Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2024

Supporting Information

Quantum Chemical Studies of Transition Metal Single-Atom Catalysts: Catalytic Descriptors Exploration

Bo Li[a],‡ Mingyue Zheng[b],‡ Shichen Lin,[c] Feng Long Gu[d], Jun Jiang[e], and Chuanyi Jia[a,*]

[a]Guizhou Provincial Key Laboratory of Computational Nano-Material Science, Institute of Applied Physics, Guizhou Education University, Guiyang, Guizhou 550018, China

[b]Department of Investigation, Shandong Police College, Jinan, Shandong 250200, China

[c]Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-Park, Fukuoka 816-8580, Japan

[d]MOE Key Laboratory of Environmental Theoretical Chemistry and SCNU Environmental Research Institute, Guangdong Provincial Key Laboratory of Chemical Pollution and Environmental Safety & School of Environment, South China Normal University, Guangzhou 510006, China

[e]Key Laboratory of Precision and Intelligent Chemistry, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, Anhui 230026, China

Corresponding Author

*cyjia@gznc.edu.cn

1. Binding Stabilities and Optimized Electronic and Atomic Structures of NC Supported Fe, Co, and Ni Single-Atom Catalysts (SACs) with Different Spin States.

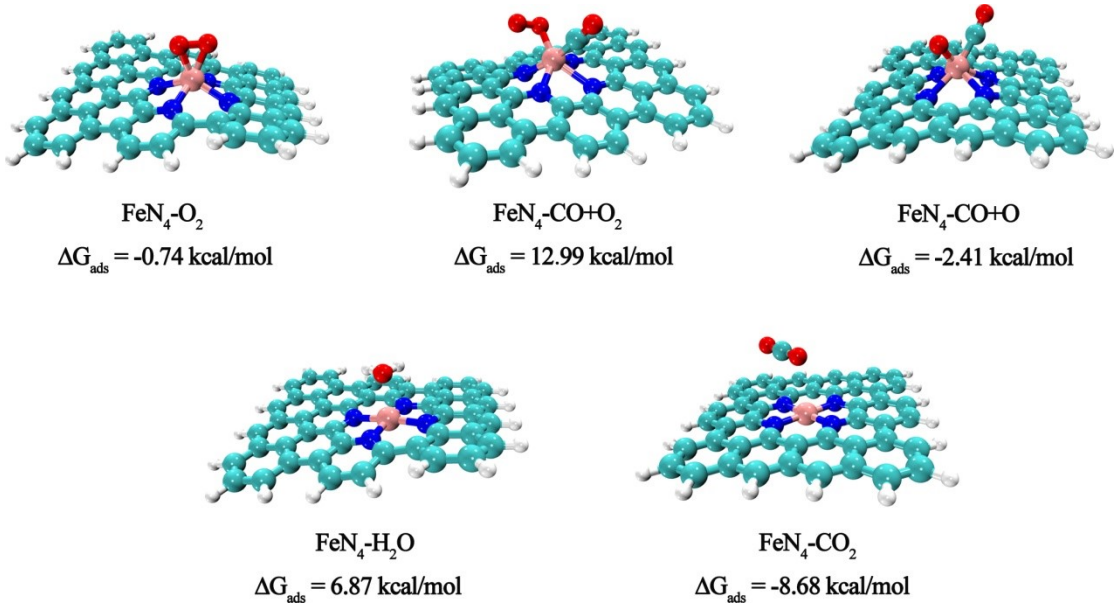

Figure S1. Optimized structures and adsorption Gibbs free energies (ΔG_{ads}) of O_2, $CO+O_2$, $CO+O$, H_2O, and CO_2 on N_4-coordinated Fe-SACs (S = 1). Fe atoms are in pink, C in cyan, H in white, and N in deep blue.

Table S1. Adsorption Gibbs free energies (ΔG_{TM}, kcal/mol) of transition metals (TMs); electronic spin moments (μ_B) of TMs before/after O adsorption under different spin states; Mulliken charges (e^-) of O (Δq, after reactants adsorption) on TMs.

	ΔG_{TM}	μ_B	Δq
Fe(II)(S=0)	-151.72	--	-0.43
Fe(III)(S=1/2)	-160.50	0.00/2.56	-0.44
Fe(II)(S=1)	-116.68	0.09/2.63	-0.47
Fe(III)(S=3/2)	-108.78	1.95/2.75	-0.44
Fe(II)(S=2)	-155.49	3.52/2.72	-0.46
Fe(III)(S=5/2)	-86.74	3.51/2.64	-0.44
Co(III)(S=0)	-80.22	--	--
Co(II)(S=1/2)	-190.89	2.00/1.55	-0.47
Co(III)(S=1)	-88.07	2.59/1.62	-0.44
Co(II)(S=3/2)	-126.79	2.27/1.61	-0.47
Co(III)(S=2)	-186.30	2.57/1.63	-0.44
Co(II)(S=5/2)	-143.51	2.66/2.82	-0.47
Ni(II)(S=0)	--	--	--
Ni(III)(S=1/2)	-131.59	1.64/1.34	-0.38
Ni(II)(S=1)	-166.32	1.62/1.70	-0.42
Ni(III)(S=3/2)	-92.46	1.64/1.69	-0.44
Ni(II)(S=2)	-227.25	1.68/1.70	-0.46
Ni(III)(S=5/2)	-172.48	1.69/1.69	-0.44

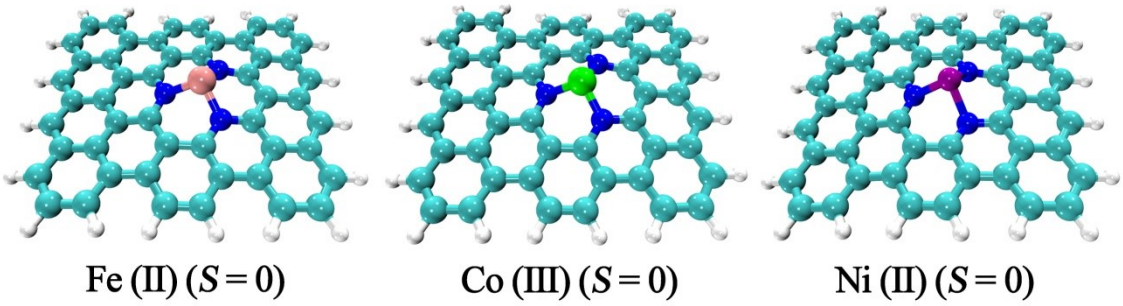

Figure S2. Optimized structures of NC supported Fe, Co, and Ni SACs (S = 0). Co atoms are in green, Ni in brown, and other atoms are the same as in Figure S1.

