260311
60	H	0.583668272	0.858269896	0.453260311
61	H	0.917001645	0.191603209	0.453260311
62	H	0.917001645	0.524936523	0.453260311
63	H	0.917001645	0.858269896	0.453260311
64	H	0.204730027	0.283066911	0.445935530
65	H	0.204730027	0.616400224	0.445935530
66	H	0.204730027	0.949733597	0.445935530
67	H	0.538063385	0.283066911	0.445935530
68	H	0.538063385	0.616400224	0.445935530
69	H	0.538063385	0.949733597	0.445935530
70	H	0.871396699	0.283066911	0.445935530
71	H	0.871396699	0.616400224	0.445935530
72	H	0.871396699	0.949733597	0.445935530
73	H	0.238942793	0.216454263	0.176521183
74	H	0.238942793	0.549787592	0.176521183
75	H	0.238942793	0.883120905	0.176521183
76	H	0.572276106	0.216454263	0.176521183
77	H	0.572276106	0.549787592	0.176521183
78	H	0.572276106	0.883120905	0.176521183
79	H	0.905609479	0.216454263	0.176521183
80	H	0.905609479	0.549787592	0.176521183
81	H	0.905609479	0.883120905	0.176521183
82	H	0.127554781	0.105007431	0.380830998
83	H	0.127554781	0.438340767	0.380830998
84	H	0.127554781	0.771674081	0.380830998
85	H	0.460888124	0.105007431	0.380830998
86	H	0.460888124	0.438340767	0.380830998

87	H	0.460888124	0.771674081	0.380830998
88	H	0.794221468	0.105007431	0.380830998
89	H	0.794221468	0.438340767	0.380830998
90	H	0.794221468	0.771674081	0.380830998
91	C	0.016116434	0.327777412	0.278653712
92	C	0.016116434	0.661110726	0.278653712
93	C	0.016116434	0.994444099	0.278653712
94	C	0.349449757	0.327777412	0.278653712
95	C	0.349449757	0.661110726	0.278653712
96	C	0.349449757	0.994444099	0.278653712
97	C	0.682783100	0.327777412	0.278653712
98	C	0.682783100	0.661110726	0.278653712
99	C	0.682783100	0.994444099	0.278653712
100	Sc	0.238090462	0.217112283	0.337295072
101	Sc	0.238090462	0.550445611	0.337295072
102	Sc	0.238090462	0.883778924	0.337295072
103	Sc	0.571423820	0.217112283	0.337295072
104	Sc	0.571423820	0.550445611	0.337295072
105	Sc	0.571423820	0.883778924	0.337295072
106	Sc	0.904757133	0.217112283	0.337295072
107	Sc	0.904757133	0.550445611	0.337295072
108	Sc	0.904757133	0.883778924	0.337295072
109	Sc	0.126841559	0.105895579	0.220026616
110	Sc	0.126841559	0.439228914	0.220026616
111	Sc	0.126841559	0.772562228	0.220026616
112	Sc	0.460174887	0.105895579	0.220026616
113	Sc	0.460174887	0.439228914	0.220026616
114	Sc	0.460174887	0.772562228	0.220026616
115	Sc	0.793508201	0.105895579	0.220026616
116	Sc	0.793508201	0.439228914	0.220026616
117	Sc	0.793508201	0.772562228	0.220026616

S2. Vibrational frequencies

All values shown here are in cm^{-1}. The normal mode analysis yield 3N modes. For free H_2 in the gas phase, we have removed five modes with low-lying or imaginary frequencies which are associated with the translation and rotation. For Sc_2C with different adsorbates, we have, if not stated otherwise, removed three modes with low-lying or imaginary frequencies which correspond to the translation of the whole simulation cell.

S2.1. Free H_2

No.	Freq (cm^{-1})
1	4181.691954

S2.2. Sc_2C (S)

