Supplementary Information

Theoretical Study of Catalytic Activity Modifications in CO_2 Methanation Induced by an Electric Field in Solid-Oxide Cells

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The electric dipole moment and polarizability values of surface adsorbed species with an electric field

Adsorption energy dependence on external electric fields is described as following Eq. S1, and the electric dipole moment and the effective polarizability values of adsorbed species on catalytic surfaces can be obtained by this equation[1,2].

$$E_{ads,\ with\ EF} = E_{ads,\ without\ EF} - d \cdot F - \frac{\alpha}{2}F^2 \ [S1]$$

where $E_{ads,\ with\ EF}$ is the adsorption energy with external electric fields, $E_{ads,\ without\ EF}$ is the adsorption energy without external electric fields, $\boldsymbol{d}$ is an electric dipole moment, α is effective polarizability and $\boldsymbol{F}$ is an external electric field. Eq. S1 is based on Eqs. 17 and 18, meaning that the effect of $\boldsymbol{d}$ is larger than that of $\boldsymbol{p}$ when the magnitude of electric fields is small ($\boldsymbol{F} < 1$ V/Å, F^2 works for $\boldsymbol{d}$). Still, the effect of $\boldsymbol{p}$ becomes the same degree as that of $\boldsymbol{d}$ when the magnitude of electric fields is large ($\boldsymbol{F} \geq 1$ V/Å). The electric dipole moment and the effective polarizability values for adsorbed species on Ni (111) surface in this study and the early study reported by F. Che et al.[1] obtained by the equation mentioned above are shown in Table S1. The comparisons of the adsorption energy plots of H atom, C atom, CH and CH_3 with external electric fields between our calculation and the early report by F. Che et al. are shown in Fig. S1. Comparing these calculation results with their results, our results have a few differences. In the electric dipole moment values, positive and negative sign tendencies agree, although the magnitude of each adsorbed species is a little larger in our results. In the calculation reported by F. Che et al., 4 Ni metal layers with 11 Å vacuum layer is used as a slab model and the Perdew-Wang 91 (PW91) functional[3] is used as an exchange-correlation functional unlike our calculation. This may be why the magnitude of the electric dipole moment values is slightly different. In the effective polarizability values, the magnitude of each adsorbed species is also a little different from their reports and positive and negative sign tendencies (except for the H atom) do not agree with their reports. A little magnitude difference of the effective polarizability values is probably caused by the difference of calculation conditions as well as the case of electric dipole moment values. In addition, as the reason why our results have a few differences in the electric dipole moment and effective polarizability values ($\boldsymbol{d}$ and $\boldsymbol{\alpha}$), the difference in electric field impression regions is considered. In the previous report, they used a wider external electric field range from -1.0 to 1.0 V/Å than ours from -0.5 to 0.5 V/Å, so we estimated the effective polarizability values ($\boldsymbol{\alpha}$) where the effort of

the electric dipole moment induced by atomic polarization (***p***) is small.

Table S1. Electric dipole moment and the effective polarizability values for adsorbed species on the Ni (111) surface in this study and the early study[1].

Species on slab	In this study		In the early study	
	d [eVÅV^{-1}]	α [Å^{2}V^{-1}]	***d*** [eVÅV^{-1}]	α [Å^{2}V^{-1}]
H	-0.034	-0.044	-0.010	-0.062
O	-0.155	-0.031	—	—
CH	0.139	0.191	0.076	-0.193
CO	-0.380	0.438	—	—
CH_3	0.390	0.348	0.191	-0.148
CO_2	-0.137	0.683	—	—
CHO	0.081	0.432	—	—
C	-0.127	0.058	-0.066	-0.18
OH	0.516	0.188	—	—
S	-0.025	0.310	—	—

