Electronic Supplementary Material (ESI) for Catalysis Science & Technology.
This journal is © The Royal Society of Chemistry 2023

Supporting information

Theoretical Study on Dry Reforming of Methane over a Ni(111) Surface under Electric Fields and with Alkali Metal Additives

Hui Jiao [a], Gui-Chang Wang [a,b,*]

([a] Frontiers Science Center for New Organic Matter, Tianjin Key Lab and Molecule-Based Material Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China; [b] Haihe Laboratory of Sustainable Chemical Transformation, Tianjin 300192, China）

*corresponding author

Tel. +86-22-23502458.

E-mail: wangguichang@nankai.edu.cn.

Table S1. Calculation settings for each element in DRM reaction (PAW potential and valence Z_{val}).

	potential	Z_{val}
Ni	PAW_PBE Ni_pv 06Sep2000	16
C	PAW_PBE C 08Apr2002	4
H	PAW_PBE H 15Jun2001	1
O	PAW_PBE O 08Apr2002	6
Li	PAW_PBE Li 17Jan2003	1
Na	PAW_PBE Na_pv 05Jan2001	7
K	PAW_PBE K_sv 06Sep2000	9
Rb	PAW_PBE Rb_pv 06Sep2000	7
Cs	PAW_PBE Cs_sv 08Apr2002	9

Table S2. The electronic adsorption energy (ΔE_{ads}) in eV and adsorption sites of species involved in DRM on Ni(111) under electric fields of 0, −0.6, +0.6 V/Å and K additive.

Species	Site	Ni(111)	ΔE_{ads} (eV)		Site	ΔE_{ads}(eV)
		F=0.0 V/Å	F= −0.6 V/Å	F= +0.6 V/Å		K/Ni(111)
CH_4*		-0.11(0.00[a], -0.02[b], -0.12[d])	-0.10	-0.13		-0.18(-0.05[a])
CH_3*	Fcc	-1.59(-1.89 [a], -1.91 [b], -1.81[c])	-1.46(-1.92[e])	-1.65(-2.15 [e])	Top	-1.46(-1.59 [a])
CH_2*	Fcc	-3.59(-4.03 [a], -4.01 [b], -3.85[c])	-3.60(-4.12 [e])	-3.61(-4.28 [e])	Fcc	-3.53(-3.90 [a])
CH*	Fcc	-5.96(-6.41 [a], -6.43 [b], -6.27[c])	-6.06(-6.47 [e])	-5.82(-6.56 [e])	Fcc	-5.91(-6.38 [a])
C*	Hcp	-6.34(-6.89 [a], -6.78 [b], -6.61 [c])	-6.23(-6.95 [e])	-6.17(-6.87 [e])	Hcp	-6.55(-7.06 [a])
H*	Fcc	-2.71(-2.80 [a], -2.81 [b], -2.77 [c], -2.89 [f])	-2.71	-2.69	Fcc	-2.75(-2.81 [a])
CO_2*		-0.16(-0.01 [a], -0.02 [b], -0.20 [d])	-0.16	-0.17		-0.40(-0.29 [a])
CO*	Hcp	-1.59(-1.93 [a], -1.92 [b], -1.45 [d], -1.26 [f])	-1.73	-1.46	Hcp	-2.10(-2.35 [a])
O*	Fcc	-5.32(-5.39 [a], -5.67 [b], -5.47 [d], -5.13 [f])	-5.26	-4.91	Fcc	-5.60(-5.65 [a])
COOH*	Bridge	-2.05(-2.25 [a], -2.26 [b], -2.14 [d])	-2.22	-1.79	Top	-2.69(-2.73 [a])
CHO*	Fcc	-2.03(-2.27 [a], -2.26 [b], -2.24 [d])	-1.86	-1.86	Fcc	-2.34(-2.49 [a])
CH_2O*	Fcc	-0.54(-0.75[b], -0.55 [d])	-0.27	-0.38	Fcc	-0.68
OH*	Fcc	-3.19(-3.27 [a], -3.42 [b], -3.46 [d])	-2.72	-2.98	Bridge	-3.29(-3.24 [a])
H_2O*	Top	-0.23(-0.27 [a], -0.29 [b], -0.48 [d])	-0.12	-0.23	Top	-0.65(-0.68 [a])
H_2*	Top	0.05(-0.25 [a], -0.22 [b], -0.38 [d])	0.14	-0.01	Top	0.22(-0.06 [a])

[a] From ref. 1. [b] From ref. 2. [c] From ref. 3. [d] From ref. 4. [e] From ref. 5. [f] From ref. 6.

Table S3. Electron transfer (|e|) of species involved in DRM on Ni(111) under electric fields of 0, −0.6, +0.6 V/Å and K additive.

Species	F=0.0 V/Å	F= −0.6 V/Å	F= +0.6 V/Å	K/Ni(111)
CH_3*	-0.32	-0.37	-0.27	-0.46
CH_2*	-0.39	-0.46	-0.33	-0.55
CH*	-0.42	-0.47	-0.38	-0.58
C*	-0.56	-0.60	-0.52	-0.71
H*	-0.26	-0.27	-0.24	-0.31
CO_2*	-0.51	-0.60	-0.29	-0.86
CO*	-0.40	-0.46	-0.33	-0.61
O*	-0.89	-0.92	-0.85	-1.00
COOH*	-0.34	-0.42	-0.27	-0.51
CHO*	-0.45	-0.53	-0.38	-0.70
CH_2O*	-0.50	-0.57	-0.42	-0.77
OH*	-0.55	-0.59	-0.52	-0.64

Table S4. The activation energy (ΔE_a) and reaction energy (ΔE) in eV of all elementary reactions involved in DRM on Ni(111) under electric fields of 0, −0.6, +0.6 V/Å and K additive.

