

Supporting Information

Rational design of B-Site single-atom doped LaMnO₃ for CO chemical looping combustion: a DFT study

Supplementary Figures

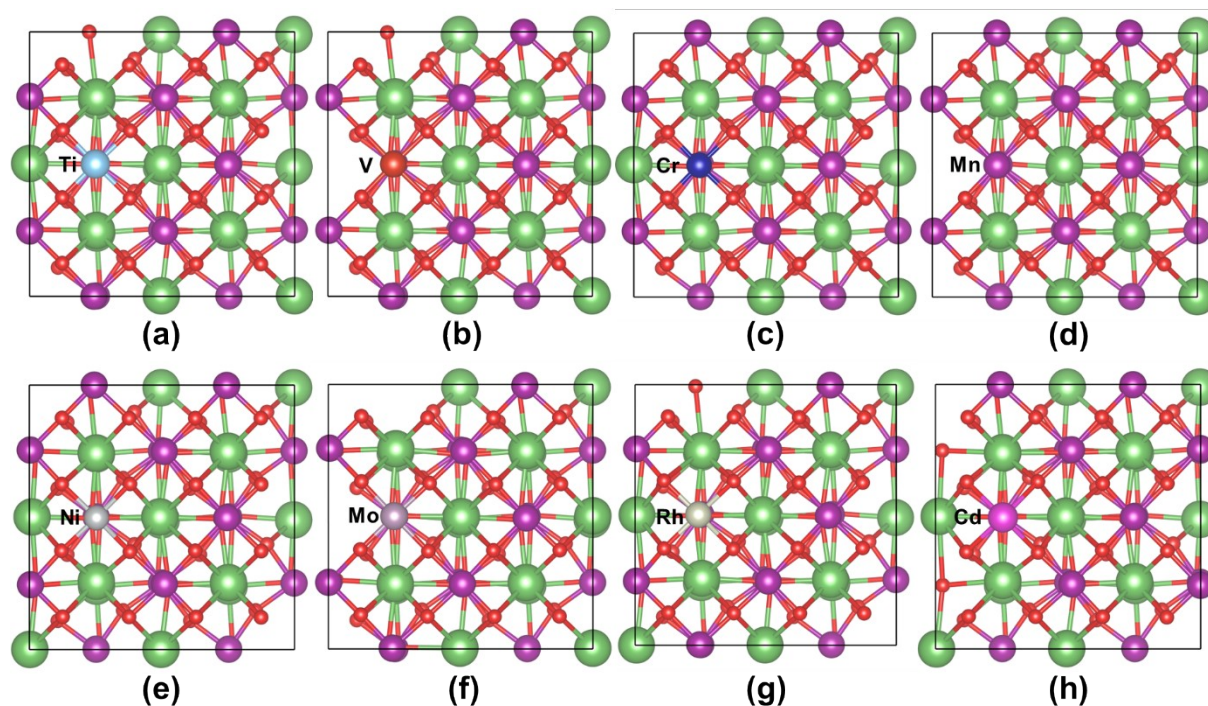
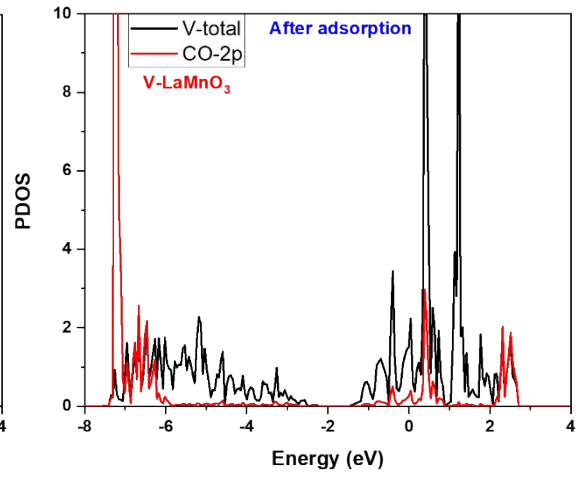
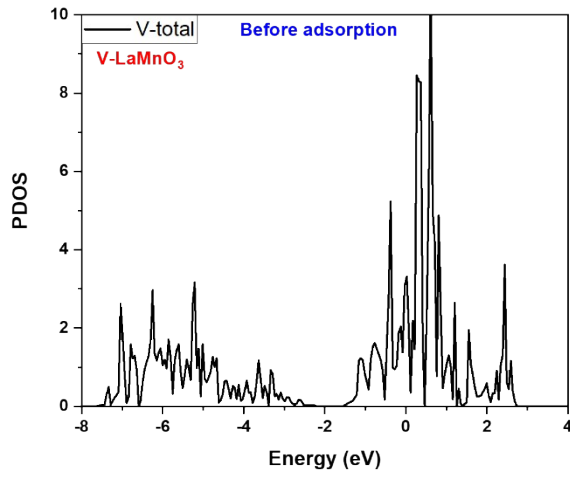
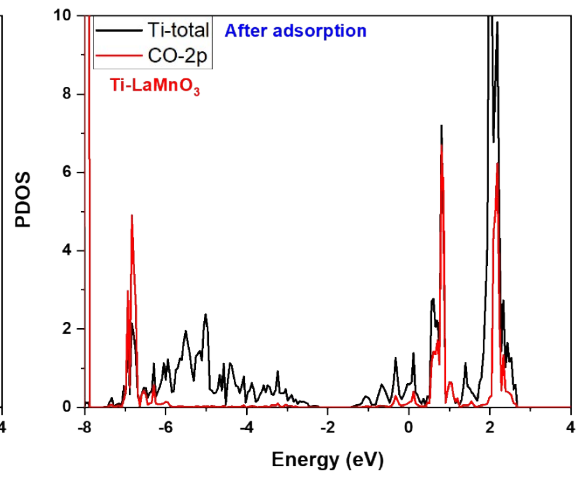
