Supporting Information

Coverage Dependent Structure and Energy of Water Dissociative Adsorption on Clean and O-Pre-covered Ni (100) and Ni(110)

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Content

Ab initio atomistic thermodynamics

According to previous literature, we took H_2O desorption on Ni(111) surface: H_2O/Ni → Ni + H_2O(g) as an example; and the change of Gibbs free energy (ΔG) for this reaction can be described as equation (1):

$$\Delta G = G[Ni(111)] + G_{gas}(H_2O) - G[\{H_2O\}/Ni(111)] \quad (1)$$

In this equation, G[Ni(111)] is the Gibbs free energy of the Ni(111) surface. G[{H_2O}/Ni(111)] is the Gibbs free energy of the Ni(111) surface with H_2O molecule. We apply the DFT calculated total energy to replace the Gibbs free energy of the solid surfaces[i]

The $G_{gas}(H_2O)$ term is equal to $\mu(H_2O)$. The H_2O chemical potential can be described as

$$\mu_{H_2O}(T,p) = E_{H_2O}^{total} + \tilde{\mu}_{H_2O}(T,p^0) + k_B T ln(p_{H_2O}/p^0)$$

$E_{H_2O}^{total}$ is the DFT calculated energy of the isolated H_2O molecule (including zero point energy), $\tilde{\mu}_{H_2O}(T,p^0)$ term is the chemical potential at different temperatures, which can be found in thermodynamic tables; and $k_B T ln(p_{H_2O}/p^0)$ is the contribution of temperature and H_2O partial pressure to the H_2O chemical potential. Therefore equation (1) can be rewritten as

$$\Delta G = E[Ni(111)] - G[\{H_2O\}/Ni(111)] + E_{H_2O}^{total} + \tilde{\mu}_{H_2O}(T,p^0) + k_B T ln(p_{H_2O}/p^0) \quad (2)$$

Figure S1. Computed $8H_2O$ configurations on the (4 X 4) slab Ni (110) surface; four periodic structures for (a): with H-bonding and (b): c(2 x 2) without H-bonding (O/red; H/white; the first layer/blue, the second layer/purple)

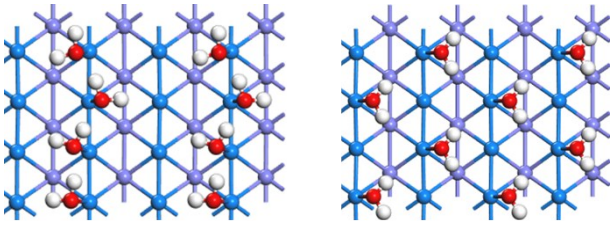

Figure S2. PBE-D3 optimized structures and the adsorption energy (eV) of $2H_2O$ dissociation for the stationary points on Ni(100) surface (O/red; H/white; the first layer/blue, the second layer/purple)