No.	Freq (cm^{-1})	No.	Freq (cm^{-1})	No.	Freq (cm^{-1})	No.	Freq (cm^{-1})
1	548.425147	21	438.579838	41	242.825289	61	182.090887
2	548.351082	22	438.544083	42	242.745648	62	181.994740
3	548.330910	23	438.511655	43	237.800977	63	181.873417
4	548.275081	24	438.489323	44	237.685944	64	181.648645
5	542.344027	25	429.495945	45	236.826899	65	181.635660
6	542.110322	26	429.418723	46	236.695071	66	181.461760
7	527.361711	27	312.392973	47	220.738821	67	157.386708
8	527.321813	28	305.152489	48	220.643239	68	157.379026
9	519.315564	29	305.085788	49	220.632957	69	156.024410
10	519.155313	30	305.049678	50	220.511653	70	155.915062
11	493.699263	31	305.020630	51	220.499332	71	155.394793
12	487.563251	32	304.923273	52	220.464490	72	155.294817
13	486.242075	33	304.831698	53	220.224525	73	116.554533
14	486.223838	34	285.288051	54	220.206178	74	116.500808
15	480.052462	35	280.604832	55	220.148929	75	116.044594
16	479.880184	36	280.477575	56	220.084883	76	116.020464
17	479.760759	37	243.495066	57	218.631089	77	115.614820
18	479.640907	38	243.475150	58	217.865066	78	115.572761
19	438.629387	39	243.193758	59	191.105843		
20	438.605146	40	243.162573	60	190.975123		

S2.3. Sc_2CH_2 (SH)

No.	Freq (cm^{-1})	No.	Freq (cm^{-1})	No.	Freq (cm^{-1})	No.	Freq (cm^{-1})
1	1023.514787	34	924.498026	67	485.007788	100	296.719650
2	1023.495736	35	924.474769	68	484.566760	101	267.229440
3	1023.098966	36	922.876910	69	484.563636	102	267.223930
4	1023.078747	37	921.969050	70	483.623500	103	267.130997
5	1022.663086	38	907.981354	71	483.575046	104	267.113945
6	1022.514115	39	832.503899	72	441.540563	105	267.034872
7	993.095178	40	832.501780	73	441.531455	106	267.031100
8	993.083395	41	832.092862	74	422.867503	107	250.315666
9	992.131324	42	832.072264	75	422.805819	108	250.295987
10	992.105546	43	831.346403	76	420.540787	109	238.896776
11	991.926419	44	831.344587	77	420.540720	110	238.891410
12	991.772364	45	830.428828	78	417.132700	111	238.036761
13	976.397447	46	830.424260	79	417.073120	112	238.025885
14	976.296095	47	829.842799	80	389.314702	113	224.611825
15	971.441005	48	829.833173	81	384.099883	114	224.586593
16	971.389610	49	829.556165	82	343.955821	115	224.527115
17	966.665581	50	829.547455	83	339.171074	116	224.523539
18	966.580043	51	807.424689	84	339.142314	117	224.392444
19	964.392053	52	807.421223	85	337.497219	118	224.371486
20	964.387645	53	806.238919	86	337.486233	119	204.659430
21	939.588651	54	806.235883	87	337.451276	120	204.383880
22	937.561753	55	670.757024	88	337.436342	121	177.421007
23	930.381954	56	606.013269	89	337.277394	122	177.383164
24	930.266070	57	605.984646	90	337.235361	123	177.157639
25	930.190878	58	604.128083	91	301.037596	124	177.155433
26	930.189142	59	604.003011	92	301.033724	125	177.120333
27	929.072157	60	602.755209	93	300.468971	126	177.077550
28	928.946160	61	602.735294	94	300.440675	127	162.070731
29	926.756608	62	550.781545	95	297.255867	128	162.043165
30	926.755914	63	550.754024	96	297.249123	129	161.605696
31	925.876873	64	546.139645	97	297.053263	130	161.594037
32	925.851821	65	546.107507	98	297.040122	131	161.104392
33	924.803449	66	485.012627	99	296.726374	132	161.094387

S2.4. $Sc_2CH_2\_(H_2)_2$ ($SH\_(H_2)$)

Apart from the three modes with imaginary frequencies associated with the translation modes, there are two further modes with small imaginary frequencies that could not be eliminated by the geometry optimization. The two imaginary frequencies have been, more or less arbitrarily, replaced by the value of 10.0 cm^{-1} which is used for the evaluation of the partition below.

