Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information (ESI)

Trends in water-promoted oxygen dissociation on transition metal surfaces from first principles

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Table S1 The experiential lattice parameters of nine transition metals

Metals	a/ Å	b/ Å	c/ Å	References
Co	2.51	2.51	4.07	[52]
Rh	3.80	3.80	3.80	[53]
Ir	3.84	3.84	3.84	[54]
Ni	3.52	3.52	3.52	[55]
Pd	3.89	3.89	3.89	[56]
Pt	3.92	3.92	3.92	[57]
Cu	3.62	3.62	3.62	[58]
Ag	4.09	4.09	4.09	[59]
Au	4.08	4.08	4.08	[53]

Table S2 Calculated adsorption characteristics of O_2 and H_2O on selected transition metal surfaces using DFT method

Surfaces	$E_{ads}(O_2)^a$	$E_{ads}(H_2O)^b$	E_{ads} $(O_2\cdots H_2O)^c$	$\Delta E_{ads}{}^d$	$d(O-O)^e$
Co(0001)	−2.08	−0.43	−2.90	−0.39	1.51
Rh(111)	−1.61	−0.55	−2.52	−0.36	1.42
Ir(111)	−1.20	−0.52	−1.94	−0.21	1.44
Ni(111)	−1.84	−0.37	−2.72	−0.52	1.46
Pd(111)	−0.83	−0.40	−1.49	−0.29	1.36
Pt(111)	−0.53	−0.41	−1.13	−0.19	1.36
Cu(111)	−0.49	−0.26	−1.06	−0.32	1.44
Ag(111)	0.27	−0.18	−0.34	−0.43	1.35
Au(111)	−0.05	−0.17	0.39	0.61	1.23

[a]$E_{ads}(O_2)$ represents the adsorption energy of O_2; [b]$E_{ads}(H_2O)$ represents the adsorption energy of H_2O; [c]$E_{ads}(O_2\cdots H_2O)$ represents the co-adsorption energy of O_2 and H_2O; [d]$\Delta E_{ads} = E_{ads}(O_2\cdots H_2O) - (E_{ads}(O_2) + E_{ads}(H_2O))$; [e]$d(O-O)$ represents the distance between two O atoms of O_2. The unit of energy, bond length and charge is eV, Å, and e, respectively.

The Gibbs free energy is calculated as follows (eq (2), eq (3)):

$$G(T) = H(T) - TS(T) \quad (2)$$

$$H(T) = U(T) + k_BT \quad (3)$$

Where T represents the temperature, $G(T)$, $H(T)$, $S(T)$, $U(T)$ represent the Gibbs free energy, the corresponding enthalpy, the entropy, the internal thermal energy at T K at the standard conditions, respectively. k_B is the Boltzmann constant.

Table S3 The individual adsorption energies of O_2 and H_2O, the co-adsorption energies of O_2 and H_2O on transition metal surfaces

