Electronic Supplementary Information for

Synergetic Catalysis of *p-d* Hybridized Single-atom Catalysts: First-principles Investigations

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Table S1 Lattice parameter and pore size of TM-HHB Monolayer.

TM-HHB	Cr	Mn	Fe	Co	Ni	Cu	Mo	Ru	Rh	Pd	Ag	Pt	Au
Lattice (Å)	13.66	13.91	13.69	13.63	12.99	13.25	14.06	13.73	13.6	13.46	15.01	13.52	14.00
D_M (Å)	6.83	6.93	6.85	6.82	6.50	6.63	7.03	6.86	6.80	6.73	7.50	6.76	7.00
D_P (Å)	13.66	13.91	13.69	13.63	12.99	13.25	14.06	13.73	13.6	13.46	15.01	13.52	14.00

Table S2 Bond lengths of each part of the structure when O_2 and CO are adsorbed.

TM-HHB		Cr	Mn	Fe	Co	Ru	Rh	Ni	Cu	Mo
Adsorption of O_2	O_2-TM (Å)	1.98	2.13	1.96	2.03	1.94	2.00	2.89	2.62	1.93
	O_2-C (Å)	3.23	2.41	2.13	2.52	3.20	3.14	2.89	2.60	
	O-O (Å)	1.28	1.29	1.33	1.28	1.28	1.27	1.24	1.26	1.48
Adsorption of CO	C-TM (Å)	2.40	2.31	2.03	1.96	1.78	1.84	1.84	1.80	2.02
	C-O (Å)	1.14	1.14	1.15	1.14	1.17	1.16	1.15	1.15	1.16

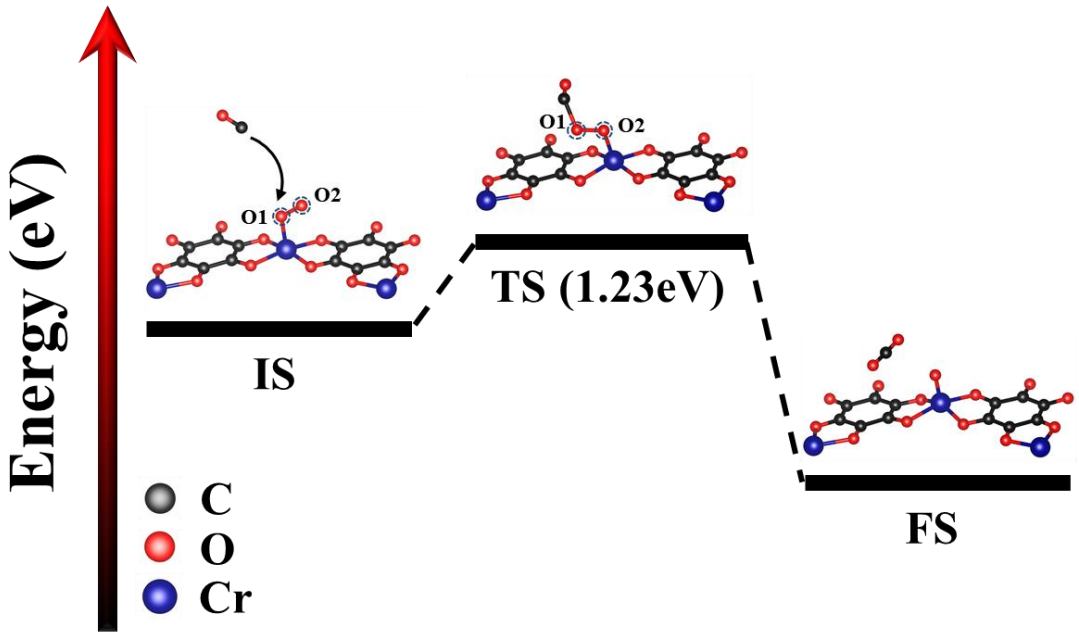

Fig. S1 MEP for the incoming CO molecule directly attacks the oxygen atom bonded with the Cr-SA site.