No.	Freq (cm^{-1})	No.	Freq (cm^{-1})	No.	Freq (cm^{-1})	No.	Freq (cm^{-1})
1	3910.710188	44	1008.802931	87	626.210378	130	345.028129
2	3910.689737	45	1008.737606	88	611.685571	131	344.958464
3	3909.274497	46	1002.839999	89	611.556075	132	341.864422
4	3909.253518	47	1002.803935	90	608.443806	133	341.799438
5	3906.479402	48	1001.241570	91	608.417699	134	340.929201
6	3906.347921	49	983.204556	92	584.615794	135	338.312293
7	3905.822206	50	983.107360	93	584.581006	136	337.903371
8	3905.237767	51	982.661902	94	563.978750	137	337.099947
9	3904.537737	52	982.637060	95	563.853216	138	336.984441
10	3904.529253	53	978.534884	96	561.584763	139	335.192898
11	3904.473277	54	978.524574	97	561.556215	140	335.064112
12	3904.459545	55	974.997250	98	550.770527	141	329.122013
13	3901.432673	56	962.038348	99	550.706522	142	328.882379
14	3900.891785	57	911.481296	100	541.029581	143	328.685396
15	3900.667439	58	911.475304	101	541.017061	144	328.527522
16	3900.265004	59	911.013167	102	454.485218	145	302.740616
17	3898.679240	60	910.977964	103	454.467870	146	302.709476
18	3894.798259	61	908.916931	104	449.814501	147	301.377181
19	1095.862426	62	908.910531	105	449.773882	148	301.371343
20	1095.842290	63	901.475418	106	449.492252	149	299.182136
21	1095.784356	64	901.460167	107	449.486475	150	299.035954
22	1095.755112	65	900.709783	108	407.667404	151	298.103257
23	1082.307599	66	900.661866	109	407.588550	152	298.075674
24	1082.247406	67	900.281918	110	407.313779	153	297.787650
25	1062.931917	68	900.270543	111	407.224089	154	297.668547
26	1062.901758	69	899.560849	112	403.807408	155	276.288608
27	1059.252247	70	899.547786	113	403.805337	156	276.204827
28	1059.210319	71	896.920673	114	400.084257	157	274.064044
29	1058.354073	72	896.908703	115	400.075856	158	273.617082
30	1055.146537	73	665.588601	116	369.607248	159	273.387739
31	1055.113150	74	649.184000	117	360.285626	160	273.341203
32	1052.472508	75	649.115093	118	356.458434	161	273.216410
33	1051.268016	76	647.037479	119	356.321298	162	271.783599
34	1051.220774	77	647.016392	120	355.811693	163	263.147775
35	1049.150590	78	639.327838	121	355.740632	164	262.690860
36	1049.101551	79	639.286744	122	349.192377	165	260.412424
37	1023.981995	80	635.336981	123	349.053802	166	260.256729
38	1023.939930	81	633.869526	124	348.942575	167	259.949768
39	1018.515936	82	627.524378	125	348.772343	168	259.497480
40	1018.449262	83	627.430946	126	348.740134	169	259.171610
41	1013.838575	84	626.572779	127	347.780350	170	258.800966
42	1013.780167	85	626.532853	128	347.638073	171	256.947739
43	1009.844580	86	626.229449	129	347.380993	172	256.938520

No.	Freq (cm^{-1})	No.	Freq (cm^{-1})	No.	Freq (cm^{-1})	No.	Freq (cm^{-1})
173	248.777016	190	211.641144	207	179.731552	224	141.028000
174	248.690753	191	210.497723	208	178.632889	225	132.570588
175	247.652859	192	210.328706	209	178.524566	226	132.458125
176	246.612779	193	205.230280	210	174.783051	227	121.602149
177	236.067382	194	205.139723	211	173.054313	228	121.175201
178	235.713249	195	204.116810	212	171.591468	229	114.160385
179	235.493026	196	201.137871	213	170.731370	230	113.227243
180	234.567158	197	200.938523	214	170.449295	231	112.091537
181	224.510933	198	198.416615	215	169.842480	232	111.609967
182	224.356713	199	193.416145	216	169.653243	233	91.821994
183	222.993451	200	192.499488	217	167.267832	234	91.486659
184	222.915306	201	186.164634	218	166.950757	235	66.589147
185	219.415242	202	182.439387	219	158.409345	236	66.160788
186	219.271970	203	182.184029	220	158.057125	237	65.090039
187	215.760016	204	181.539065	221	142.188814	238	63.733971
188	215.486180	205	181.485014	222	141.930335	239	10.000000
189	215.014049	206	179.785722	223	141.384425	240	10.000000

S2.5. $Sc_2CH_2\_(H_2)_4$ ($SH\_(H_2)_2$)

Apart from the three modes with imaginary frequencies associated with the translation modes, there are several other modes showing imaginary frequencies. These modes are associated with the rotation and the translation of the H_2 molecules in the second layer. Therefore, we have assumed all H_2 molecules from the second layer behave like a particle in a box in two dimensions, and that they can freely rotate in one dimension. Thus, we have removed 54 modes below, even if not all of them feature imaginary frequencies. When calculating the partition function, we treat these modes as translational and rotational degrees of freedom.

