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Atomic Ru cluster supported on CeO_2(110) for effective catalyzing electrochemical N_2 reduction reaction: insights from density functional theory

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Table S1 Calculated binding energy of Ru_n (n=1-6, 10) on CeO_2(110), the optimized bond lengths and Bader charge and the related donations of atoms are shown in Figure S3.

Ru_n/CeO_2(110)	E_b / eV	Bond	Bond length/Å	Atom	Bader charge/|e|
Ru_1/CeO_2(110)	-6.97	Ru-O1	1.962	Ru	0.93
		Ru-O2	2.025	O1	-0.95
		Ru-O3	2.008	O2	-0.53
		Ru-O4	1.988	O3	-0.43
				O4	-0.93
				O5	-1.31
				O6	-1.18
				Ce1	2.42
				Ce2	0.52
				Ce3	2.34
				Ce4	2.10
Ru_2/CeO_2	-8.83	Ru1-Ru2	2.239	Ru1	1.50
		Ru1-O1	1.861	Ru2	0.18
		Ru1-O2	1.782	O1	-0.95
		Ru2-O3	1.876	O2	-1.04
		Ru2-O4	1.799	O3	-1.01
				O4	-1.04
				O5	-1.08
				O6	-0.78
				Ce1	1.79
				Ce2	0.93
				Ce3	1.67
Ru_3/CeO_2	-9.27	Ru1-Ru2	2.511	Ru1	0.94
		Ru1-Ru3	2.339	Ru2	0.60
		Ru2-Ru3	2.224	Ru3	0.54
		Ru1-O1	1.899	O1	-1.55
		Ru1-O2	1.790	O2	-1.25
		Ru2-O3	1.991	O3	-1.47
		Ru2-O4	2.013	O4	-1.50
		Ru3-O5	1.812	O5	-1.20
				O6	-1.60
				O7	-1.63
				Ce1	2.79
				Ce2	2.98
				Ce3	2.61
Ru_4/CeO_2	-10.29	Ru1-Ru2	2.223	Ru1	-0.34
		Ru1-Ru4	2.234	Ru2	0.44
		Ru2-Ru3	2.352	Ru3	1.27
		Ru3-Ru4	2.241	Ru4	0.82
		Ru2-O1	1.938	O1	-0.91

		Ru2-O2	1.938	O2	-1.06
		Ru3-O3	1.822	O3	-1.13
		Ru3-O4	1.864	O4	-0.96
		Ru4-O5	1.817	O5	-1.19
				O6	-1.21
				O7	-1.19
				Ce1	2.16
				Ce2	2.31
				Ce3	1.42
Ru_5/CeO_2	-9.97	Ru1-Ru2	2.280	Ru1	0.41
		Ru1-Ru3	2.626	Ru2	0.23
		Ru1-Ru4	2.645	Ru3	0.49
		Ru1-Ru5	2.274	Ru4	0.11
		Ru2-Ru3	2.374	Ru5	0.05
		Ru2-Ru5	2.892	O1	-0.85
		Ru3-Ru4	2.256	O2	-1.13
		Ru4-Ru5	2.389	O3	-1.26
		Ru2-O1	1.800	O4	-0.90
		Ru3-O2	1.926	O5	-0.74
		Ru4-O3	1.912	O6	-1.16
		Ru5-O4	1.776	Ce1	2.12
				Ce2	1.93
				Ce3	0.26
Ru_6/CeO_2	-10.47	Ru1-Ru2	2.365	Ru1	-0.18
		Ru1-Ru3	2.342	Ru2	1.0
		Ru1-Ru6	2.240	Ru3	0.68
		Ru2-Ru3	2.499	Ru4	-0.15
		Ru2-Ru5	2.269	Ru5	0.06
		Ru3-Ru4	2.270	Ru6	-0.09
		Ru4-Ru5	2.605	O1	-0.94
		Ru4-Ru6	2.313	O2	-1.24
		Ru5-Ru6	2.356	O3	-1.01
		Ru2-O1	1.949	O4	-1.07
		Ru2-O2	1.974	O5	-0.95
		Ru3-O3	1.818	O6	-1.24
		Ru5-O4	2.019	O7	-1.38
		Ru5-O5	1.978	Ce1	2.21
				Ce2	2.45
				Ce3	1.93
Ru_{10}/CeO_2	-11.46	Ru1-Ru2	2.270	Ru1	-0.22
		Ru1-Ru5	2.379	Ru2	0.45
		Ru1-Ru6	2.303	Ru3	0.19
		Ru2-Ru3	2.502	Ru4	0.97
		Ru2-Ru7	2.233	Ru5	0.27