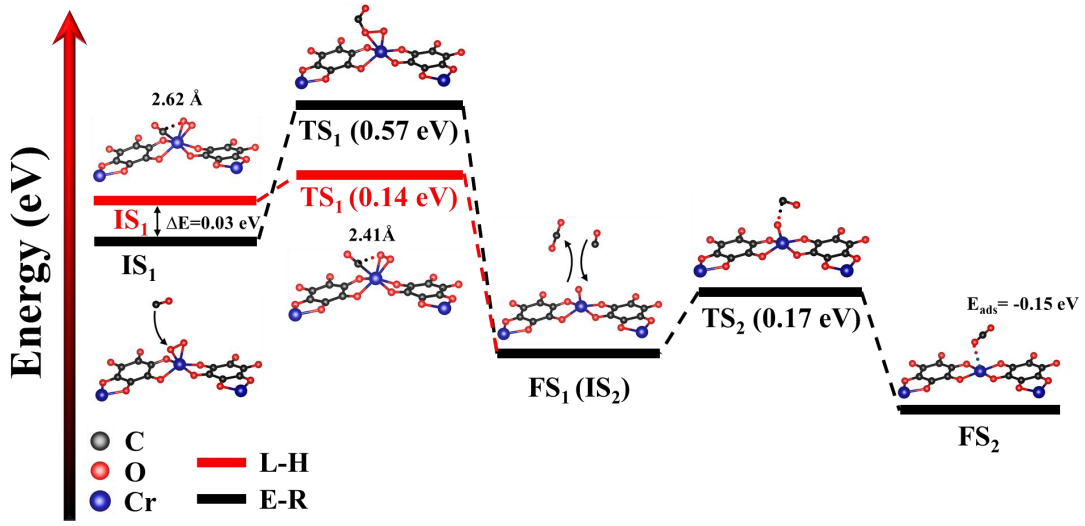

Fig. S2 Minimum energy pathways (MEP) and corresponding energy barriers (E_{bar}) for CO oxidation via L-H and E-R mechanism on 2D Cr-HHB without Hubbard U correction (U_{eff} = 0 eV). For the second round of CO oxidation, the initial state (termed IS_2) is based on the FS_1 with releasing the CO_2 molecule.

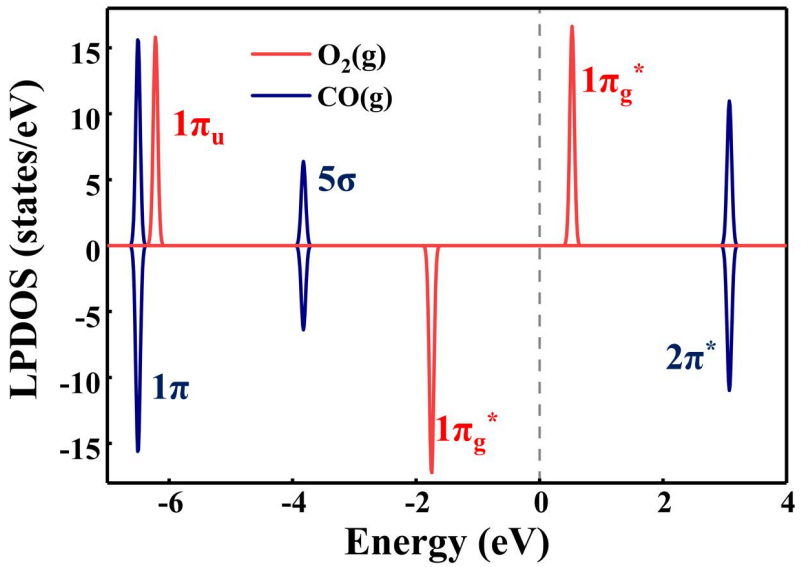

Fig. S3 LPDOS of the CO and O_2 molecules about 5 Å above the Ni-HHB monolayer are also presented in blue and red solid lines, with the Fermi levels shifted to zero.

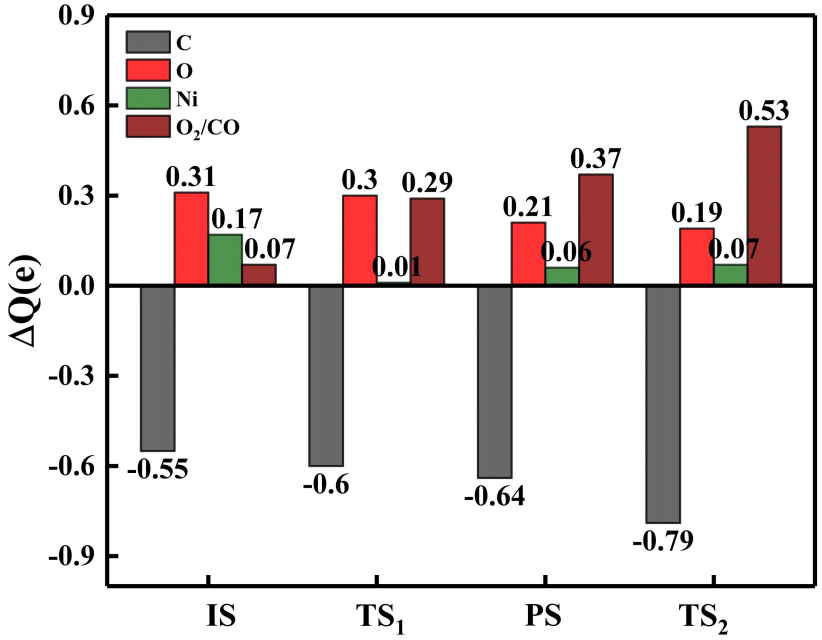

Fig. S4 Charge transfer evolution of the key steps presented in the TER process of CO oxidation on Ni-HHB.

