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Supporting information

A DFT study on the selective adsorption of CO from water-gas shift reaction tail gas by 3d transition metal porphyrins

Kaili Lyu, Nuo Chen, Yaxing Dong, Wencai Peng*

[a] School of Chemistry and Chemical Engineering, Shihezi University, Shihezi 832003, Xinjiang, China

* Corresponding author, Email: pengwencai@shzu.edu.cn

The most stable structure of each compound was used as the reference point (typically set at 0), and the total energy difference between a given structure and this reference was defined as the relative energy. The calculation formula is as follows:

$$\Delta E = E_{structure} - E_{RP}$$

where ΔE represents relative energy, $E_{structure}$ denotes the total energy of the computed structure, and E_{RP} is the total energy of the reference structure.

Table S1 Relative energies (kcal/mol) of complexes in different spin states

		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	L	0	14.43	26.80	78.26	40.13	29.48	0	0	0	0
MP	I				45.77	2.77	0	18.71	10.64		
	H		0	0	0	0	10.99				
	L	0	10.61	18.22	33.31	0	0	0	0	0	0
MP-CO	I				7.25	3.90	15.18	13.30	3.97		
	H		0	0	0	2.34	13.01				
	L	0	10.62	24.74	68.50	35.43	21.96	0	0	0	0
MP-CO_2	I				50.66	5.34	0	17.21	8.05		
	H		0	0	0	0	9.49				
	L	0	7.35	21.58	58.38	23.97	16.33	0	0	0	0
MP-H_2	I				26.99	2.57	0	17.54	10.95		
	H		0	0	0	0	33.23				
	L	0	7.09	22.44	60.73	26.73	15.83	0	0	0	0
MP-H_2O	I				37.79	0	0	7.76	1.94		
	H		0	0	0	9.85	7.91				

Table S2 Bond lengths (M-N, C-O, Å), frontier molecular orbital energies (E_{HOMO}, E_{LUMO}, eV), HOMO-LUMO energy gap (E_g, eV), polarizability (α, a.u.), and dipole moment (μ, Debye) of MP-CO.

	ScP	TiP	VP	CrP	MnP	FeP	CoP	NiP	CuP	ZnP
M-N (Å)	2.144	2.095	2.076	2.052	2.027	2.011	2.011	1.979	2.028	2.062
C-O (Å)	1.145	1.151	1.144	1.338	1.152	1.147	1.346	1.132	1.131	1.130
E_{HOMO} (eV)	-3.91	-4.68	-5.22	-5.58	-5.62	-5.63	-5.42	-5.61	-5.60	-5.53
E_{LUMO} (eV)	-2.77	-2.53	-2.49	-2.70	-2.54	-2.52	-2.50	-2.52	-2.56	-2.55
E_g (eV)	1.14	2.15	2.73	2.88	3.08	3.11	2.92	3.09	3.04	2.99
α (a.u.)	409.4	383.8	378.0	374.3	365.4	363.9	365.2	361.9	366.7	370.4
μ (Debye)	0.269	1.594	0.820	0.135	1.531	0.946	0.051	0.223	0.095	0.404

Table S3 Bond lengths (M-N, Å), frontier molecular orbital energies (E_{HOMO}, E_{LUMO}, eV), HOMO-LUMO energy gap (E_g, eV), polarizability (α, a.u.), and dipole moment (μ, Debye) of MP-CO_2.

	ScP	TiP	VP	CrP	MnP	FeP	CoP	NiP	CuP	ZnP
M-N (Å)	2.125	2.080	2.069	2.051	2.096	2.008	1.996	1.978	2.027	2.060
E_{HOMO} (eV)	-3.73	-4.23	-4.79	-5.58	-4.44	-5.20	-5.57	-5.62	-5.61	-5.58
E_{LUMO} (eV)	-2.56	-2.27	-2.35	-2.69	-2.55	-2.71	-2.48	-2.53	-2.57	-2.57
E_g (eV)	1.18	1.97	2.44	2.90	1.89	2.49	3.09	3.09	3.04	3.01
α (a.u.)	390.5	379.3	375.4	372.9	377.5	367.4	364.4	362.6	368.0	371.3
μ (Debye)	2.758	1.049	0.921	0.183	0.476	0.216	0.208	0.259	0.211	0.225

Table S4 Bond lengths (M-N, Å), frontier molecular orbital energies (E_{HOMO}, E_{LUMO}, eV), HOMO-LUMO energy gap (E_g, eV), polarizability (α, a.u.), and dipole moment (μ, Debye) of MP-H_2