Ru3-Ru4	2.300	Ru6	0.02
Ru3-Ru8	2.242	Ru7	-0.28
Ru4-Ru5	2.341	Ru8	0.3
Ru4-Ru9	2.312	Ru9	-0.24
Ru5-Ru10	2.265	Ru10	0.31
Ru6-Ru7	2.293	O1	-0.98
Ru6-Ru10	2.292	O2	-0.42
Ru7-Ru8	2.415	O3	-1.26
Ru8-Ru9	2.298	O4	-0.72
Ru9-Ru10	2.290	O5	-1.18
Ru1-O1	1.877	O6	-1.04
Ru2-O3	1.971	Ce1	2.36
Ru3-O3	1.929	Ce2	-0.04
Ru4-O5	1.797	Ce3	1.71
Ru5-O6	1.901		

Table S2 Calculated N-Ru bond length ($L_{N\text{-}Ru}$) of N_2 adsorbed on Ru_n (n=1-6,10)/CeO_2(110) in end-on and side-on modes.

Ru_n/CeO_2(110)	$L_{N\text{-}Ru}$ / Å			
	End-on		Side-on	
	N-Ru	length	N-Ru	length
Ru_1/CeO_2	N2-Ru1	1.863	N1-Ru1	2.201
			N2-Ru1	2.156
Ru_2/CeO_2	N2-Ru1	1.976	N2-Ru1	2.048
			N2-Ru1	2.139
			N1-Ru2	2.062
			N2-Ru2	2.115
Ru_3/CeO_2	N2-Ru3	1.951	N1-Ru3	1.982
			N2-Ru2	1.948
Ru_4/CeO_2	N2-Ru4	1.953	N1-Ru1	2.012
			N2-Ru4	2.113
Ru_5/CeO_2	N2-Ru1	1.950	N1-Ru2	1.993
			N2-Ru1	1.873
Ru_6/CeO_2	N2-Ru6	1.974	N1-Ru4	2.023
			N2-Ru6	1.998
Ru_{10}/CeO_2	N2-Ru8	1.950	N1-Ru8	2.221
			N2-Ru8	2.079

Table S3 Calculated Bader charge of N atom in the gas N_2 and the end-on and side on adsorbed N_2 on Ru_n (n=1-6, 10)/CeO_2(110).

Species		Bader charge of N / |e|		Bader charge of N / |e|	
gas N_2		5.11		4.89	
		End-on		Side-on	
	Ru_1/CeO_2	5.26	5.10	5.17	5.15
	Ru_2/CeO_2	5.39	5.00	5.61	5.37
N_2 on	Ru_3/CeO_2	5.57	4.97	5.46	5.36
Ru_n/CeO_2(110)	Ru_4/CeO_2	5.40	5.06	5.38	5.31
	Ru_5/CeO_2	5.73	4.75	5.51	5.37
	Ru_6/CeO_2	5.42	5.00	5.31	5.38
	Ru_{10}/CeO_2	5.78	4.63	5.20	5.33

Table S4 The Gibbs free energy change of N_2 (ΔG(*N_2)) and H (ΔG(*H)) adsorption on Ru_n/CeO_2(110).

Ru_n/CeO_2(110)	ΔG(*N_2)/eV		ΔG(*H)/eV
	end on	side on	
Ru_1/CeO_2	-0.96	-0.35	-0.06
Ru_2/CeO_2	0.30	0.77	-0.01
Ru_3/CeO_2	-0.56	-0.22	-0.92
Ru_4/CeO_2	-0.30	0.30	-0.24
Ru_5/CeO_2	-0.28	0.12	-0.33
Ru_6/CeO_2	-0.56	-0.03	-0.39
Ru_{10}/CeO_2	-0.72	-0.25	-0.84

