Supporting information

Mechanistic of Coke-Resistance Ni/ZrO_2 Catalyst for Dry Reforming of Methane Under External Electric Fields: A Combined First-Principles and Microkinetic Modeling Study

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

([a] Tianjin Key Lab and Molecule-Based Material Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China)

*corresponding author

Tel. +86-22-23502458.

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

Table S1. The electronic adsorption energy (ΔE_{ads}) in eV and adsorption sites of species on Ni(111) and Ni_{16}/ZrO_2 under electric fields.

Species	Ni(111)[1]			$Ni_{16}/ZrO_2(110)$			Ni_{13}/ZrO_2 (101)[2]	Ni_{25}/ZrO_2 (101)[3]	Ni_{13}/CeO_2 (111)[4]	Ni_{12}/MgO (100)[5]	Ni_{55}/Al_2O_3 (110)[6]
Field (V/Å)	0.0	-0.6	+0.6	0.0	-0.6	+0.6					
CH_4*	-0.11	-0.10	-0.13	-0.22	-0.45	-0.30	-0.31	-0.35	-0.44	-0.05	0.00
CH_3*	-1.59	-1.46	-1.65	-2.29	-2.09	-2.49	-1.95	-1.49	-2.57	-2.12	--
CH_2*	-3.59	-3.60	-3.61	-4.30	-3.98	-4.36	-4.37	-1.98	-4.52	-4.03	--
CH*	-5.96	-6.06	-5.82	-6.25	-6.28	-6.42	-6.19	-2.97	-7.20	-6.24	--
C*	-6.34	-6.23	-6.17	-7.07	-6.52	-6.68	-8.71	--	-7.88	-8.15	--
H*	-2.71	-2.71	-2.69	-3.61	-2.76	-2.71	-3.89	--	-2.68	-0.20	--
CO_2*	-0.16	-0.16	-0.17	-0.66	-0.88	-0.48	-1.51	--	--	-0.76	-1.49
CO*	-1.59	-1.73	-1.46	-2.20	-2.28	-2.24	-2.09	-1.35	-2.18	-1.81	-1.48
O*	-5.32	-5.26	-4.91	-5.65	-5.55	-5.52	-7.70	--	-5.86	-2.42	-6.05
CHO*	-2.03	-1.86	-1.86	-2.65	-2.47	-2.77	-2.43	--	--	-2.38	--
CH_2O*	-0.54	-0.27	-0.38	-1.38	-0.60	-1.00	-0.50	--	--	--	--
COOH*	-2.05	-2.22	-1.79	-2.71	-2.81	-2.62	--	--	--	--	--
OH*	-3.19	-2.72	-2.98	-4.18	-3.75	-3.88	-3.73	--	-3.97	--	-3.76
H_2O*	-0.23	-0.12	-0.23	-0.53	-0.68	-0.41	0.10	--	--	--	-0.48
H_2*	0.05	0.14	-0.01	-0.40	-0.68	-0.61	--	--	-0.47	--	--

Table S2. The activation energy (ΔE_a) and reaction energy (ΔE) in eV of all elementary reactions on Ni_{16}/ZrO_2 under electric fields.