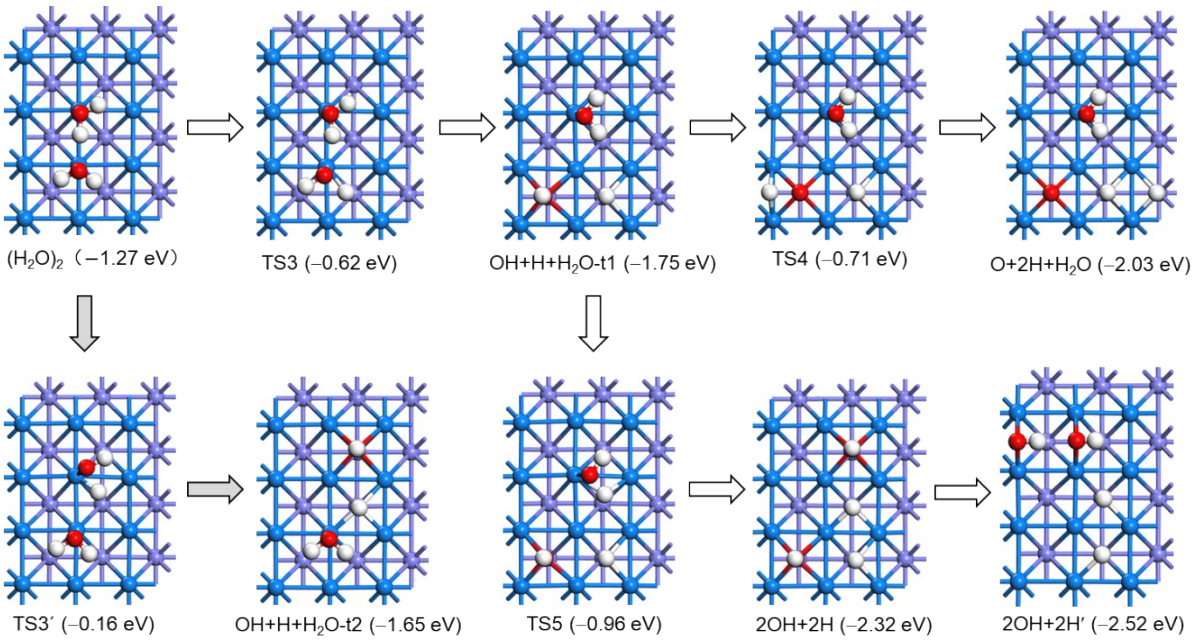

Table S1. Adsorption energy (E_{ads}, eV) and shortest distances (d, Å) of the IS and FS for H_2O direct dissociation and $2H_2O$ dissociation on Ni(100) surface using PBE-D3

	E_{ads}	d_{Ni-O}	d_{Ni-H}
		H_2O direct dissociation	
H_2O	−0.57	2.110	
OH+H	−1.29	2.110; 2.113; 2.111; 2.115	1.816; 1.844; 1.850; 1.866
O+2H	−1.73	1.946; 1.945; 1.952; 1.942	1.795; 1.846; 1.836; 1.845; 1.809; 1.839; 1.865; 1.854
		$2H_2O$ dissociation	
H_2O+H_2O	−1.27	2.040; 2.813	
H_2O+OH+H	−1.75	2.141; 2.004; 2.010; 2.194; 2.242	1.741; 1.770; 1.908; 1.950
H_2O+O+2H	−2.03	2.141; 2.004; 2.010; 2.194; 2.242	1.741; 1.770; 1.908; 1.950
2OH+2H	−2.04	2.043; 2.043; 2.194; 2.217; 2.038; 2.057; 2.181; 2.209	1.764; 1.773; 1.858; 1.915; 1.708; 1.748; 1.906; 1.983

Table S2. PBE-D3 computed dissociation barriers and energies (E_a and E_r, eV), bond distances (d_{Ni-X}, Å) and the breaking O-H bond distance (d_{O-H}, Å) in the transition state for H_2O direct dissociation and $2H_2O$ dissociation on Ni(100) surface

	E_a	E_r	d_{Ni-O}	d_{Ni-H}	d_{O-H}
			$H_2O \rightarrow TS1 \rightarrow OH + H$		
TS1	0.82	−0.72	1.919	1.663; 1.898	1.598
			OH + H → TS2 → O + 2H		
TS2	1.14	−0.44	1.933; 2.051; 2.069; 2.177	1.668; 1.818; 1.760; 1.736; 1.928; 1.931	1.402
			$2H_2O \rightarrow TS3 \rightarrow H_2O + OH + H$		
TS3	0.65	−0.48	2.058; 1.983	1.794; 1.970	1.536
			$H_2O + OH + H \rightarrow TS4 \rightarrow H_2O + O + 2H$		
TS4	1.04	−0.28	2.105; 2.035; 2.042; 2.042; 2.069	1.671; 1.713; 1.749; 1,767; 1.885; 1.933	1.389
			$H_2O + OH + H \rightarrow TS5 \rightarrow 2OH + 2H'$		
TS5	0.79	−0.77	1.919; 2.030; 2.037; 2.212; 2.245	1.755; 1.761; 1.904; 1.953	1.519