Reaction	Ni (111)						K/Ni (111)	
	F=0.0 V/Å		F= −0.6 V/Å		F= +0.6 V/Å			
	ΔE_a	ΔE	ΔE_a	ΔE	ΔE_a	ΔE	ΔE_a	ΔE
$CH_{4(g)} \rightarrow CH_3$*+H*	0.98 (0.71[a]) (0.91[b])	0.30 (-0.11[a]) (0.01[b])	1.10 (0.87[a])	0.42 (0.09[a])	0.89 (0.62[a])	0.23 (-0.16[a])	1.11	0.4 (0.32[c])
CH_3* $\rightarrow CH_2$*+H*	0.66 (0.55[a]) (0.70[b])	0.10 (-0.01[a]) (0.07[b])	0.66 (0.52[a])	0.05 (-0.06[a])	0.68 (0.56[a])	0.12 (0.06[a])	0.73	0.05 (-0.16[c])
CH_2* $\rightarrow$ CH*+H*	0.32 (0.25[a]) (0.35[b])	-0.32 (-0.41[a]) (-0.34[b])	0.31 (0.23[a])	-0.34 (-0.46[a])	0.34 (0.27[a])	-0.27 (-0.34[a])	0.27	-0.36 (-0.48[c])
CH* $\rightarrow$ C*+H*	1.37 (1.23[a]) (1.33[b])	0.60 (0.45[a]) (0.52[b])	1.30 (1.14[a])	0.52 (0.34[a])	1.44 (1.37[a])	0.70 (0.63[a])	1.10	0.44 (0.32[c])
$CO_{2(g)} \rightarrow$ CO*+O*	0.69 (0.67[b])	-0.72 (-0.98[b])	0.55	-0.87	0.88	-0.55	0.06 (-0.08[c])	-1.29 (-0.79[c])
$CO_{2(g)}$+H* $\rightarrow$ COOH*	1.17 (1.13[b])	0.35 (0.28[b])	1.02	0.29	1.32	0.38	0.32 (0.22[c])	-0.22 (-0.22[c])
COOH* $\rightarrow$ CO*+OH*	0.36 (0.57[b])	-1.04 (-1.08[b])	0.53	-0.97	0.33	-1.07	0.45 (0.40[c])	-0.53 (-0.89[c])

$C^*+O^* \rightarrow CO^*$	2.07 (2.17 [a]) (1.59 [b])	-1.61 (-1.48 [a]) (-1.35 [b])	2.05 (2.12 [a])	-1.65 (-1.56 [a])	2.09 (2.19 [a])	-1.59 (-1.49 [a])	1.08 (1.55 [c])	-1.87 (-1.30 [c])
$CH^*+O^* \rightarrow CHO^*$	1.19 (1.14 [a]) (1.53 [b])	0.13 (0.55 [a]) (0.45 [b])	1.19 (1.15 [a])	0.12 (0.11 [a])	1.18 (1.13 [a])	0.11 (0.06 [a])	1.19 (1.52 [c])	0.09 (0.51 [c])
$CHO^* \rightarrow CO^*+H^*$	0.19 (0.13 [a]) (0.20 [b])	-1.21 (-1.33 [a]) (-1.28 [b])	0.16 (0.08 [a])	-1.33 (-1.53 [a])	0.22 (0.20 [a])	-1.08 (-1.11 [a])	0.07 (0.05 [c])	-1.39 (-1.49 [c])
$CH_2^*+O^* \rightarrow CH_2O^*$	1.19 (1.13 [a]) (1.45 [b])	0.19 (0.39 [a]) (0.50 [b])	1.21 (1.17 [a])	0.11 (0.33 [a])	1.16 (1.49 [a])	0.16 (0.36 [a])	1.21	0.22
$CH_2O^* \rightarrow CHO^*+H^*$	0.36 (0.18 [a]) (0.36 [b])	-0.26 (-0.55 [a]) (-0.38 [b])	0.32 (0.17 [a])	-0.32 (-0.54 [a])	0.41 (0.25 [a])	-0.22 (-0.45 [a])	0.23	-0.41
$O^*+H^* \rightarrow OH^*$	1.23 (1.24 [a]) (1.35 [b])	0.09 (0.27 [a]) (0.19 [b])	1.26 (1.30 [a])	0.28 (0.58 [a])	1.19 (1.18 [a])	-0.11 (-0.07 [a])	1.11 (1.21 [c])	0.29 (0.50 [c])
$OH^*+H^* \rightarrow H_2O_{(g)}$	1.10 (1.11 [a]) (1.33 [b])	0.45 (0.42 [a]) (0.70 [b])	1.00 (0.81 [a])	0.11 (0.07 [a])	1.25 (1.32 [a])	0.38 (0.30 [a])	0.69 (0.80 [c])	0.49 (0.67 [c])
$H^*+H^* \rightarrow H_{2(g)}$	0.81 (0.88 [a]) (0.92 [b])	0.66 (0.87 [a]) (1.08 [b])	0.85 (0.96 [a])	0.66 (0.98 [a])	0.76 (0.78 [a])	0.63 (0.72 [a])	0.87	0.58
$2CO_* \rightarrow CO_{2(g)}+C^*$	1.80 (1.59[c])	0.53 (0.36 [c])	1.62	0.55	1.9	0.51	0.86 (0.87 [c])	0.58 (0.64 [c])
C*, diffusion	0.33 (0.66[d])	-0.03	0.32	-0.04	0.32	-0.05	0.33	-0.04
$2C^* \rightarrow C\text{-}C^*$	0.66 (0.70 [d])	-0.94 (-0.89 [d])	0.63	-0.96	0.63	-0.97	0.61	-0.90

Note: Zero-point energy (ZPE) correction is included. [a] From ref. 7. [b] From ref. 2. [c] From ref. 1. [d] From ref. 8.