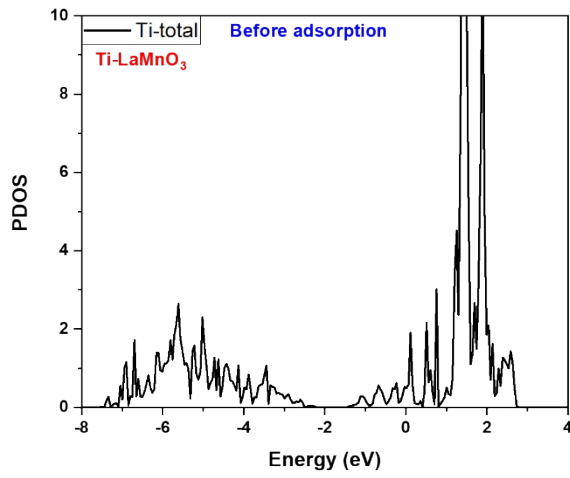
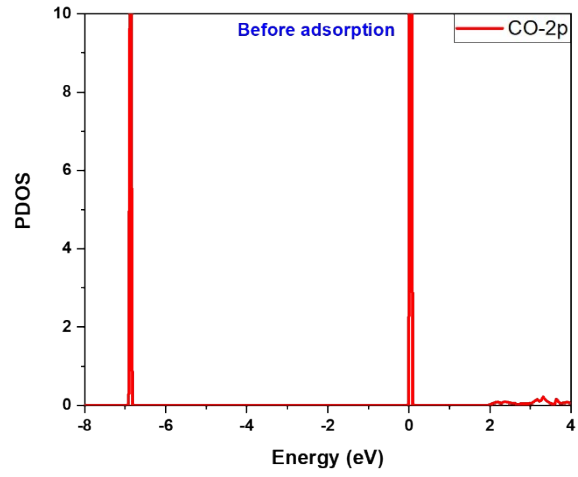
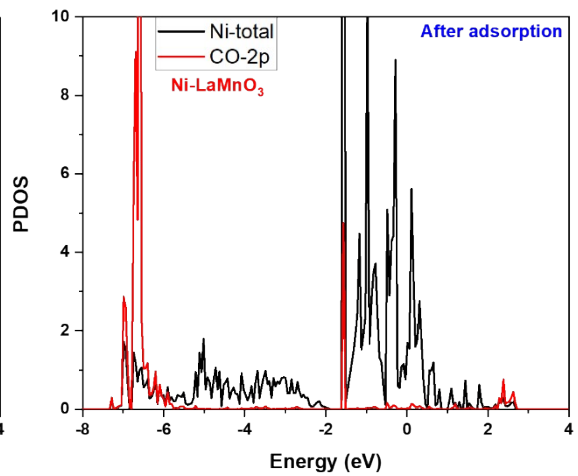
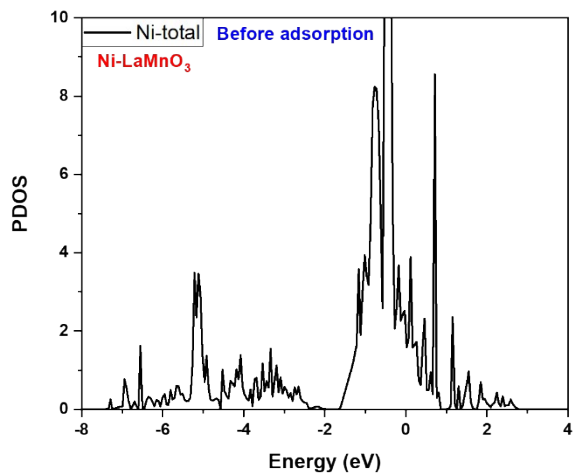
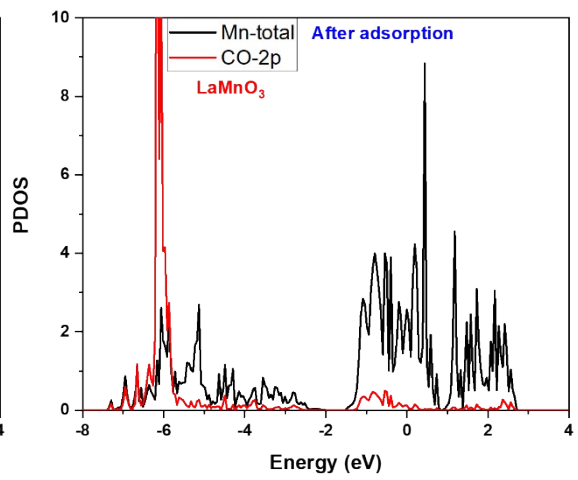
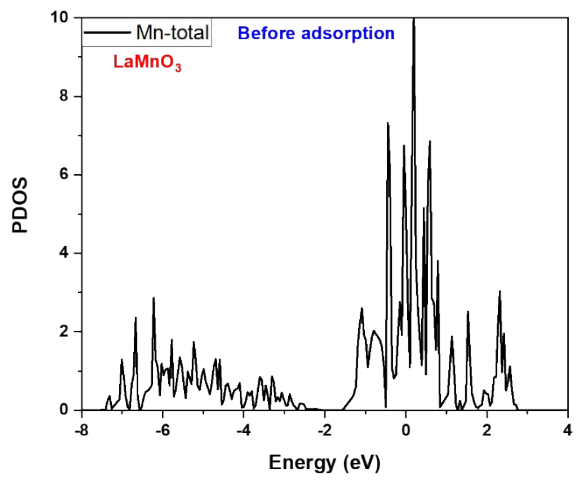
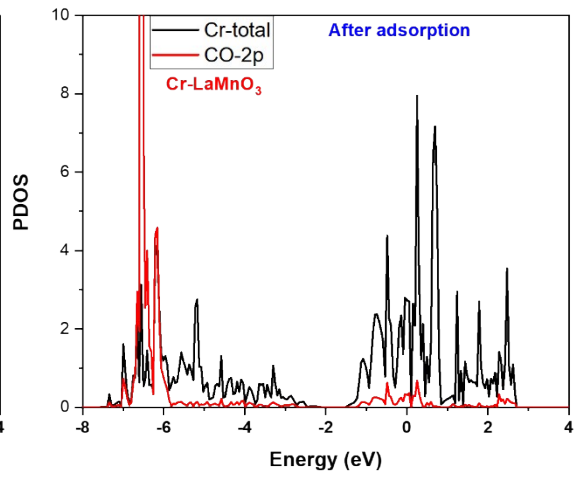
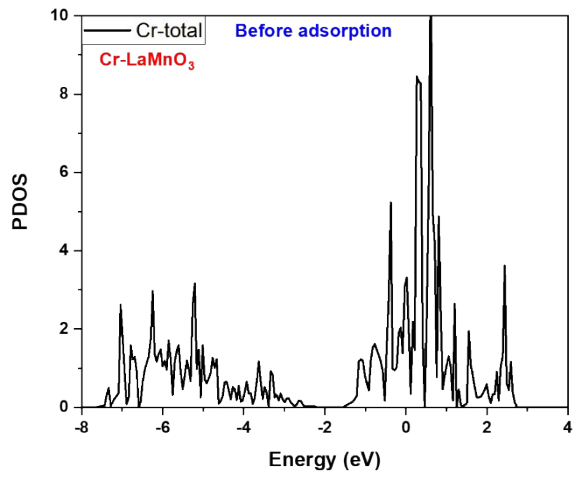