Model	Ni_{16}/ZrO_2					
Electric field	0.0 V/Å		-0.6 V/Å		+0.6 V/Å	
Reaction	ΔE_a	ΔE	ΔE_a	ΔE	ΔE_a	ΔE
$CH_{4(g)} \rightarrow CH_3$*+H*	0.78	-0.11	0.67	0.17	0.57	-0.02
$CH_{4(g)} \rightarrow CH_3$*+H-$O_L$*	0.61	-1.01	0.35	-1.03	0.27	-1.35
CH_3* $\rightarrow$ CH_2*+H*	0.45	0.01	0.62	-0.07	0.75	0.20
CH_2* $\rightarrow$ CH*+H*	0.40	-0.27	0.37	-0.35	0.34	-0.24
CH* $\rightarrow$ C*+H*	1.19	0.74	1.14	0.62	1.37	0.90
$CO_{2(g)} \rightarrow$ CO*+O*	0.13	-1.73	-0.18	-1.62	0.14	-1.76
$CO_{2(g)}$+H* $\rightarrow$ COOH*	0.23	-0.10	0.35	-0.12	0.65	-0.16
COOH* $\rightarrow$ CO*+OH*	0.10	-1.30	0.33	-1.40	0.40	-1.36
C*+O* $\rightarrow$ CO*	1.23	-1.79	1.29	-1.39	1.20	-1.93
CH*+O* $\rightarrow$ CHO*	1.14	0.07	1.03	0.20	0.87	0.02
CHO* $\rightarrow$ CO*+H*	0.25	-1.14	0.39	-1.07	0.48	-0.60
CH_2*+O* $\rightarrow$ CH_2O*	1.25	0.41	1.31	0.48	1.25	0.34
CH_2O* $\rightarrow$ CHO*+H*	0.51	-0.29	0.42	-0.52	0.50	0.04
O*+H* $\rightarrow$ OH*	1.38	-0.05	1.48	-0.38	1.50	-0.35
OH*+H* $\rightarrow$ $H_2O_{(g)}$	1.42	0.95	1.32	0.64	1.58	1.12
H*+H* $\rightarrow$ $H_{2(g)}$	0.61	0.82	0.74	1.10	0.82	1.26
$2CO_{(g)} \rightarrow CO_{2(g)}$+C*	1.45	1.24	0.74	0.55	0.86	0.64
C*, diffusion	0.49	-0.22	0.49	-0.21	0.59	-0.12
2C* $\rightarrow$ C-C*	0.45	-0.79	0.48	-0.77	0.32	-0.90
2CH*$\rightarrow$ CH-CH*	0.27	-0.55	0.35	-0.37	0.21	-0.56

Note: Zero-point energy (ZPE) correction is included.

Table S3. The activation energy (ΔE_a) and reaction energy (ΔE) in eV of elementary reactions on other Ni-supported catalysts reported in literature.

Model	Ni_{16}/ $ZrO_2(110)$		Ni_{13}/ $ZrO_2(101)$[2]		Ni_{25}/ $ZrO_2(101)$[3]		Ni_{13}/ $CeO_2(111)$[4]		Ni_{12}/ MgO(100)[5]	
Reaction	ΔE_a	ΔE	ΔE_a	ΔE	ΔE_a	ΔE	ΔE_a	ΔE	ΔE_a	ΔE
$CH_{4(g)} \rightarrow CH_3$*+H*	0.78	-0.11	-0.10	-0.87	0.57	0.21	-0.10	-0.12	3.40	0.05
$CH_{4(g)} \rightarrow CH_3$*+H-$O_L$*	0.61	-1.01	--	--	--	--	--	--	--	--
CH_3* $\rightarrow$ CH_2*+H*	0.45	0.01	0.37	-0.34	0.80	0.52	0.68	0.34	2.58	0.77
CH_2* $\rightarrow$ CH*+H*	0.40	-0.27	0.36	-0.52	0.71	0.54	0.36	-0.78	1.92	-0.13
CH* $\rightarrow$ C*+H*	1.19	0.74	0.38	-0.15	1.32	0.89	0.72	-0.16	1.39	0.55
$CO_{2(g)} \rightarrow$ CO*+O*	0.13	-1.73	-0.07	-1.30	--	--	--	--	-0.33	-0.79
$CO_{2(g)}$+H* $\rightarrow$ COOH*	0.23	-0.10	--	--	--	--	--	--	--	--
COOH* $\rightarrow$ CO*+OH*	0.10	-1.30	--	--	--	--	--	--	--	--
C*+O* $\rightarrow$ CO*	1.23	-1.79	1.12	-0.47	1.31	-1.43	1.47	-0.31	2.24	-1.76
CH*+O* $\rightarrow$ CHO*	1.14	0.07	2.61	0.79	--	--	--	--	3.28	0.44
CHO* $\rightarrow$ CO*+H*	0.25	-1.14	--	--	--	--	--	--	1.64	-1.31
CH_2*+O* $\rightarrow$ CH_2O*	1.25	0.41	2.18	1.14	--	--	--	--	--	--
CH_2O* $\rightarrow$ CHO*+H*	0.51	-0.29	--	--	--	--	--	--	--	--
O*+H* $\rightarrow$ OH*	1.38	-0.05	1.10	0.09	--	--	--	--	--	--
OH*+H* $\rightarrow$ $H_2O_{(g)}$	1.42	0.95	1.77	1.51	--	--	--	--	--	--
H*+H* $\rightarrow$ $H_{2(g)}$	0.61	0.82	0.48	0.41	--	--	0.62	0.94	--	--
$2CO_{(g)} \rightarrow CO_{2(g)}$+C*	1.45	1.24	--	--	--	--	--	--	--	--
C*, diffusion	0.49	-0.22	--	--	--	--	--	--	--	--
2C* $\rightarrow$ C-C*	0.45	-0.79	--	--	0.42	-1.39	--	--	--	--
2CH* $\rightarrow$ CH-CH*	0.27	-0.55	--	--	--	--	--	--	--	--