	ScP	TiP	VP	CrP	MnP	FeP	CoP	NiP	CuP	ZnP
M-N (Å)	2.118	2.082	2.072	2.051	2.094	2.009	1.997	1.979	2.026	2.058
E_{HOMO} (eV)	-3.83	-4.32	-4.94	-5.55	-4.43	-5.21	-5.55	-5.59	-5.59	-5.56
E_{LUMO} (eV)	-2.62	-2.28	-2.35	-2.66	-2.52	-2.69	-2.46	-2.50	-2.55	-2.54
E_g (eV)	1.21	2.03	2.58	2.90	1.91	2.52	3.09	3.09	3.05	3.02
α (a.u.)	381.8	369.8	366.3	364.6	368.9	359.2	356.2	356.1	360.0	363.0
μ (Debye)	1.845	0.584	0.625	0.182	0.427	0.297	0.274	0.068	0.033	0.182

Table S5 Bond lengths (M-N, Å), frontier molecular orbital energies (E_{HOMO}, E_{LUMO}, eV), HOMO-LUMO energy gap (E_g, eV), polarizability (α, a.u.), and dipole moment (μ, Debye) of MP-H_2O.

	ScP	TiP	VP	CrP	MnP	FeP	CoP	NiP	CuP	ZnP
M-N (Å)	2.129	2.078	2.070	2.055	2.018	2.014	2.001	1.977	2.030	2.071
E_{HOMO} (eV)	-3.54	-3.97	-4.54	-5.21	-3.96	-5.04	-5.50	-5.76	-5.66	-5.44
E_{LUMO} (eV)	-2.36	-2.19	-2.25	-2.46	-2.60	-2.62	-2.41	-2.67	-2.62	-2.48
E_g (eV)	1.18	1.78	2.29	2.75	1.36	2.42	3.09	3.09	3.04	2.96
α (a.u.)	385.0	373.9	369.2	367.7	366.1	362.4	359.6	357.4	362.6	366.7
μ (Debye)	5.295	2.523	2.162	1.031	1.831	1.346	1.376	2.489	1.428	1.619

Table S6 CDA Analysis Results for α Orbitals of the ScP-CO Complex: Orbital Number of the Complex (Orb.), Occupation Number of the Complex Orbital (Occ.), Number of Electrons Transferred from MP to CO (d), Number of Electrons Transferred from CO to MP (b), Net Electron Transfer from CO to MP (b-d), Charge Polarization of Occupied Orbitals (r).

Orb.	Occ.	d	b	b-d	r
11	1	0	0.002	0.002	0
32	1	0.001	0	-0.001	0.001
33	1	-0.001	0	0.001	0.005
36	1	0	0.004	0.004	0
54	1	0	0.003	0.003	-0.005
67	1	0	0.002	0.002	0.002
69	1	-0.001	0.049	0.050	0.015
71	1	0.002	0.038	0.037	-0.040
73	1	0	0.002	0.002	-0.002
85	1	0	0.003	0.002	-0.015
92	1	-0.002	-0.001	0.001	-0.007
93	1	0.003	0	-0.003	-0.001
94	1	0.002	0	-0.002	-0.001
98	1	0.029	-0.001	-0.030	-0.003
Sum:	98	0.034	0.099	0.066	-0.052

Table S7 CDA Analysis Results for β Orbitals of the ScP-CO Complex: Orbital Number of the Complex (Orb.), Occupation Number of the Complex Orbital (Occ.), Number of Electrons Transferred from MP to CO (d), Number of Electrons Transferred from CO to MP (b), Net Electron Transfer from CO to MP (b-d), Charge Polarization of Occupied Orbitals (r).

Orb.	Occ.	d	b	b-d	r
11	1	0	0.002	0.002	0
32	1	0.001	0.000	-0.001	0.001
34	1	-0.001	0.000	0.001	0.005
36	1	0	0.004	0.004	0
57	1	0	0.002	0.003	-0.004
69	1	-0.001	0.022	0.023	0.021
72	1	0	0.003	0.003	-0.002
73	1	0.002	0.071	0.069	-0.044
85	1	0	0.003	0.003	-0.015
92	1	-0.002	-0.001	0.001	-0.007
93	1	0.002	0	-0.002	-0.001
94	1	0.002	0	-0.002	-0.001
Sum:	97	0.003	0.105	0.102	-0.047

Table S8 CDA Analysis Results for α Orbitals of the TiP-CO Complex: Orbital Number of the Complex (Orb.), Occupation Number of the Complex Orbital (Occ.), Number of Electrons Transferred from MP to CO (d), Number of Electrons Transferred from CO to MP (b), Net Electron Transfer from CO to MP (b-d), Charge Polarization of Occupied Orbitals (r).