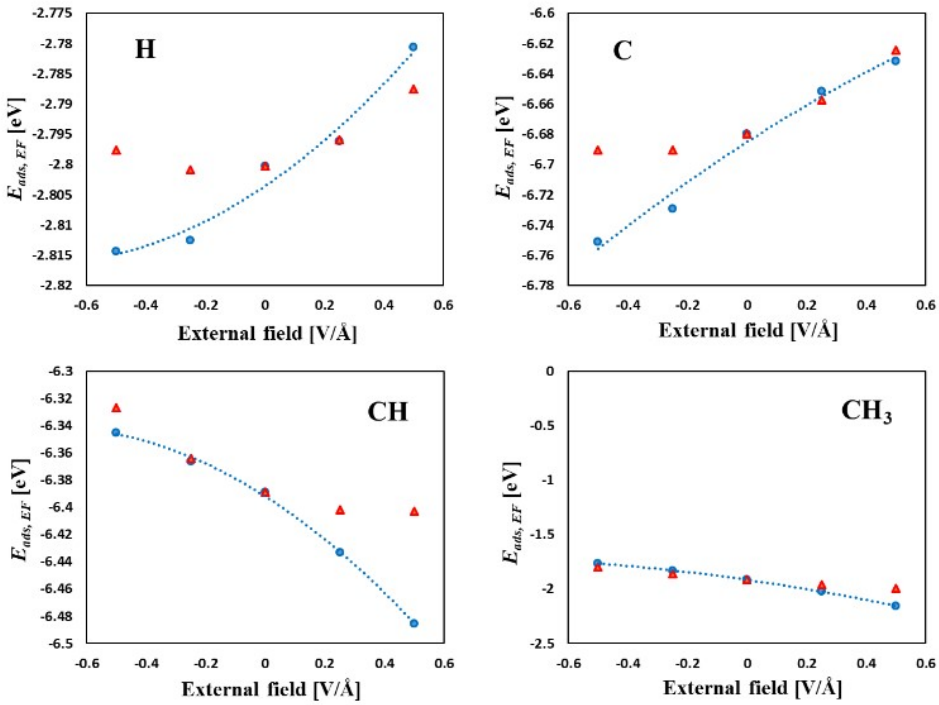

Fig. S1. Adsorption energy plots of H atom, C atom, CH and CH_3 with external electric fields in this study (circle markers) and the early study (triangle markers)[1].

Table S2. Elementary steps in CO_2 methanation. (Reaction 1-51)