Table S4. The distance of TS in all elementary reactions on Ni_{16}/ZrO_2 under electric fields. (Unit: Å)

	Ni_{16}/ZrO_2		
Reaction (distance of TS)	0.0 V/Å	-0.6 V/Å	+0.6 V/Å
$CH_{4(g)} \rightarrow CH_3^* + H^*$ (d_{C-H})	1.658	1.641	1.679
$CH_{4(g)} \rightarrow CH_3^* + OH^*$ (d_{C-H})	1.358	1.357	1.360
$CH_3^* \rightarrow CH_2^* + H^*$ (d_{C-H})	1.793	1.812	1.794
$CH_2^* \rightarrow CH^* + H^*$ (d_{C-H})	1.714	1.711	1.638
$CH^* \rightarrow C^* + H^*$ (d_{C-H})	1.629	1.610	1.609
$CO_2^* \rightarrow CO^* + O^*$ (d_{C-O})	1.730	1.773	1.729
$CO_2^* + H^* \rightarrow COOH^*$ (d_{C-H})	1.408	1.406	1.407
$COOH^* \rightarrow CO^* + OH^*$ (d_{C-O})	1.621	1.697	1.660
$C^* + O^* \rightarrow CO^*$ (d_{C-O})	1.915	1.913	1.908
$CH^* + O^* \rightarrow CHO^*$ (d_{C-O})	1.884	1.879	1.887
$CHO^* \rightarrow CO^* + H^*$ (d_{C-H})	1.191	1.180	1.175
$CH_2^* + O^* \rightarrow CH_2O^*$ (d_{C-O})	1.929	1.927	1.931
$CH_2O^* \rightarrow CHO^* + H^*$ (d_{C-H})	1.715	1.672	1.577
$O^* + H^* \rightarrow OH^*$ (d_{O-H})	1.392	1.388	1.363
$OH^* + H^* \rightarrow H_2O^*$ (d_{O-H})	1.509	1.492	1.532
$H^* + H^* \rightarrow H_2^*$ (d_{H-H})	1.313	1.316	1.303
$2CO^* \rightarrow CO_2^* + C^*$ (d_{C-O})	1.916	1.756	2.033
$2C^* \rightarrow C_2^*$ (d_{C-C})	2.029	2.024	2.021
$2CH^* \rightarrow C_2H_2^*$ (d_{C-C})	2.014	2.005	2.024