Orb.	Occ.	d	b	b-d	r
11	1	0	0.002	0.002	0.001
32	1	0.002	0	-0.002	0.003
33	1	-0.001	0	0.001	0.007
36	1	0	0.006	0.006	0.004
59	1	-0.001	0	0.001	-0.010
65	1	0	0.001	0.001	0.008
66	1	0	0.002	0.001	0.007
69	1	-0.002	0.003	0.005	0.046
73	1	0.001	0	-0.001	-0.006
74	1	0.001	0	-0.001	-0.006
75	1	0.001	0.025	0.024	0.060
85	1	0.001	0.003	0.002	-0.026
92	1	-0.005	-0.003	0.002	-0.019
93	1	0.008	0	-0.008	-0.004
94	1	0.007	0	-0.007	-0.003
97	1	-0.002	-0.001	0.001	-0.006
98	1	0.011	-0.004	-0.015	-0.003
99	1	0.017	-0.003	-0.020	-0.004
Sum:	99	0.040	0.031	-0.009	0.078

Table S9 CDA Analysis Results for β Orbitals of the TiP-CO Complex: Orbital Number of the Complex (Orb.), Occupation Number of the Complex Orbital (Occ.), Number of Electrons Transferred from MP to CO (d), Number of Electrons Transferred from CO to MP (b), Net Electron Transfer from CO to MP (b-d), Charge Polarization of Occupied Orbitals (r).

Orb.	Occ.	d	b	b-d	r
11	1	0	0.003	0.003	0
32	1	0.002	0	-0.002	0.004
35	1	-0.001	0	0.001	0.007
36	1	0	0.007	0.008	0
58	1	0	0.002	0.002	0.013
59	1	-0.001	0.004	0.005	-0.020
67	1	0.001	0	-0.001	0.009
68	1	0.001	0	-0.001	0.008
69	1	-0.001	0.004	0.005	0.017
73	1	0.001	0	0.000	-0.008
74	1	0.001	0.001	0.000	-0.009
76	1	0.002	0.092	0.090	-0.039
85	1	0.003	0.012	0.009	-0.038
92	1	-0.005	-0.004	0.001	-0.019
93	1	0.004	0	-0.004	-0.002
94	1	0.004	0	-0.004	-0.002
96	1	-0.001	0	0.001	-0.004
Sum:	97	0.007	0.121	0.114	-0.083

Table S10 CDA Analysis Results for α Orbitals of the VP-CO Complex: Orbital Number of the Complex (Orb.), Occupation Number of the Complex Orbital (Occ.), Number of Electrons Transferred from MP to CO (d), Number of Electrons Transferred from CO to MP (b), Net Electron Transfer from CO to MP (b-d), Charge Polarization of Occupied Orbitals (r).

Orb.	Occ.	d	b	b-d	r
11	1	0	0.003	0.003	0
32	1	0.002	0	-0.002	0.003
36	1	0	0.007	0.007	0.001
57	1	0	0.010	0.010	-0.002
59	1	-0.002	-0.001	0.002	-0.004
67	1	-0.001	0.007	0.008	0.007
68	1	-0.003	0.055	0.058	0.026
72	1	0.002	0.020	0.018	-0.022
73	1	0.002	0.022	0.020	-0.028
74	1	0.002	0	-0.002	-0.004
75	1	0.002	0	-0.002	-0.004
85	1	0	0.007	0.007	-0.042
92	1	0.012	0	-0.012	-0.005
93	1	0.012	0	-0.012	-0.005
94	1	-0.004	-0.001	0.003	-0.020
97	1	-0.001	0	0.002	-0.006
99	1	0.030	0	-0.031	-0.006
100	1	0.030	0	-0.031	-0.006
Sum:	100	0.083	0.129	0.046	-0.098

Table S11 CDA Analysis Results for β Orbitals of the VP-CO Complex: Orbital Number of the Complex (Orb.), Occupation Number of the Complex Orbital (Occ.), Number of Electrons Transferred from MP to CO (d), Number of Electrons Transferred from CO to MP (b), Net Electron Transfer from CO to MP (b-d), Charge Polarization of Occupied Orbitals (r).

Orb.	Occ.	d	b	b-d	r
11	1	0	0.003	0.003	0
32	1	0.002	0	-0.002	0.003
36	1	0	0.007	0.007	0.001
57	1	0	0.004	0.004	-0.001
59	1	-0.001	0	0.001	-0.004
69	1	-0.003	0.026	0.029	0.035
72	1	0	0.001	0.001	0.000
73	1	0.004	0.068	0.064	-0.054
74	1	0.002	0	-0.001	-0.005
75	1	0.002	0	-0.001	-0.005
85	1	0.003	0.010	0.007	-0.040
92	1	-0.004	-0.002	0.003	-0.021
93	1	0.005	0	-0.005	-0.002
94	1	0.005	0	-0.005	-0.002
96	1	-0.001	0	0.001	-0.006
Sum:	97	0.011	0.118	0.107	-0.085

Table S12 CDA Analysis Results for α(β) Orbitals of the FeP-CO Complex: Orbital Number of the Complex (Orb.), Occupation Number of the Complex Orbital (Occ.), Number of Electrons Transferred from MP to CO (d), Number of Electrons Transferred from CO to MP (b), Net Electron Transfer from CO to MP (b-d), Charge Polarization of Occupied Orbitals (r).