Figure S1 Structures of (a) Ti–LaMnO₃, (b) V–LaMnO₃, (c) Cr–LaMnO₃, (d) pristine LaMnO₃, (e) Ni–LaMnO₃, (f) Mo–LaMnO₃, (g) Rh–LaMnO₃, and (h) Cd–LaMnO₃. Atom colours: Mn (purple), La (green), O (red), and C (brown).





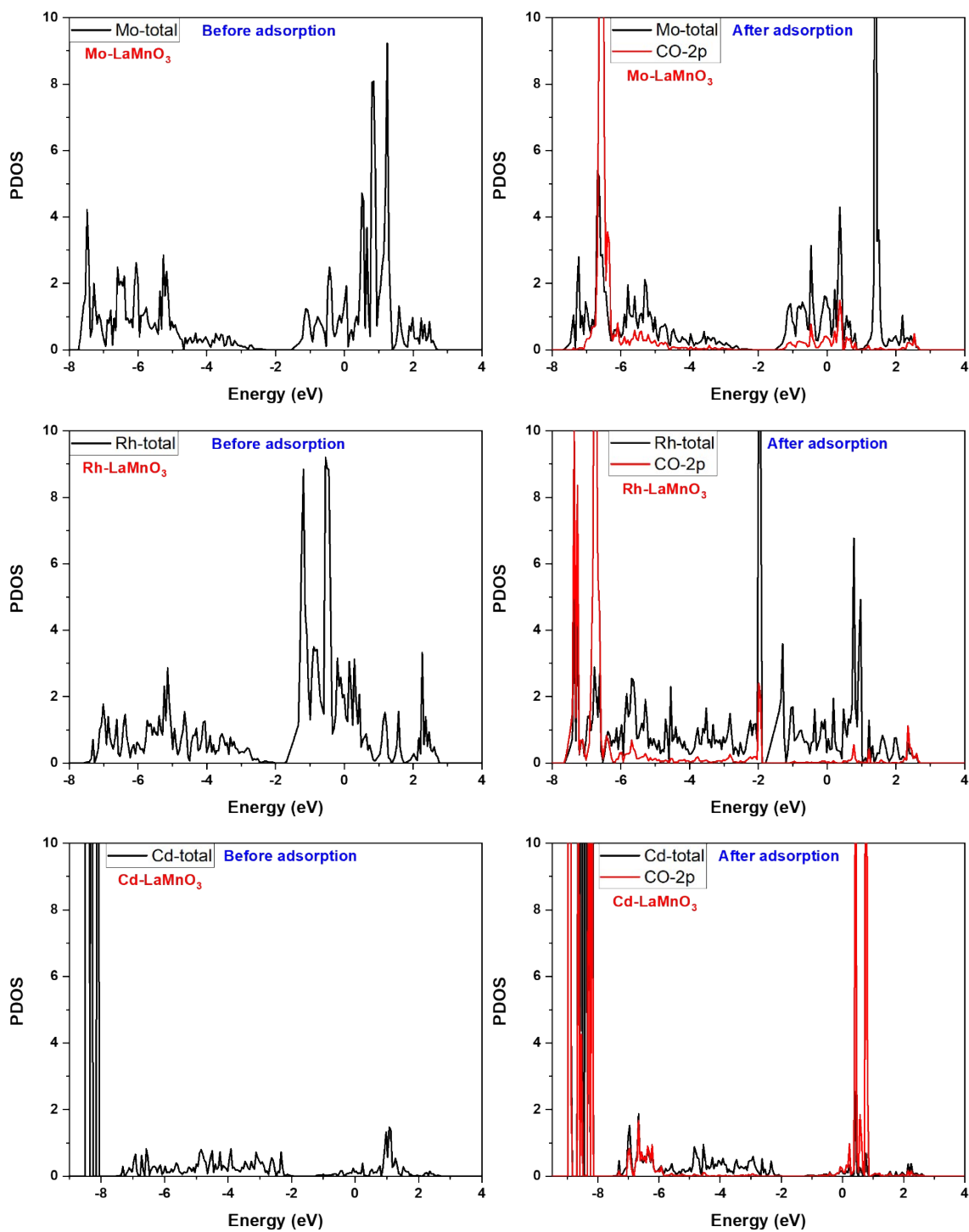
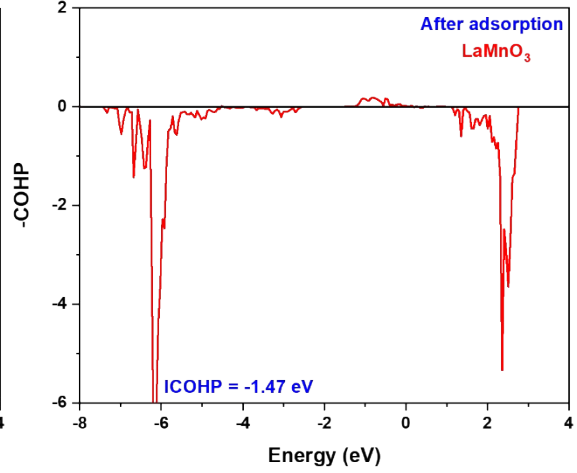
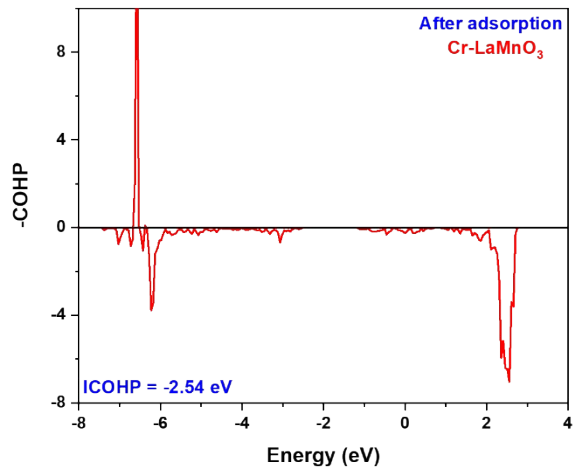
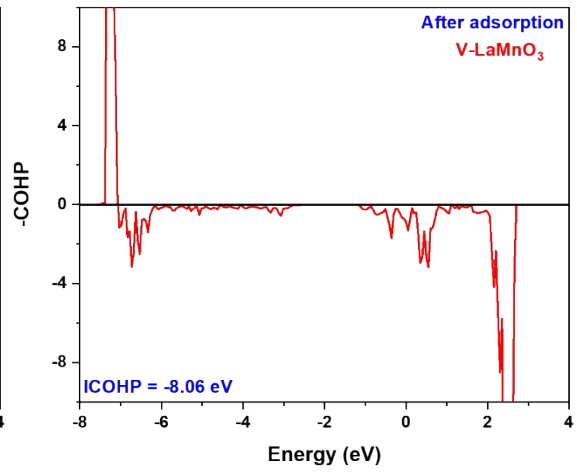
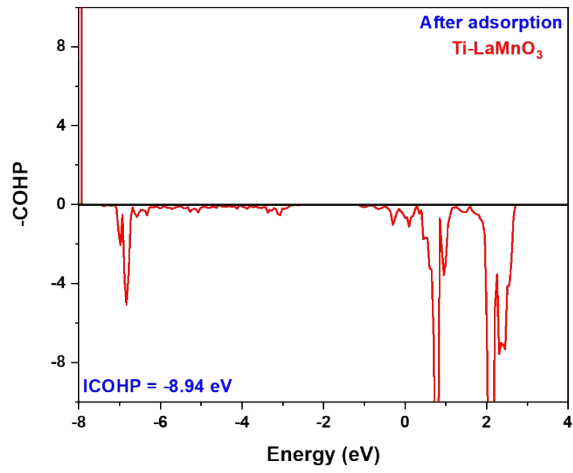
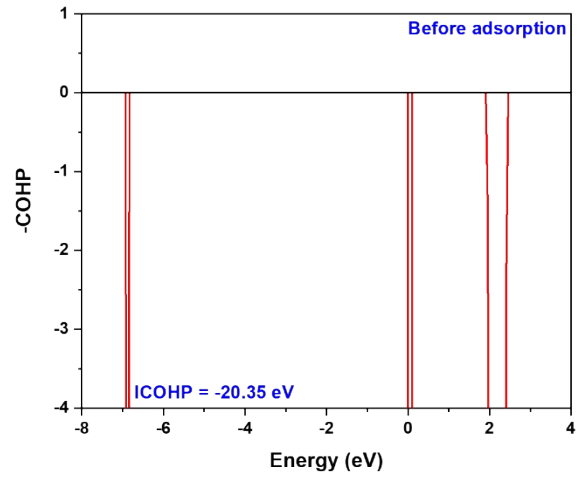