Table S3. PBE-D3 computed adsorption energies (E_{ads}, eV) and bond lengths (d_{Ni-X}, Å) of the IS and FS for H_2O dissociation on O pre-covered Ni(100)

	E_{ads}	d_{Ni-O}	d_{Ni-H}
		1O assisted H_2O dissociation	
O+H_2O	−1.02	1.952; 1.959; 1.952; 1.961; 2.115	
O+H_2O'	−0.91	2.154; 1.893; 1.938; 1.945; 2.225	
2OH	−1.52	1.910; 1.911; 1.954; 1.955	
O+H+OH	−1.62	2.207; 2.111; 2.112; 2.060; 1.931; 1.956; 1.960; 1.997	1.804; 1.872; 1.827; 1.862
2O+2H	−2.04	1.949; 1.940; 1.43; 1.929; 1.943; 1.927; 1.941; 1.949	1.815; 1.799; 1.857; 1.848; 1.800; 1.813; 1.849; 1.856
		2O assisted H_2O dissociation	
2O+H_2O	−1.12	1.884; 2.064; 1.887; 2.080; 2.114	
2O+H_2O'	−0.93	2.222; 1.877; 1.879; 1.956; 2.025	
O+2OH	−2.54	1.929; 1.935; 1.926; 1.937	
2O+H+OH	−1.49	2.109; 2.217; 2.116; 2.049; 1.931; 1.933; 1.992; 1.952; 1.958; 1.941; 1.937; 1.930	1.787; 1.815; 1.846; 1.859
3O+2H	−1.06	1.999; 1.940; 1.908; 1.911; 1.926; 1.932; 1.920; 1.931; 1.950; 1.937; 1.917; 1.952	1.715; 1.721; 1.927; 1.932; 1.804; 1.808; 1.820; 1.860

Table S4. PBE-D3 computed energy barriers and reaction energies (E_a and E_r, eV), bond distances (d_{Ni-X}, Å) and the breaking O-H bond distances (d_{O-H}, Å) of the TS for H_2O dissociation on O pre-covered Ni(100) surface

	E_a	E_r	d_{Ni-O}	d_{Ni-H}	d_{O-H}
			1O + H_2O → TS6 → 2OH		
TS6	0.53	−0.61	1.891; 1.953; 2.009; 2.098; 2.442		1.859
			2OH → TS7 → O + H + OH		
TS7	1.38	−0.10	1.939; 1.944; 1.926; 1.990; 2.122; 2.172	1.615; 1.899	1.390
			O + H + OH → TS8 → 2O + 2H		
TS8	1.24	−0.42	1.817; 1.842; 1.889; 1.936; 1.953; 2.015	1.731; 1.750; 1.922; 1.924; 1.654; 1.863; 1.937; 2.202	1.543
			2O + H_2O → TS9 → O + 2OH		
TS9	0.67	−0.61	1.925; 1.950; 2.094; 2.452		1.620
			O + 2OH → TS10 → 2O + H + OH		
TS10	1.20	−0.38	1.844; 1.859; 1.920; 1.937	1.848; 1.876; 2.096; 2.125	1.466
			2O + H + OH →TS11 → 3O + 2H		
TS11	2.22	−0.22	1.890; 1.932; 1.961; 2.004; 1.822; 1.824	1.694; 1.712; 1.983; 2.043; 1.971; 1.998; 1.762; 1.823	1.577

Figure S3. Optimized structures and the adsorption energy (eV) H_2O dissociation for the stationary points on the O pre-covered Ni(100) surface (O/red; H/white; the first layer/blue, the second layer/purple)