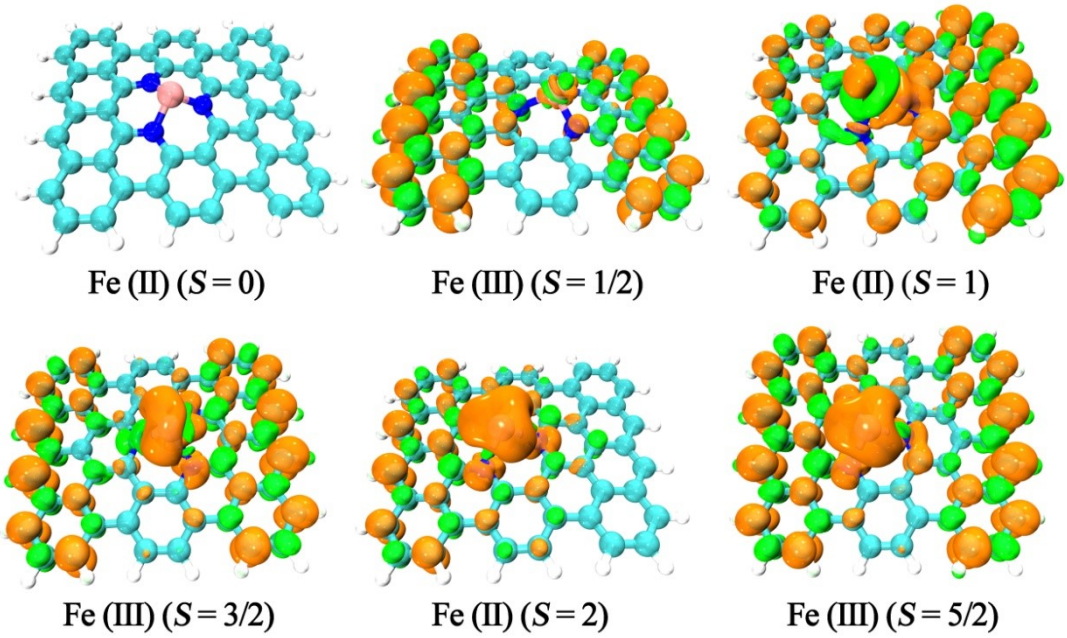

Figure S3. Structures and spin densities (isovalue is 0.001) of NC supported Fe(II) and Fe(III) SACs with different spin states. See Figure S1 for color coding.

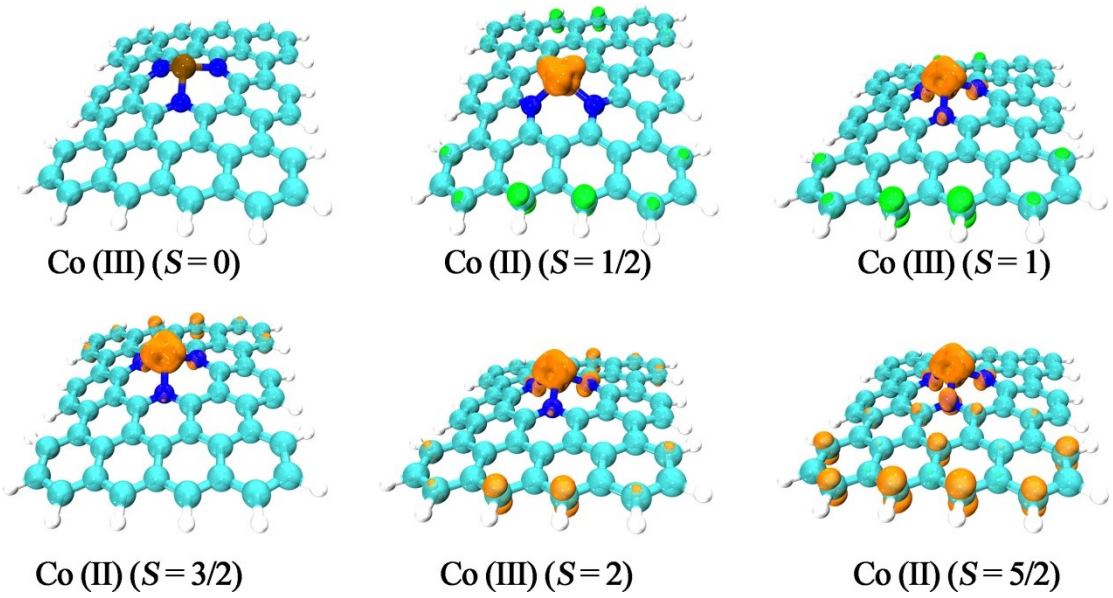

Figure S4. Structures and spin densities (isovalue is 0.009) of NC supported Co(II) and Co(III) SACs with different spin states. See Figure S2 for color coding.