Figure S2 The partial density of states (PDOS) of Ti-LaMnO₃, V-LaMnO₃, Cr-LaMnO₃, pristine LaMnO₃, Ni-LaMnO₃, Mo-LaMnO₃, Rh-LaMnO₃, and Cd-LaMnO₃, showing the total PDOS and the CO-2p states before and after CO adsorption on the catalysts.



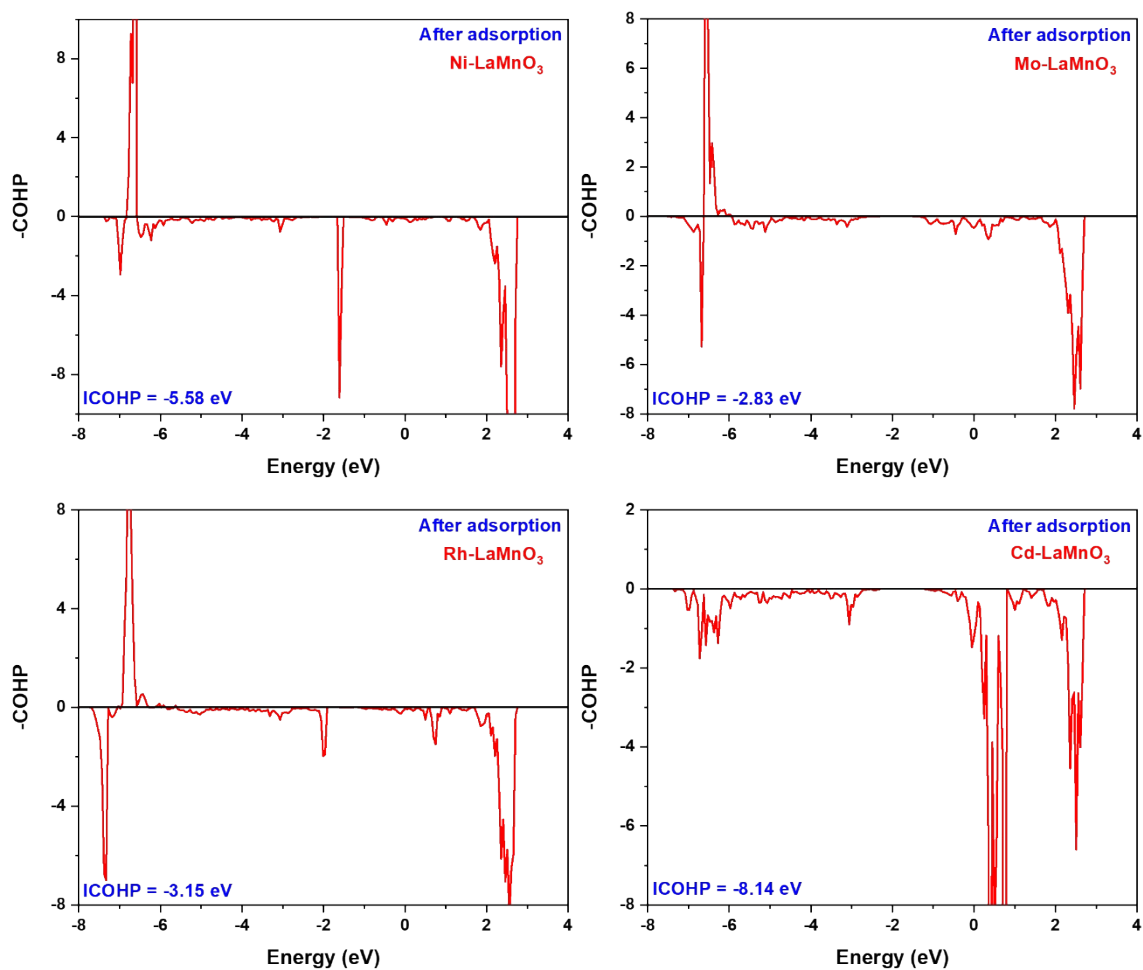


Figure S3 Crystal orbital Hamilton population (COHP) for C-O interaction of CO before and after adsorption on Ti-LaMnO₃, V-LaMnO₃, Cr-LaMnO₃, pristine LaMnO₃, Ni-LaMnO₃, Mo-LaMnO₃, Rh-LaMnO₃, and Cd-LaMnO₃.