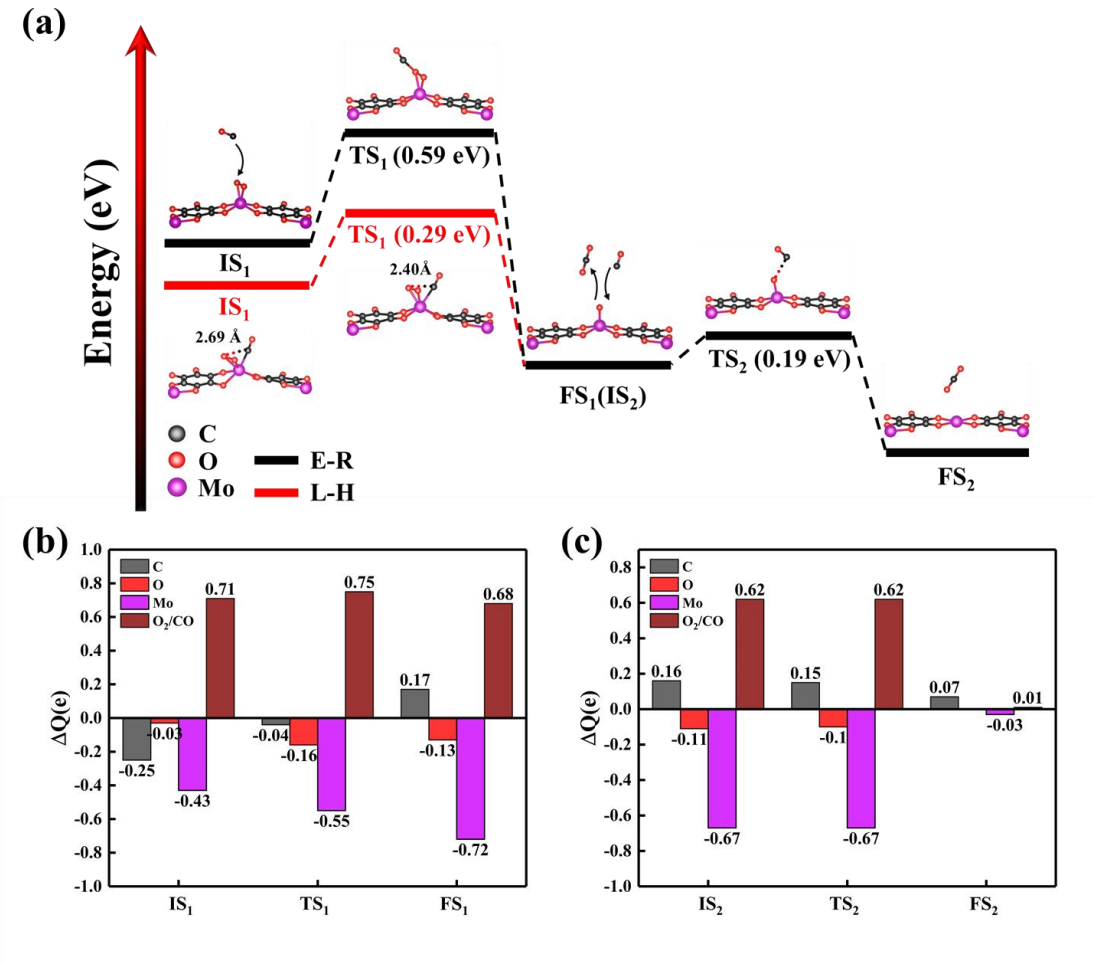

Fig. S5 (a) Minimum energy pathways (MEP) and corresponding energy barriers (E_{bar}) for CO oxidation via E-R and L-H mechanism on 2D Mo-HHB. For the second round of CO oxidation, the initial state (termed IS_2) is based on the FS_1 with releasing the CO_2 molecule. Evolution of the ΔQ in the key steps presented in the L-H processes of (b) the first and (c) the second round of CO oxidation on Mo-HHB.