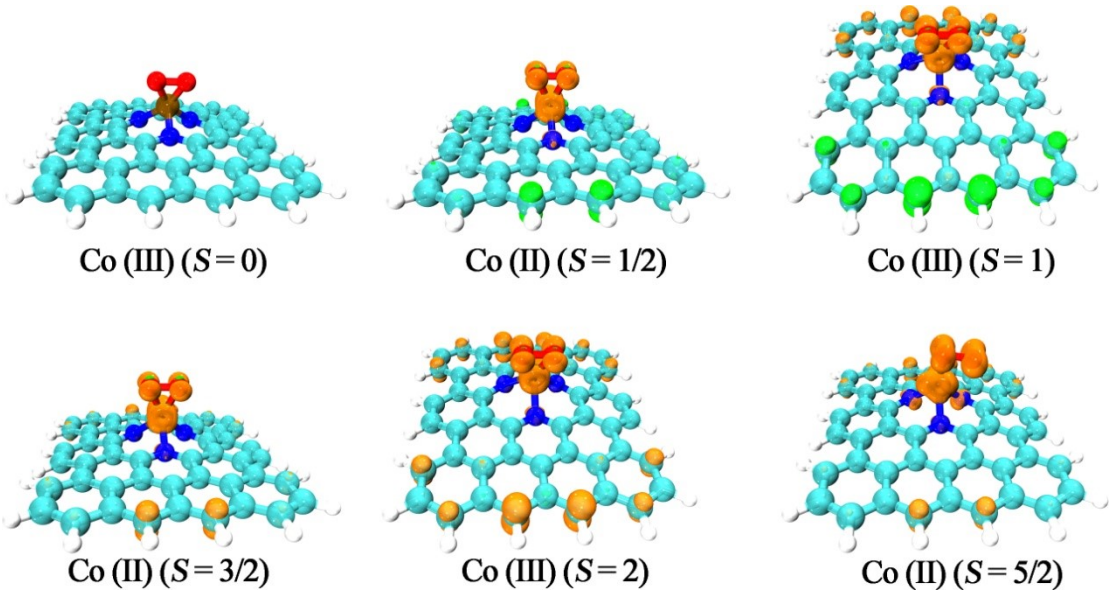

Figure S5. Structures and spin densities (isovalue is 0.009) of O_2 adsorption on NC supported Co(II) and Co(III) SACs with different spin states. See Figure S2 for color coding.

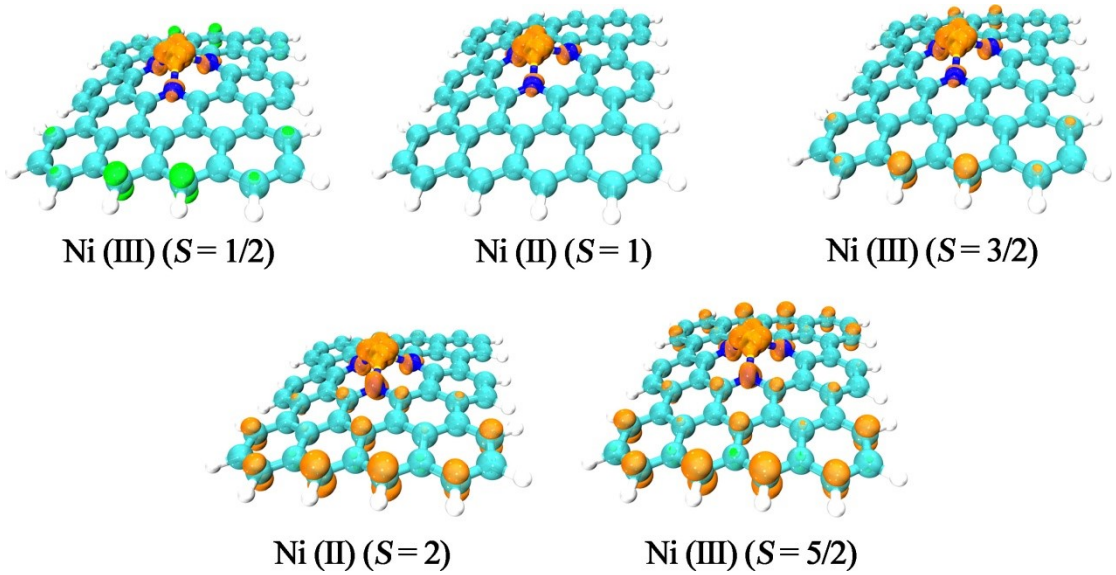

Figure S6. Structures and spin densities (isovalue is 0.009) of NC supported Ni(II) and Ni(III) SACs with different spin states. See Figure S2 for color coding.

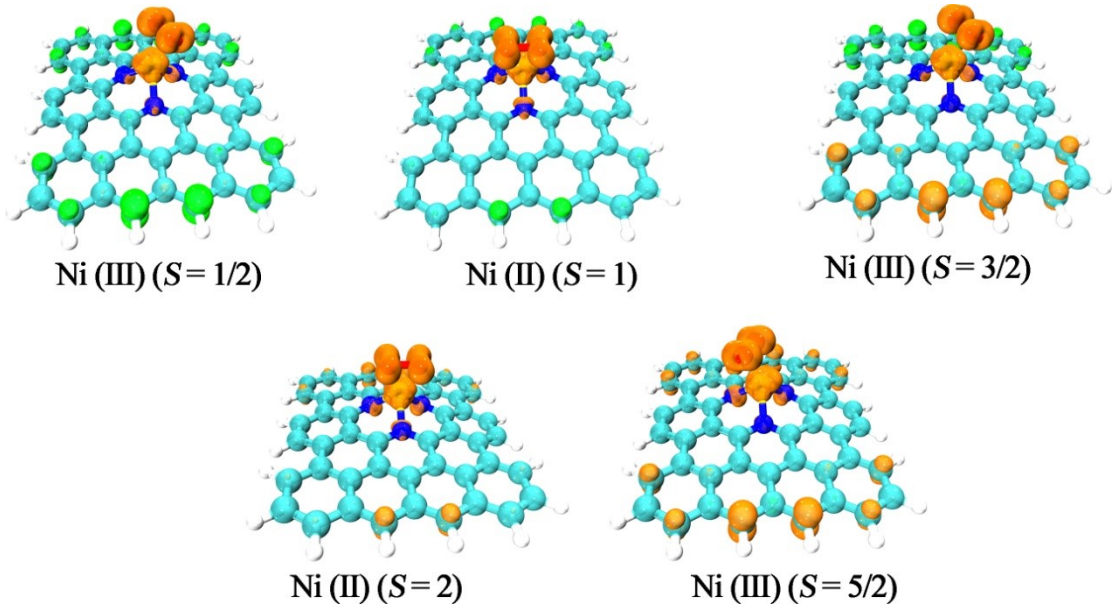

Figure S7. Structures and spin densities (isovalue is 0.009) of O_2 adsorption on NC supported Ni(II) and Ni(III) SACs with different spin states. See Figure S2 for color coding.

2. Detailed Data and Corresponding Correlations for the Catalytic Properties of NC Supported Fe, Co, and Ni SACs with Different Spin States.

Table S2. Electronic spin moments (μ_B) of transition metals (TMs) before/after O_2, $CO+O_2$, CO+O, H_2O, and CO_2 adsorption under different spin states.

