Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2019

Understanding deep dehydrogenation and cracking of n-butane on Ni (111) surface by a DFT study

Chan Wu[a, b], Li Wang[a], Zhourong Xiao [a], Guozhu Li[*a], Lichang Wang[*b]

[a] Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Collaborative Innovative Center of Chemical Science and Engineering (Tianjin), Tianjin University, Tianjin 300072, China. E-mail: gzli@tju.edu.cn

[b] Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901, United States. E-mail: lwang@chem.siu.edu

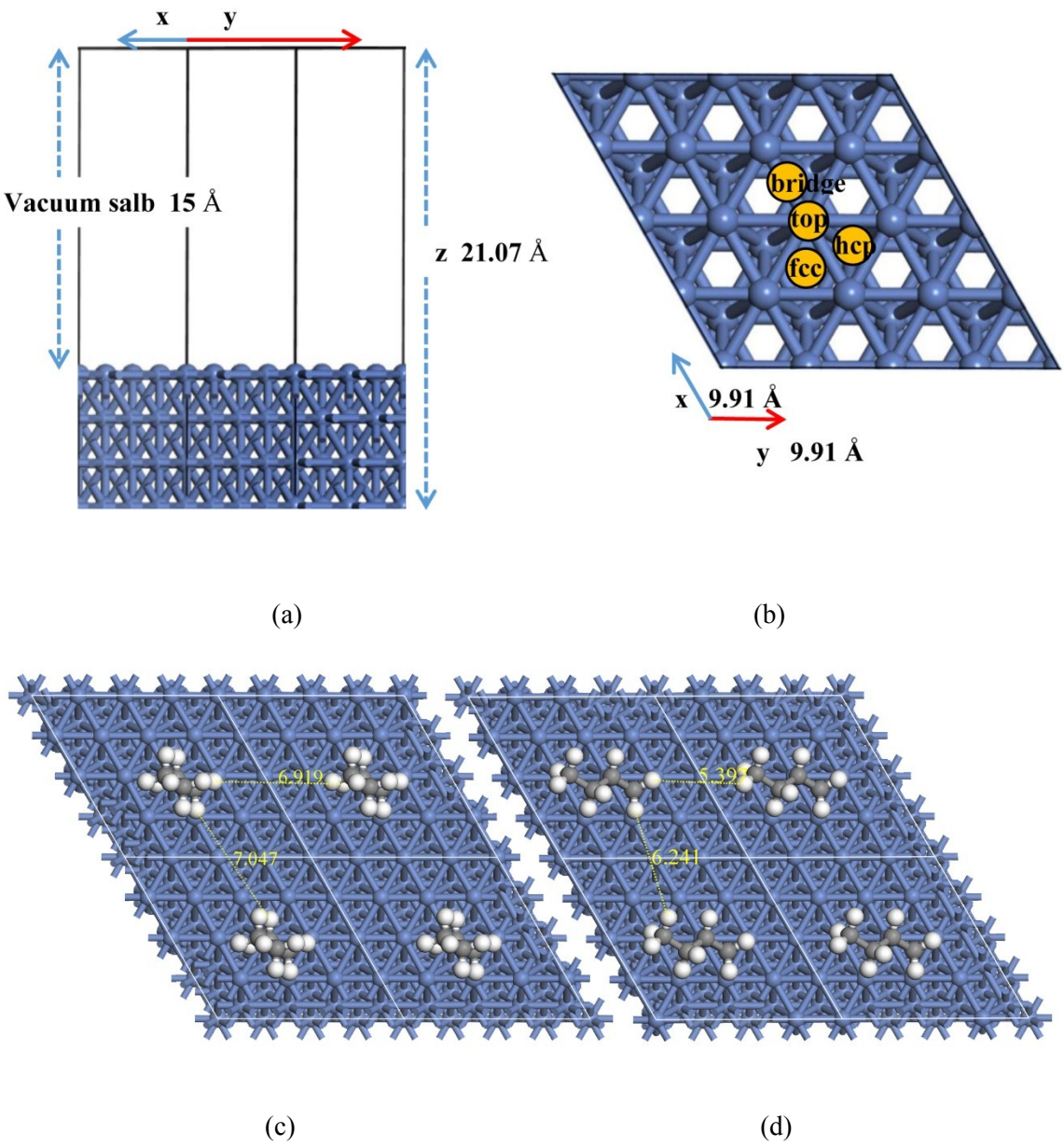


Fig. S1. (a) Side view of Ni (111) surface and (b) top view with four adsorption sites on Ni (111) surface; The periodic model of 1-butyl (c) and 1-butane (d) adsorption on Ni (111). White lines are lattice lines, and yellow dotted lines are the closest distances to periodic atoms, distances were labeled. The colors of atoms: Ni is dark blue, C is gray, and H is white.