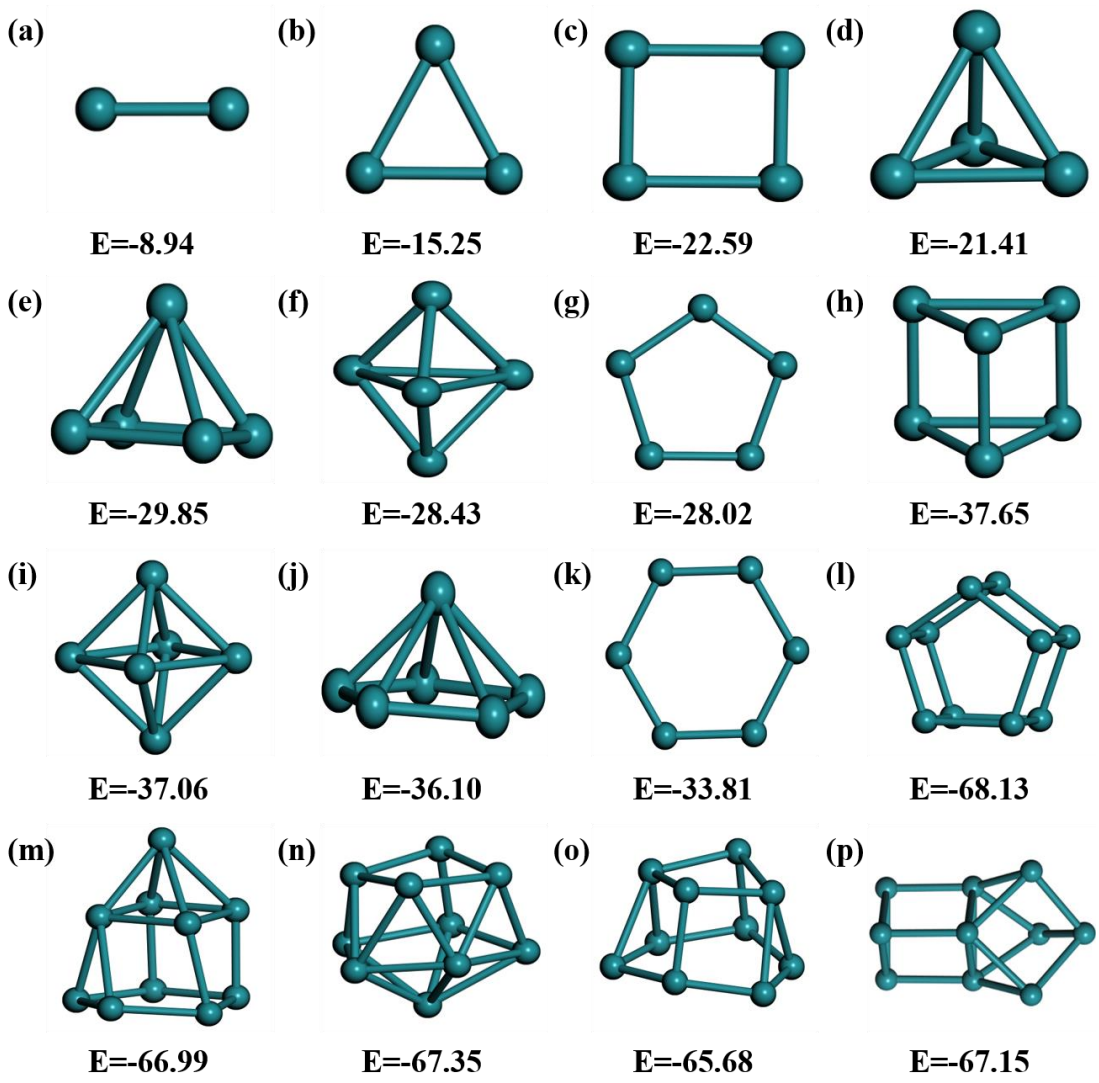

Figure S1. Configurations of Ru_n (n=2-6,10) cluster. The values in figure indicate the calculated total energy in eV by DFT.