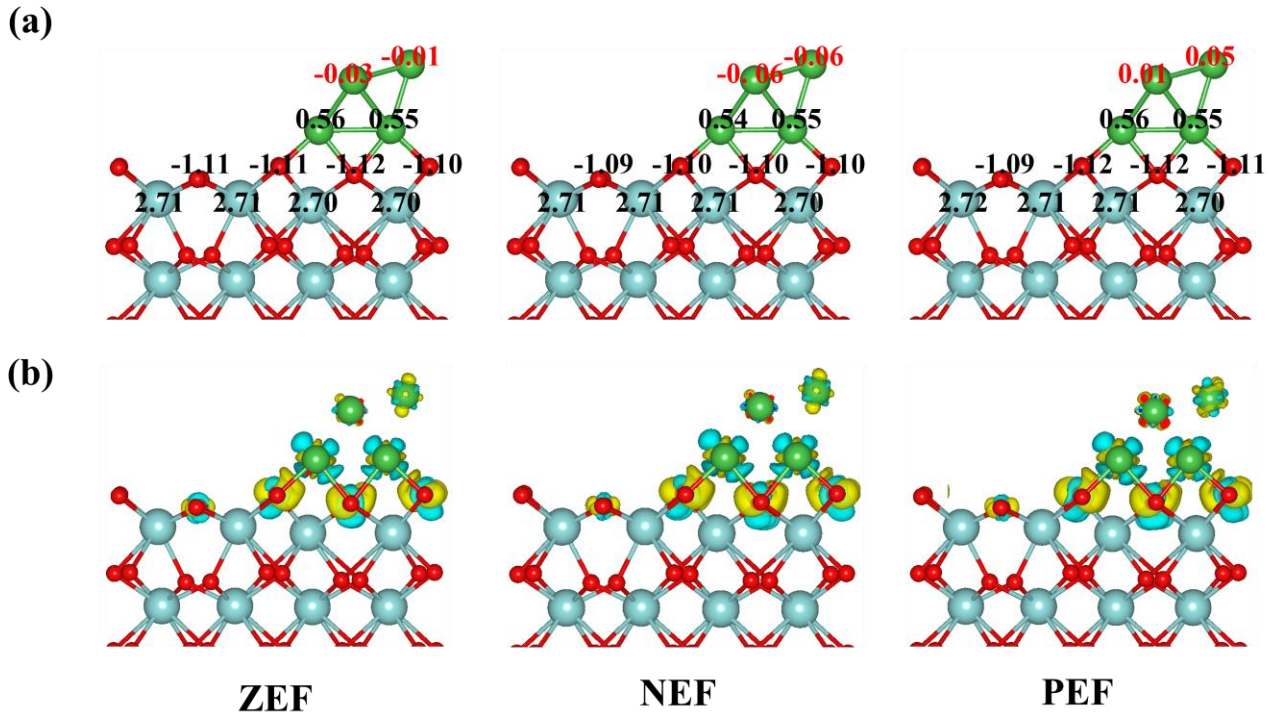


Figure S1. The (a) Bader charge and (b) charge density difference plot of Ni_{16}/ZrO_2 with ZEF, NEF and PEF. (The values in the figure represent the charge of single atom.) The green, red, grayish-green, and purple represent Ni, O, and Zr, respectively. Isosurface level used for the charge density plot was 0.007 e/Bohr^3. The yellow (cyan) color represents the charge accumulation (depletion).