No.	Freq (cm^{-1})	No.	Freq (cm^{-1})	No.	Freq (cm^{-1})	No.	Freq (cm^{-1})
1	4130.783192	15	4121.594013	29	3867.391971	43	1076.405215
2	4130.776390	16	4121.472379	30	3866.809951	44	1076.361796
3	4130.234578	17	4117.106146	31	3866.087291	45	1072.147169
4	4130.228116	18	4115.213372	32	3866.085867	46	1072.077426
5	4128.710116	19	3872.069577	33	3865.974581	47	1072.046547
6	4128.658779	20	3871.982665	34	3865.970183	48	1069.084638
7	4128.344624	21	3871.175140	35	3861.613242	49	1064.947226
8	4128.309013	22	3870.889424	36	3859.459905	50	1064.842163
9	4123.594555	23	3870.666927	37	1105.332546	51	1064.031600
10	4123.586200	24	3870.656386	38	1105.331587	52	1063.991266
11	4122.983133	25	3869.243470	39	1104.884251	53	1062.110114
12	4122.974174	26	3869.242408	40	1104.873050	54	1062.027303
13	4121.739385	27	3868.798509	41	1093.101002	55	1033.961629
14	4121.707514	28	3867.949944	42	1093.025236	56	1033.905297

No.	Freq (cm^{-1})	No.	Freq (cm^{-1})	No.	Freq (cm^{-1})	No.	Freq (cm^{-1})
57	1026.351125	100	677.182990	143	375.709994	186	299.598338
58	1026.277879	101	674.151543	144	375.488215	187	299.143307
59	1025.005302	102	674.046156	145	372.598881	188	299.061419
60	1024.947962	103	673.488897	146	367.944162	189	296.663604
61	1019.098316	104	673.359289	147	367.305021	190	296.633391
62	1014.557489	105	661.808620	148	364.854833	191	295.779108
63	1014.475074	106	661.201030	149	364.746621	192	293.924369
64	1011.825377	107	661.183988	150	363.652205	193	292.917558
65	1008.507086	108	653.613431	151	363.452475	194	290.955409
66	1008.446840	109	653.574059	152	360.731066	195	289.987915
67	991.177263	110	588.126069	153	357.612114	196	289.562641
68	991.126509	111	588.086888	154	355.896711	197	285.690182
69	990.310438	112	572.641747	155	344.001722	198	285.280801
70	990.299293	113	572.625839	156	343.867546	199	283.288627
71	980.492191	114	571.390414	157	342.113221	200	283.173719
72	980.423989	115	571.277635	158	341.919237	201	282.763619
73	969.414098	116	549.451930	159	341.286015	202	282.653459
74	953.341381	117	549.394387	160	341.275064	203	275.522669
75	912.009217	118	543.968208	161	338.454242	204	274.980959
76	912.004500	119	543.959075	162	338.379431	205	274.726772
77	911.280976	120	456.788048	163	325.272542	206	274.572890
78	911.221674	121	456.764791	164	323.300822	207	265.642328
79	907.825252	122	453.145437	165	323.206548	208	265.584652
80	907.815247	123	453.125656	166	321.012014	209	261.974270
81	903.464015	124	452.216457	167	320.911727	210	261.856731
82	903.438460	125	452.195759	168	320.814973	211	261.427746
83	901.932250	126	422.757189	169	318.782799	212	260.611460
84	901.906230	127	422.576416	170	318.631462	213	259.353663
85	897.161645	128	405.696302	171	318.498043	214	258.140892
86	897.129768	129	405.642865	172	318.288340	215	247.326696
87	896.950975	130	405.268826	173	317.780868	216	246.693691
88	896.940816	131	405.252745	174	317.566028	217	242.334211
89	893.226636	132	402.010340	175	315.878806	218	238.589609
90	893.199376	133	401.981167	176	313.223724	219	238.406175
91	690.866010	134	391.941896	177	313.188718	220	235.753788
92	686.733478	135	391.679133	178	312.897716	221	235.642703
93	686.729907	136	390.943176	179	312.819217	222	234.520810
94	684.813623	137	390.879592	180	312.741581	223	234.506422
95	684.787362	138	384.594969	181	312.141454	224	234.318981
96	683.799467	139	380.765650	182	304.639969	225	234.113038
97	683.793880	140	380.609194	183	304.548760	226	233.302196
98	681.679139	141	378.162269	184	302.535359	227	233.244031
99	677.253717	142	378.129383	185	302.137509	228	231.614479