Number	Reaction	A	E_a [J/mol]	ΔH [J/mol]	ΔS [J/mol · K]
1	H_2 +2 (111)* = 2 H(111)*	3.941×10^{8}	23060	-41774	-82.717
2	H_2O + (111)* = H_2O(111)*	1.031	0	-18000	-85.1
3	CO + (111)* = CO(111)*	0.827	0	-34664	-51.237
4	CH_4 +2 (111)* = CH_3(111)* + H(111)*	2.673×10^{8}	129000	28611	-109.84
5	CH_2O + (111)* = CH_2O(111)*	0.798	0	-51000	-156.57
6	CH_3OH + (111)* = CH_3OH(111)*	0.773	0	-48000	-101.94
7	CO_2 + (111)* = CO_2(111)*	0.66	0	-32000	-90.72
8	CH_3(111)* + (111)* = CH_2(111)* + H(111)*	5.354×10^{13}	66660	3000	-0.79
9	CH_2(111)* + (111)* = CH(111)* + H(111)*	9.484×10^{12}	26030	-38000	-14.02
10	CH(111)* + (111)* = C(111)* + H(111)*	2.321×10^{14}	135740	54000	-2.33
11	H_2O(111)* + (111)* = H(111)* + OH(111)*	2.301×10^{11}	91100	-9000	-55.54
12	OH(111)* + (111)* = H(111)* + O(111)*	1.002×10^{13}	82810	-33000	-17.61
13	C(111)* + O(111)* = CO(111)* + (111)*	1.072×10^{15}	206130	-144000	32.73
14	C(111)* + OH(111)* = COH(111)* + (111)*	3.025×10^{13}	125710	-83000	15.11
15	CH(111)* + O(111)* = CHO(111)* + (111)*	3.132×10^{12}	118277	25000	17.38
16	CH(111)* + OH(111)* = CHOH(111)* + (111)*	1.081×1013	123000	48000	8.49
17	CHO(111)* + (111)* = H(111)* + CO(111)*	9.561×1012	20140	24829	143.33
18	COH(111)* + (111)* = H(111)* + CO(111)*	4.309×1012	86220	-94000	0
19	CHOH(111)* + (111)* = H(111)* + CHO(111)*	7.98×1012	59623	-57000	-8.72
20	CHOH(111)* + (111)* = H(111)* + COH(111)*	4.942×1012	8760	-77000	4.29
21	CH_2(111)* + O(111)* = CH_2O(111)* + (111)*	7.146×1012	130470	28000	-4.18
22	CH_2O(111)* + (111)* = H(111)* + CHO(111)*	5.086×1013	31000	-42000	7.54
23	CH_2O(111)* = CHOH(111)*	1.0×1013	174540	15000	16.26
24	CH_2(111)* + OH(111)* = CH_2OH(111)* + (111)*	3.297×1012	84770	17000	3.07
25	CH_2OH(111)* + (111)* = H(111)* + CHOH(111)*	7.077×1012	35700	-6000	-8.6
26	CH_2OH(111)* + (111)* = H(111)* + CH_2O(111)*	5.113×1012	59410	-22000	-24.87