Orb.	Occ.	d	b	b-d	r
2	1	0.001	-0.001	-0.002	0.001
11	1	0	0.003	0.003	0
32	1	0.001	0	-0.001	0.004
36	1	-0.001	0.012	0.013	0.002
37	1	-0.004	-0.001	0.003	-0.003
44	1	-0.003	0	0.003	-0.001
57	1	-0.002	0.024	0.027	0.038
59	1	-0.007	-0.005	0.002	-0.046
65	1	-0.006	0.027	0.033	0.026
66	1	0.002	-0.001	-0.003	0.026
67	1	0.002	-0.001	-0.003	0.026
68	1	-0.004	0.037	0.041	0.018
72	1	0.003	0.016	0.013	-0.018
73	1	0.003	0.017	0.014	-0.030
74	1	0.002	0	-0.002	-0.016
75	1	0.002	0	-0.002	-0.016
84	1	-0.003	0.012	0.015	-0.090
92	1	0.024	0	-0.024	-0.015
93	1	0.024	0	-0.024	-0.015
94	1	-0.002	0.002	0.004	-0.022
97	1	0.010	0	-0.010	-0.003
98	1	0.010	0	-0.010	-0.003
Sum:	100	0.054	0.143	0.089	-0.143

Table S13 CDA Analysis Results for α Orbitals of the CoP-CO Complex: Orbital Number of the Complex (Orb.), Occupation Number of the Complex Orbital (Occ.), Number of Electrons Transferred from MP to CO (d), Number of Electrons Transferred from CO to MP (b), Net Electron Transfer from CO to MP (b-d), Charge Polarization of Occupied Orbitals (r).

Orb.	Occ.	d	b	b-d	r
36	1	0	0.003	0.003	0.001
37	1	-0.001	0	0.001	-0.001
44	1	-0.001	0	0.001	0
57	1	0	0.003	0.003	0.023
59	1	-0.005	-0.001	0.004	-0.004
67	1	-0.004	0.012	0.017	0.054
68	1	-0.004	0.016	0.020	0.067
72	1	0.002	0.008	0.006	0.001
73	1	0.002	0.005	0.004	-0.007
74	1	0.002	0	-0.002	-0.006
75	1	0.002	0	-0.002	-0.006
81	1	-0.004	-0.003	0.001	-0.022
90	1	0.009	0	-0.009	-0.003
91	1	0.009	0	-0.009	-0.003
92	1	0.005	0	-0.005	-0.002
93	1	0.005	0	-0.005	-0.002
95	1	0.001	0.003	0.002	-0.006
97	1	0.003	0.023	0.020	-0.087
99	1	0.004	0.018	0.014	-0.075
101	1	0.004	0.021	0.017	-0.088
Sum:	101	0.032	0.110	0.079	-0.143

Table S14 CDA Analysis Results for β Orbitals of the CoP-CO Complex: Orbital Number of the Complex (Orb.), Occupation Number of the Complex Orbital (Occ.), Number of Electrons Transferred from MP to CO (d), Number of Electrons Transferred from CO to MP (b), Net Electron Transfer from CO to MP (b-d), Charge Polarization of Occupied Orbitals (r).

Orb.	Occ.	d	b	b-d	r
11	1	0	0.001	0.001	0
36	1	0	0.003	0.003	0
37	1	-0.001	0	0.001	-0.001
44	1	-0.001	0	0.001	0
57	1	0	0.006	0.006	0.013
59	1	-0.005	-0.001	0.004	-0.004
65	1	0	0.002	0.001	0.009
67	1	-0.001	0.005	0.007	0.012
68	1	-0.005	0.032	0.038	0.054
72	1	0	0.006	0.005	0
73	1	0.002	0	-0.002	-0.005
74	1	0.002	0.001	-0.001	-0.006
75	1	0.002	0.034	0.032	-0.020
84	1	-0.001	0.020	0.021	-0.106
92	1	0.013	0	-0.013	-0.004
93	1	0.013	0	-0.013	-0.005
94	1	0.001	0.004	0.004	-0.021
97	1	0.003	0	-0.003	-0.001
98	1	0.003	0	-0.003	-0.001
100	1	0	0.002	0.002	-0.009
Sum:	100	0.027	0.117	0.089	-0.088

Table S15 CDA Analysis Results for α Orbitals of the FeP-H_2O Complex: Orbital Number of the Complex (Orb.), Occupation Number of the Complex Orbital (Occ.), Number of Electrons Transferred from MP to H_2O (d), Number of Electrons Transferred from H_2O to MP (b), Net Electron Transfer from H_2O to MP (b-d), Charge Polarization of Occupied Orbitals (r).