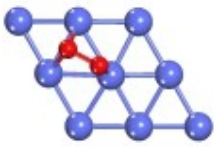
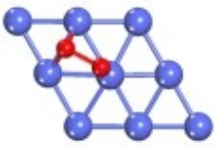
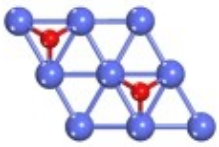
Surfaces	E_{ads} $(O_2)^a$	E_{ads} $(H_2O)^b$	E_{ads} $(O_2\cdots H_2O)^c$	E_{ads}^{ZPE} $(O_2)^d$	E_{ads}^{ZPE} $(H_2O)^e$	E_{ads}^{ZPE} $(O_2\cdots H_2O)^f$	ΔG_{ads} $(O_2)^g$	ΔG_{ads} $(H_2O)^h$	ΔG_{ads} $(O_2\cdots H_2O)^i$
Co(0001)	−2.26	−0.72	−3.40	−2.25	−0.66	−3.32	−2.28	−0.70	−3.41
Rh(111)	−1.74	−0.79	−2.93	−1.70	−0.71	−2.79	−1.74	−0.74	−2.83
Ir(111)	−1.24	−0.74	−2.40	−1.21	−0.66	−2.25	−1.23	−0.72	−2.28
Ni(111)	−2.01	−0.66	−3.22	−1.98	−0.60	−3.11	−2.03	−0.65	−3.20
Pd(111)	−0.91	−0.54	−1.74	−0.87	−0.47	−1.60	−0.90	−0.54	−1.66
Pt(111)	−0.60	−0.60	−1.46	−0.56	−0.53	−1.31	−0.58	−0.62	−1.37
Cu(111)	−0.60	−0.44	−1.40	−0.58	−0.38	−1.29	−0.62	−0.44	−1.55
Ag(111)	0.19	−0.31	−0.57	−0.20	−0.26	−0.47	0.14	−0.35	−0.57
Au(111)	−0.11	−0.29	0.17	−0.10	−0.24	0.27	−0.14	−0.33	0.12

[a]$E_{ads}(O_2)$ represents the adsorption energy of O_2; [b]$E_{ads}(H_2O)$ represents the adsorption energy of H_2O; [c]$E_{ads}(O_2\cdots H_2O)$ represents the co−adsorption energy of O_2 and H_2O; [d]$E_{ads}^{ZPE}(O_2)$, [e]$E_{ads}^{ZPE}(H_2O)$, [f]$E_{ads}^{ZPE}(O_2\cdots H_2O)$ represent the adsorption energies of O_2, H_2O and $O_2\cdots H_2O$ with zero point energy corrections, respectively; [g]$\Delta G_{ads}(O_2)$, [h]$\Delta G_{ads}(H_2O)$ and [i]$\Delta G_{ads}(O_2\cdots H_2O)$ represent the adsorption free energies of O_2, H_2O and $O_2\cdots H_2O$ at 298.15 K, respectively. The unit of energy is eV.

Table S4 The spin states of adsorbed O_2 on nine transition metal surfaces

Surfaces	Molecular adsorbed O_2		
	Spin (S_{O_2})	Spin Multiplicity ($2S_{O_2}+1$)	Spin state
Co(0001)	0.23	1.46	singlet
Rh(111)	0	1	singlet
Ir(111)	0	1	singlet
Ni(111)	0.14	1.28	singlet
Pd(111)	0	1	singlet
Pt(111)	0	1	singlet
Cu(111)	0	1	singlet
Ag(111)	0	1	singlet
Au(111)	1	3	triplet

Table S5 The optimized structures of initial states, transition states and final states of adsorbed O_2 and $O_2\cdots H_2O$ on transition metal surfaces

Surfaces	Structures		
Co(0001)			
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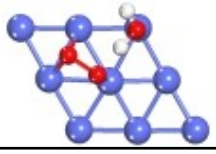
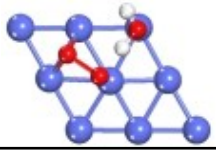
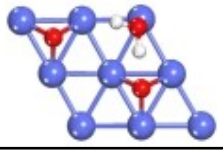
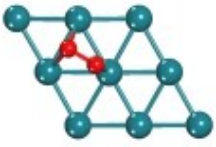
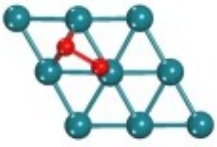
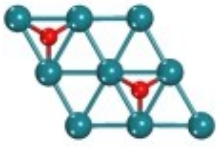
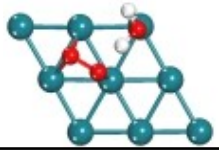
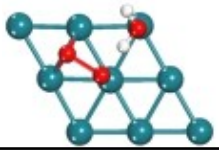
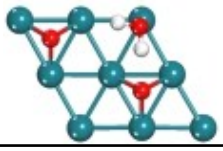
			