	O_2	$CO+O_2$	CO+O	H_2O	CO_2
Fe(III)(S=1/2)	0.00/0.50	0.00/0.02	0.00/0.70	0.00/0.00	0.00/3.07
Fe(II)(S=1)	0.09/2.75	0.09/0.08	0.09/2.39	0.09/1.96	0.09/3.04
Fe(III)(S=3/2)	1.95/2.83	1.95/0.09	1.95/2.38	1.95/3.57	1.95/3.07
Fe(II)(S=2)	3.52/2.82	3.52/2.00	3.52/2.40	3.52/3.54	3.52/3.11
Fe(III)(S=5/2)	3.51/2.85	3.51/1.99	3.51/2.39	3.51/3.56	3.51/3.26
Co(II)(S=1/2)	2.00/1.44	2.00/-0.02	2.00/1.28	2.00/2.22	2.00/2.00
Co(III)(S=1)	2.59/1.37	2.59/-0.03	2.59/1.26	2.59/2.60	2.59/1.95
Co(II)(S=3/2)	2.27/1.44	2.27/1.01	2.27/1.28	2.27/2.58	2.27/2.00
Co(III)(S=2)	2.57/1.36	2.57/1.00	2.57/1.24	2.57/2.59	2.57/1.94
Co(II)(S=5/2)	2.66/2.55	2.66/2.40	2.66/2.72	2.66/2.61	2.66/2.06
Ni(III)(S=1/2)	1.64/1.53	1.64/1.41	1.64/--	1.64/1.63	1.64/1.03
Ni(II)(S=1)	1.62/1.54	1.62/1.43	1.62/--	1.62/1.62	1.62/1.03
Ni(III)(S=3/2)	1.64/1.53	1.64/1.41	1.64/1.55	1.64/1.62	1.64/1.03
Ni(II)(S=2)	1.68/1.55	1.68/1.43	1.68/0.90	1.68/1.64	1.68/1.06
Ni(III)(S=5/2)	1.69/1.54	1.69/1.42	1.69/1.57	1.69/1.65	1.69/1.89

Table S3. Adsorption Gibbs free energies (ΔG_{ads}, kcal/mol) of the molecular products (CO_2/CO in corresponding steps; the rate determining step (RDS) of CO_2 dissociation.

	CO_2 ($CO+O_2 \rightarrow CO_2+O$)	**CO_2 ($CO+O \rightarrow CO_2$)**	**CO ($CO_2 \rightarrow CO+O$)**	**RDS ($CO_2 \rightarrow CO+O$)**
Fe(II)(S=0)	1.59	-2.37	-16.50	30.60
Fe(III)(S=1/2)	1.93	-18.85	-35.76	38.12
Fe(II)(S=1)	1.47	-35.06	-36.35	36.35
Fe(III)(S=3/2)	3.69	-21.02	-34.32	34.32
Fe(II)(S=2)	-1.99	-9.58	-36.81	36.81
Fe(III)(S=5/2)	-1.90	-6.63	-39.24	39.24
Co(III)(S=0)	--	--	--	--
Co(II)(S=1/2)	0.11	-7.37	-47.65	47.65
Co(III)(S=1)	2.59	-1.36	-48.91	48.91
Co(II)(S=3/2)	-10.19	-5.36	-47.65	47.65
Co(III)(S=2)	-9.89	-1.11	-48.74	48.74
Co(II)(S=5/2)	-0.01	-0.58	-19.95	27.70
Ni(II)(S=0)	--	--	--	--
Ni(III)(S=1/2)	2.79	--	--	--
Ni(II)(S=1)	0.76	--	--	--
Ni(III)(S=3/2)	0.87	--	--	--
Ni(II)(S=2)	0.59	-0.22	-34.02	36.93
Ni(III)(S=5/2)	--	6.62	-31.01	35.56

Table S4. TM-O bond lengths (L/Å) of adsorbed O_2, $CO+O_2$, CO+O, H_2O, and CO_2 under different spin states. Specifically, for the reactant that has two TM-O bonds (O_2/$CO+O_2$), L(TM-O) is the average length of these two bonds.

	O_2	**$CO+O_2$**	**CO+O**	**H_2O**	**CO_2**
Fe(II)(S=0)	1.84	1.92	1.65	2.12	2.17
Fe(III)(S=1/2)	1.83	1.96	1.65	2.09	1.95
Fe(II)(S=1)	1.82	1.96	1.66	2.08	1.95
Fe(III)(S=3/2)	1.82	1.96	1.66	2.13	1.94
Fe(II)(S=2)	1.82	2.17	1.67	2.16	1.97
Fe(III)(S=5/2)	1.82	2.15	1.66	2.12	2.01
Co(III)(S=0)	1.84	1.90	--	2.04	1.92
Co(II)(S=1/2)	1.84	1.90	1.68	2.15	1.96
Co(III)(S=1)	1.85	1.89	1.68	2.09	2.06
Co(II)(S=3/2)	1.84	2.21	1.68	2.14	1.96
Co(III)(S=2)	1.85	2.18	1.68	2.08	2.06
Co(II)(S=5/2)	1.57	2.17	1.69	2.15	1.97
Ni(II)(S=0)	--	--	--	--	--
Ni(III)(S=1/2)	2.01	2.11	--	2.10	1.98
Ni(II)(S=1)	2.02	2.12	--	2.12	1.98
Ni(III)(S=3/2)	2.00	2.11	1.75	2.09	1.98
Ni(II)(S=2)	2.02	2.12	1.75	2.13	1.98
Ni(III)(S=5/2)	2.01	2.11	1.75	2.10	2.29

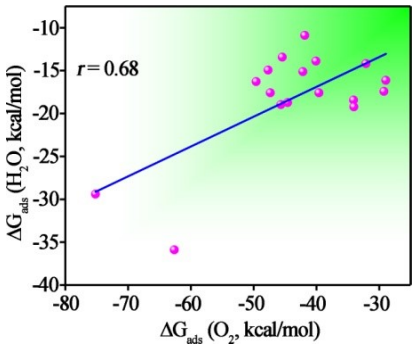

Figure S8. Correlation between the binding stability (ΔG_{ads}) of O_2 and H_2O. Colored background indicates the change trend of the linear relationship.