Table S5. The Bader charge of Ni(111) surface with alkali metals.

Atom	Li	Na	K	Rb	Cs
AM	0.926	0.770	0.779	0.780	0.757
Ni (Near to AM)	-0.277	-0.178	-0.146	-0.142	-0.124
Ni (other)	-0.055	-0.065	-0.081	-0.081	-0.085

Table S6. The activation energy (ΔE_a) and reaction energy (ΔE) in eV of important reactions involved in DRM on Ni(111) with AMs additives. (Zero point energy (ZPE), thermal and entropic contributions were not included.)

Reaction	$CH_{4(g)} \rightarrow CH_3$*+H*		CH* → C*+H*		$CO_{2(g)} \rightarrow$ CO*+O*	
Surfaces	ΔE_a	ΔE	ΔE_a	ΔE	ΔE_a	ΔE
Ni(111)	1.12	0.44	1.37	0.60	0.77	-0.68
Li/Ni(111)	1.26	0.63	1.09	0.42	0.38	-1.03
Na/Ni(111)	1.28	0.61	1.28	0.59	0.37	-0.96
K/Ni(111)	1.27	0.52	1.25	0.52	0.07	-1.23
Rb/Ni(111)	1.26	0.51	1.26	0.51	0.04	-1.12
Cs/Ni(111)	1.24	0.64	1.29	0.51	0.02	-1.21

Table S7. The rates of all elementary reactions involved in DRM on Ni(111) under electric fields of 0, −0.6, +0.6 V/Å and K additive at 1073.15K and 1 bar.

Reaction	Ni (111)			K/Ni (111)
	F= 0.0 V/Å	F= −0.6 V/Å	F= +0.6 V/Å	
CH_4*→ CH_3*+H*	1.19E-02	3.46E-03	2.69E-02	3.12E-03
CH_3* → CH_2*+H*	9.47E-01	4.39E-03	6.37E+00	3.13E-03
CH_2* → CH*+H*	3.83E+03	1.15E+01	3.09E+04	5.71E-01
CH* → C*+H*	4.15E+02	5.23E+00	4.15E+02	1.49E+00
CO_2* → CO*+O*	9.81E-03	4.77E-02	1.01E-02	1.95E+01
CO_2*+H* → COOH*	1.83E-07	5.30E-07	1.83E-08	4.07E-03
COOH* → CO*+OH*	4.50E-07	1.69E-06	7.08E-08	2.78E-02
C*+O* → CO*	3.50E-07	6.91E-07	1.27E-07	3.53E-03
CH*+O* → CHO*	9.23E-03	3.46E-03	1.01E-02	2.97E-04
CHO* → CO*+H*	2.34E-01	1.12E-01	1.71E-01	1.16E+01
CH_2*+O* → CH_2O*	1.03E-06	1.44E-07	1.44E-06	1.15E-08
CH_2O* → CHO*+H*	7.86E-06	1.36E-06	6.12E-06	6.66E-05
O*+H* → OH*	1.70E-01	4.35E+00	1.54E-02	7.38E+01
OH*+H* → H_2O*	8.56E-04	6.77E-03	5.67E-05	8.33E-01
H*+H* → H_2*	1.64E+04	3.55E+03	1.23E+04	4.57E+03
2CO* → CO_2*+C*	8.31E-13	1.47E-11	1.86E-13	1.73E-06
C*, diffusion	7.43E+02	6.09E-01	2.29E+04	1.73E-03
2C* → C-C*	2.95E+01	3.69E-02	1.25E+03	1.32E-04