Orb.	Occ.	d	b	b-d	r
35	1	0.000	0.007	0.007	0.005
56	1	0.000	0.002	0.002	0.007
66	1	0.002	0.000	-0.002	0.003
70	1	0.000	0.001	0.001	0.014
71	1	0.001	0.000	-0.001	-0.004
72	1	0.000	0.000	0.000	0.000
73	1	-0.001	0.010	0.011	0.009
83	1	-0.001	0.012	0.013	0.040
91	1	0.002	0.000	-0.002	-0.003
92	1	0.001	0.000	-0.001	0.000
95	1	0.001	0.002	0.000	-0.010
96	1	0.003	0.011	0.008	-0.070
99	1	0.002	0.003	0.000	-0.018
Sum:	99.000	0.014	0.050	0.036	-0.046

Table S16 CDA Analysis Results for β Orbitals of the FeP-H_2O Complex: Orbital Number of the Complex (Orb.), Occupation Number of the Complex Orbital (Occ.), Number of Electrons Transferred from MP to H_2O (d), Number of Electrons Transferred from H_2O to MP (b), Net Electron Transfer from H_2O to MP (b-d), Charge Polarization of Occupied Orbitals (r).

Orb.	Occ.	d	b	b-d	r
35	1	0.000	0.008	0.008	0.003
56	1	0.000	0.002	0.002	0.006
66	1	0.002	0.000	-0.002	0.003
70	1	0.000	0.001	0.001	0.011
71	1	0.001	0.000	-0.001	-0.004
72	1	0.000	0.000	0.000	0.000
73	1	-0.001	0.012	0.012	0.000
83	1	0.001	0.023	0.022	-0.003
87	1	0.000	0.002	0.001	-0.010
90	1	0.002	0.000	-0.002	-0.002
91	1	0.003	0.002	-0.002	-0.010
94	1	0.000	0.002	0.001	-0.006
96	1	0.002	0.002	0.000	-0.009
97	1	0.001	0	-0.001	0.000
Sum:	97	0.012	0.055	0.042	-0.022

Table S17 CDA Analysis Results for α Orbitals of the CoP-H_2O Complex: Orbital Number of the Complex (Orb.), Occupation Number of the Complex Orbital (Occ.), Number of Electrons Transferred from MP to H_2O (d), Number of Electrons Transferred from H_2O to MP (b), Net Electron Transfer from H_2O to MP (b-d), Charge Polarization of Occupied Orbitals (r).

Orb.	Occ.	d	b	b-d	r
35	1	0.000	0.007	0.007	0.006
56	1	0.000	0.002	0.002	0.007
66	1	0.002	0.000	-0.002	0.003
70	1	0.000	0.002	0.001	0.016
71	1	0.001	0.000	-0.001	-0.004
73	1	-0.001	0.009	0.010	0.010
83	1	-0.001	0.011	0.012	0.040
90	1	0.002	0.000	-0.002	-0.003
91	1	0.001	0.000	-0.001	-0.007
92	1	0.001	0.000	-0.001	0.000
95	1	0.005	0.015	0.010	-0.091
99	1	0.003	0.003	0.000	-0.017
Sum:	99	0.015	0.051	0.036	-0.048

Table S18 CDA Analysis Results for β Orbitals of the CoP-H_2O Complex: Orbital Number of the Complex (Orb.), Occupation Number of the Complex Orbital (Occ.), Number of Electrons Transferred from MP to H_2O (d), Number of Electrons Transferred from H_2O to MP (b), Net Electron Transfer from H_2O to MP (b-d), Charge Polarization of Occupied Orbitals (r).

Orb.	Occ.	d	b	b-d	r
35	1	0.000	0.009	0.009	0.003
56	1	0.000	0.002	0.002	0.007
66	1	0.002	0.000	-0.002	0.003
70	1	0.000	0.001	0.001	0.013
71	1	0.001	0.000	-0.001	-0.004
73	1	-0.001	0.011	0.012	0.002
74	1	0.000	0.000	0.000	0.000
75	1	0.000	0.002	0.002	-0.002
83	1	0.001	0.026	0.025	-0.010
87	1	0.000	0.002	0.001	-0.009
90	1	0.002	0.000	-0.002	-0.003
91	1	0.002	0.001	-0.001	-0.009
92	1	0.003	0.002	-0.001	-0.009
98	1	0.002	0.001	0.000	-0.006
Sum:	98	0.013	0.058	0.045	-0.023

Table S19 Summary of CDA Analysis Results for MP-CO/H_2O Complex Orbitals: Orbital Number of the Complex (Orb.), Occupation Number of the Complex Orbital (Occ.), Number of Electrons Transferred from MP to CO/H_2O (d), Number of Electrons Transferred from CO/H_2O to MP (b), Net Electron Transfer from CO/H_2O to MP (b-d), Charge Polarization of Occupied Orbitals (r).

	d	b	b-d	r
ScP-CO	0.037	0.204	0.168	-0.099
TiP-CO	0.046	0.152	0.105	-0.006
VP-CO	0.094	0.247	0.153	-0.183
FeP-CO	0.108	0.287	0.178	-0.287
FeP-H_2O	0.026	0.104	0.078	-0.068
CoP-CO	0.059	0.227	0.168	-0.231
CoP-H_2O	0.028	0.108	0.081	-0.023

Table S20 CDA Analysis Results for Orbitals of NiP: Orbital Number of NiP (Orb.), Occupation Number of the NiP Orbital (Occ.), Number of Electrons Transferred from P to Ni (d), Number of Electrons Transferred from Ni to P (b), Net Electron Transfer from Ni to P (b-d), Charge Polarization of Occupied Orbitals (r)..