No.	Freq (cm^{-1})	No.	Freq (cm^{-1})	No.	Freq (cm^{-1})	No.	Freq (cm^{-1})
229	219.888071	246	196.951189	263	162.403744	280	118.475525
230	219.649468	247	189.845346	264	162.118441	281	117.273936
231	218.823628	248	189.738308	265	160.316712	282	115.840490
232	218.821853	249	188.718343	266	160.133290	283	115.458363
233	214.808814	250	184.717416	267	152.439885	284	112.767308
234	214.521311	251	181.508826	268	152.146834	285	109.596705
235	212.131986	252	181.375948	269	141.344274	286	108.852309
236	211.622892	253	179.379685	270	140.853427	287	106.638403
237	208.459840	254	179.190433	271	137.300572	288	105.855295
238	208.270505	255	176.211846	272	137.250781	289	104.537667
239	202.052428	256	175.767378	273	127.393726	290	103.300856
240	201.611106	257	166.612790	274	124.186702	291	103.148557
241	200.324888	258	166.282666	275	123.907558	292	102.248395
242	200.087347	259	165.972705	276	123.178752	293	101.103073
243	199.886916	260	165.796822	277	122.931642	294	92.576590
244	199.765451	261	165.050359	278	120.132024		
245	198.041581	262	164.912258	279	119.768442		

S3. Partition functions

In the following, we define the molecular partition functions for free H_2 as well as for a surface adsorption site with different amounts of hydrogen adsorbed. The partition functions are required for the evaluation of Eq 6 of the main text.

S3.1. Free H_2

The partition function q_{H_2} of one H_2 molecule in the gas phase can be separated into contributions from the translational, rotational and vibrational degrees of freedom:

$$q_{H_2} = q_{trans} q_{rot} q_{vib} \tag{S1}$$

The different contributions can be calculated via the following expressions

$$q_{trans} = \left(k_B T / p_{H_2}\right) \left(\sqrt{2\pi m k_B T}/h\right)^3 \tag{S2}$$

$$q_{rot} = \left(8\pi^2 I_{H_2,gas} k_B T\right)/\left(h^2 \sigma\right) \tag{S3}$$

$$q_{vib} = \prod_k \left\{ \exp\left(-\frac{h\nu_k}{2k_B T}\right) \Big/ \left[1 - \exp\left(-\frac{h\nu_k}{k_B T}\right)\right] \right\} \tag{S4}$$

In these formulae, p_{H_2} stands for the H_2 pressure, while $I_{H_2,gas}$ refers to the moment of inertia of a free H_2, which is calculated via the H-H bond length of 0.76 Å as determined by the LDA method. σ is the symmetry number, which is 2 for H_2. The expression in Eq S4 is a product over the frequencies ν_k of all vibrational modes of a system, as displayed in Section S2. As there is only one vibrational mode for H_2, Eq S4 reduces to a single term. A superscript "0" added to q_{H_2} as encountered in Eq 6 of the main text means that the translational contributions to the partition function are evaluated for $p_{H_2} = p^0$, i.e., the standard pressure of 1 bar.

S3.2. Adsorption site with no hydrogen, chemisorbed H, one chemisorbed H and a molecular H_2

For the partition functions q_X for an adsorption site without any hydrogen (X=S), with one chemisorbed H atom, (X=SH), as well as with one chemisorbed H and molecular H_2 (X=SH_(H_2)),

we assume that all degrees of freedom can be described by vibrational modes. Thus, q_X only contains contributions from vibrational terms as displayed in Eq S4:

$$q_X = \sqrt[18]{\prod_k \left\{ \exp\left(-\frac{h\nu_k}{2k_BT}\right) \Big/ \left[1 - \exp\left(-\frac{h\nu_k}{k_BT}\right)\right]\right\}} \quad \text{(S5)}$$

Also here, the partition function is a product over the frequencies shown in Sections S2.2 to S2.4. However, frequencies in S2.2 to S2.4 are evaluated for a 3×3 supercell with 18 adsorption sites. To obtain the partition function for a single adsorption site, we need to pull the 18-th root out of the product over the frequencies.