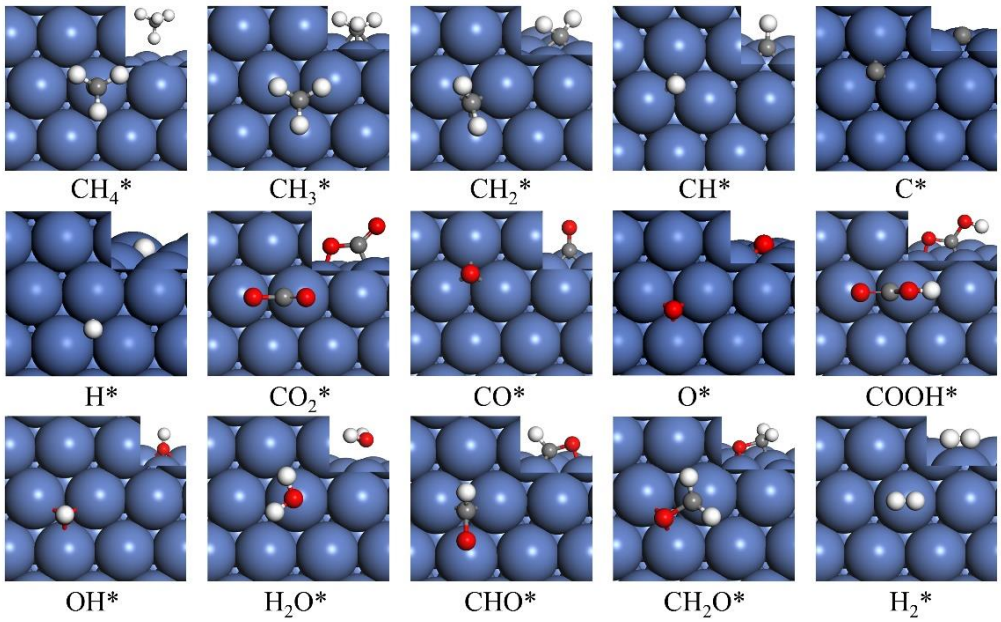

Figure S1. The top and side views of the most stable configurations of the DRM intermediates on Ni(111) surface. Blue, grey, red, and white represent Ni, C, O, and H, respectively.

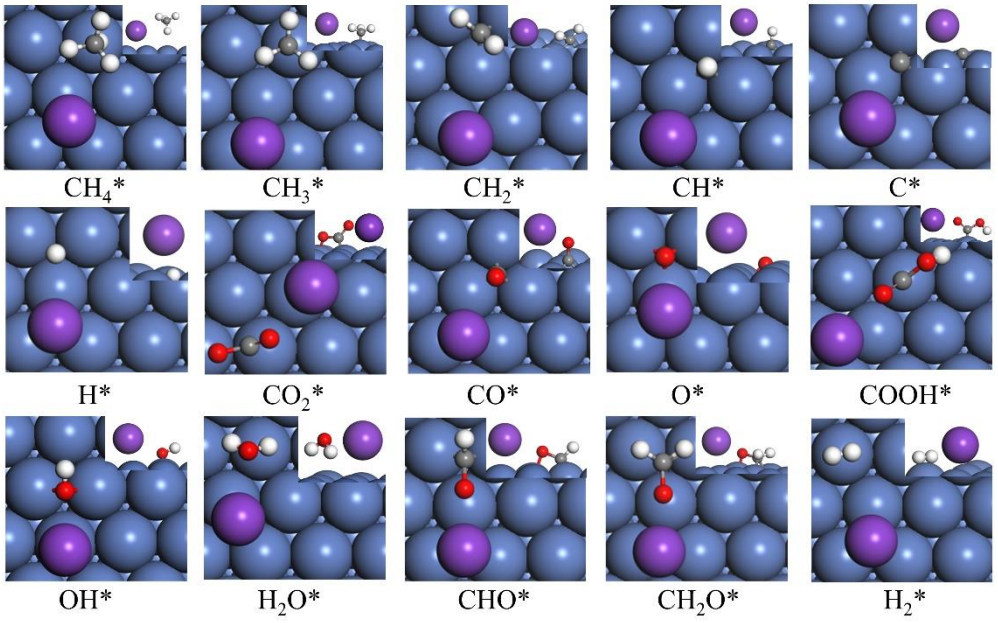

Figure S2. The top and side views of the most stable configurations of the DRM intermediates on K/Ni(111) surface. Blue, purple, grey, red, and white represents Ni, K, C, O, and H, respectively.

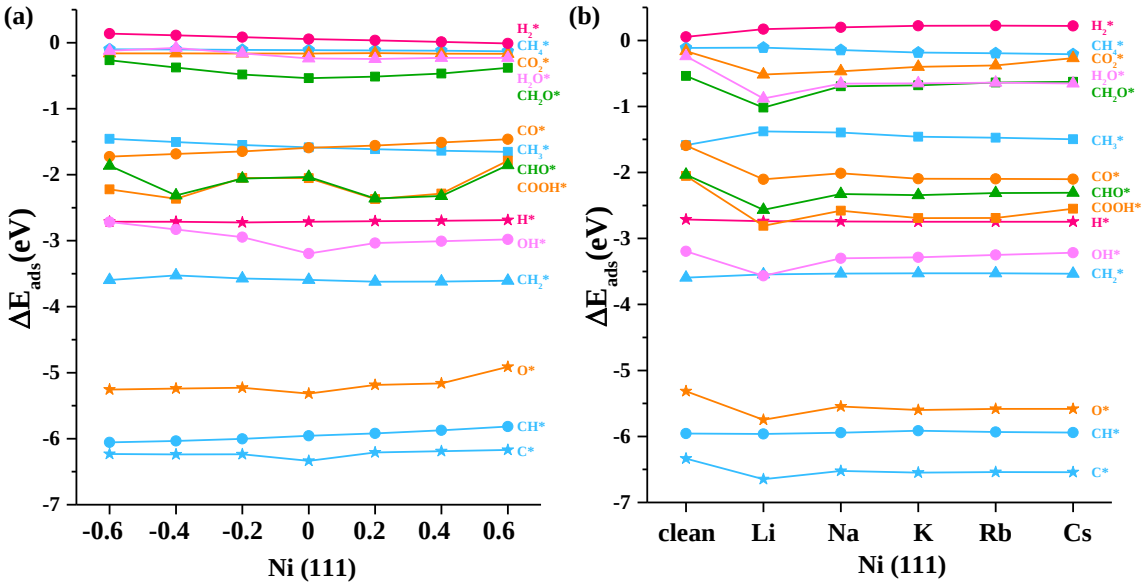

Figure S3. The electronic adsorption energy (ΔE_{ads}) of species involved in DRM on Ni(111) under (a) electric fields from −0.6 to +0.6 V/Å and (b) alkali metals.