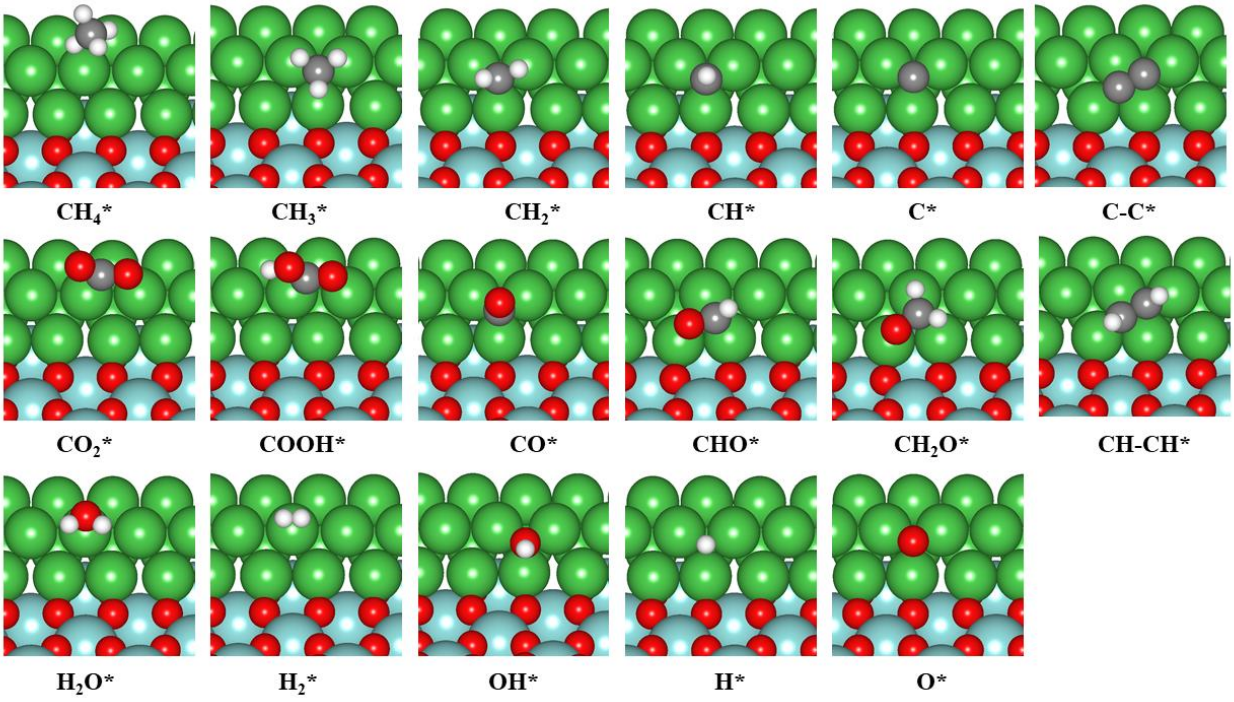


Figure S2. The front view of the DRM intermediates on Ni_{16}/ZrO_2 interface. The green, red, and grayish-green represent Ni, O, and Zr, respectively.