Orb.	Occ.	d	b	b-d	r
35	2	0.011	0.000	-0.011	-0.001
36	2	0.011	0.000	-0.011	-0.001
55	2	0.012	0.000	-0.012	0.073
58	2	0.010	0.000	-0.010	0.019
63	2	0.011	0.000	-0.011	-0.001
70	2	0.020	0.000	-0.020	-0.003
71	2	0.020	0.000	-0.020	-0.003
72	2	0.020	0.001	-0.019	0.039
74	2	0.027	-0.006	-0.033	0.178
79	2	0.042	0.002	-0.040	0.080
81	2	0.097	0.000	-0.097	-0.021
82	2	0.097	0.000	-0.097	-0.021
83	2	0.002	0.026	0.025	-0.052
86	2	-0.001	0.012	0.013	0.060
87	2	-0.002	0.013	0.014	0.062
88	2	0.019	0.000	-0.020	-0.001
Sum:	188	0.418	0.068	-0.350	0.362

The CDA analysis results of NiP show a net charge transfer of 0.35 e^-, with the direction from porphyrin to Ni (where σ-donation is 0.418 e^- from porphyrin → Ni, while π-backdonation is only 0.068 e^- from Ni → porphyrin). This significant accumulation of net negative charge on Ni fundamentally changes its electronic structure. The increased d-electron density effectively screens the nuclear charge, transforming Ni from an electrophilic center (as in Fe/Co analogs with positive ESP) into a locally electron-rich nucleophilic site, reflected in a negative ESP maximum. For

Ni(II) with a d^8 configuration, the net negative charge further stabilizes the square-planar field, maintaining a closed-shell singlet ground state (diamagnetic), and promotes metal-to-ligand charge transfer (MLCT) transitions due to the high d-electron density.

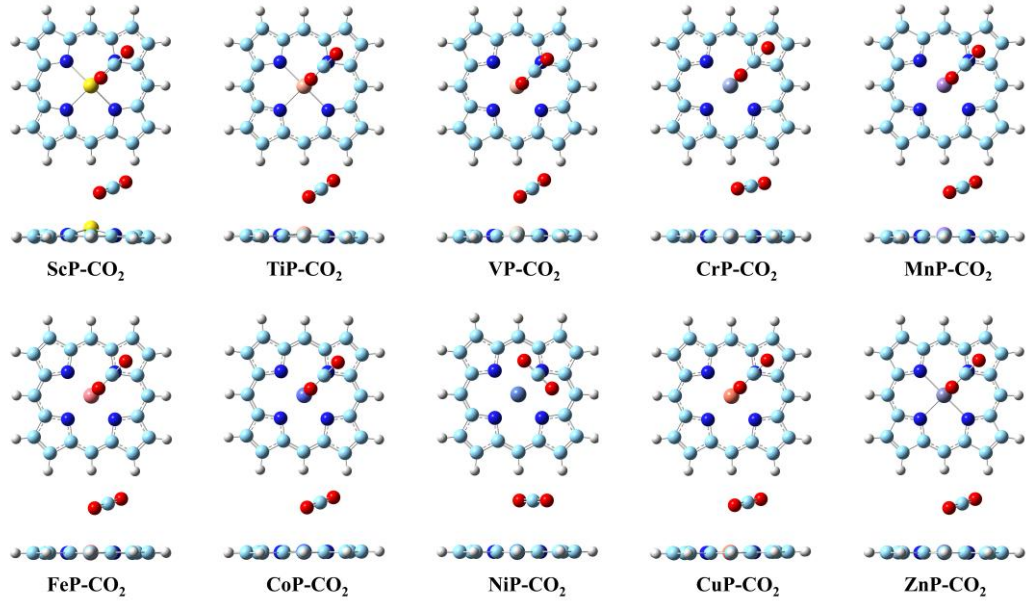

Fig. S1 Optimized structure of the MP-CO_2 complex (central atom: transition metal; color scheme: dark blue - N, light blue - C, red - O, silver grey - H).