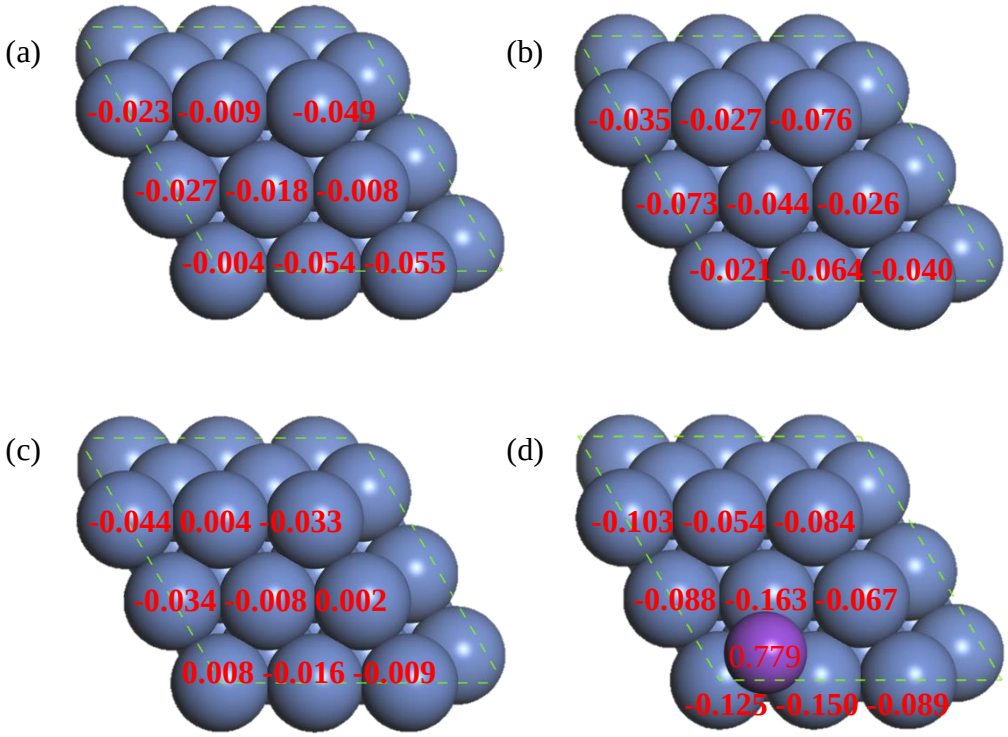

Figure S4. The Bader charge of Ni(111) under electric fields of (a) 0, (b) −0.6, (c) +0.6 V/Å and (d) K additive.