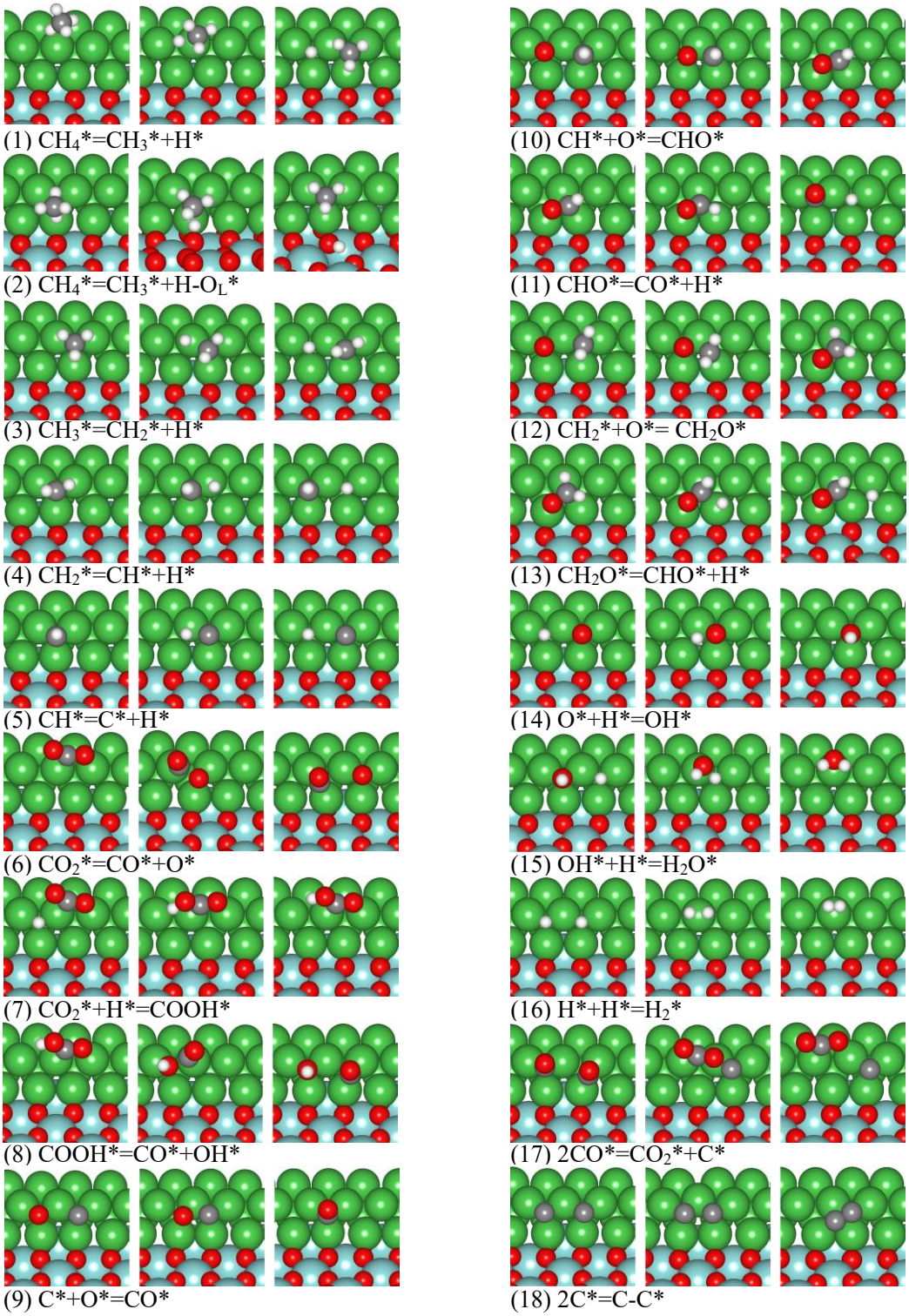


Figure S3. The front view of IS, TS, and FS of elementary reaction involved in