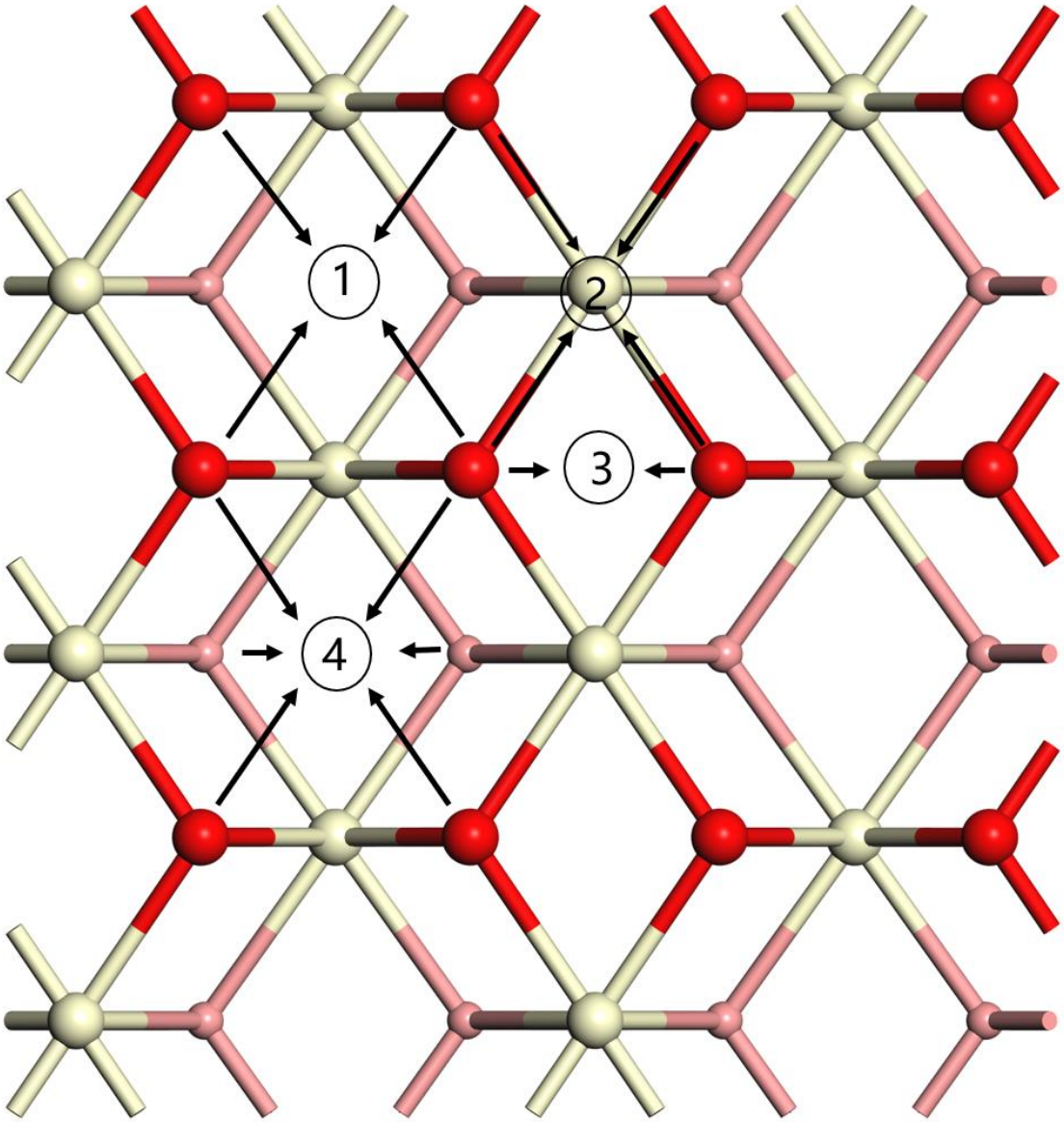

Figure S2. Possible location sites of Ru_n(n=1-6,10) on CeO_2(110). Color code: surface O: red; second layer O: pink; Ce: yellow.