27	CH_2OH(111)* = CH_3O(111)*	1.0×1013	188530	-38000	-11.32
28	H(111)* + CH_2OH(111)* = CH_3OH(111)* + (111)*	1.0×1013	142800	-26000	38.16
29	CH_3(111)* + O(111)* = CH_3O(111)* + (111)*	3.256×1013	151480	15000	8.57
30	CH_3O(111)* + (111)* = H(111)* + CH_2O(111)*	1.0×1013	60780	17000	-13.54
31	CH_3(111)* + OH(111)* = CH_3OH(111)* + (111)*	1.0×1013	124660	-6000	40.45
32	CH_3OH(111)* + (111)* = H(111)* + CH_3O(111)*	1.0×1013	60780	-13000	-49.49
33	OH(111)* + CO(111)* = COOH(111)* + (111)*	1.0×1013	101000	63000	-37.33
34	COOH(111)* + (111)* = H(111)* + CO_2(111)*	1.0×1013	97000	-73000	63.1
35	O(111)* + CO(111)* = CO_2(111)* + (111)*	1.0×1013	149000	23000	43.37
36	2 CO(111)* = C(111)* + CO_2(111)*	1.0×1013	318000	167000	10.65
37	C(111)* = (111)* + Carbon(111)*	17000	80000	0	0
38	H_2 +2 (211)* = 2 H(211)*	3.941×108	11000	-46774	-82.717
39	H_2O + (211)* = H_2O(211)*	1.031	0	-12000	-85.1
40	CO + (211)* = CO(211)*	0.827	0	-44664	-51.237
41	CH_4 +2 (211)* = H(211)* + CH_3(211)*	7.03×109	116350.8	-34000	-124.39
42	CO_2 + (211)* = CO_2(211)*	0.66	0	-26000	-90.72
43	(211)* + CH_3(211)* = H(211)* + CH_2(211)*	5.354×1013	59000	26000	-0.79
44	(211)* + CH_2(211)* = H(211)* + CH(211)*	9.484×1012	46000	-45000	-14.02
45	(211)* + CH(211)* = H(211)* + C(211)*	2.321×1014	88000	-17000	-2.33
46	(211)* + H_2O(211)* = H(211)* + OH(211)*	2.301×1011	38000	-51000	-55.54
47	(211)* + OH(211)* = H(211)* + O(211)*	1.002×1013	76000	-16000	-17.61
48	C(211)* + O(211)* = (211)* + CO(211)*	1.6×1013	160000	-48000	32.73
49	C(211)* + OH(211)* = (211)* + COH(211)*	8.33×1012	147000	63000	15.11
50	CH(211)* + O(211)* = (211)* + CHO(211)*	4.1×1015	123263.1	58000	17.38
51	(211)* + CHO(211)* = H(211)* + CO(211)*	9.561×1012	20000	32440	157.88

Table S3. Elementary steps in CO_2 methanation (Reaction 52-101).