DRM reaction on Ni_{16}/ZrO_2 surface.

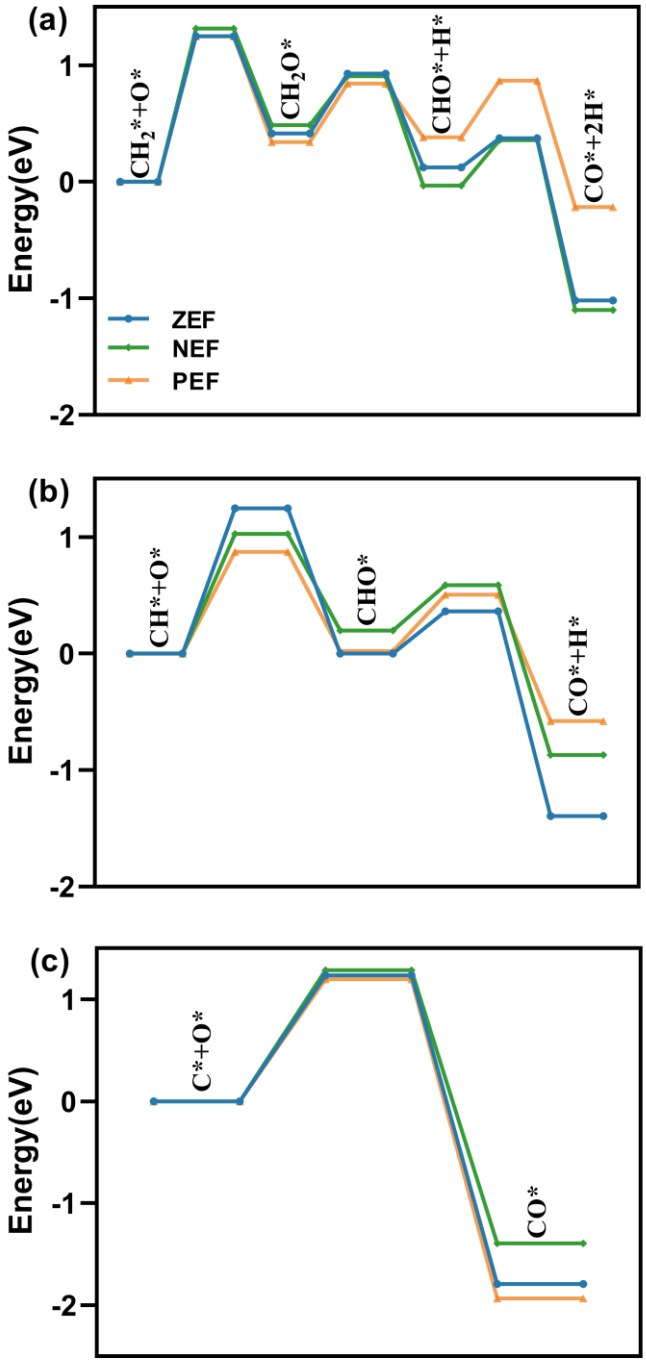
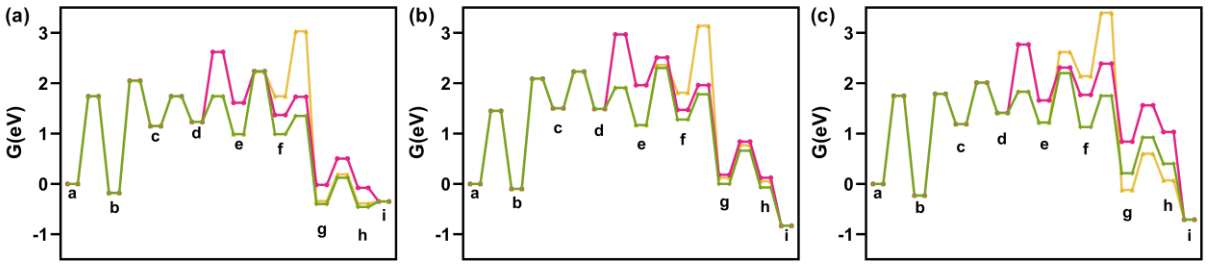