Table S1. ZPE-corrected adsorption energies of C_4H_x species (x = 6–10) on the Ni (111) surface.

	Species	Favored	E_{ads}(eV)
C_4H_{10}*	n-butane	Top	-0.06
C_4H_9*	1-butyl	Fcc	-1.49
	2-butyl	Top	-1.00
C_4H_8*	1-butene	Fcc+top	-0.73
	trans-2-butene	Bridge	-0.25
C_4H_7*	1-butenyl	Fcc+top	-2.78
	1-buten-2-yl	Bridge+bridge	-2.44
	2-buten-2-yl	Bridge+top	-2.18
C_4H_6*	1-butyne	Fcc+hcp	-2.29
	2-butyne	Fcc+hcp	-2.03

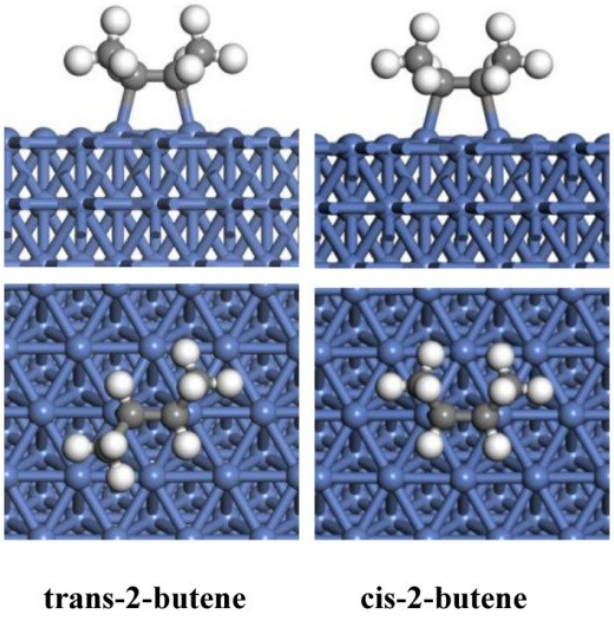


Fig. S2. Adsorption configurations of trans-2-butene and cis-2-butene on Ni (111) surface.

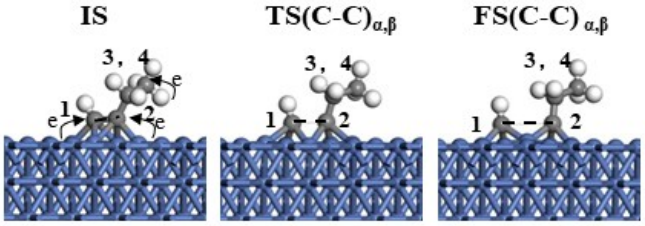
Table S2. The INCAR file of optimizing n-butane adsorption on Ni (111) surface with DFT used by VASP

SYSTEM = n-butane on Ni	EDIFF = 1E-05
NPAR= 4	ISMEAR = 1
GGA= PE	SIGMA = 0.1
ISTART = 0	EDIFFG = -0.02
ICHARG = 2	IBRION = 2
ISIF= 2	NSW = 300
ISYM= 0	POTIM = 0.2
ISPIN = 2	LORBIT= 11
ENCUT = 400 eV	PREC= Accurate
ALGO= Fast	LCHARG = .F.
NELM = 300	LWAVE = .F.
NELMIN= 5	LREAL = Auto
NELMDL= -5	MAGMOM= 64*0.7 10*0 4*0