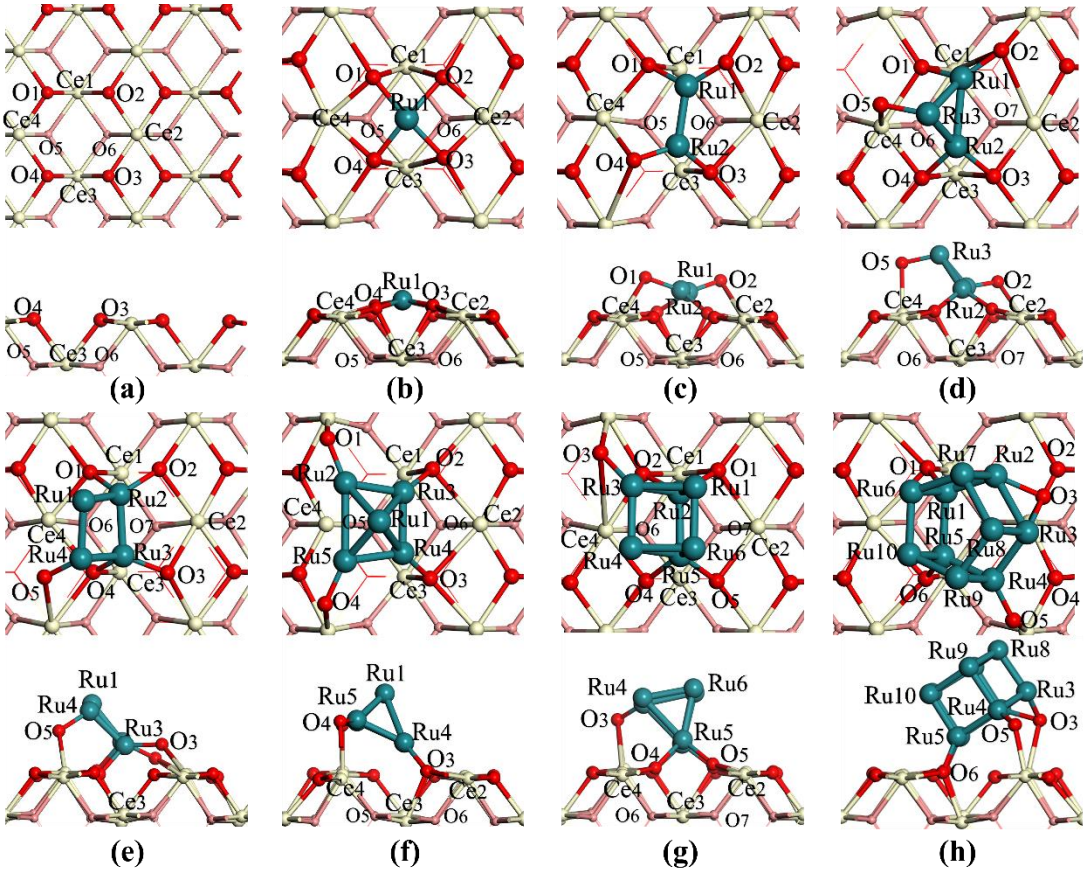

Figure S3. Top views of $CeO_2(110)$ and $Ru_n(n=1\text{-}6,10)/CeO_2(110)$. (a) $CeO_2(110)$, (b) $Ru_1/CeO_2(110)$, (c) $Ru_2/CeO_2(110)$, (d) $Ru_3/CeO_2(110)$, (e) $Ru_4/CeO_2(110)$, (f) $Ru_5/CeO_2(110)$, (g) $Ru_6/CeO_2(110)$, (h) $Ru_{10}/CeO_2(110)$. Color scheme: oxygen: red (surface O), pink (third layer O), Ce: yellow, Ru: cyan.

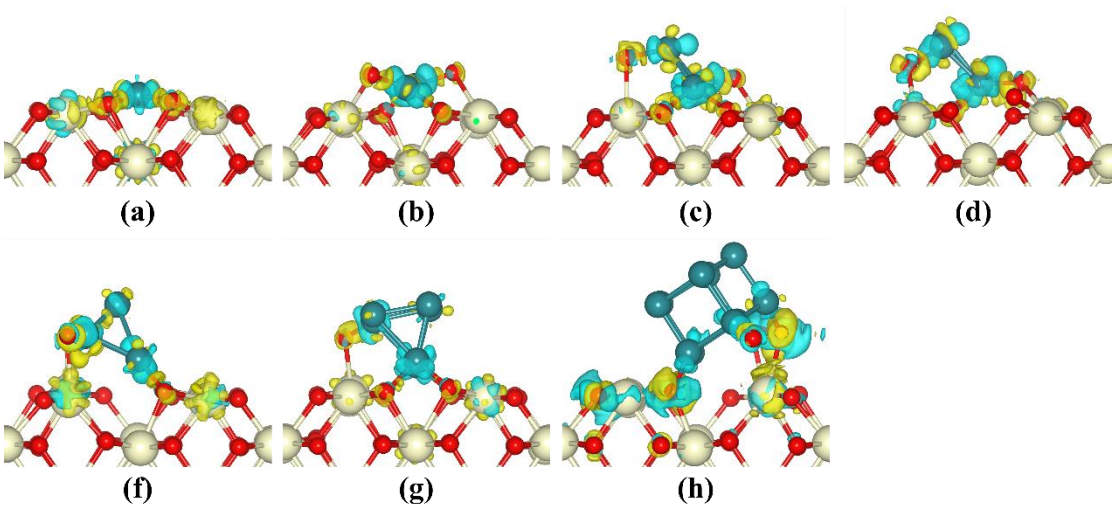

Figure S4. Calculated differential charge density of Ru_n(n=1-6,10)/CeO_2(110). The yellow and cyan regions represent the accumulation and consumption of electrons, respectively. Color code: O: red; Ce: yellow; Ru: cyan.