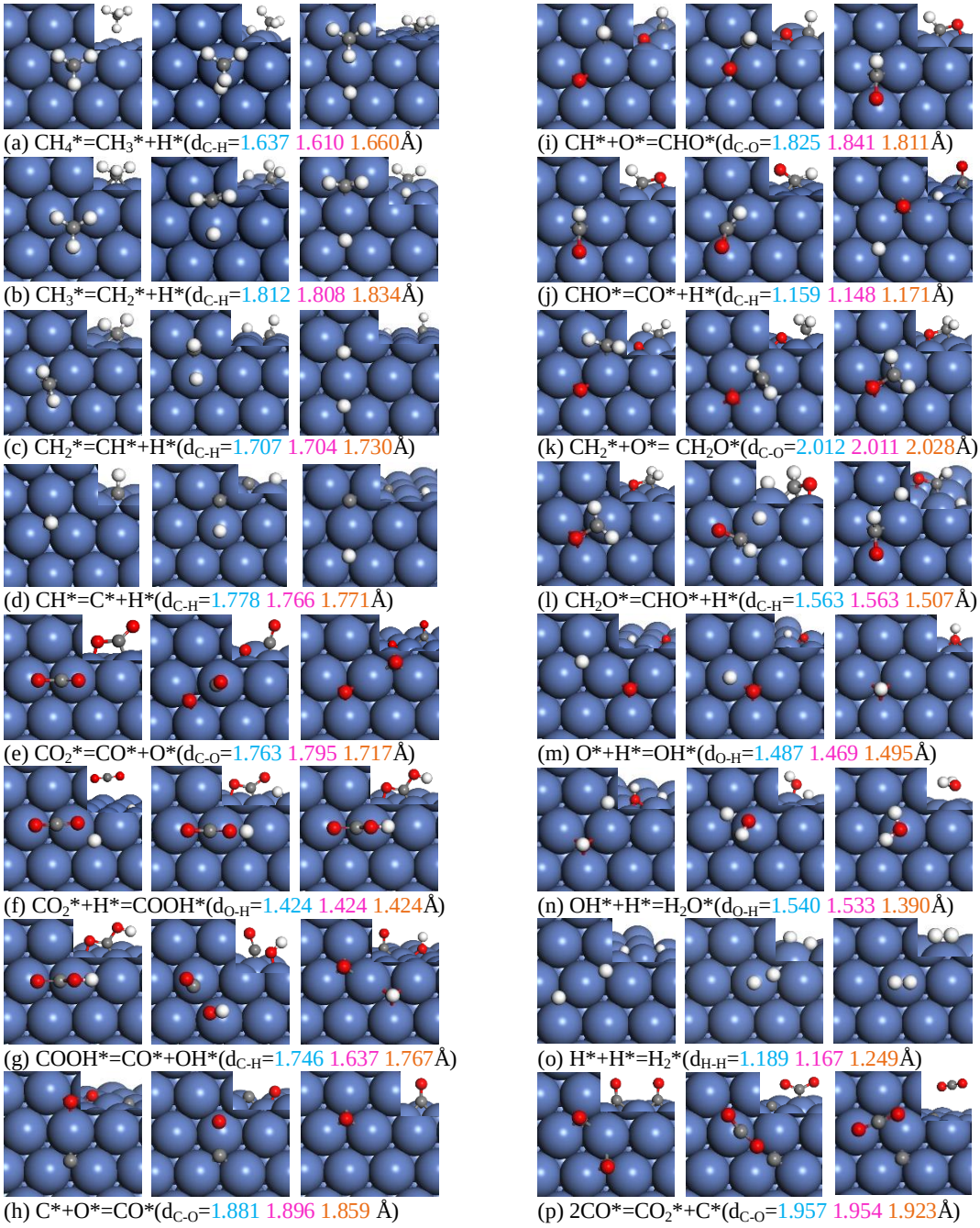

Figure S5. The top and side views of IS, TS, and FS of elementary reaction involved in DRM reaction on Ni (111) surface. The distance between the bonding or breaking atoms in the transition state structure is expressed in parentheses, where blue, purple and orange indicate electric fields of 0, −0.6, and +0.6 V/Å, respectively.

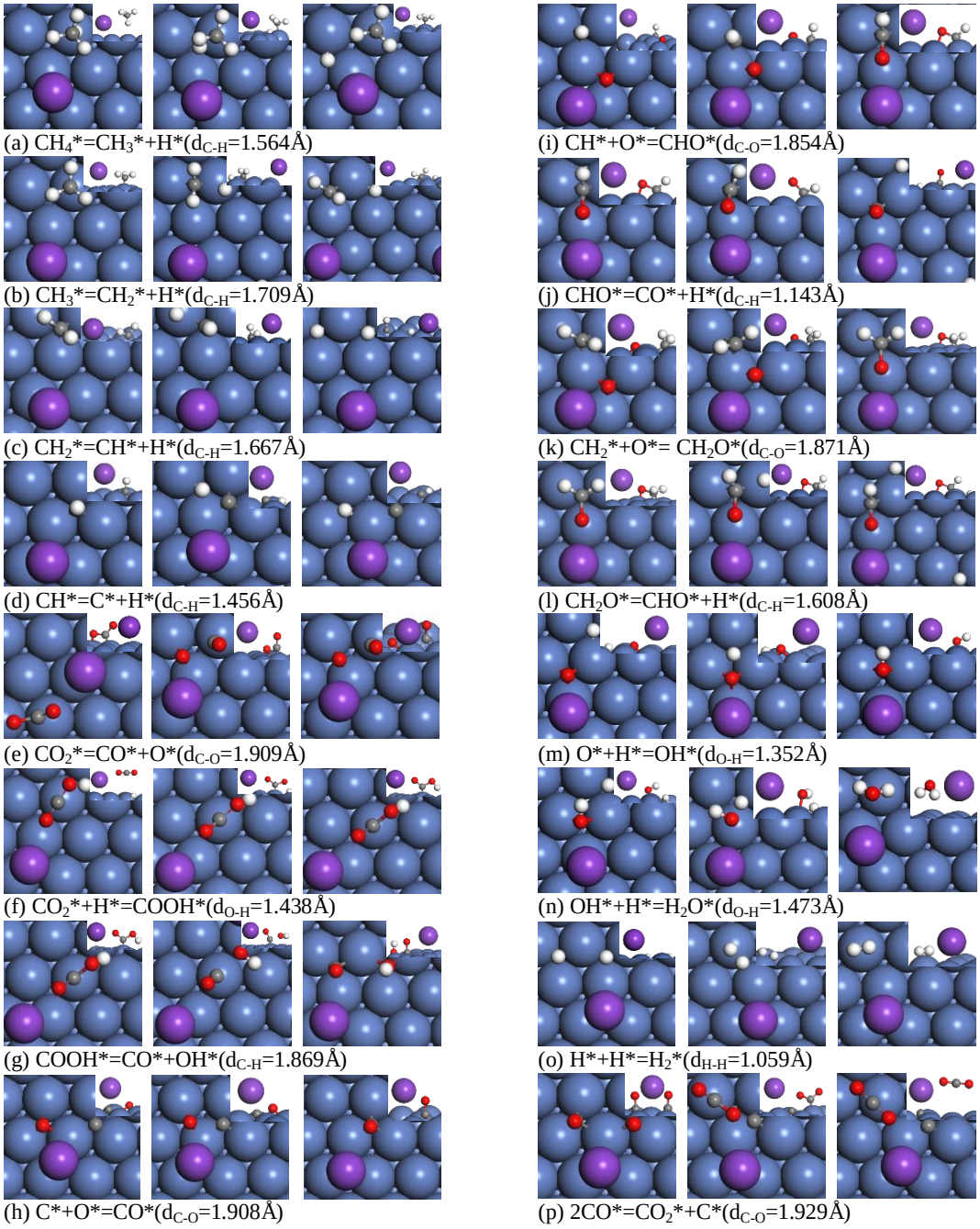

Figure S6. The top and side views of IS, TS, and FS of elementary reaction involved in DRM reaction on K/Ni (111) surface. The distance between the bonding or breaking atoms in the transition state structure is expressed in parentheses.