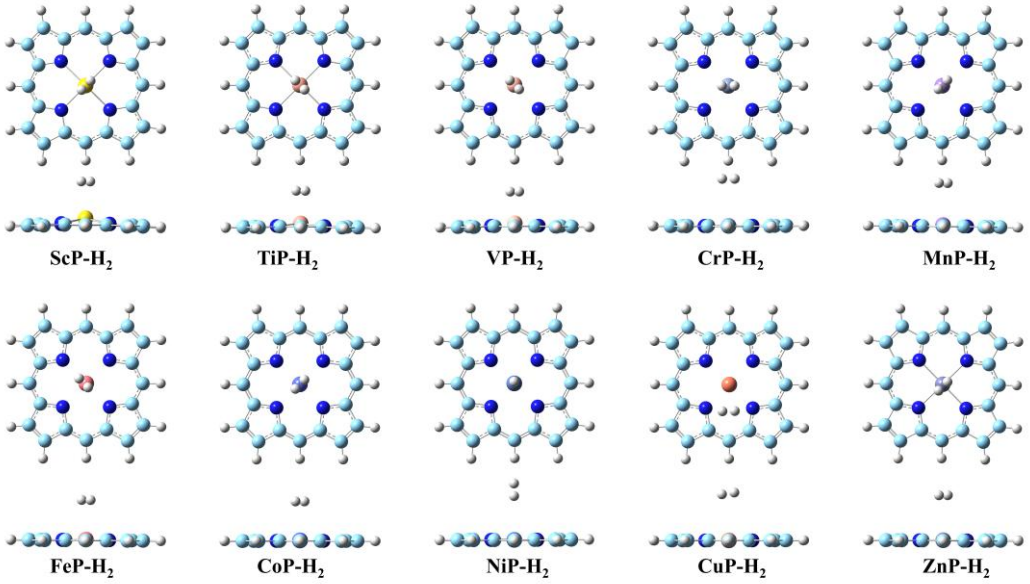

Fig. S2 Optimized structure of MP-H_2 (central atom: transition metal; color scheme: dark blue - N, light blue - C, silver grey - H).

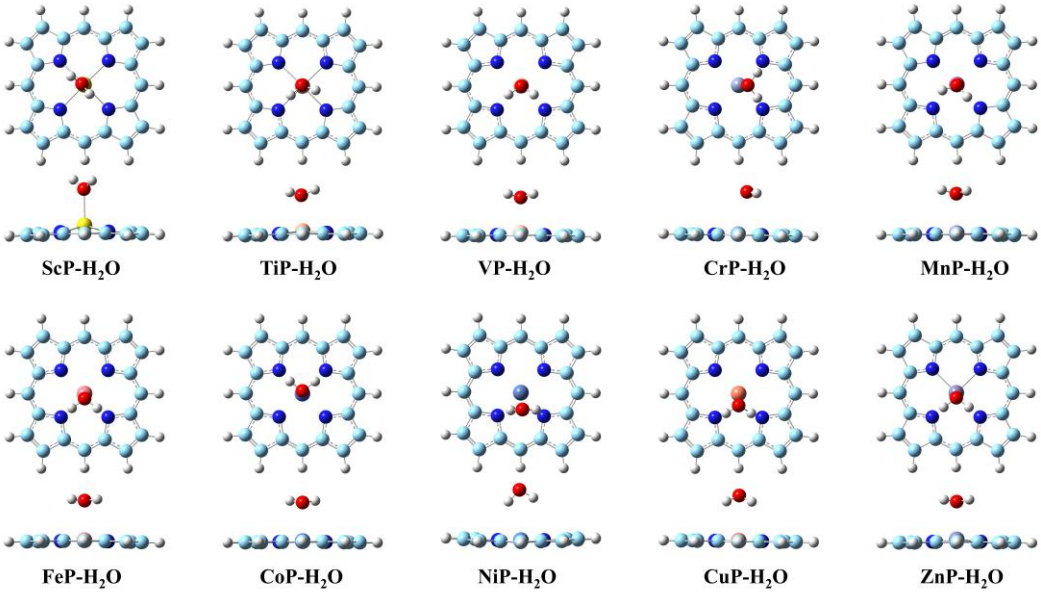

Fig. S3 Optimized structure of MP-H_2O (central atom: transition metal; color scheme: dark blue - N, light blue - C, red - O, silver grey - H).

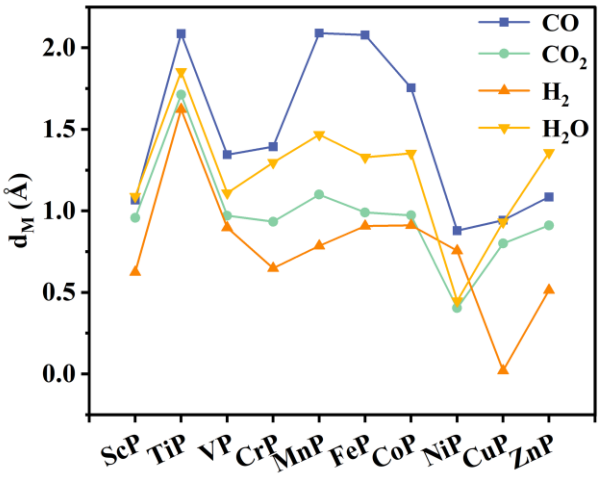

Fig. S4 Interpenetration distance (d_M, Å) of the electrostatic potential surfaces between MP and $CO/CO_2/H_2/H_2O$ complexes.