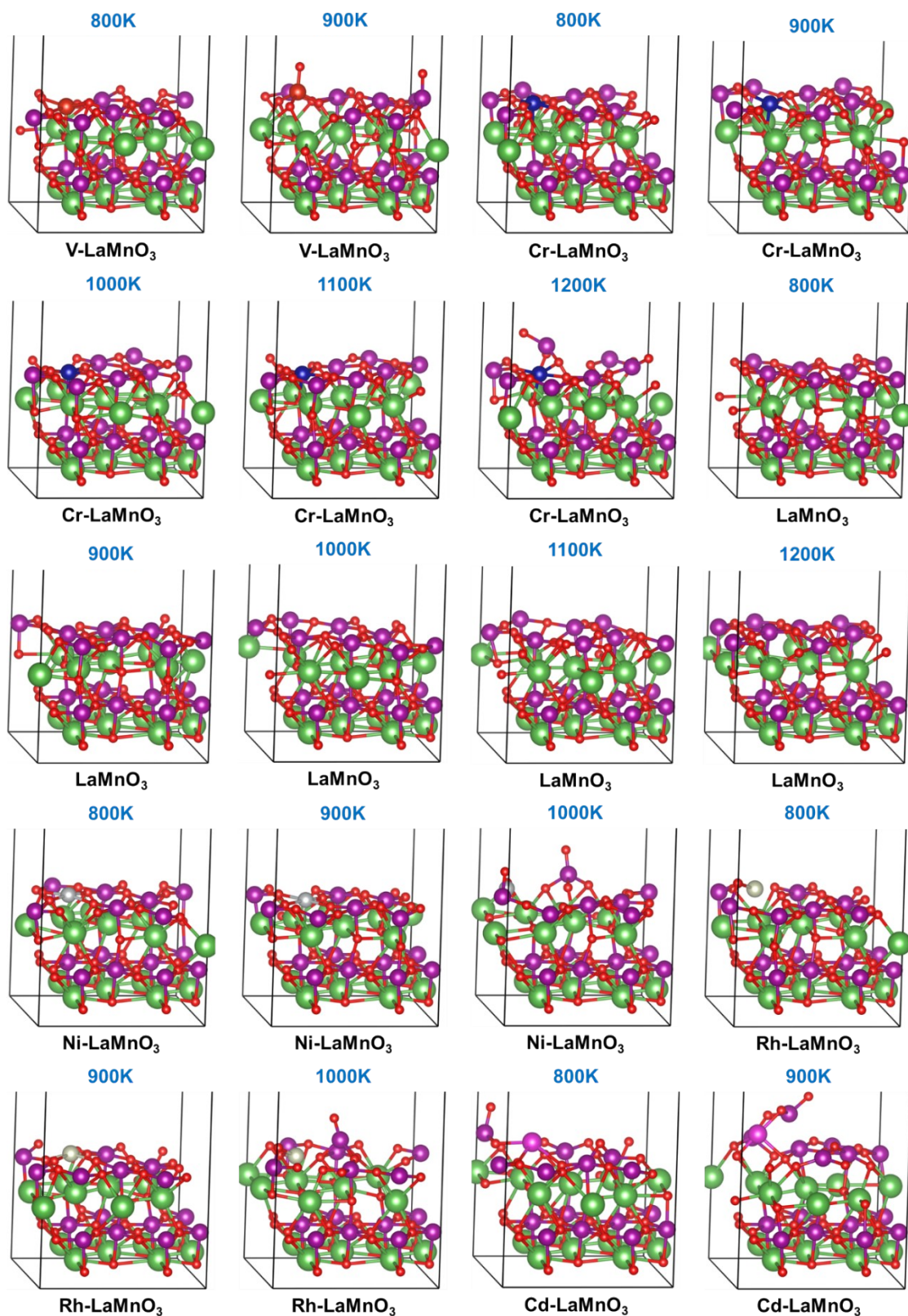


Figure S4 Final configurations obtained from AIMD simulations of V-LaMnO₃, Cr-LaMnO₃, pristine LaMnO₃, Ni-LaMnO₃, Rh-LaMnO₃, and Cd-LaMnO₃ at different temperatures (800–1200 K). Atom colours: Mn (purple), La (green), O (red), and C (brown).