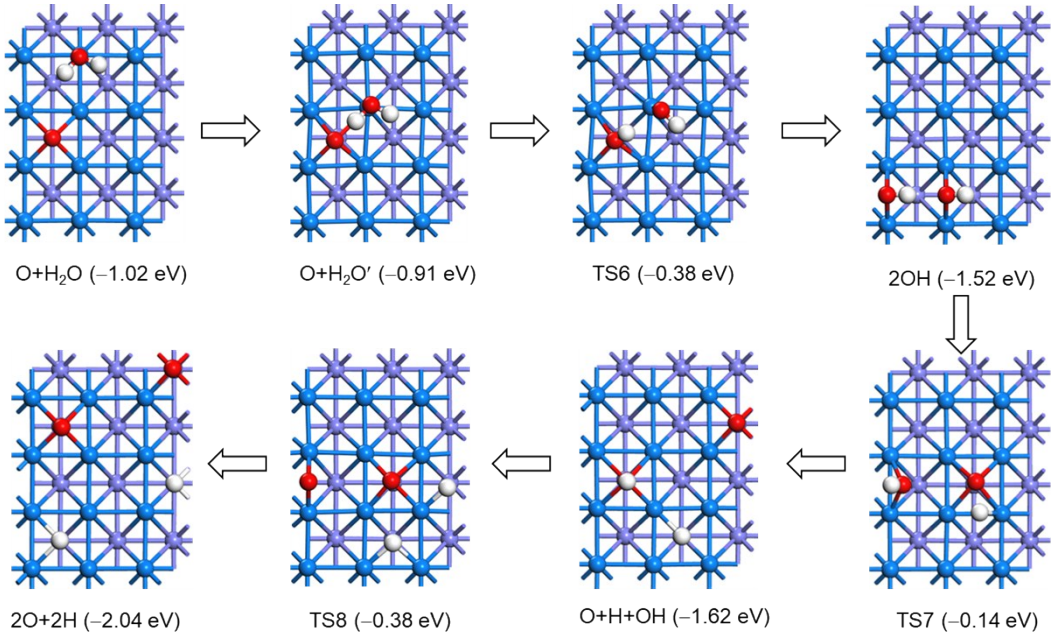

Figure S4. Optimized structures and the adsorption energy (eV) H_2O dissociation for the stationary points on the 2O pre-covered Ni(100) surface (O/red; H/white; the first layer/blue, the second layer/purple)

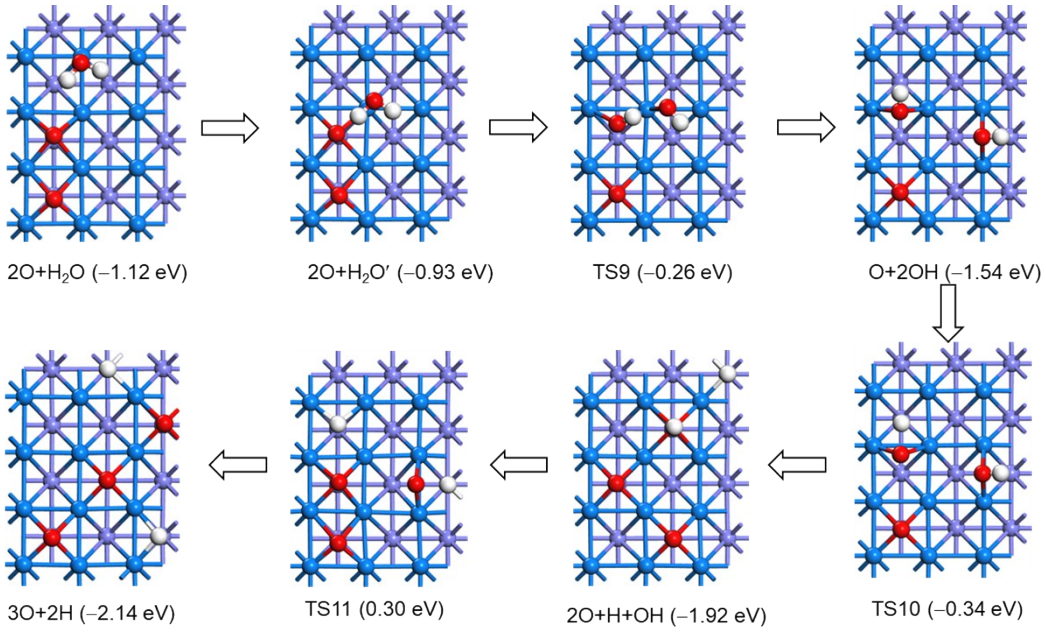

Figure S5. E-D3 optimized structures and the adsorption energy (eV) of $2H_2O$ dissociation for the stationary points on Ni(110) surface (O/red; H/white; the first layer/blue, the second layer/purple)

