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

Supporting Information

Phosphomolybdic Acid Supported Single-Metal-Atom Catalysis in CO Oxidation: First-Principles Calculations

*Ming'an Yu, Yingxin Feng, Liye Gao and Sen Lin**

State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350002, China

**Corresponding author. Email: slin@fzu.edu.cn*

Table S1 Structure parameters for the reaction intermediates of CO oxidation following LH mechanism on *M*-PMAs (*M*=Pt, Fe, Ir, Rh and Ru).

	Pt-PMA	Fe-PMA	Ir-PMA	Rh-PMA	Ru-PMA
			State ii		
d_{O-O}（Å）	1.27	1.27	1.28	1.26	1.26
d_{M-O}（Å）	2.10，2.88	1.86, 2.80	1.93，2.84	1.93, 2.82	1.91, 2.98
			State iii		
d_{M-C}（Å）	1.91	2.00	3.07	2.07	2.07
d_{C-O}（Å）	1.69	1.15	0.98	1.16	1.16
d_{O-O}（Å）	1.37	1.34	2.06	1.36	1.36
E_{b-O}（eV)	0.12	-0.87	-1.41	-0.65	-2.78
			State v		
d_{C-O}（Å）	1.14	1.16	1.15	1.14	1.14
			State vi		
d_{M-C}（Å）	2.29	2.43	3.27	1.96	1.84