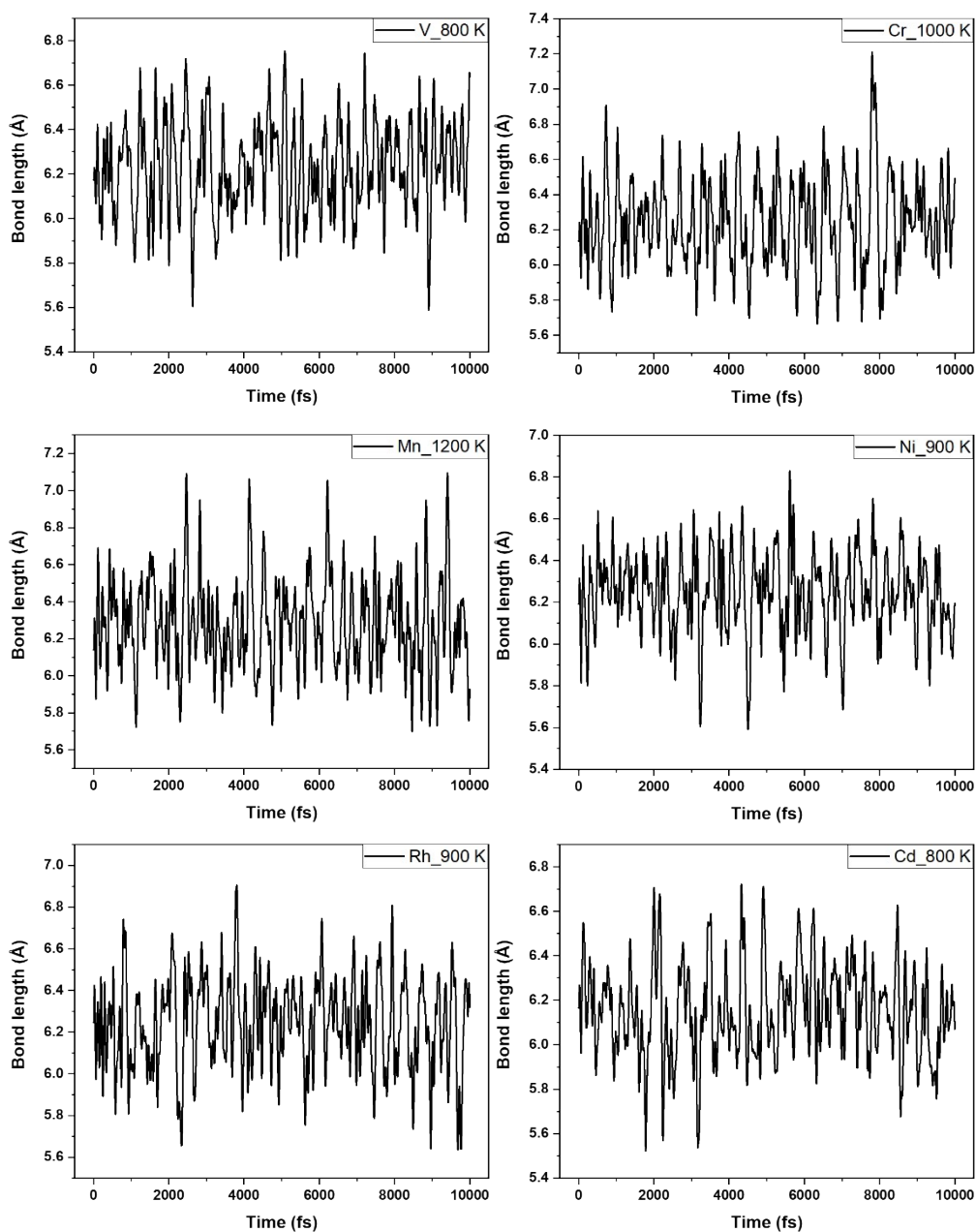


Figure S5 Variation of the M–O₁ bond length during AIMD simulations for V–LaMnO₃ (800 K), Cr–LaMnO₃ (1000 K), pristine LaMnO₃ (1200 K), Ni–LaMnO₃ (900 K), Rh–LaMnO₃ (900 K), and Cd–LaMnO₃ (800 K).

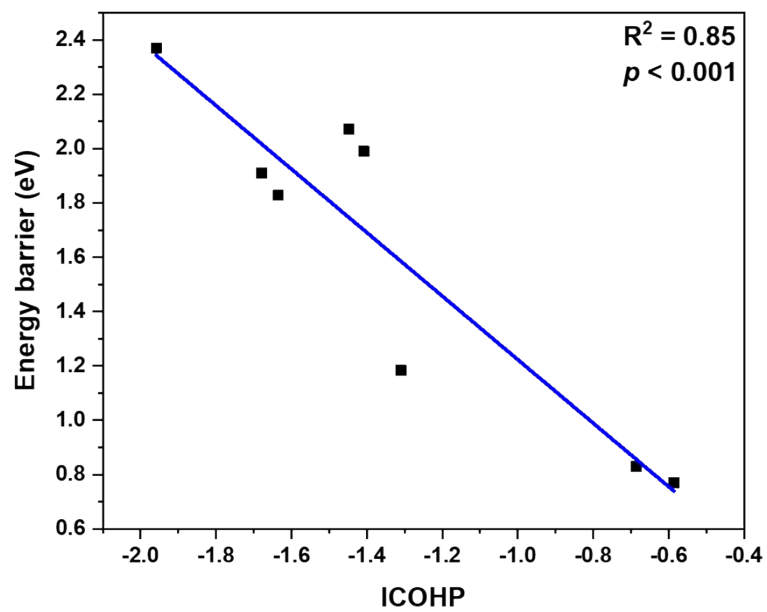


Figure S6 Relationship between the reaction energy barrier and the M–O₁ bond strength as quantified by ICOHP.