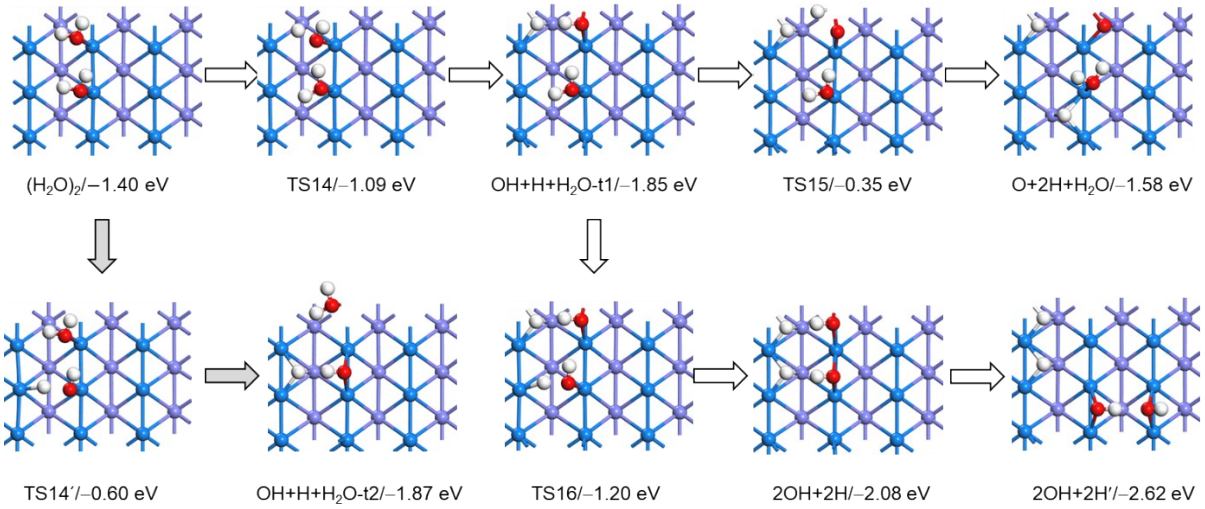

Table S5. Adsorption energy (E_{ads}, eV) and shortest distances (d, Å) of the IS and FS for H_2O direct dissociation and $2H_2O$ dissociation on Ni(110) surface using PBE-D3

	E_{ads}	d_{Ni-O}	d_{Ni-H}
		H_2O direct dissociation	
H_2O	−0.62	2.101	
OH+H	−1.20	1.929; 1.922	1.669; 1.669; 1.788
O+2H	−1.02	1.821; 1.834; 1.930	1.655; 1.664; 1.742; 1.659; 1.696; 1.718
		$2H_2O$ dissociation	
H_2O+H_2O	−1.40	2.079; 2.224	
H_2O+OH+H	−1.85	2.086; 1.927; 1.944	1.667; 1.669; 1.798
H_2O+O+2H	−1.58	2.143; 1.839; 1.834; 1.952	1.686; 1.659; 1.736; 1.677; 1.753; 1.702
2OH+2H	−2.08	1.869; 1.992; 1.868; 1.992	1.666; 1.669; 1.789; 1.665; 1.668; 1.792
2OH+2H′	−2.62	1.899; 1.898; 1.949; 1.949	1.688; 1.737; 1.700; 1.700; 1.689; 1.736

Table S6. PBE-D3 computed dissociation barriers and energies (E_a and E_r, eV), bond distances (d_{Ni-X}, Å) and the breaking O-H bond distance (d_{O-H}, Å) in the transition state for H_2O direct dissociation and $2H_2O$ dissociation on Ni(110) surface