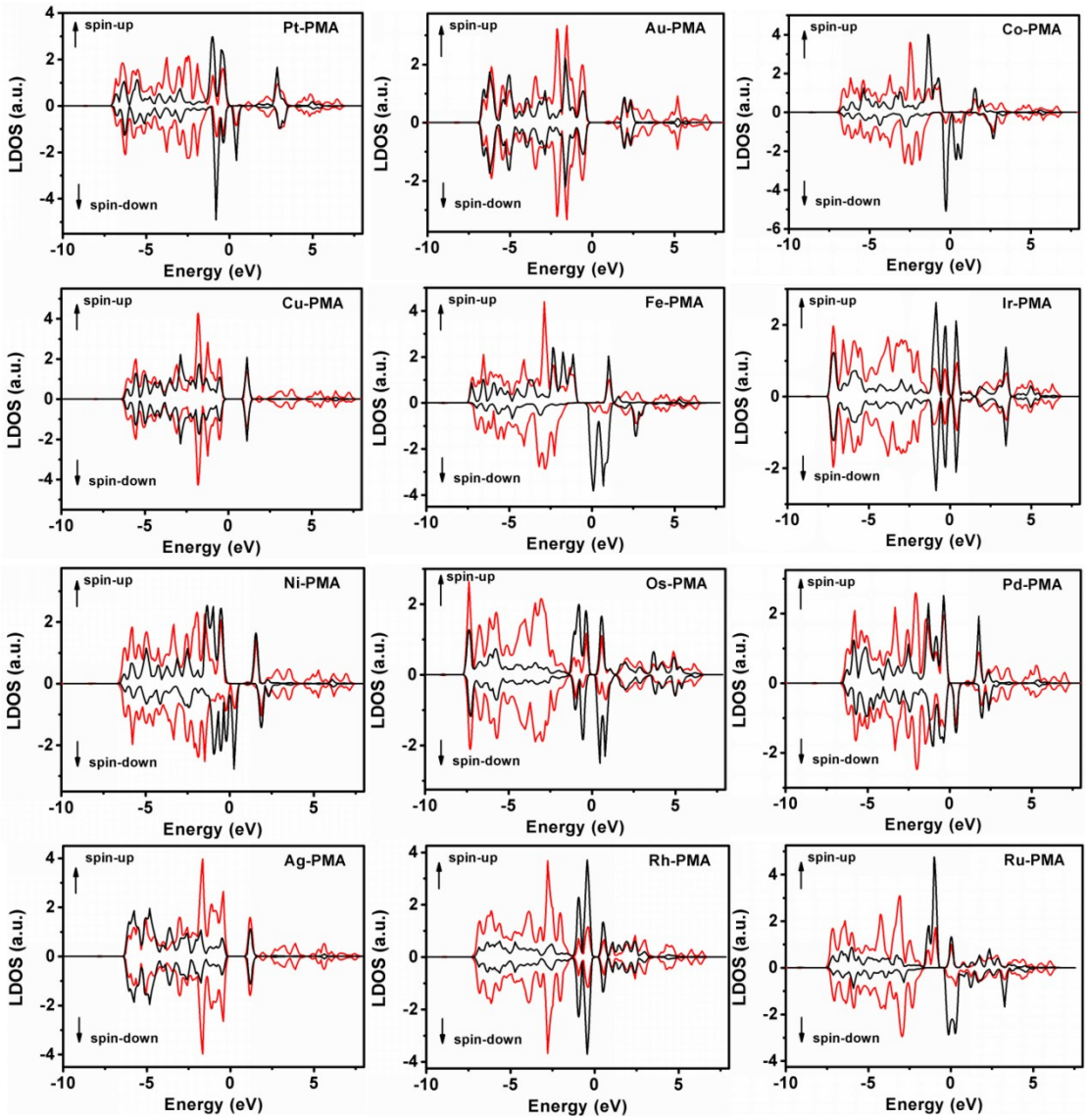

Fig. S1 Corresponding spin-polarized LDOSs of *M*-3d and neighboring O-2*p* orbitals of *M*-PMA (*M* = Pt, Au, Co, Fe, Ir, Ni, Pd, Ag, Rh, Cu, Os and Ru). Black and red curves denote *d* orbitals of metal and *p* orbitals of O, respectively. Fermi level is set to 0 eV.

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Table S2 Calculated M-O -distances (d/Å) and ∠*OMO*（°）for *M* at the anchoring sites of the *M*-PMA，CO-M-PMA and O_2-M-PMA systems.

M	d_{M-O}（Å）	d_{M-O} (CO)	d_{M-O}(O_2)	∠*OMO*	∠*OMO*(CO)	∠*OMO*(O_2)
Pt	1.94, 1.94, 2.04, 2.04	1.98, 2.16, 2.10, 2.08	2.00, 2.00, 2.04, 2.10	87.3, 87.5, 87.5, 87.4	78.6, 78.1, 77.5, 78.2	76.4, 76.8, 77.4, 76.9
Au	2.00, 2.00, 2.02, 2.02	2.00, 2.08, 2.16, 2.10	1.98, 1.95, 2.04, 2.04,	88.2, 88.2, 88.2, 88.2	78.1, 78.6, 77.5, 78.2	86.0, 85.8, 86.0, 86.1
Co	1.81, 1.81, 1.83, 1.83	1.83, 1.83, 1.89, 1.88	1.81, 1.81, 1.93, 1.93	87.9, 87.9, 87.9, 87.9	87.4, 87.4, 87.1, 87.1	84.2, 84.2, 84.3, 84.3
Cu	1.82, 1.82, 1.84, 1.84	1.84, 1.84, 1.85, 1.86	1.81, 1.82, 1.82, 1.83	89.3, 89.3, 89.3, 89.3	88.3, 87.8, 88.1, 88.3	89.7, 89.5, 89.8, 90.0
Fe	1.81, 1.81, 1.84, 1.84	1.81, 1.82, 1.84, 1.84	1.88, 1.88, 1.91, 1.91	88.6, 88.6, 88.6, 88.6	88.3, 88.3, 88.4, 88.3	82.0, 82.0, 81.8, 81.8
Ir	1.86, 1.85, 2.06, 2.04	1.95, 1.98, 2.07, 2.08	2.00, 2.00, 2.03, 2.00	80.1, 85.3, 85.3, 80.2	81.1, 80.6, 78.8, 79.2	78.7, 78.8, 78.7, 78.6
Ni	1.78, 1.78, 1.87, 1.87	1.86, 1.86, 1.89, 1.89	1.77, 1.77, 1.88, 1.88	88.6, 88.6, 88.6, 88.6	86.3, 86.4, 86.2, 86.5	89.7, 89.6, 89.5, 89.6
Os	1.88, 1.86, 1.96, 2.01	2.08, 2.08, 2.11, 2.08	1.87, 1.88, 2.03, 2.04	79.5, 82.2, 82.2,78.8	87.0, 91.1, 90.8, 87.6	81.0, 80.7, 81.2, 80.6
Pd	1.94, 1.94, 2.04, 2.04	1.95, 2.15, 2.10, 2.11	1.97, 1.99, 2.06, 2.07	85.7, 85.7, 85.7, 85.7	77.4, 77.6, 78.9, 78.8	81.9, 81.6, 81.1, 82.5
Ag	2.01, 2.01, 2.02, 2.02	2.13, 2.16, 2.11, 2.14	2.01, 2.01, 2.02, 2.02	86.9, 86.9, 86.9, 86.9	78.3, 77.7, 77.3, 78.5	86.8, 86.8, 86.8, 86.8
Rh	1.88, 1.88, 2.08, 2.08	1.99, 1.99, 2.03, 2.03	1.97, 1.96, 2.05, 2.04	82.3, 82.3, 82.3, 82.3	85.1, 87.1, 84.8, 87.4	79.8, 78.5, 80.0, 80.0
Ru	1.90, 1.90, 2.03, 2.03	1.97, 2.02, 2.02, 2.02	2.00, 2.00, 2.01, 2.03,	80.8, 82.8, 82.8, 80.9	79.2, 78.6, 78.5, 79.3	78.6, 78.7, 78.6, 78.7