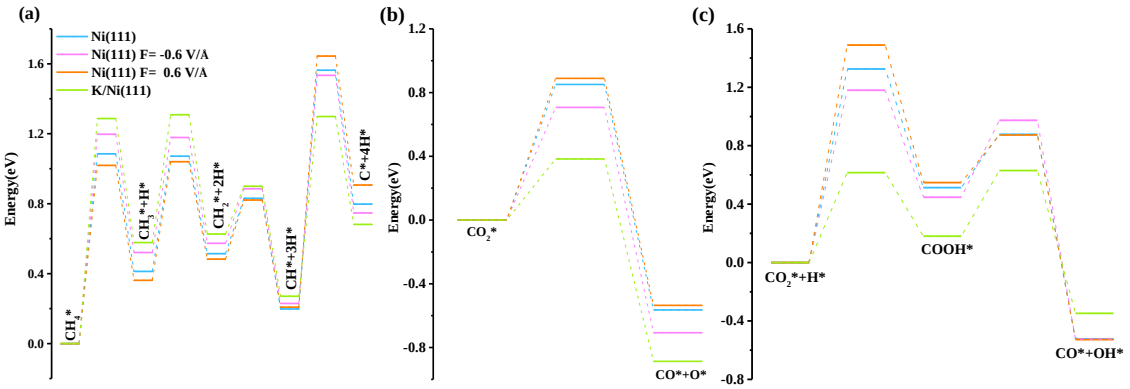

Figure S7. Electronic energy profiles of (a) CH_4 dissociation, (b) CO_2 direct dissociation, (c) CO_2 dissociation by H assistance on Ni(111) under electric fields of 0, −0.6, +0.6 V/Å and K additive.

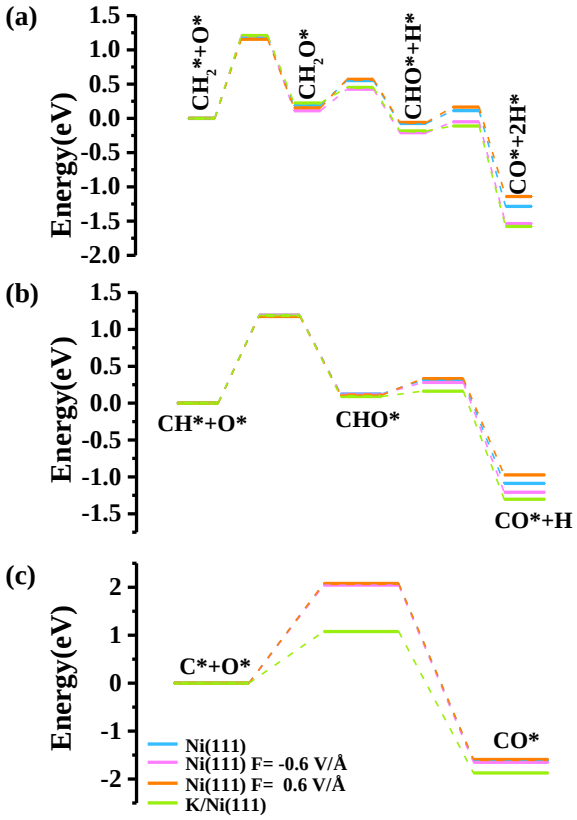

Figure S8. Potential energy profiles of (a) CH_2-O oxidation, (b) CH-O oxidation, and (c) C-O oxidation on Ni(111) under electric fields of 0, −0.6, +0.6 V/Å and K additive.

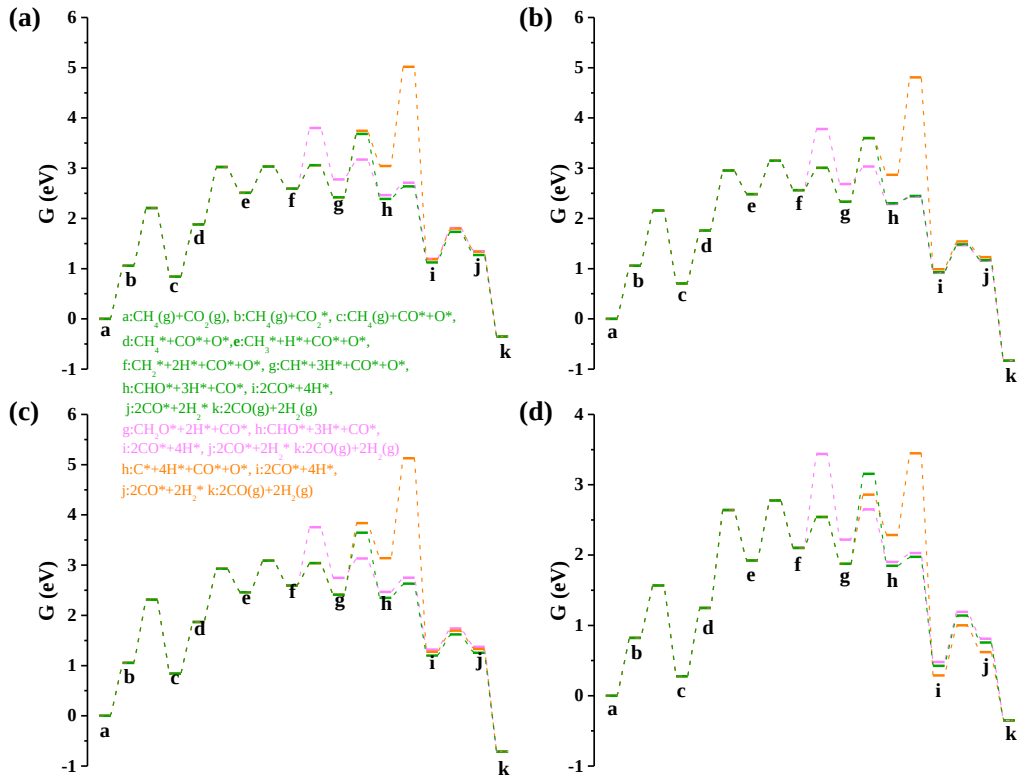

Figure S9. Gibbs free energy profiles of CH_2-O oxidation, CH-O oxidation, and C-O oxidation DRM reaction pathways on Ni(111) under electric fields of (a) 0, (b) −0.6, (c) +0.6 V/Å and (d) K additive at 1073.15 K.