	IS4’	TS4’	FS4’
Rh(111)			
	IS5	TS5	FS5

Surfaces	Structures		
Rh(111)			
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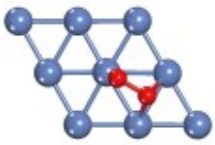
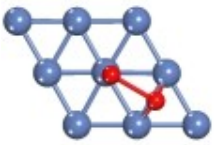
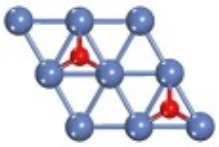
Ni(111)			
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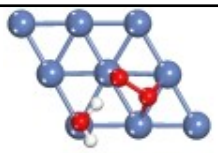
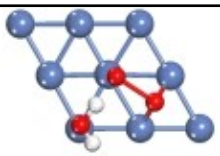
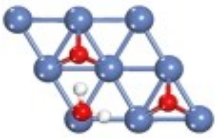
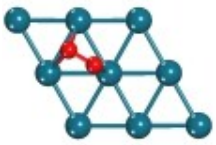
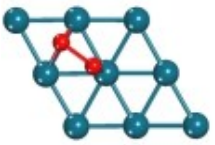
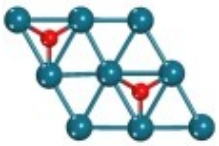
			
	IS6′	TS6′	FS6′
Pd(111)			
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	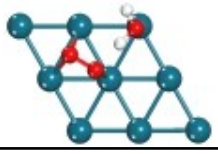	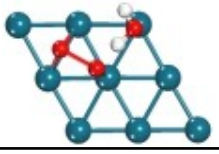	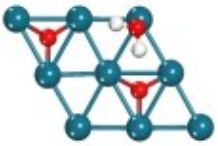
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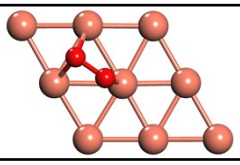
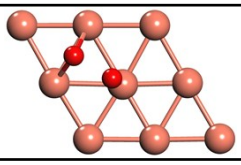
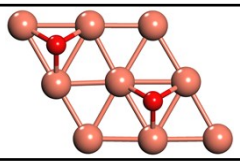
Cu(111)			
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	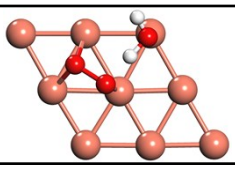	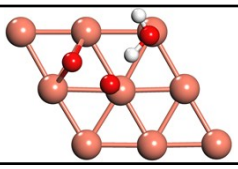	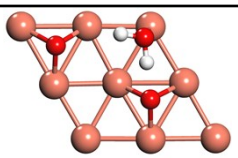
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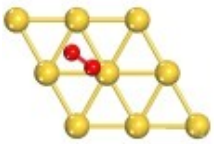
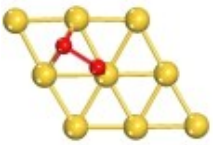
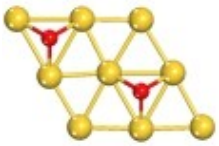
Au(111)			
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	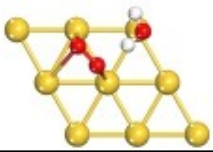	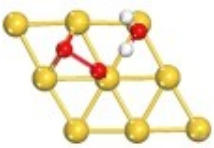	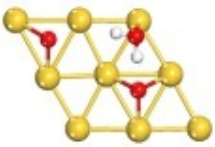
	IS9′	TS9′	FS9′

The *d*-band center which is generally used to describe the *d*-state of metal surfaces is calculated as：

$$\text{d band center} = \frac{E_d}{N_d} = \frac{\int_{-\infty}^{0} \rho E dE}{\int_{-\infty}^{0} \rho dE}$$

where E_d is the total energy of occupied *d* electrons, N_d the total number of occupied d electrons, ρ the density of d states.