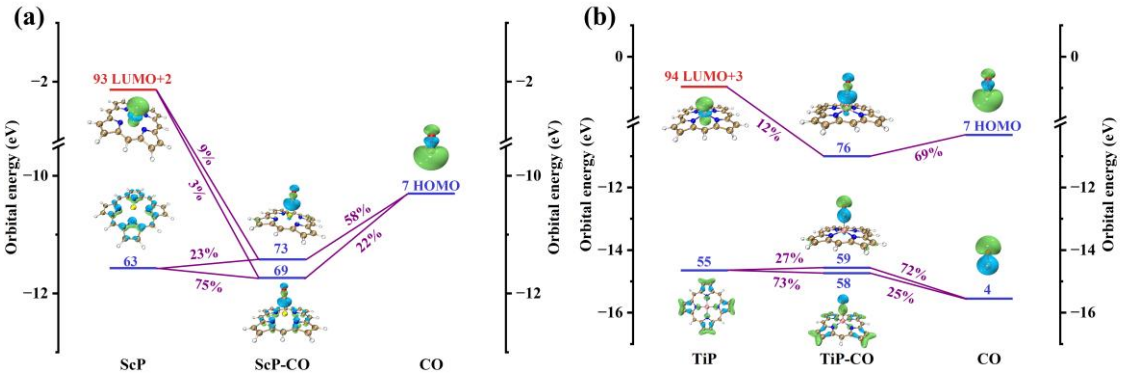

Fig. S5 Orbital interaction diagrams: (a) β orbitals of the ScP-CO system, (b) β orbitals of the TiP-CO system.

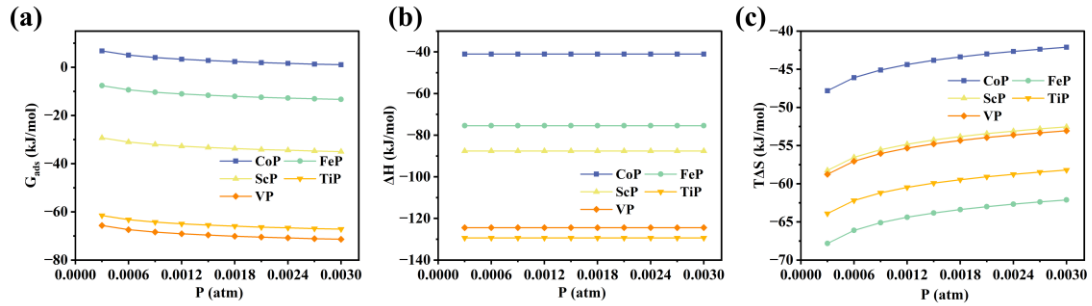

Fig. S6 Thermodynamic properties of desorption under variable pressure ((a) G_{ads}, (b) ΔH, (c) TΔS).

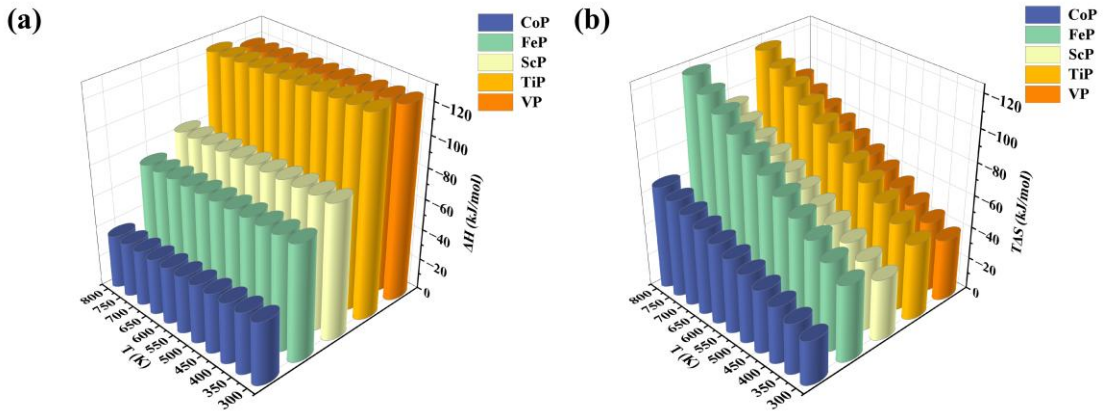

Fig. S7 Thermodynamic properties of desorption under variable temperature ((a) ΔH, (b) TΔS).