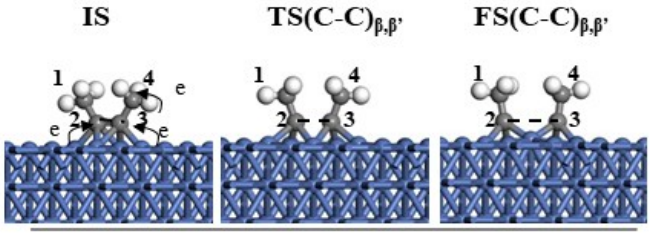
Table S3. The Cartesian coordinates (Å) of optimized n-butane adsorption structure on Ni (111) surface by DFT

Tag	Atom	X	Y	Z	Tag	Atom	X	Y	Z
1	Ni	0.000000	0.000000	0.000000	29	Ni	2.476690	2.861373	4.053756
2	Ni	0.000000	0.000000	21.071301	30	Ni	-2.482121	8.583106	6.060138
3	Ni	-4.957250	8.586209	0.000000	31	Ni	4.957250	0.000000	0.000000
4	Ni	-4.957250	8.586209	21.071301	32	Ni	4.957250	0.000000	21.071301
5	Ni	9.914500	0.000000	0.000000	33	Ni	0.000000	8.586209	0.000000
6	Ni	9.914500	0.000000	21.071301	34	Ni	0.000000	8.586209	21.071301
7	Ni	4.957250	8.586209	0.000000	35	Ni	7.435826	1.431063	2.023688
8	Ni	4.957250	8.586209	21.071301	36	Ni	4.954033	2.861315	4.051417
9	Ni	2.478576	1.431063	2.023688	37	Ni	-0.002369	8.583473	6.063698
10	Ni	-0.001527	2.861073	4.049055	38	Ni	3.717937	2.146552	0.000000
11	Ni	4.952471	8.583551	6.063821	39	Ni	3.717937	2.146552	21.071301
12	Ni	-1.239313	2.146552	0.000000	40	Ni	6.196513	3.577616	2.023688
13	Ni	-1.239313	2.146552	21.071301	41	Ni	6.194483	0.714307	4.049674
14	Ni	8.675188	2.146552	0.000000	42	Ni	3.714801	2.141860	6.069427
15	Ni	8.675188	2.146552	21.071301	43	Ni	6.196562	2.146552	0.000000
16	Ni	1.239263	3.577616	2.023688	44	Ni	6.196562	2.146552	21.071301
17	Ni	1.237135	0.715374	4.050291	45	Ni	3.717888	3.577616	2.023688
18	Ni	8.669897	2.144718	6.061186	46	Ni	8.673338	0.714504	4.050299
19	Ni	1.239313	2.146552	0.000000	47	Ni	6.195150	2.143857	6.058682
20	Ni	1.239313	2.146552	21.071301	48	Ni	7.435875	0.000000	0.000000
21	Ni	-1.239362	3.577616	2.023688	49	Ni	7.435875	0.000000	21.071301
22	Ni	3.716392	0.715538	4.050542	50	Ni	2.478625	8.586209	0.000000
23	Ni	1.232105	2.142565	6.065585	51	Ni	2.478625	8.586209	21.071301
24	Ni	2.478625	0.000000	0.000000	52	Ni	4.957201	1.431063	2.023688
25	Ni	2.478625	0.000000	21.071301	53	Ni	7.433906	2.861979	4.048838
26	Ni	-2.478625	8.586209	0.000000	54	Ni	2.474792	8.584263	6.064649
27	Ni	-2.478625	8.586209	21.071301	55	Ni	-2.478625	4.293105	0.000000
28	Ni	-0.000050	1.431063	2.023688	56	Ni	-2.478625	4.293105	21.071301