Table S6 The *d*-band centers for the adsorption sites of the nine transition metal surfaces

Surfaces	*d*-band center / eV	Surfaces	*d*-band center / eV	Surfaces	*d*-band center / eV
Co(0001)	-2.26	Ni(111)	-1.98	Cu(111)	-2.55
Rh(111)	-2.55	Pd(111)	-2.95	Ag(111)	-4.00
Ir(111)	-3.04	Pt(111)	-2.58	Au(111)	-3.48

Table S7 The activation barriers and reaction energies of O_2 dissociation without and with co-adsorbed H_2O on transition metal surfaces

Surfaces	Without H_2O						With H_2O					
	E_a [a]	ΔE [b]	E_a^{ZPE} [c]	ΔE^{ZPE} [d]	ΔG_a [e]	ΔG [f]	E_a [a]	ΔE [b]	E_a^{ZPE} [c]	ΔE^{ZPE} [d]	ΔG_a [e]	ΔG [f]
Co(0001)	0.04	−3.27	−0.03	−3.23	0.03	−3.20	0.01	−3.19	0.00	−3.12	0.00	−3.08
Rh(111)	0.22	−2.37	−0.21	−2.34	0.20	−2.33	0.14	−2.21	0.09	−2.18	0.09	−2.18
Ir(111)	0.71	−2.13	−0.65	−2.11	0.62	−2.08	0.45	−1.88	0.37	−1.89	0.37	−1.91
Ni(111)	0.28	−2.64	−0.27	−2.60	0.26	−2.57	0.14	−2.54	0.11	−2.50	0.11	−2.48
Pd(111)	0.71	−1.76	−0.67	−1.75	0.65	−1.72	0.49	−1.60	0.43	−1.60	0.43	−1.60
Pt(111)	1.02	−1.02	−0.95	−1.02	0.92	−0.98	0.75	−0.78	0.68	−0.79	0.65	−0.79
Cu(111)	0.51	−2.11	−0.47	−2.08	0.45	−2.04	0.33	−2.02	0.30	−1.99	0.28	−1.98
Ag(111)	1.10	−0.32	−1.07	−0.31	1.07	−0.26	0.85	−0.41	0.81	−0.40	0.81	−0.37
Au(111)	2.52	1.24	−2.49	1.25	2.50	1.28	1.50	0.36	1.44	0.36	1.45	0.44

[a]E_a represents the activation barrier of O_2 dissociation; [b]ΔE represents the reaction energy of O_2 dissociation; [c]E_a^{ZPE} and [d]ΔE^{ZPE} represent the activation barrier and the reaction energy of O_2 dissociation with zero point energy corrections; [e]ΔG_a and [f]ΔG represent the free energy barrier and reaction free energy of O_2 dissociation at 298.15 K. The unit of energy is eV.

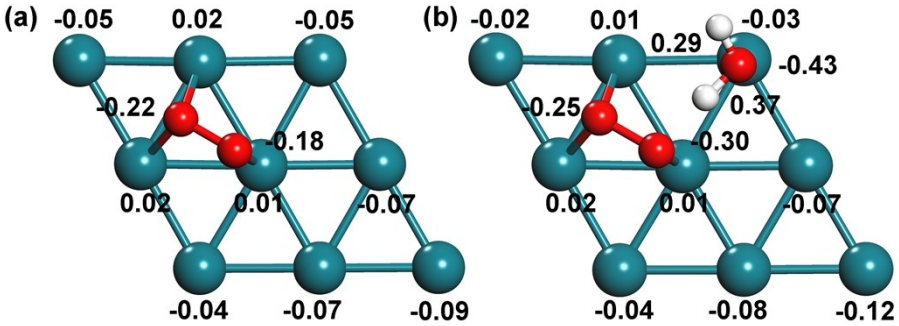

Fig. S1 Mulliken charge distribution of Rh(111) surface adsorbed with O_2 (a) and $O_2\cdots H_2O$ (b).