Number	Reaction	A	E_a [J/mol]	ΔH [J/mol]	ΔS [J/mol · K]
52	(211)* + COH(211)* = H(211)* + CO(211)*	7.3×1012	43000	-127000	0
53	CO(211)* + OH(211)* = (211)* + COOH(211)*	1.0×1013	111000	106500	-37.33
54	(211)* + COOH(211)* = H(211)* + CO_2(211)*	1.0×1013	97000	-69500	63.1
55	CO(211)* + O(211)* = (211)* + CO_2(211)*	1.35×1014	145880.4	53000	43.37
56	2 CO(211)* = CO_2(211)* + C(211)*	1.0×1013	326000	101000	10.65
57	C(211)* = (211)* + Carbon(211)*	17000	80000	0	0
58	CH_3(111)* + (211)* = (111)* + CH_3(211)*	1.0×1013	25000	-60111	-14.55
59	CH_2(111)* + (211)* = (111)* + CH_2(211)*	1.0×1013	25000	-34611	-14.55
60	CH(111)* + (211)* = (111)* + CH(211)*	1.0×1013	46000	-39111	-14.55
61	C(111)* + (211)* = (111)* + C(211)*	1.0×1013	50000	-107611	-14.55
62	H(111)* + (211)* = (111)* + H(211)*	1.0×1013	13000	-2500	0
63	H_2O(111)* + (211)* = (111)* + H_2O(211)*	1.0×1013	300	6000	0
64	OH(111)* + (211)* = (111)* + OH(211)*	1.0×1013	25000	-33500	0
65	O(111)* + (211)* = (111)* + O(211)*	1.0×1013	48000	-14000	0
66	CO(111)* + (211)* = (111)* + CO(211)*	1.0×1013	10000	-10000	0
67	CHO(111)* + (211)* = (111)* + CHO(211)*	1.0×1013	13000	-20111	-14.55
68	COH(111)* + (211)* = (111)* + COH(211)*	1.0×1013	25000	20500	0
69	CO_2(111)* + (211)* = (111)* + CO_2(211)*	1.0×1013	0	6000	0
70	H_2 +2 (100)* = 2 H(100)*	3.507×108	11000	-43774	-82.717
71	H_2O + (100)* = H_2O(100)*	1.031	0	-12000	-85.1
72	CO + (100)* = CO(100)*	0.827	0	-35664	-51.237
73	CH_4 +2 (100)* = H(100)* + CH_3(100)*	2.495×108	117000	156440	20.48
74	CO_2 + (100)* = CO_2(100)*	0.66	0	-26000	-90.72
75	(100)* + CH_3(100)* = H(100)* + CH_2(100)*	5.354×1013	59000	-15000	-0.79
76	(100)* + CH_2(100)* = H(100)* + CH(100)*	9.484×1012	46000	-70000	-14.02
77	(100)* + CH(100)* = H(100)* + C(100)*	2.321×1014	88000	-22000	-2.33
78	(100)* + H_2O(100)* = H(100)* + OH(100)*	2.301×1011	38000	-47000	-55.54
79	(100)* + OH(100)* = H(100)* + O(100)*	1.002×1013	114000	-30000	-17.61
80	C(100)* + O(100)* = (100)* + CO(100)*	1.110×1013	202000	16000	32.73
81	C(100)* + OH(100)* = (100)* + COH(100)*	1.018×1013	154000	63000	15.11
82	CH(100)* + O(100)* = (100)* + CHO(100)*	1.214×1013	195000	72000	17.38
83	(100)* + CHO(100)* = H(100)* + CO(100)*	9.561×1012	20000	-10374	76.04
84	(100)* + COH(100)* = H(100)* + CO(100)*	2.513×1013	93000	-77000	0
85	CO(100)* + OH(100)* = (100)* + COOH(100)*	1.0×1013	111000	95000	-37.33
86	(100)* + COOH(100)* = H(100)* + CO_2(100)*	1.0×1013	97000	-68000	63.1
87	CO(100)* + O(100)* = (100)* + CO_2(100)*	1.0×1013	149000	57000	43.37
88	2 CO(100)* = CO_2(100)* + C(100)*	1.0×1013	326000	41000	10.65
89	C(100)* = (100)* + Carbon(100)*	1.0×1013	80000	0	0
90	CH_3(211)* + (100)* = (211)* + CH_3(100)*	1.0×1013	25000	188940	144.87
91	CH_2(211)* + (100)* = (211)* + CH_2(100)*	1.0×1013	25000	146440	144.87
92	CH(211)* + (100)* = (211)* + CH(100)*	1.0×1013	119000	119940	144.87
93	C(211)* + (100)* = (211)* + C(100)*	1.0×1013	196000	113440	144.87
94	H(211)* + (100)* = (211)* + H(100)*	1.0×1013	13000	1500	0
95	H_2O(211)* + (100)* = (211)* + H_2O(100)*	1.0×1013	300	0	0
96	OH(211)* + (100)* = (211)* + OH(100)*	1.0×1013	19000	2500	0
97	O(211)* + (100)* = (211)* + O(100)*	1.0×1013	61000	-13000	0
98	CO(211)* + (100)* = (211)* + CO(100)*	1.0×1013	3000	9000	0
99	CHO(211)* + (100)* = (211)* + CHO(100)*	9.87×1011	6333	53314	81.84
100	COH(211)* + (100)* = (211)* + COH(100)*	1.0×1013	25000	-39500	0
101	CO_2(211)* + (100)* = (211)* + CO_2(100)*	1.0×1013	0	0	0