S3.3. Adsorption site with one chemisorbed H and two molecular H_2

As mentioned in Section S2.5, the molecular hydrogen in the second layer will be treated as a two-dimensional particle-in-a-box (translation in two dimensions) and as a one-dimensional rotor. Thus, the partition function for adsorption sites with one chemisorbed H and two molecular H_2 also contains contributions from rotation and translation:

$$q_{SH\_(H_2)_2} = q_{trans\_2D} q_{rot\_1D} q_{vib} \quad \text{(S6)}$$

While the vibrational term is calculated exactly as described in Eq S5 via the frequencies shown in Section S2.5, the translational and rotational terms are:

$$q_{trans\_2D} = \left(2\pi m k_B T\, A\right)/h^2 \quad \text{(S7)}$$

$$q_{rot\_1D} = 2\pi\sqrt{2\pi I_{H_2,ads} k_B T}/\sigma h \quad \text{(S8)}$$

A is the area in which an H_2 can freely translate. We have estimated this value to be 9.10 Å^2, the average area for each adsorption site. $I_{H_2,ads}$ in Eq S8 refers to the moment of inertia of the H_2 molecules adsorbed in the second layer. This parameter is calculated based on an H-H bond length of 0.77 Å for adsorbed H_2.

S3.4. Calculation of equilibrium constants

The following equation is Eq 6 from the main text

$$K_X^{ads} = \left[q_{X,product} \Big/ \left(q_{X,initial} \cdot q_{H_2}^0\right)\right] exp\left(-\Delta E_X^{ads}/k_BT\right) \quad \text{(S9)}$$

which is used for the calculation of the adsorption constants for the adsorption processes in Eqs 1-3 of the main text (or Eqs 10, 13, and 16 below). In the following, we will define $q_{X,initial}$ and $q_{X,product}$ for each process:

For X= SH, and the reaction

$2S + H_2 \rightarrow 2SH$ (S10)

we have

$q_{SH,initial} = (q_S)^2$ (S11)

and

$q_{SH,product} = (q_{SH})^2$ (S12)

For X= SH_(H_2), and the reaction

$SH + H_2 \rightarrow SH\_(H_2)$ (S13)

we have

$q_{SH\_(H_2),initial} = q_{SH}$ (S14)

and

$q_{SH\_(H_2),product} = q_{SH\_(H_2)}$ (S15)

And finally, for X= SH_$(H_2)_2$, and the reaction

$SH\_(H_2) + H_2 \rightarrow SH\_(H_2)_2$ (S16)

we have

$q_{SH\_(H_2)_2,initial} = q_{SH\_(H_2)}$ (S17)

and

$q_{SH\_(H_2)_2,product} = q_{SH\_(H_2)_2}$ (S18)