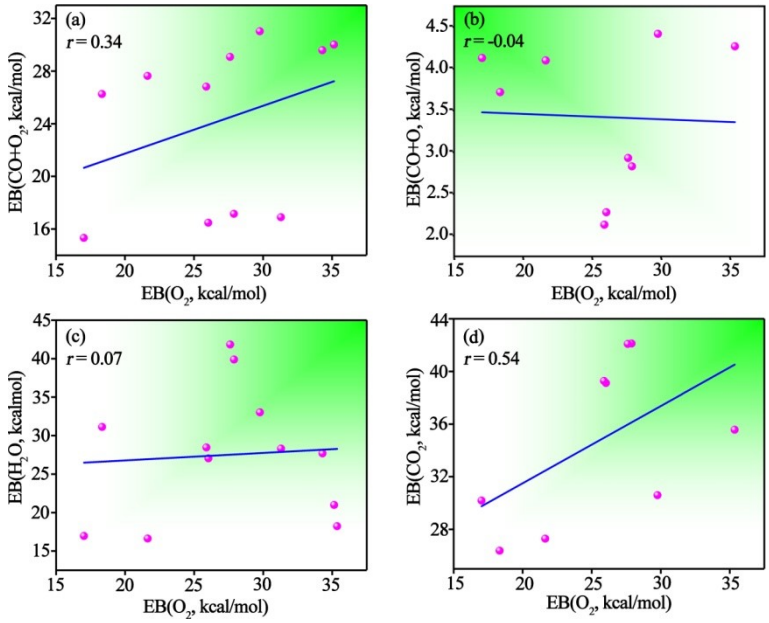

Figure S9. Correlations between the energy barrier (EB) of O_2 and EB of $CO+O_2$ (a), CO+O (b), H_2O (c), and CO_2 (d). Colored backgrounds indicate the change trends of the linear relationships.

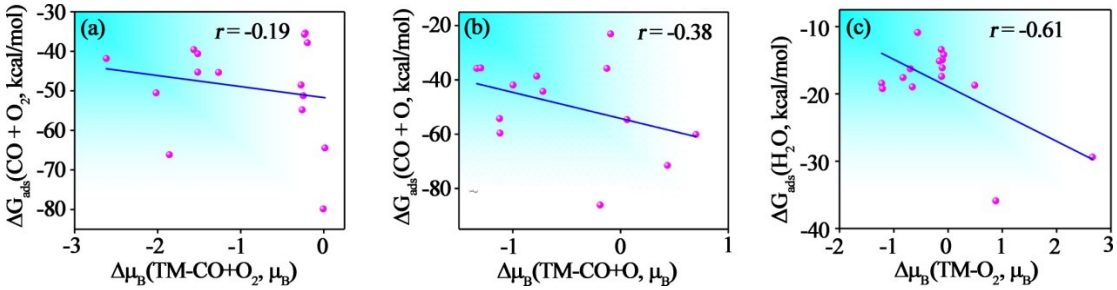

Figure S10. Correlations between the variation of electronic spin moment ($\Delta\mu_B$) of TM (before and after reactants adsorption) and ΔG_{ads} of $CO+O_2$ (a) and CO+O (b); Correlation between the $\Delta\mu_B$ of TM (before and after O_2 adsorption) and ΔG_{ads} of H_2O (c). Detailed data is shown in Table S2. Colored backgrounds indicate the change trends of the linear relationships.

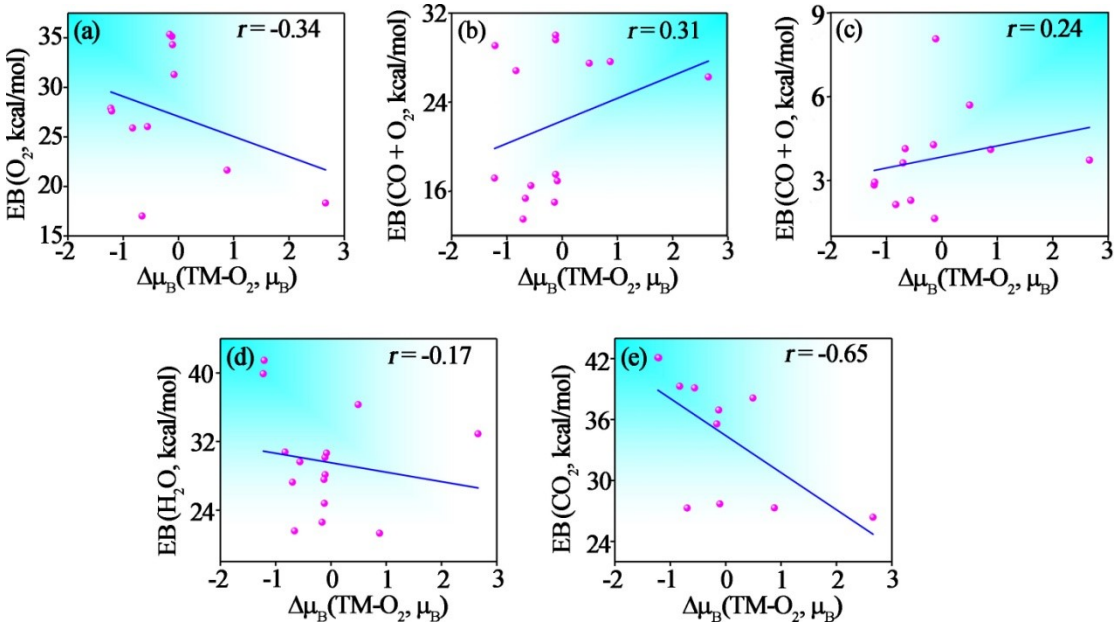

Figure S11. Correlations between the variation of electronic spin moment ($\Delta\mu_B$) of TM (before and after O_2 adsorption) and EB of O_2 (a), $CO+O_2$ (b), CO+O (c), H_2O (d), and CO_2 (e). Detailed data is shown in Table S2. Colored backgrounds indicate the change trends of the linear relationships.