	E_a	E_r	d_{Ni-O}	d_{Ni-H}	d_{O-H}
			$H_2O \rightarrow TS12 \rightarrow OH + H$		
TS12	0.58	−0.58	1.898	1.724	1.557
			OH + H → TS13 → O + 2H		
TS13	1.60	0.18	1.776; 1.818	1.660; 1.679; 1.772; 1.498	1.609
			$2H_2O \rightarrow TS14 \rightarrow H_2O + OH + H$		
TS14	0.31	−0.45	1.980; 2.051		1.517
			H_2O + OH + H → TS15 → H_2O + O + 2H		
TS15	1.50	0.27	1.798; 1.832; 2.087	1.537; 1.675; 1.656; 1.785	1.590
			H_2O + OH + H → TS16 → 2OH + 2H′		
TS16	0.65	−0.77	1.894; 1.936; 1.920	1.669; 1.666; 1.670;1.789	1.560

Table S7. PBE-D3 computed adsorption energies (E_{ads}, eV) and bond lengths (d_{Ni-X}, Å) of the IS and FS for H_2O dissociation on O pre-covered Ni(110)

	E_{ads}	d_{Ni-O}	d_{Ni-H}
		1O assisted H_2O dissociation	
O+H_2O	−0.92	1.846; 1.844; 2.006; 2.036	
2OH	−1.57	1.900; 1.900; 1.950; 1.950	
O+H+OH	−1.31	1.906; 1.906; 1.800; 1.811; 1.994	1.656; 1.728; 1.709
2O+2H	−1.00	1.841; 1.823; 1.938; 1.819; 1.813; 1.937	1.667; 1.697; 1.720; 1.655; 1.731; 1.716
		2O assisted H_2O dissociation	
2O+H_2O	−0.62	2.033; 1.807; 1.880; 1.971	
O+2OH	−1.30	1.865; 1.938; 1.953; 1.940	
2O+H+OH	−1.08	1.873; 1.942; 1.823; 1.794; 1.966	1.661; 1.718; 1.714
3O+2H	−0.94	1.819; 1.797; 1.915; 2.001; 2.082; 1.945; 1.979	1.631; 1.717; 1.727; 1.662; 1.717; 1.704

Table S8. PBE-D3 computed energy barriers and reaction energies (E_a and E_r, eV), bond distances (d_{Ni-X}, Å) and the breaking O-H bond distances (d_{O-H}, Å) of the TS for H_2O dissociation on O pre-covered Ni(110) surface

	E_a	E_r	d_{Ni-O}	d_{Ni-H}	d_{O-H}
			2OH → TS17 → O + H + OH		
TS17	1.50	0.26	1.898; 1.895; 1.794; 1.830	1.507	1.541
			O + H + OH → TS18 → 2O + 2H		
TS18	1.77	0.31	1.778; 1.809; 1.796; 1.794; 1.964	1.657; 1.726; 1.712; 1.498;	1.630
			O + 2OH → TS19 → 2O + H + OH		
TS19	1.45	0.22	1.858; 1.935; 1.823; 1.832	1.510	1.522
			2O + H + OH →TS20 → 3O + 2H		
TS20	1.83	0.14	1.793; 1.801; 1.809; 1.793; 1.945	1.661; 1.717; 1.714; 1.491	1.579

Figure S6. Optimized structures and the adsorption energy H_2O dissociation for the stationary points on the O pre-covered Ni(110) surface (O/red; H/white; the first layer/blue, the second layer/purple)