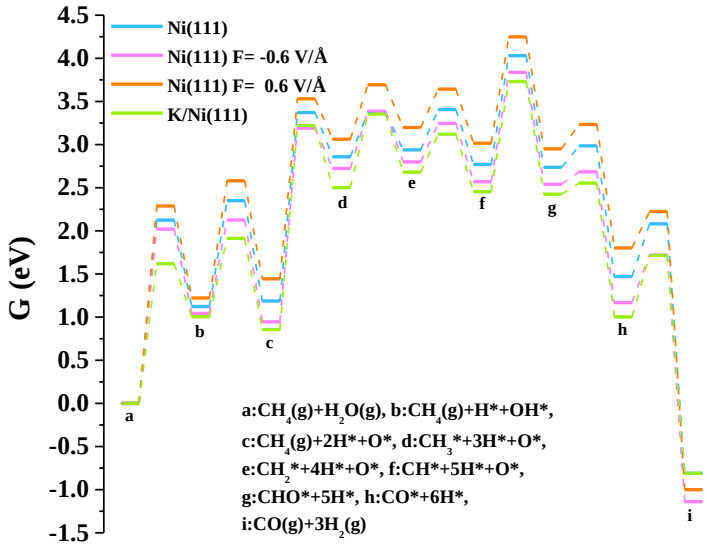

Figure S10. Gibbs free energy profiles of the most favorable SRM reaction pathway (CH-O) on Ni(111) under electric fields of 0, −0.6, +0.6 V/Å and K additive at 1073.15 K.

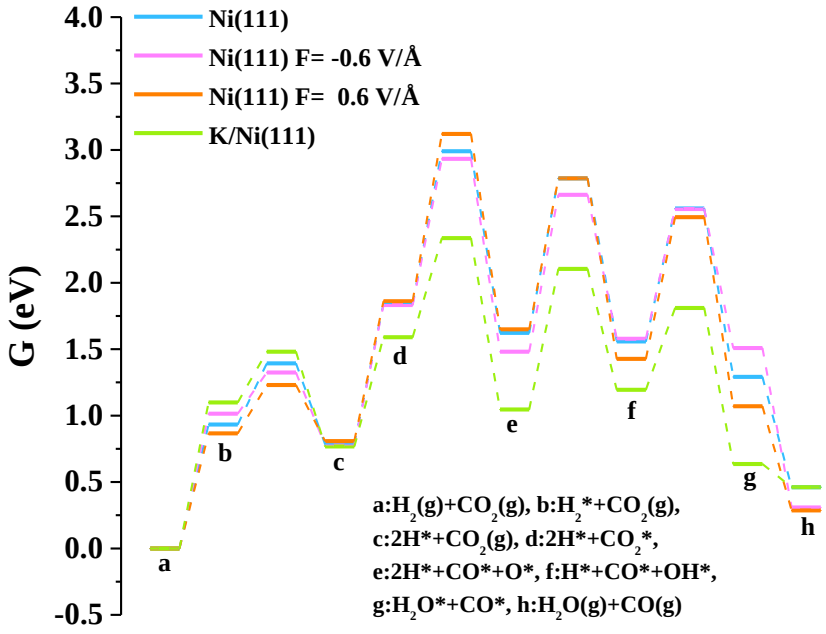

Figure S11. Gibbs free energy profiles of RWGS reaction on Ni(111) under electric fields of 0, −0.6, +0.6 V/Å and K additive at 1073.15 K.

References

1 M. Zhou and B. Liu, *ChemCatChem*, 2015, **7**, 3928–3935.

2 Y.-A. Zhu, D. Chen, X.-G. Zhou and W.-K. Yuan, *Catal. Today*, 2009, **148**, 260–267.

3 S.-G. Wang, D.-B. Cao, Y.-W. Li, J. Wang and H. Jiao, *Surf. Sci.*, 2006, **600**, 3226–3234.

4 W.-Y. Wang and G.-C. Wang, *J. Phys. Chem. C*, 2021, **125**, 18653–18664.

5 F. Che, R. Zhang, A. J. Hensley, S. Ha and J.-S. McEwen, *Phys. Chem. Chem. Phys.*, 2014, **16**, 2399–2410.

6 J. Wellendorff, T. L. Silbaugh, D. Garcia-Pintos, J. K. Nørskov, T. Bligaard, F. Studt and C. T. Campbell, *Surf. Sci.*, 2015, **640**, 36–44.

7 F. Che, J. T. Gray, S. Ha and J.-S. McEwen, *ACS Catal.*, 2017, **7**, 551–562.

8 L. Foppa, M.-C. Silaghi, K. Larmier and A. Comas-Vives, *J. Catal.*, 2016, **343**, 196–207.