Figure S4. Potential energy profiles of (a) CH_2-O, (b) CH-O, and (c) C-O oxidation on Ni_{16}/ZrO_2 and under electric fields.



a:CH_4(g)+CO_2(g), b:CH_4(g)+CO*+O*, c:CH_3*+H*+CO*+O*, d:CH_2*+2H*+CO*+O*,
e:CH_2O*+2H*+CO*, f:CHO*+3H*+CO*, g:2CO*+4H*, h:2CO*+$2H_2$*, i:2CO(g)+$2H_2$(g)
e:CH*+3H*+CO*+O*, f:CHO*+3H*+CO*, g:2CO*+4H*, h:2CO*+$2H_2$*, i:2CO(g)+$2H_2$(g)
e:CH*+3H*+CO*+O*, f:C*+4H*+CO*+O*, g:2CO*+4H*, h:2CO*+$2H_2$*, i:2CO(g)+$2H_2$(g)

Figure S5. Gibbs free energy profiles of CH_x-O (0-2) oxidation DRM reaction pathways on Ni_{16}/ZrO_2 under (a) ZEF, (b) NEF, and (c) PEF at 1073.15 K.

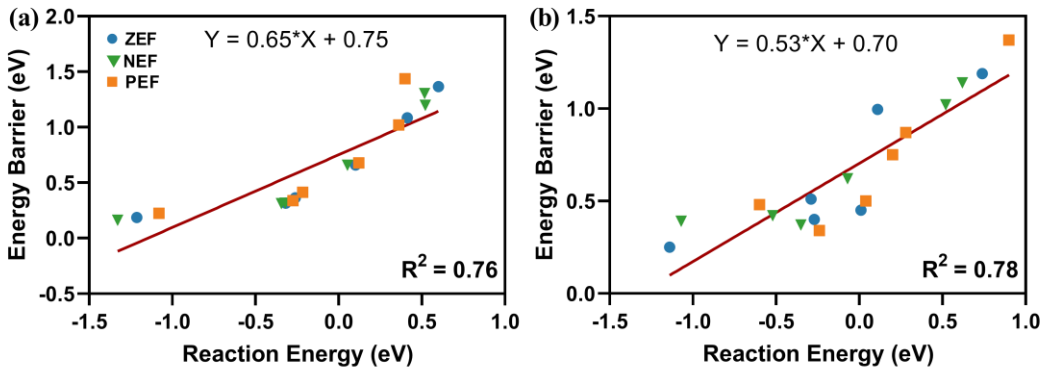
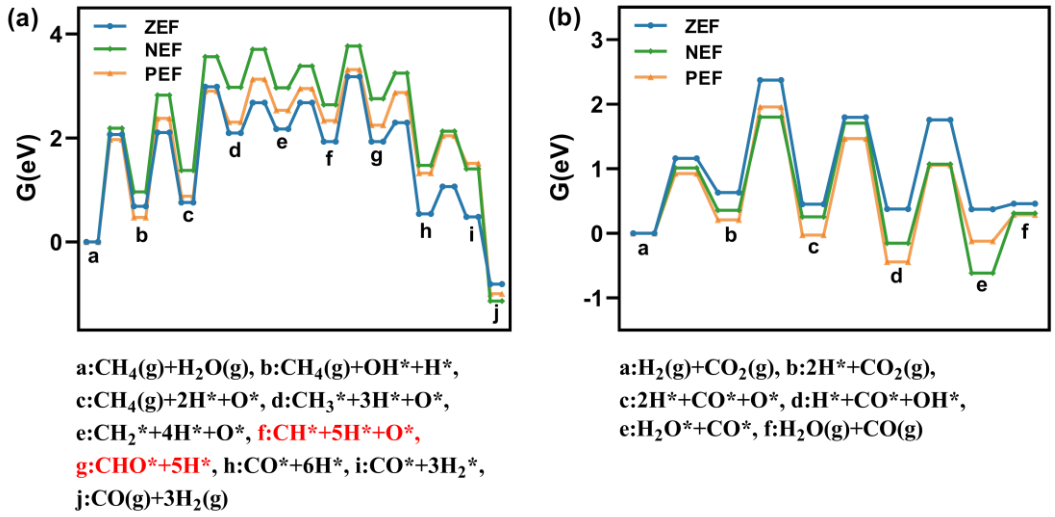


Figure S6. Relationship of the energy barrier and reaction energy for C–H breaking (R1, R3-5, R11, and R13) elementary reactions involved in the DRM reaction on (a) Ni(111) and (b) Ni_{16}/ZrO_2 under electric fields.



a:CH_4(g)+H_2O(g), b:CH_4(g)+OH*+H*, c:CH_4(g)+2H*+O*, d:CH_3*+3H*+O*, e:CH_2*+4H*+O*, f:CH*+5H*+O*, g:CHO*+5H*, h:CO*+6H*, i:CO*+$3H_2$*, j:CO(g)+$3H_2$(g)

a:H_2(g)+CO_2(g), b:2H*+CO_2(g), c:2H*+CO*+O*, d:H*+CO*+OH*, e:H_2O*+CO*, f:H_2O(g)+CO(g)

Figure S7. Gibbs free energy profiles of the most favorable (a) SRM reaction and (b) RWGS reaction on Ni_{16}/ZrO_2 under electric fields at 1073.15 K.

References

1 H. Jiao and G.-C. Wang, *Catal. Sci. Technol.*, 2023, **13**, 5407–5421.

2 H. Yang, H. Wang, L. Wei, Y. Yang, Y.-W. Li, X. Wen and H. Jiao, *Phys. Chem. Chem. Phys.*, 2021, **23**, 26392–26400.

3 J. Niu, C. Zhang, K. Li, H. Liu, Y. Jin and J. Ran, *Int. J. Hydrogen Energy*, 2024, **59**, 1399–1408.

4 A. Salcedo, P. G. Lustemberg, N. Rui, R. M. Palomino, Z. Liu, S. Nemsak, S. D. Senanayake, J. A. Rodriguez, M. V. Ganduglia-Pirovano and B. Irigoyen, *ACS Catal.*, 2021, **11**, 8327–8337.

5 Y. Guo, J. Feng and W. Li, *Chin. J. Chem. Eng*, 2017, **25**, 1442–1448.

6 L. Foppa, T. Margossian, S. M. Kim, C. Müller, C. Copéret, K. Larmier and A. Comas-Vives, *J. Am. Chem. Soc.*, 2017, **139**, 17128–17139.