S4. Comment on the kMC results

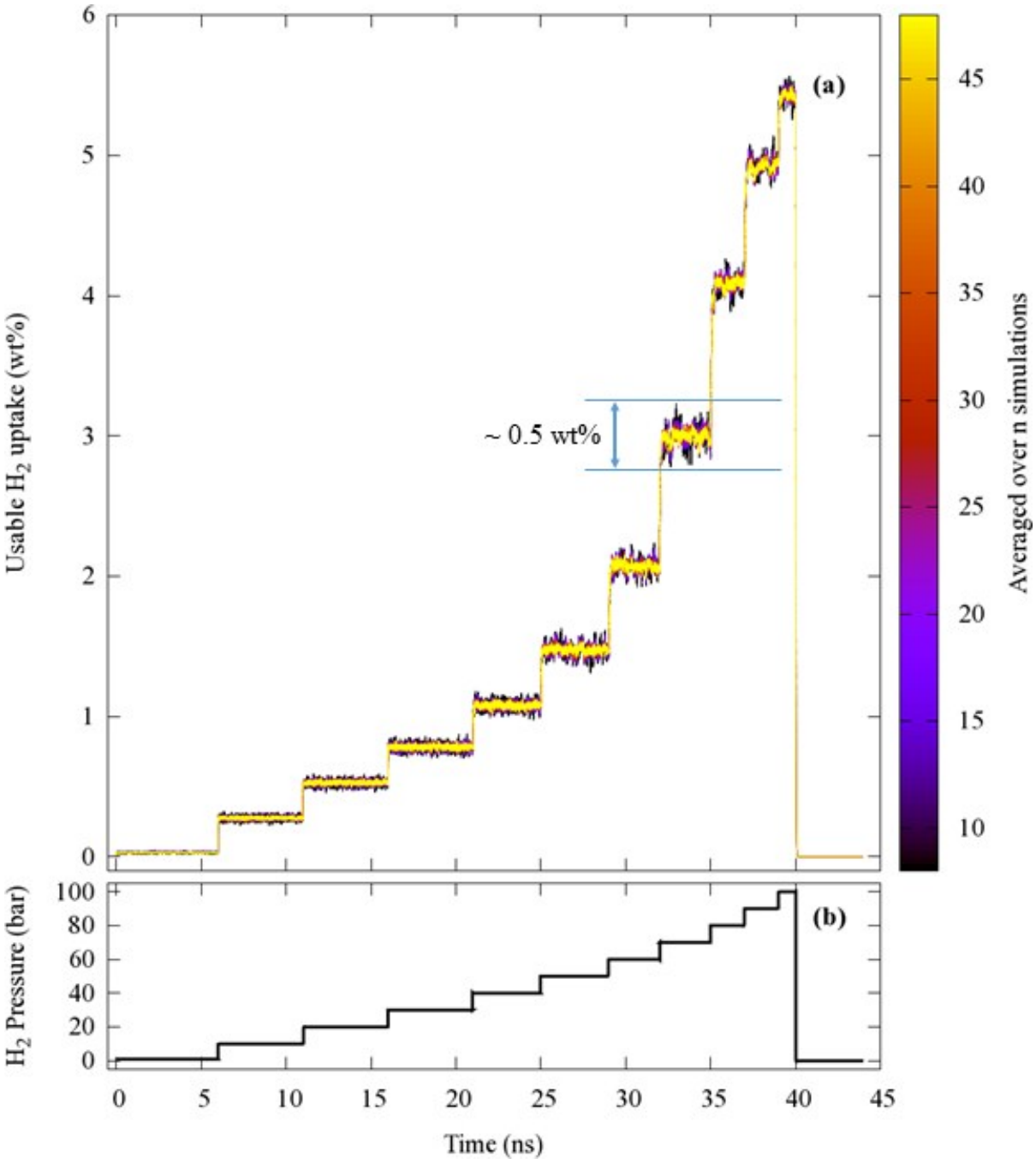

Figure S1. (a) The time-dependent, average gravimetric uptake of usable H_2 at 175 K calculated with the kMC model starting from an empty Sc_2CH_2 surface at time = 0. The different colors indicate results obtained by averaging different numbers of simulations (from 8 to 48) using identical settings. The H_2 pressure is varied over the simulation time, with the pressure profile being shown in (b).

As mentioned in the main text, the presented kMC results are obtained by averaging over 16 simulations using identical settings. A question that naturally arises is whether and how the results would change if the number of simulations N is varied. As visible from Figure 7 of the main text, the fluctuation in the calculated H_2 uptake is the strongest at intermediate hydrogen uptakes. Thus, we have used the hydrogen uptake at 175 K as a test system to evaluate how the N affects the calculated results. It can be seen from Figure S1: the overall trends are not affected. Only the fluctuation of the calculated results becomes smaller with increasing N. So, the question that remains is, how many simulations are required to obtain a smooth curve. Only the results obtained by averaging over 8 simulations (darkest line in Figure S1) shows some significant fluctuations of up to 0.5 wt%.

The number of simulations N to achieve a smooth curve depends, on the one hand, on what is perceived as "smooth" and, on the other hand, on the size of the simulation cell in the kMC model. In the present case, a 25×25 lattice (with 625 adsorption sites) is used. Thus, averaging over N simulations is equivalent to the simulation using a cell with 625×N adsorption sites. This in return means, each adsorption and desorption step changes the average surface coverage rate in increments of $1/(625\times4\times N) = 0.0016N^{-1}$ if the full coverage is normalized to 1. The factor of 4 comes in as two H_2 can adsorb on each site of Sc_2CH_2. Figure S2 illustrates how these increments change as N is increased and to what values in wt% these increments correspond to. Figure S2 shows that, when N=16, as used in this study, the increments are less than 0.001 wt%, which should be sufficiently "smooth."