Table S4. Direct effects on the adsorption energy with an electric field.

External field [V/Å]	$E_{ads,\,EF}$ [eV]									
	H	**O**	**CH**	**CO**	**CH_3**	**CO_2**	**CHO**	**C**	**OH**	**S**
0.50	-2.78	-5.12	-6.49	-1.75	-2.16	-0.05	-3.32	-6.63	-3.44	-5.18
0.25	-2.80	-5.16	-6.43	-1.81	-2.02	-0.03	-3.27	-6.65	-3.30	-5.16
0	-2.80	-5.19	-6.39	-1.89	-1.92	-0.03	-3.23	-6.68	-3.16	-5.15
-0.25	-2.81	-5.23	-6.37	-2.00	-1.83	-0.08	-3.22	-6.73	-3.04	-5.17
-0.50	-2.81	-5.26	-6.35	-2.14	-1.76	-0.19	-3.24	-6.75	-2.93	-5.21

Table S5. Mulliken charge (upper side) and the number of electrons (bottom side) of each adsorbed species on Ni surface.

Mulliken charge [e]						
Species on slab	Atom	EF=0.5	EF=0.25	EF=0	EF=-0.25	EF=-0.5
H	H	-0.27	-0.27	-0.27	-0.27	-0.27
O	O	-0.52	-0.53	-0.55	-0.56	-0.57
CH	H	0.25	0.22	0.19	0.17	0.14
	C	-0.72	-0.73	-0.73	-0.74	-0.74
CO	C	-0.08	-0.08	-0.09	-0.09	-0.09
	O	-0.25	-0.29	-0.34	-0.38	-0.42
CH_3	H_1	0.16	0.15	0.13	0.12	0.11
	H_2	0.16	0.14	0.13	0.12	0.1
	H_3	0.16	0.15	0.13	0.12	0.11
	C	-1.04	-1.03	-1.03	-1.03	-1.03
CO_2	C	0.95	0.94	0.93	0.94	0.94
	O_1	-0.49	-0.49	-0.49	-0.49	-0.5
	O_2	-0.49	-0.49	-0.49	-0.49	-0.5
CHO	H	0.25	0.22	0.19	0.17	0.14
	C	-0.28	-0.29	-0.3	-0.3	-0.31
	O	-0.37	-0.39	-0.41	-0.44	-0.46
C	C	-0.45	-0.46	-0.48	-0.49	-0.5
OH	H	0.47	0.46	0.44	0.42	0.4
	O	-0.78	-0.78	-0.79	-0.78	-0.78
S	S	0.02	-0.03	-0.07	-0.12	-0.17

The number of electrons					
Species on slab	EF=0.5	EF=0.25	EF=0	EF=-0.25	EF=-0.5
H	1.251	1.256	1.260	1.262	1.262
O	6.519	6.528	6.544	6.551	6.567
CH	5.439	5.471	5.502	5.535	5.566
CO	10.247	10.300	10.353	10.383	10.431
CH_3	7.465	7.515	7.560	7.591	7.634
CO_2	15.770	15.794	15.794	15.799	15.794
CHO	11.297	11.377	11.431	11.496	11.547
C	4.442	4.458	4.471	4.485	4.515
OH	7.248	7.284	7.300	7.314	7.339
S	5.947	5.997	6.045	6.096	6.139

Table S6. Mulliken charge of 3-fold Ni atoms (average) or top Ni atom in the case of each adsorbed species.

Species on slab	EF=0.5	EF=0.25	EF=0	EF=-0.25	EF=-0.5
H (*fcc*)	0.07	0.06	0.05	0.03	0.02
O (*fcc*)	0.18	0.17	0.16	0.15	0.15
CH (*fcc*)	0.17	0.16	0.15	0.14	0.13
CO (*hcp*)	0.11	0.10	0.09	0.09	0.08
CH_3 (*fcc*)	0.18	0.17	0.17	0.16	0.15
CO_2 (*top*)	0.00	-0.02	-0.04	-0.05	-0.07
CHO (*hcp*)	0.13	0.13	0.13	0.13	0.12
C (*hcp*)	0.13	0.12	0.11	0.09	0.08
OH (*fcc*)	0.12	0.12	0.11	0.10	0.09
S (*fcc*)	-0.06	-0.07	-0.07	-0.08	-0.08

Table S7. Relative value of C, OH, and S species based on the adsorption energy without an electric field.

External field [V/Å]	$\Delta E_{ads,\,EF}$ [eV]		
	C	**OH**	**S**
0.50	0.05	-0.28	-0.03
0.25	0.03	-0.14	-0.01
-0.25	-0.05	0.12	-0.02
-0.50	-0.07	0.23	-0.06

Table S8. Direct effects on the surface reaction energy with an electric field.

External field [V/Å]	$E_{rxn,\,EF}$ [eV]		
	CHO* + * → CH* + O*	**CO_2* + * → CO* + O***	**CH_3* + H* → CH_4 + 2***
0.5	-0.27	-0.70	0.23
0.25	-0.31	-0.82	0.11
0	-0.33	-0.92	0.01
-0.25	-0.34	-1.02	-0.07
-0.5	-0.33	-1.08	-0.13

Table S9. Activation barrier parameters of RDSs under the electric field magnitude EF = 0, ± 0.25, or ± 0.5 V/Å.