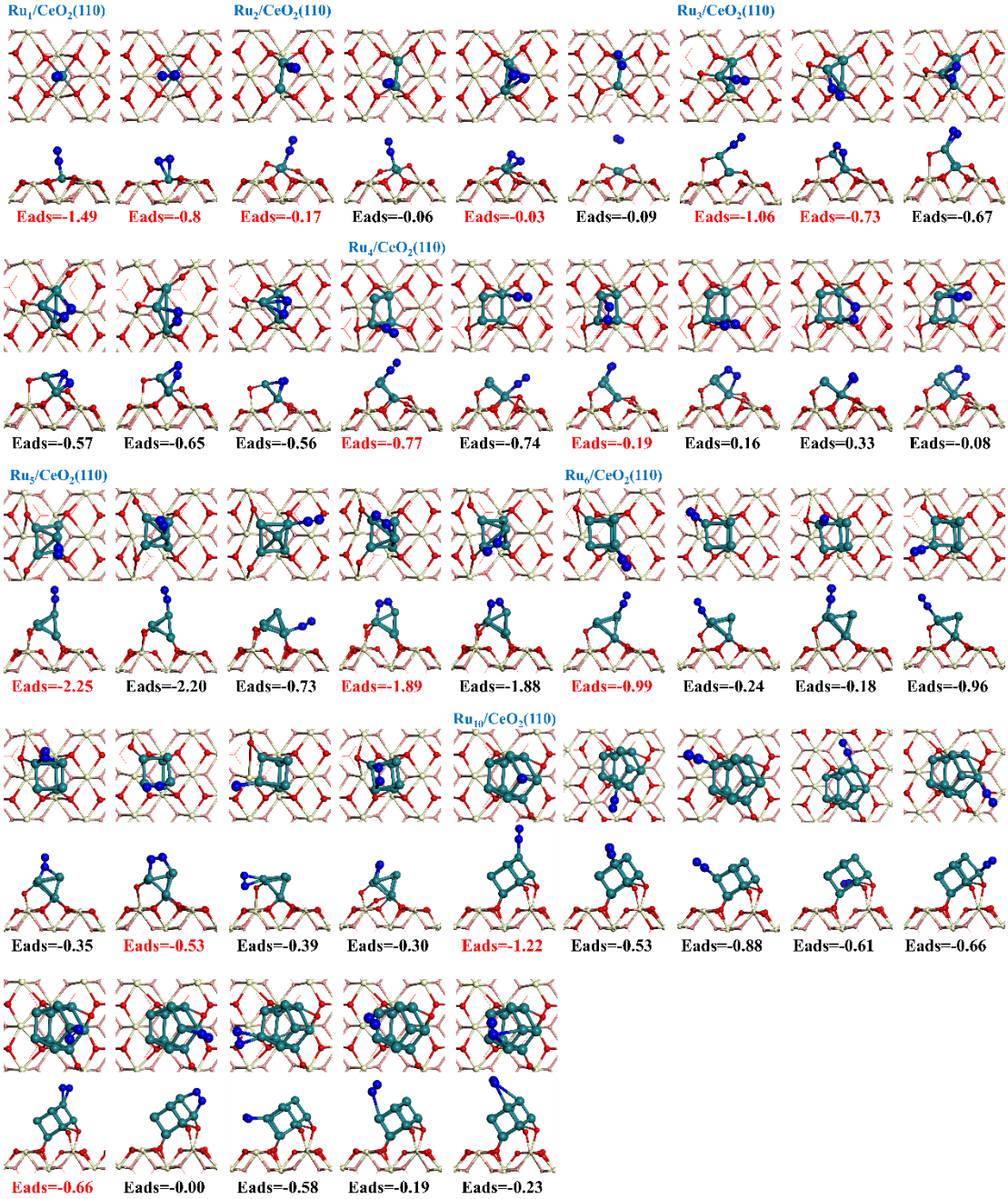

Figure S5. The top and side views of N_2 adsorbed at different site on Ru_n(n=1-6,10)/CeO_2(110) with the values of adsorption energy (E_{ads}, unit in eV). Color code: O: red; Ce: yellow; Ru: cyan; N: blue.