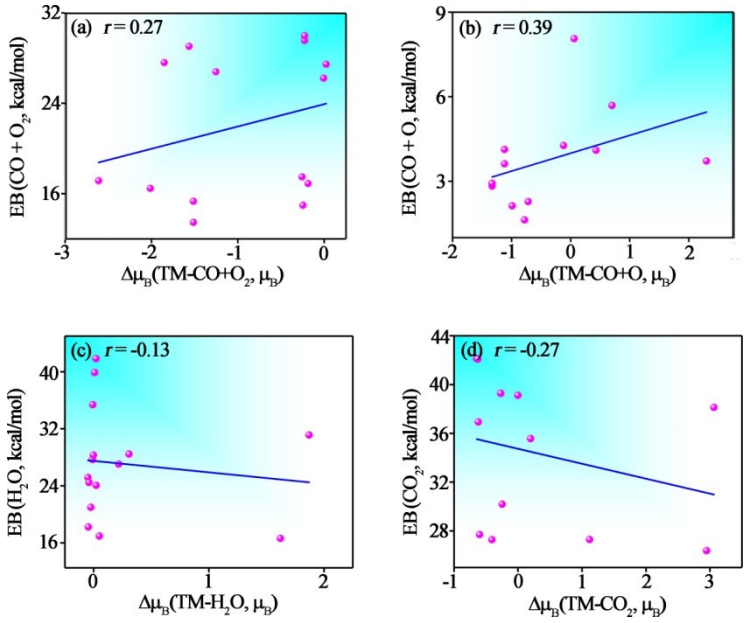

Figure S12. Correlations between the variation of electronic spin moment ($\Delta\mu_B$) of TM (before and after reactants adsorption) and EB of $CO+O_2$ (a), CO+O (b), H_2O (c), and CO_2 (d). Detailed data is shown in Table S2. Colored backgrounds indicate the change trends of the linear relationships.

Table S5. The Mulliken charges (e^-) of O_2, $CO+O_2$, CO+O, H_2O and CO_2 (Δq, after reactants adsorption) on Fe, Co, and Ni SACs with different spin states.

	O_2	**$CO+O_2$**	**CO+O**	**H_2O**	**CO_2**
Fe(II)(S=0)	-0.57	-0.30	-0.21	0.25	-0.11
Fe(III)(S=1/2)	-0.52	-0.16	-0.18	0.26	-0.25
Fe(II)(S=1)	-0.62	-0.22	-0.22	0.26	-0.30
Fe(III)(S=3/2)	-0.56	-0.15	-0.19	0.23	-0.26
Fe(II)(S=2)	-0.59	-0.25	-0.22	0.24	-0.22
Fe(III)(S=5/2)	-0.55	-0.20	-0.19	0.24	-0.14
Co(III)(S=0)	-0.51	0.01	--	0.28	-0.14
Co(II)(S=1/2)	-0.50	0.03	-0.03	0.23	-0.13
Co(III)(S=1)	-0.44	-0.01	0.01	0.23	0.37
Co(II)(S=3/2)	-0.50	-0.06	-0.03	0.24	-0.13
Co(III)(S=2)	-0.44	-0.01	0.02	0.23	0.38
Co(II)(S=5/2)	-0.44	-0.09	-0.26	0.24	-0.13
Ni(II)(S=0)	--	--	--	--	--
Ni(III)(S=1/2)	-0.38	-0.02	--	0.25	-0.07
Ni(II)(S=1)	-0.40	-0.07	--	0.25	-0.12
Ni(III)(S=3/2)	-0.38	-0.02	-0.06	0.26	-0.07
Ni(II)(S=2)	-0.41	-0.07	-0.12	0.25	-0.14
Ni(III)(S=5/2)	-0.38	-0.02	-0.08	0.25	-0.19

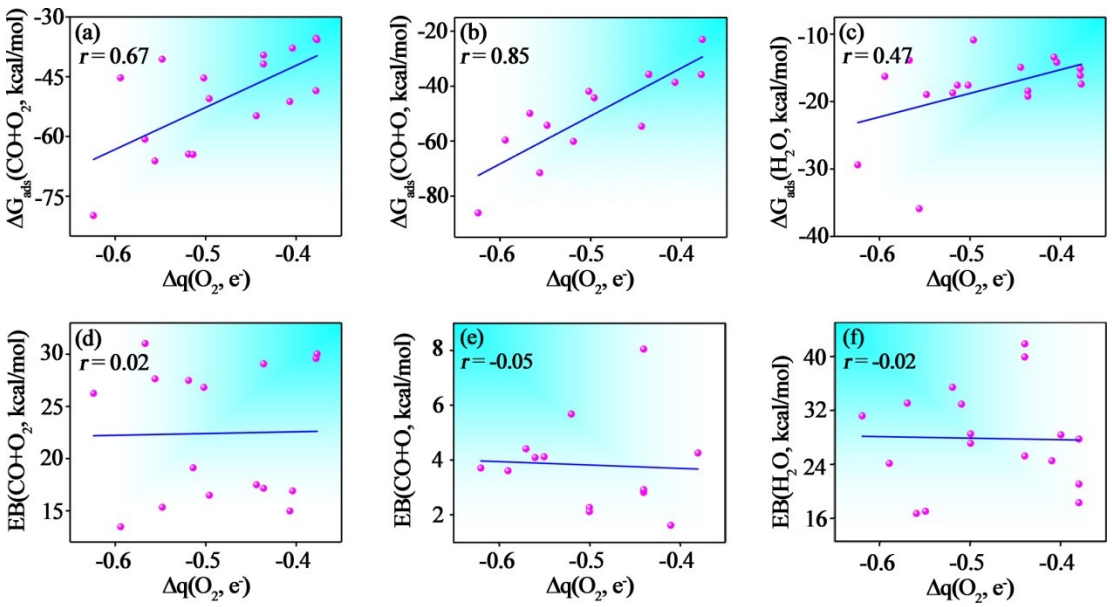

Figure S13. Correlations between the charge on O_2 ($\Delta q(O_2)$, after adsorption) and ΔG_{ads}/EB of $CO+O_2$ (a, d), CO+O (b, e), and H_2O (c, f). Detailed data is shown in Table S5. Colored backgrounds indicate the change trends of the linear relationships.