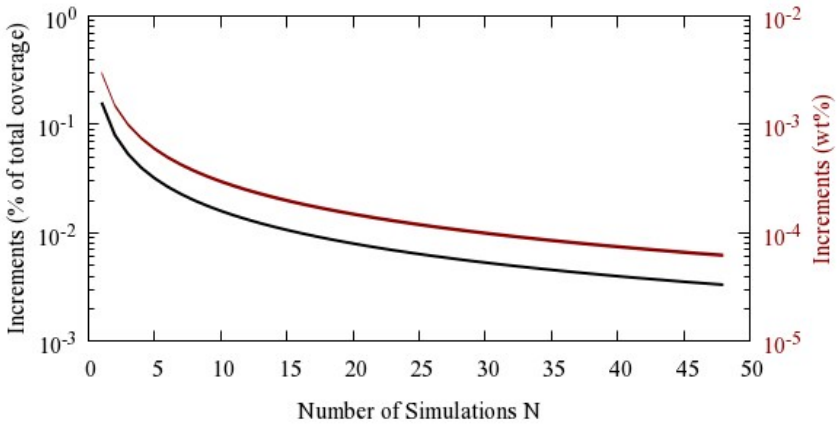

Figure S2. Increments in which the averaged calculated H_2 uptake changes with each adsorption/desorption step as a function of the number of simulations N, over which the results are averaged. The varying width of the red line (increments in wt%) reflects the circumstance that the values change slightly with the coverage rate.

S5. Spin-polarized DOS for pristine Sc_2C

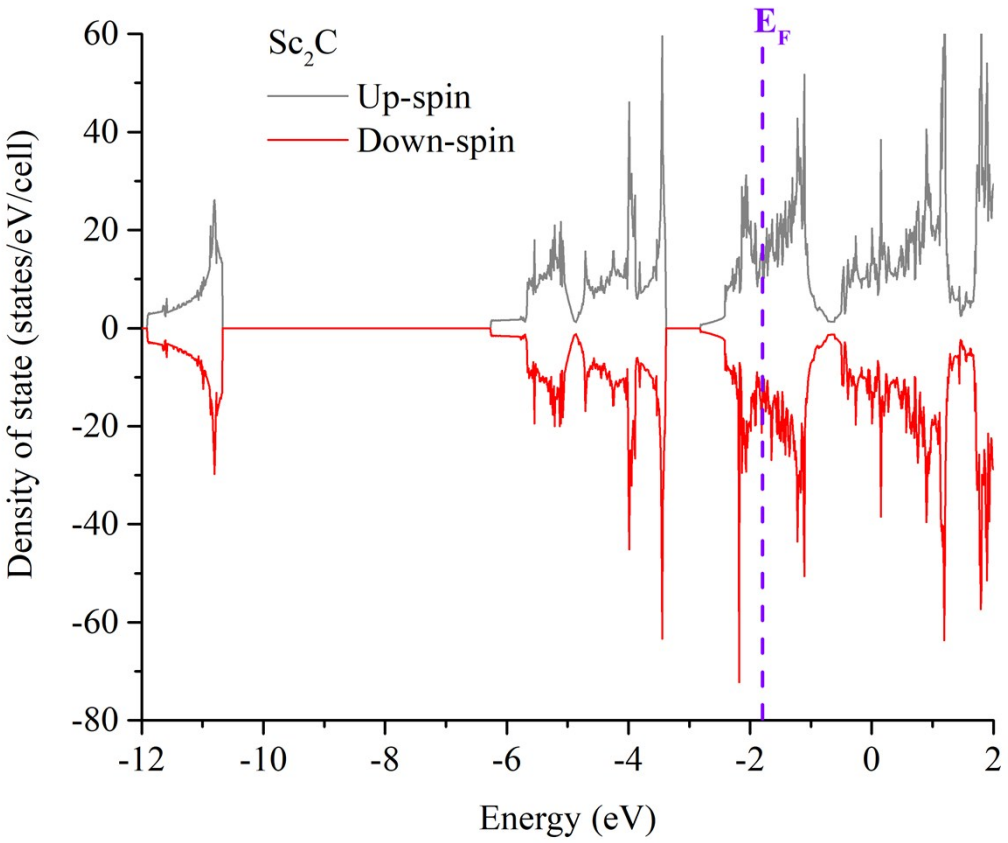

Figure S3. DOS for spin-polarized calculations of pristine Sc_2C. The vertical dash line indicates the Fermi level at -1.81 eV. To distinguish the different spin-orientations, the DOS of the spin-down component is shown as negative values.