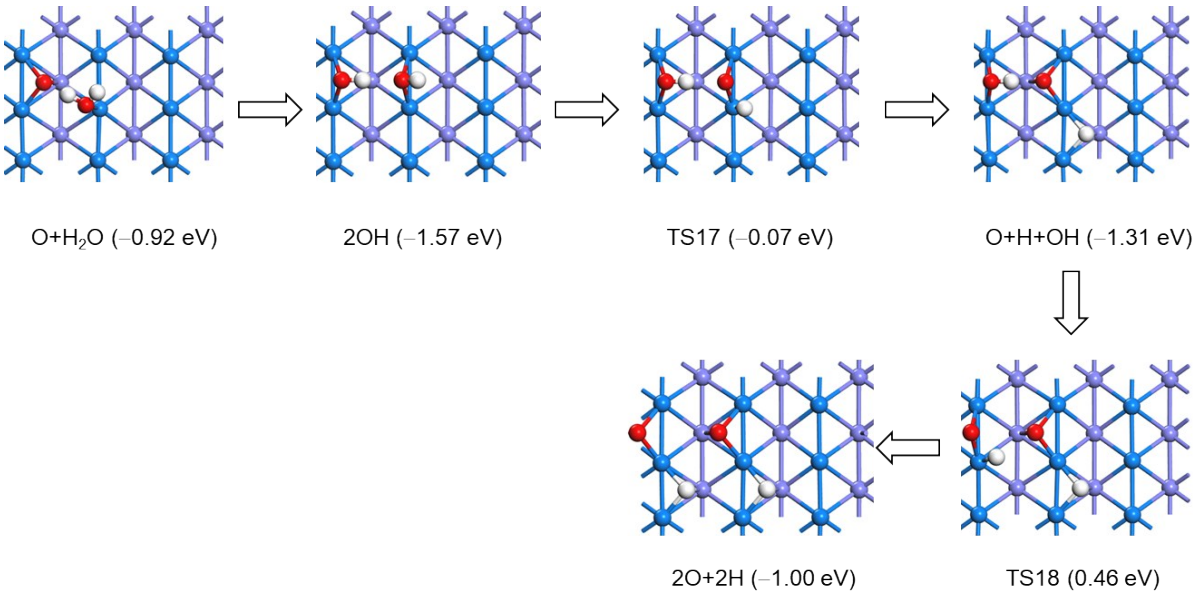

Figure S7. Optimized structures and the adsorption energy H_2O dissociation for the stationary points on the 2O pre-covered Ni(110) surface (O/red; H/white; the first layer/blue, the second layer/purple)