			E_a [J/mol]				
Facet	**Reaction**	**Reaction number**	**EF = 0.5**	**EF = 0.25**	**EF = 0**	**EF = -0.25**	**EF = -0.5**
(111)*	CH_3* + H* → CH_4 + 2*	4	150324	138872	129000	122194	115626
	CHO* + * → CH* + O*	15	125964	120826	118277	116217	116576
	CO_2* + * → CO* + O*	35	171035	158375	149000	139286	132608
(211)*	CH_3* + H* → CH_4 + 2*	41	137675	126223	116351	109545	102976
	CHO* + * → CH* + O*	50	130950	125812	123263	121203	121562
	CO_2* + * → CO* + O*	55	167916	155255	145880	136166	129489
(100)*	CH_3* + H* → CH_4 + 2*	73	138324	126872	117000	110194	103626
	CHO* + * → CH* + O*	82	202687	197549	195000	192940	193299
	CO_2* + * → CO* + O*	87	171035	158375	149000	139286	132608

Table S10. Effects on the adsorption energy with co-adsorbed oxygen atoms.

O co-adsorption coverage: θ	$E_{ads,\,co\text{-}ad\,O}$ [eV]						
	H	**O**	**CH**	**CO**	**CH_3**	**CO_2**	**CHO**
θ=0 (2x2)	-2.79	-5.18	-6.40	-1.86	-1.87	-0.06	-3.27
θ=0 (3x2)	-2.76	-5.17	-6.33	-1.82	-1.81	0.01	-3.16
θ=0 (3x3)	-2.79	-5.12	-6.37	-1.85	-1.89	-0.04	-3.21
θ=1/9	-2.78	-5.12	-6.35	-1.87	-1.94	-0.09	-3.23
θ=1/6	-2.69	-4.83	-6.11	-1.69	-1.94	-0.03	-3.01
θ=2/9	-2.74	-5.05	-6.31	-1.80	-1.92	-0.07	-3.26
θ=1/4	-2.61	-4.30	-5.86	-1.42	-1.13	-0.06	-2.49
θ=3/9	-2.56	-4.27	-5.62	-1.20	-1.04	-0.07	-2.42

Table S11. Effects on the surface reaction energy with co-adsorbed oxygen atoms.

O co-adsorption coverage: θ	$E_{rxn,co\text{-}ad\ O}$ [eV]		
	CHO* + * → CH* + O*	**CO_2* + * → CO* + O***	**CH_3* + H* → CH_4 + 2***
θ=0 (2x2)	-0.37	-0.74	-0.08
θ=0 (3x2)	-0.44	-0.80	-0.11
θ=0 (3x3)	-0.37	-0.72	-0.03
θ=1/9	-0.32	-0.69	0.01
θ=1/6	-0.01	-0.28	-0.08
θ=2/9	-0.19	-0.57	-0.06
θ=1/4	0.24	0.55	-0.97
θ=3/9	0.44	0.81	-1.11