Tag	Atom	X	Y	Z	Tag	Atom	X	Y	Z
57	Ni	7.435875	4.293105	0.000000	85	Ni	1.239313	6.439657	21.071301
58	Ni	7.435875	4.293105	21.071301	86	Ni	3.717888	7.870721	2.023688
59	Ni	-0.000050	5.724168	2.023688	87	Ni	3.716142	5.007420	4.051159
60	Ni	-2.480631	7.154428	4.048885	88	Ni	1.235095	6.439358	6.063241
61	Ni	7.433079	4.291685	6.063463	89	Ni	3.717937	6.439657	0.000000
62	Ni	-3.717937	6.439657	0.000000	90	Ni	3.717937	6.439657	21.071301
63	Ni	-3.717937	6.439657	21.071301	91	Ni	1.239263	7.870721	2.023688
64	Ni	6.196563	6.439657	0.000000	92	Ni	6.194333	5.007486	4.050389
65	Ni	6.196563	6.439657	21.071301	93	Ni	3.714742	6.440101	6.062679
66	Ni	-1.239362	7.870721	2.023688	94	Ni	4.957250	4.293105	0.000000
67	Ni	-1.241911	5.008270	4.048992	95	Ni	4.957250	4.293105	21.071301
68	Ni	6.193535	6.439035	6.062474	96	Ni	2.478575	5.724168	2.023688
69	Ni	-1.239312	6.439657	0.000000	97	Ni	4.955478	7.154696	4.049755
70	Ni	-1.239312	6.439657	21.071301	98	Ni	4.955105	4.293483	6.065118
71	Ni	-3.717988	7.870721	2.023688	99	H	4.945692	4.191207	10.616799
72	Ni	1.238177	5.007913	4.049245	100	H	4.976858	4.291761	8.843733
73	Ni	-1.243642	6.438334	6.063278	101	H	3.636490	2.015819	10.452150
74	Ni	0.000000	4.293105	0.000000	102	H	2.345645	4.243031	8.773956
75	Ni	0.000000	4.293105	21.071301	103	H	2.373570	4.231324	10.537151
76	Ni	-2.478675	5.724168	2.023688	104	H	1.035661	2.084463	8.758195
77	Ni	-0.002279	7.154597	4.050217	105	H	0.185908	3.331577	9.694295
78	Ni	-0.005016	4.293465	6.057265	106	H	5.823624	2.966872	9.668674
79	Ni	2.478625	4.293105	0.000000	107	H	1.078610	2.036929	10.531866
80	Ni	2.478625	4.293105	21.071301	108	H	3.662289	2.137134	8.693928
81	Ni	4.957201	5.724168	2.023688	109	C	4.917287	3.589564	9.694802
82	Ni	2.476643	7.154412	4.050169	110	C	3.649404	2.745724	9.623640
83	Ni	2.473946	4.295514	6.065362	111	C	2.362404	3.567634	9.654635
84	Ni	1.239313	6.439657	0.000000	112	C	1.097296	2.715660	9.664528



(C-C)α,β bond)	IS(e)	TS(e)	FS(e)
Ni surface	-0.55	-0.64	-0.68
C_4H_6*	0.55	0.36, 0.28	0.40, 0.28
4C in C_4H_6*	0.94	1.02	1.07
C_1, C_2	0.47, 0.31	0.47, 0.42	0.48, 0.43



(C-C)β,β' bond	IS(e-)	TS(e-)	FS(e-)
Ni surface	-0.49	-0.55	-0.58
C_4H_6*	0.49	0.28, 0.27	0.29, 0.29
4C in C_4H_6*	0.91	1.02	1.08
C_2, C_3	0.35, 0.35	0.40, 0.40	0.43, 0.42

Fig. S3. Bader charge analysis of cleavage $(C\text{-}C)_{\alpha,\beta}$ and $(C\text{-}C)_{\beta,\beta'}$ bonds on Ni (111) . "+" and "—" refer to accumulation and depletion of electron, respectively. C_4H_6* represents electrons of fragment in TS and FS.