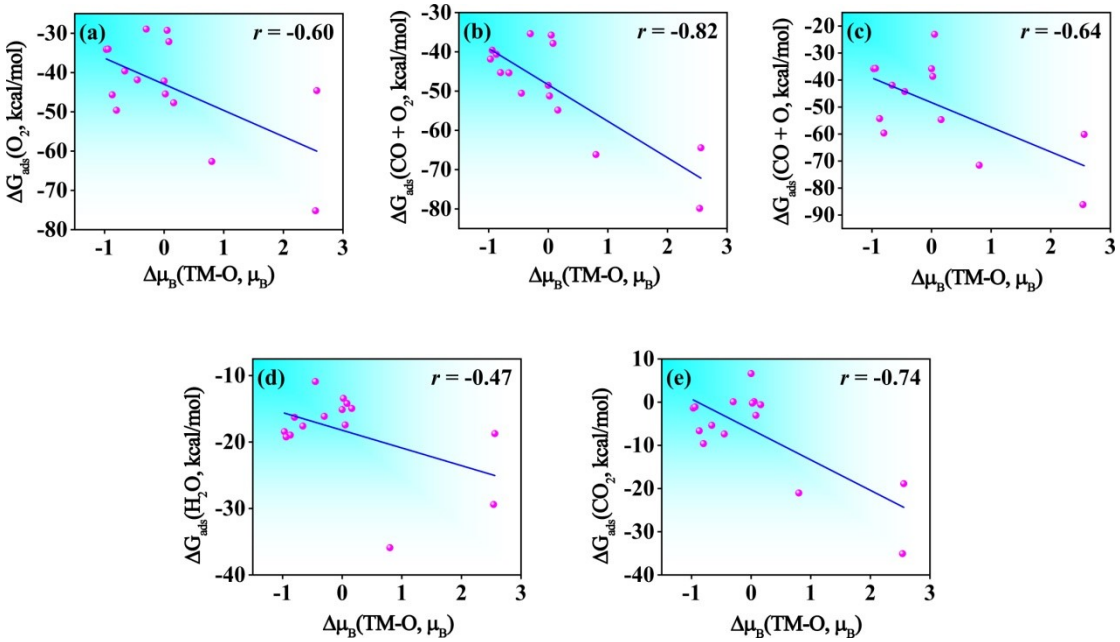

Figure S14. Correlations between the variation of electronic spin moment ($\Delta\mu_B$) of TM (before and after O adsorption) and ΔG_{ads} of O_2 (a), $CO+O_2$ (b), CO+O (c), H_2O (d), and CO_2 (e). Detailed data is shown in Table S1. Colored backgrounds indicate the change trends of the linear relationships.

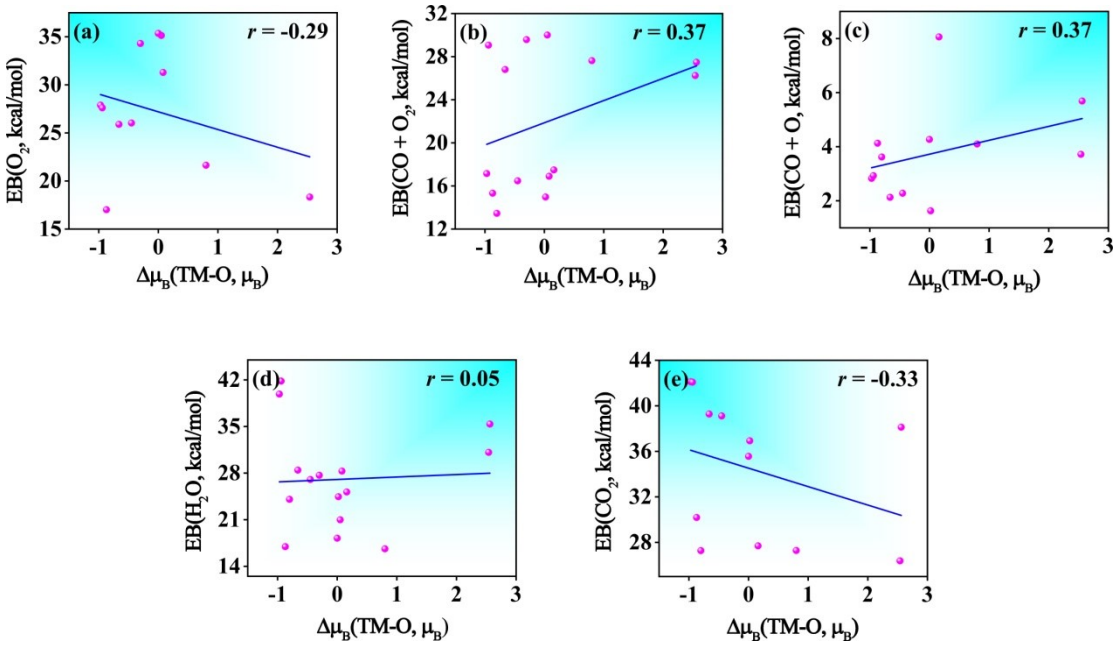

Figure S15. Correlations between the variation of electronic spin moment ($\Delta\mu_B$) of TM (before and after O adsorption) and EB of O_2 (a), CO+O_2 (b), CO+O (c), H_2O (d), and CO_2 (e). Detailed data is shown in Table S1. Colored backgrounds indicate the change trends of the linear relationships.