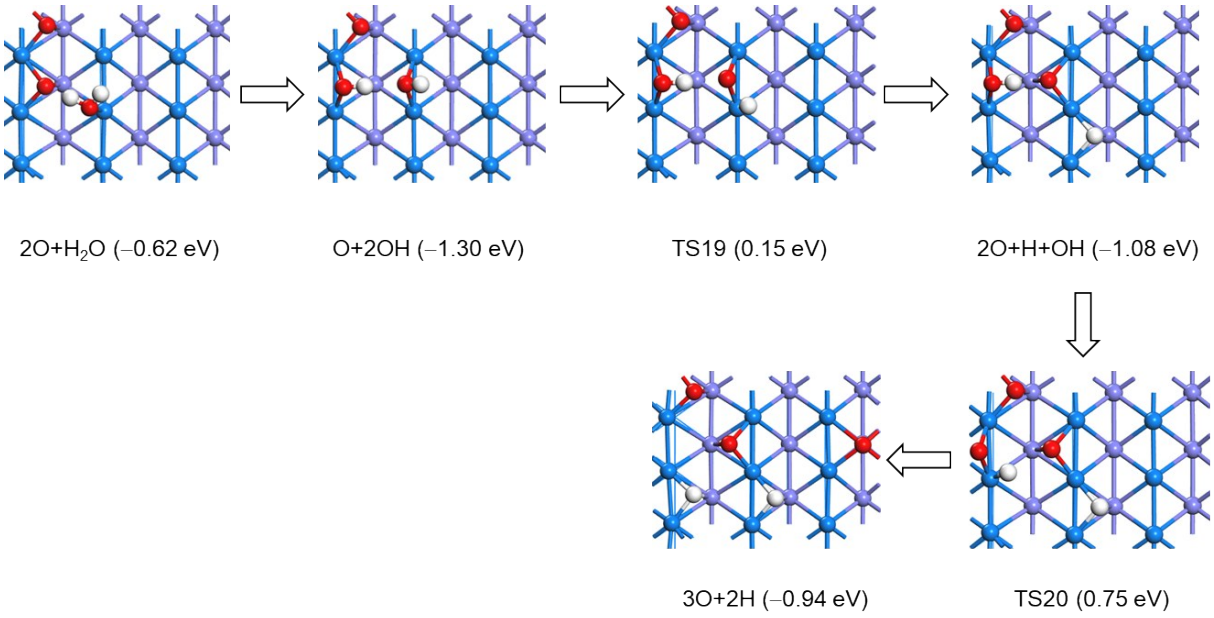

Figure S8. The computed 4O configurations on the (4 X 4) slab Ni (100) surface (O/red; H/white; the first layer/blue, the second layer/purple)

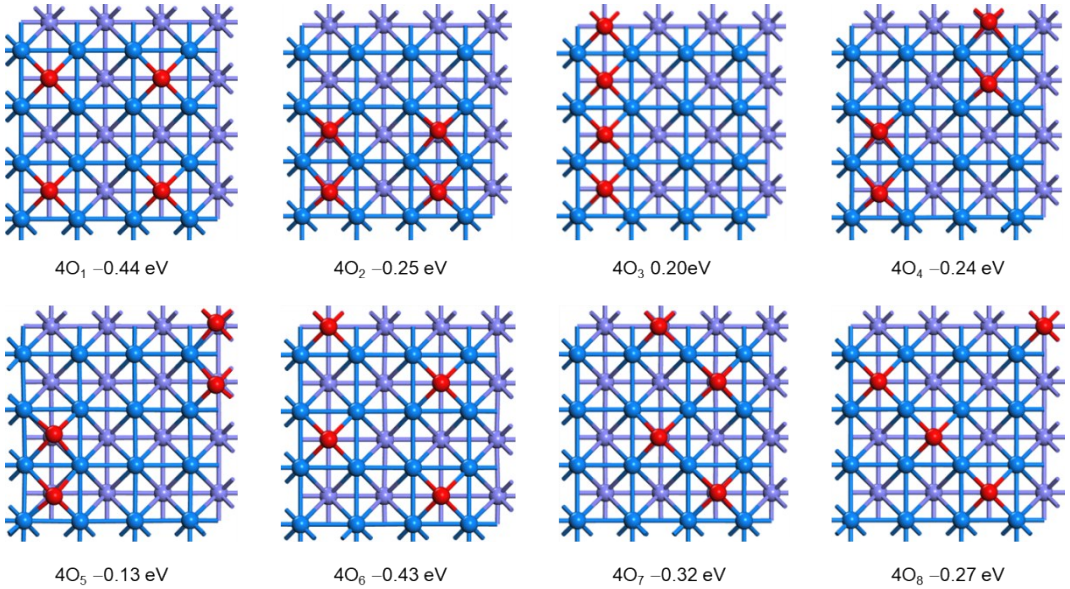

Table S9. Computed H_2O desorption temperature on the Ni (100) and Ni (110) surface (T_{des}, K; 2×10^{-10} Torr) with RPBE-D3 energies

	Ni(100)	Ni(110)
Reaction	T (RPBE-D3)	T (RPBE-D3)
$(H_2O)_n(s) = nH_2O(g)$ (n = 1-6)	128–176	163–200
$(H_2O)_2(s) = (H_2O)_2(g)$	315	358
$nO + H_2O(s) = nO + H_2O(g)$ (n = 1-2)	141–145	227–229
$OH+H = H_2O(g)$	330	302
$2OH(s) = O(s) + H_2O(g)$	390	367
$OH+H = OH + 0.5H_2(g)$	124	180
$O+2H =O + H_2(g)$	360	216

(1) Zeng, T.; Wen, X. D.; Li, Y.-W.; Jiao, H. J. Density Functional Theory Study of Triangular Molybdenum Sulfide Nanocluster and CO Adsorption on It. *J. Phys. Chem. B* **2005**, *109*, 13704-13710.