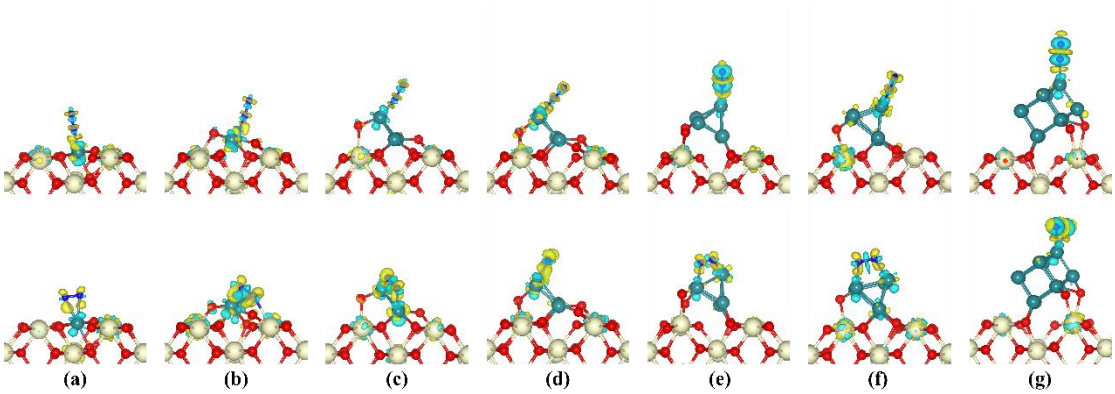

Figure S6. Calculated differential charge density of N_2 adsorbed on Ru_n(n=1-6,10)/CeO_2(110) in end-on and side-on modes. The yellow and cyan regions represent the accumulation and consumption of electrons, respectively. Color code: O: red; Ce: yellow; Ru: cyan; N: blue.

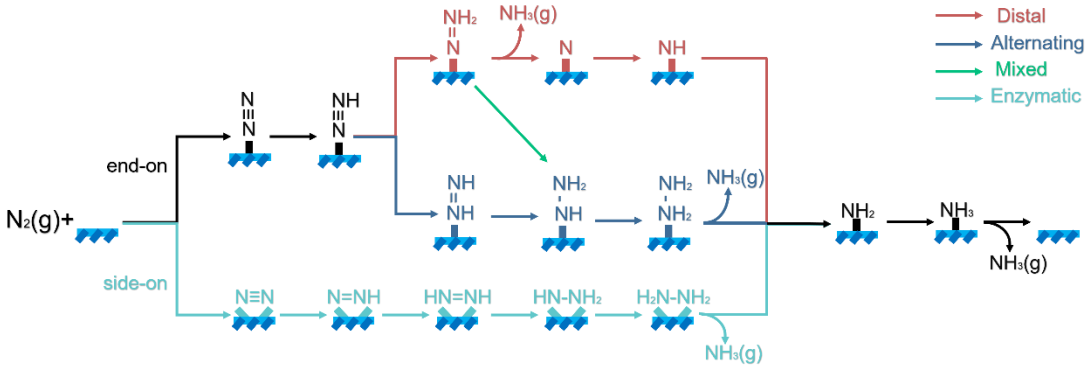

Figure S7. Scheme of possible associative reaction pathways of nitrogen reduction, i.e. the distal, alternating, enzymatic and mixed pathways.