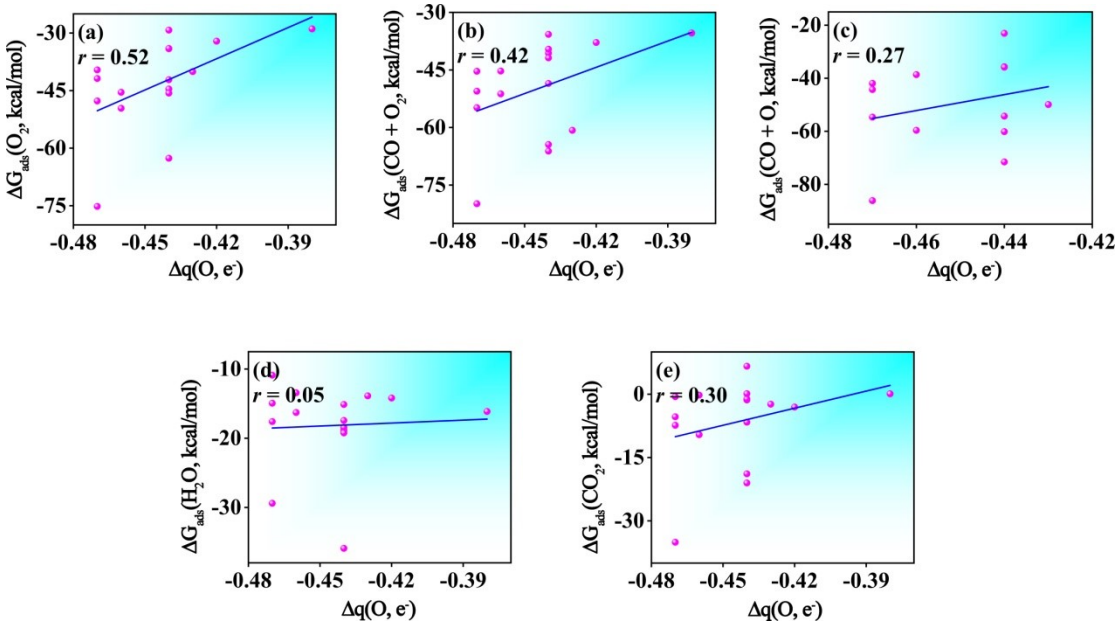

Figure S16. Correlations between the charge on O ($\Delta q(O)$, after adsorption) and ΔG_{ads} of O_2 (a), CO+O_2 (b), CO+O (c), H_2O (d), and CO_2 (e). Detailed data is shown in Table S1. Colored backgrounds indicate the change trends of the linear relationships.

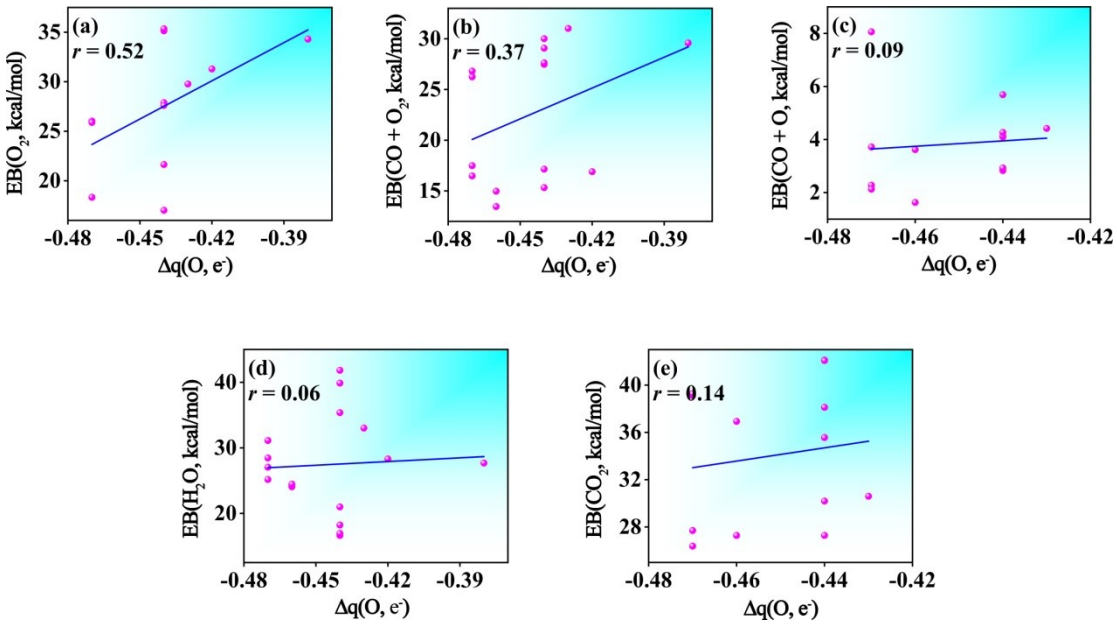

Figure S17. Correlations between the charge on O (Δq(O), after adsorption) and EB of O_2 (a), CO+O_2 (b), CO+O (c), H_2O (d), and CO_2 (e). Detailed data is shown in Table S1. Colored backgrounds indicate the change trends of the linear relationships.

Table S6. Stretching vibrational frequencies (ν/cm^{-1}) of O-O in adsorbed O_2, O-H in adsorbed H_2O, C-O in adsorbed CO_2, and TM-O in all adsorbed reactants on Fe, Co, and Ni SACs with different spin states. Specifically, for the reactant that has two TM-O bonds (O_2/CO+O_2), ν(TM-O) is the average frequency of these two bonds.

	O_2		$CO+O_2$	CO+O	H_2O		CO_2	
	O-O	**TM-O**	**TM-O**	**TM-O**	**O-H**	**TM-O**	**C-O**	**TM-O**
Fe(II)(S=0)	935.63	561.93	433.57	790.37	3724.74	353.18	2064.97	410.21
Fe(III)(S=1/2)	982.95	465.22	406.11	809.93	3744.83	355.48	1945.84	413.57
Fe(II)(S=1)	948.98	503.01	401.48	828.85	3735.14	381.37	1920.76	425.17
Fe(III)(S=3/2)	971.79	532.98	405.78	842.55	3707.86	365.92	1944.73	421.83
Fe(II)(S=2)	954.26	509.05	325.83	828.31	3770.29	341.49	1937.12	378.17
Fe(III)(S=5/2)	974.25	535.62	331.39	841.50	3706.53	366.42	2042.79	367.33
Co(III)(S=0)	965.7	525.78	524.42	--	3744.36	381.86	1932.60	476.32
Co(II)(S=1/2)	1030.62	320.89	524.67	700.43	3762.16	332.69	1985.93	443.11
Co(III)(S=1)	1076.92	319.68	531.03	699.96	3810.25	349.59	2055.67	378.62
Co(II)(S=3/2)	1021.26	319.69	398.95	700.46	3768.97	341.67	1984.95	441.93
Co(III)(S=2)	1077.77	320.84	412.51	701.77	3811.01	373.17	2055.38	379.51
Co(II)(S=5/2)	1149.18	295.93	280.55	762.71	3761.93	338.13	1984.48	436.52
Ni(II)(S=0)	--	--	--	--	--	--	--	--
Ni(III)(S=1/2)	1171.78	326.35	307.37	--	3769.69	370.75	2021.55	421.30
Ni(II)(S=1)	1164.72	317.66	304.00	--	3752.58	342.52	1992.84	420.37
Ni(III)(S=3/2)	1171.72	326.65	307.70	578.00	3767.85	348.29	2021.84	420.46
Ni(II)(S=2)	1169.52	316.08	305.19	583.85	3746.97	339.33	1983.92	420.35
Ni(III)(S=5/2)	1173.64	326.07	307.92	583.81	3693.08	346.92	2009.28	318.36