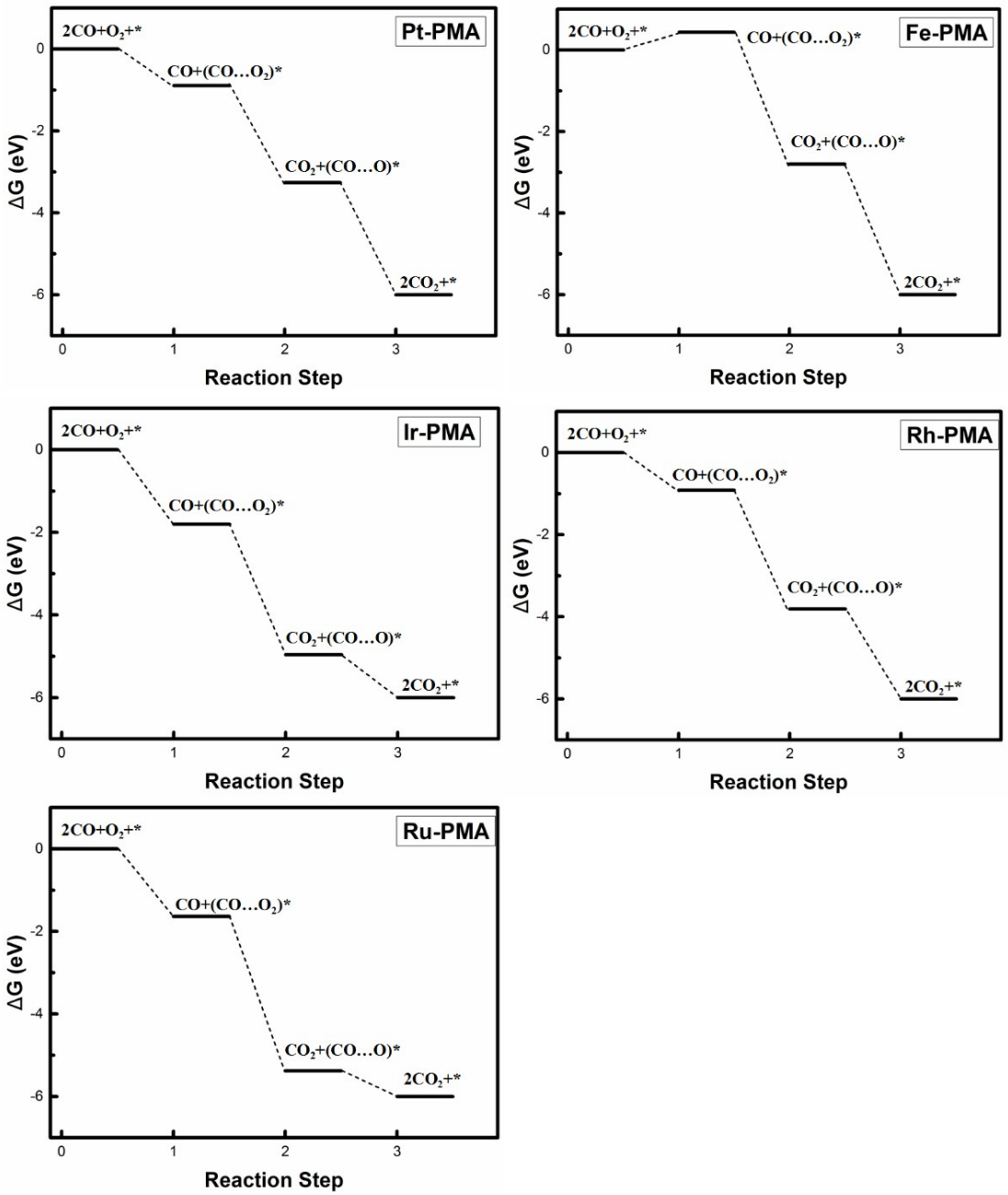

Fig. S2 Free energy (△*G*) profile with all reaction steps of CO oxidation on M-PMA.ΔG is obtained using $\Delta G = \Delta E - T\Delta S$, where ΔE is the total energy change directly from DFT calculations, Δ*S* denotes the entropy change, and the zero point energies (*ZPE*s) are assumed to be negligible. The entropies of the adsorbed state are also thought to be negligible while the Δ*S* values of the gases are obtained from the reference (P. Atkins and J. Paula, in Atkins' Physical Chemistry, ed. W. H. Freeman and Company, New York, 2006, pp. 993–1001).