Supplementary Tables

Table S1 Most stable phases according to Ellingham diagram (metal oxides at 800-1000K).

Dopant	Most stable phase	Valance	Dopant	Most stable phase	Valance
Sc	Sc ₂ O ₃	3	Rh	Rh ₂ O ₃	3
Ti	TiO ₂	4	Pd	PdO	2
V	V ₂ O ₅	5	Ag	Ag	0
Cr	Cr ₂ O ₃	3	Cd	CdO	2
Mn	Mn ₃ O ₄	2.7	Hf	HfO ₂	4
Fe	Fe ₃ O ₄	2.7	Ta	Ta ₂ O ₅	5
Co	Co ₃ O ₄	2.7	W	WO ₃	6
Ni	NiO	2	Re	ReO ₃	6
Cu	Cu ₂ O	1	Os	OsO ₂	4
Zn	ZnO	2	Ir	IrO ₂	4
Mo	MoO ₃	6	Pt	PtO	2
Tc	TcO ₂	4	Au	Au	0
Ru	RuO ₂	4			

Table S2 Summary of the electronegativity (χ), the first ionization energy (IE), the atomic radius (r_{atom}), and the +3 ionic radius (r_{ion}^{3+}) of the dopant atoms.

Dopant	χ	IE (kJ/mol)	r_{atom} (pm)	r_{ion}^{3+} (pm)
Sc	1.36	18.1	633.1	74.5
Ti	1.54	7.6	658.8	67
V	1.63	50.6	650.9	64
Cr	1.66	64.3	652.9	61.5
Mn	1.55	0	717.3	58
Fe	1.83	15.7	762.5	55
Co	1.88	63.7	760.4	54.5
Ni	1.91	112	737.1	56
Cu	1.9	118.4	745.5	54
Zn	1.65	0	906.4	none
Mo	2.16	71.9	684.3	69
Tc	1.9	53	702	none
Ru	2.2	101.3	710.2	68
Rh	2.28	109.7	719.7	66.5
Pd	2.2	53.7	804.4	76
Ag	1.93	125.6	731	75
Cd	1.69	0	867.8	none
Hf	1.3	0	658.5	none
Ta	1.5	31	761	72
W	2.36	78.6	770	none
Re	1.9	14.5	760	none
Os	2.2	106.1	840	none
Ir	2.2	151	880	68
Pt	2.28	205.3	870	none
Au	2.54	222.8	890.1	85

Table S3 Summary of d-band centre of the doped atom (ε_d), the p-band center of the O₁ atom (ε_p), the charge-transfer energy (Δ), and the Bader charge transfer of the doped atom (Δq).

Dopant	ε_d (eV)	ε_p (eV)	Δ (eV)	Δq (e)
2Ti	-0.293	-3.634	5.701	-1.813
3V	-1.138	-3.941	5.432	-1.706
4Cr	-1.204	-3.953	5.301	-1.597
5Mn	-1.029	-3.814	5.257	-1.416
8Ni	-1.138	-3.359	4.507	-0.998
11Mo	-1.874	-4.193	5.808	-1.906
14Rh	-1.707	-3.812	5.488	-0.978
17Cd	-4.138	-3.121	4.561	-1.166

Table S4 ICOHP values for La–O₁ and La–O₂ bonds in stable configurations

Dopant	La-O₁	La-O₂
Ti	-0.100	-0.250
V	-0.138	-0.336
Cr	-0.140	-0.342
Mn	-0.129	-0.279
Ni	-0.255	-0.312
Mo	-0.093	-0.331
Rh	-0.146	-0.406
Cd	-0.236	-0.282

Table S5 Comparison of adsorption site, structural parameters ($d(\text{M-C})$ and $d(\text{C-O})$, Å), Bader charge transfer (Q , e), and adsorption energies (E_{ads} , eV) for CO adsorption on Ti-, V-, Cr-, Ni-, Mo-, Rh-, and Cd-doped LaMnO_3 surfaces, obtained from non-spin-polarized (NSP) and spin-polarized (SP) calculations.

Dopant	Calculation Method	Adsorption Site	$d(\text{M-C})$	$d(\text{C-O})$	Q	E_{ads}
Ti	NSP	Ti	2.214	1.148	0.06	-0.518
Ti	SP	Ti	2.284	1.150	0.07	-0.229
V	NSP	V	1.996	1.157	0.13	-0.797
V	SP	V	1.965	1.166	0.21	-0.842
Cr	NSP	Cr	1.846	1.166	0.14	-1.215
Cr	SP	Cr	1.968	1.154	0.10	-0.960
Ni	NSP	Ni	1.763	1.162	0.14	-1.086
Ni	SP	Ni	1.794	1.163	0.24	-0.629
Mo	NSP	Mo	1.975	1.171	0.29	-1.614
Mo	SP	Mo	1.904	1.193	0.50	-1.670
Rh	NSP	Rh	1.812	1.169	0.08	-1.553
Rh	SP	Rh	1.850	1.173	0.19	-1.214
Cd	NSP	Cd	2.390	1.149	0.05	-0.277
Cd	SP	Cd	2.321	1.160	0.14	-0.305