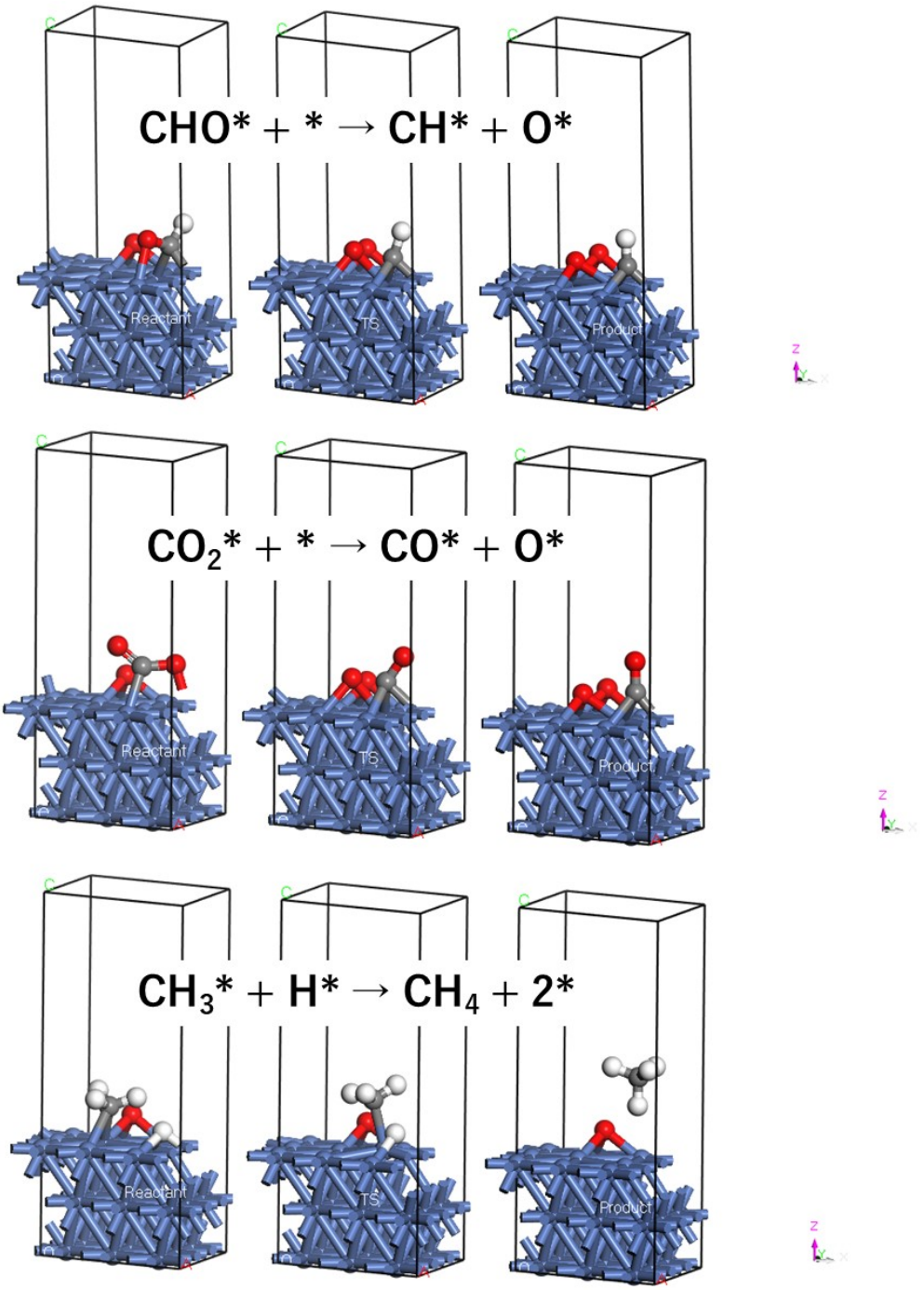

Fig. S2. Configurations of the initial step (reactants, left side), transition state (middle side), and final step (products, right side) geometries for CHO dissociation, CO_2 dissociation, and CH_4 desorption on Ni (111) facet under oxygen atom coverage θ = 1/9.

Table S12. Activation barrier parameters of RDSs under oxygen atom coverage θ = 0, 1/9, and 2/9.

			E_a [J/mol]		
Facet	**Reaction**	**Reaction number**	**θ = 0**	**θ = 1/9**	**θ = 2/9**
(111)*	CH_3* + H* → CH_4 + 2*	4	129000	79811	63772
	CHO* + * → CH* + O*	15	118277	137375	160567
	CO_2* + * → CO* + O*	35	149000	165077	165552
(211)*	CH_3* + H* → CH_4 + 2*	41	116351	67162	51122
	CHO* + * → CH* + O*	50	123263	142361	165554
	CO_2* + * → CO* + O*	55	145880	161957	162432
(100)*	CH_3* + H* → CH_4 + 2*	73	117000	67811	51772
	CHO* + * → CH* + O*	82	195000	214098	237290
	CO_2* + * → CO* + O*	87	149000	165077	165552

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