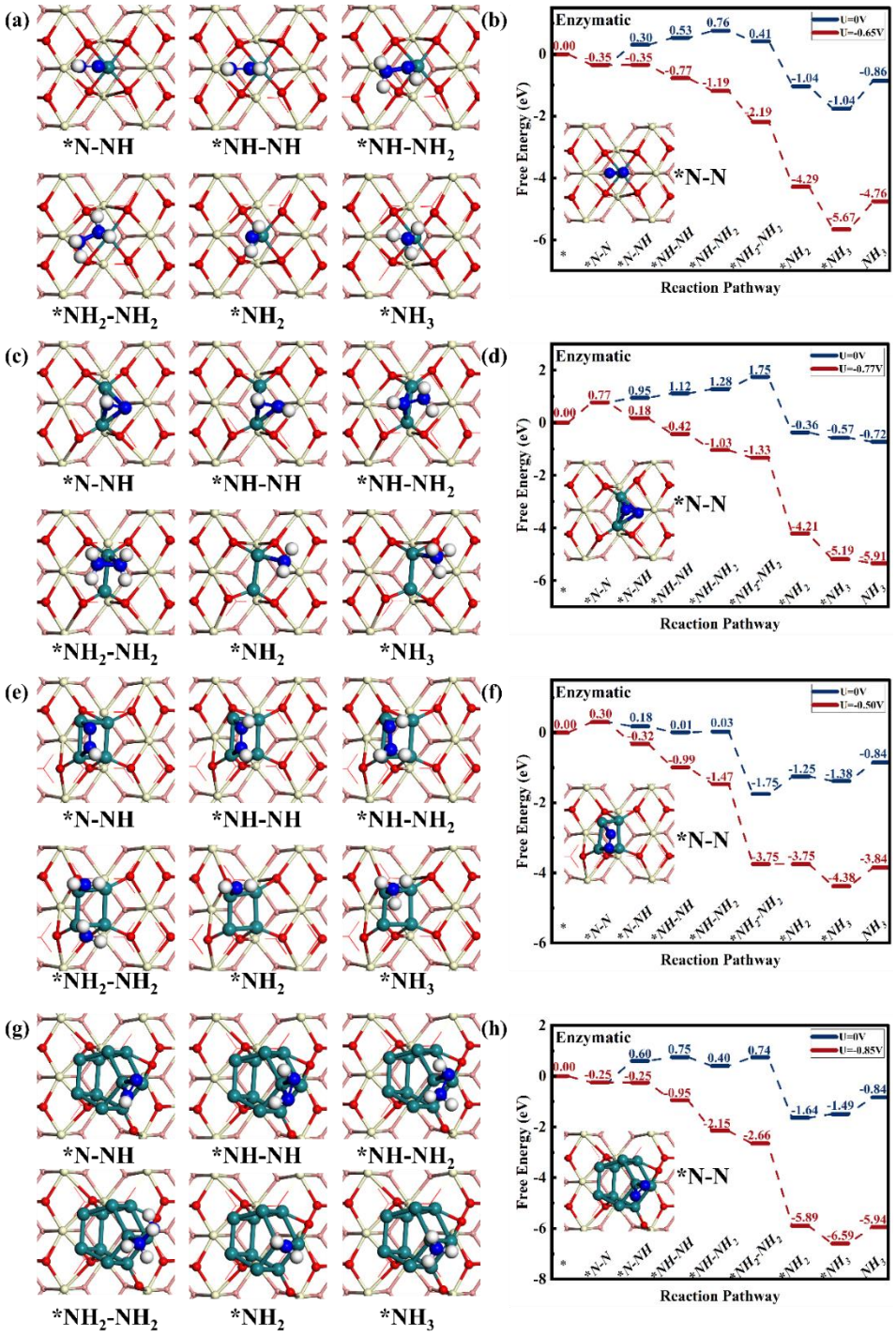

Figure S8. The optimized geometries and energy profiles of NRR on Ru_n(n=1,2,4,10)/CeO_2(110) along enzymatic pathway. (a), (b) Ru_1/CeO_2(110); (c), (d) Ru_2/CeO_2(110); (e), (f) Ru_4/CeO_2(110); (g), (h) Ru_{10}/CeO_2(110). Color code: surface O: red; second layer O: pink; Ce: yellow; Ru: cyan; N: blue; H: white.

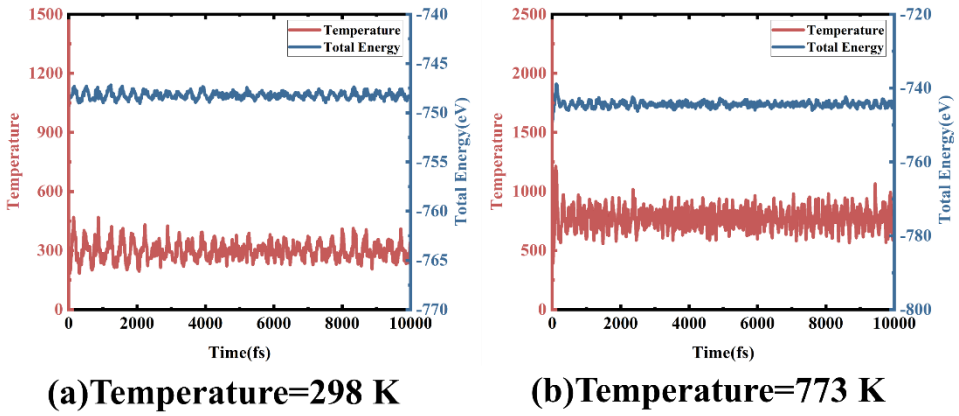

Figure S9. Temperature and energy evolution of $Ru_3/CeO_2(110)$ simulated by AIMD at 298 and 773 K, respectively. (a) 298K; (b) 773K.