Supporting Information

New Horizons of MBenes: Highly-active Catalysts for CO Oxidation Reaction

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■ Computational Details

All the energy calculated in this work was investigated in the form of Gibbs free energy, which is determined as follows:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \qquad \textbf{(eq. S1)}$$

where ΔE, ΔE_{ZPE} and ΔS represent the differences of total energy, zero-point energy and entropy between the products and reactants. In this work, temperature, T, was set to 298 K to study the COOR catalytic performance at room temperature. Zero-point energy, E_{ZPE}, was calculated using the equation:

$$E_{ZPE} = \sum_{i=1}^{3N} \frac{1}{2} h\nu_i \qquad \textbf{(eq. S2)}$$

where N represents the number of atoms of the adsorbates or isolated molecules, ν_i is the vibrational

frequency of the normal mode obtained by the first-principle calculations, and h represents Planck's constant. Entropy, S, was calculated using the following equation:

$$S = \sum_{i=1}^{3N} \left[-R\ln\left(1 - e^{-h\nu_i/k_BT}\right) + \frac{N_A h\nu_i \, e^{-h\nu_i/k_BT}}{T} \frac{1}{1 - e^{-h\nu_i/k_BT}} \right] \qquad \textbf{(eq. S3)}$$

where R, N_A and k_B represent the universal gas constant, Avogadro's number and Boltzmann's constant, respectively. The entropy of O_2, CO and CO_2 gas at 298 K and 1 bar was listed in **Table S1**, obtained from NIST Chemistry WebBook.

The formation energy of oxygen functionalized group, ΔG_f^O, was calculated as follows：

$$\Delta G_f^O = G_{M_2B_2O_2} - G_{M_2B_2} - 2\mu_O \qquad \textbf{(eq. S4)}$$

where $G_{M_2B_2O_2}$ and $G_{M_2B_2}$ represent the Gibbs free energy of $M_2B_2O_2$ and M_2B_2, respectively. μ_O is the chemical potential of oxygen, which is consumed to be half of the Gibbs free energy of O_2 here in consideration of the air atmosphere. Negative value of ΔG_f^O indicates spontaneous formation of oxygen functionalized group of $M_2B_2O_2$.

The formation energy of oxygen vacancy, ΔG_f^{Va}, was calculated using the equation:

$$\Delta G_f^{Va} = G_{M_{18}B_{18}O_{18}} - G_{M_{18}B_{18}O_{17}} - \mu_O \qquad \textbf{(eq. S5)}$$

where $G_{M_{18}B_{18}O_{17}}$ represents the Gibbs free energy of $M_2B_2O_2$ with one oxygen vacancy in a 3×3×1 supercell. In this work, the values of ΔG_f^{Va} for all the 18 $M_2B_2O_2$ are positive, implying that the formation of oxygen vacancy on all the 18 $M_2B_2O_2$ are non-spontaneous. Smaller value of ΔG_f^{Va} indicates harder formation of oxygen vacancy of $M_2B_2O_2$.
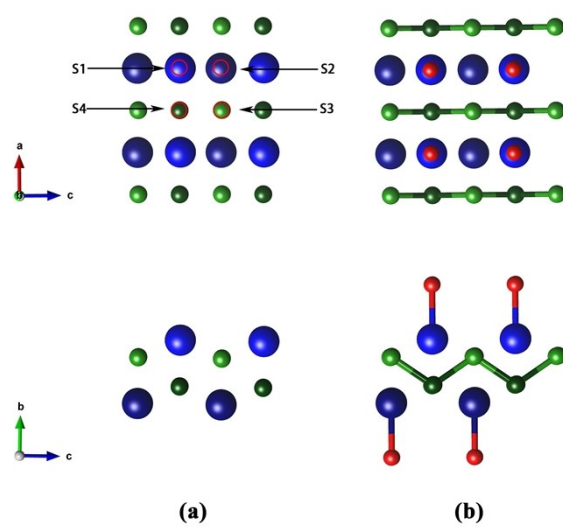
■ **Figures**

Fig. S1 (a) four different sites for O adsorption, S1, S2, S3 and S4; (b) type IV structure for orth-$M_2B_2O_2$. The light blue, dark blue, light green, dark green and red balls represent upper M atom, lower M atom, upper B atom, lower B atom and O atom, respectively.
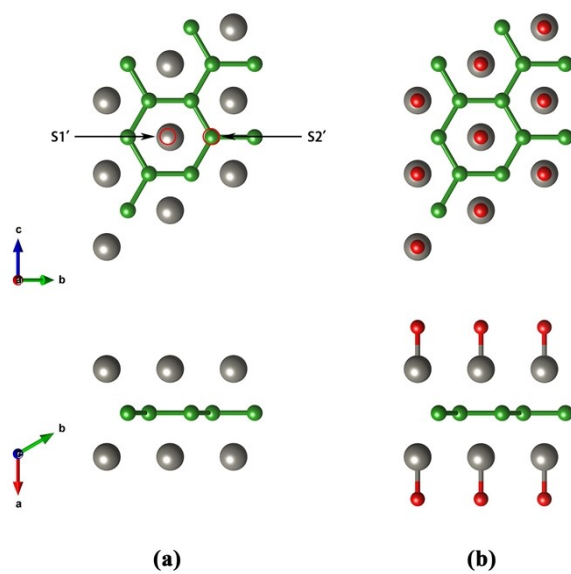

Fig. S2 (a) two different sites for O adsorption, S1' and S2'; (b) type C structure for hex-$M_2B_2O_2$. The grey, green and red balls represent M atom, B atom and O atom, respectively.
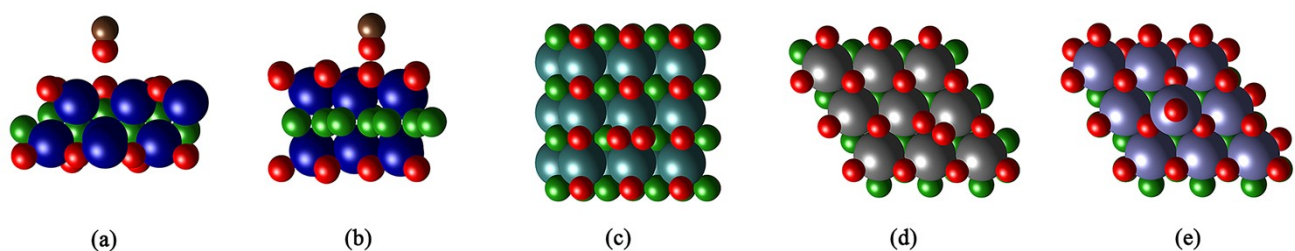
Fig. S3 Structures of (a) orth-$Cr_2B_2O_2*CO$, (b) hex-$Cr_2B_2O_2*CO$, (c) orth-$Ta_2B_2O_2*O_2$, (d) hex-$Zr_2B_2O_2*O_2$ and (e) hex-$Hf_2B_2O_2*O_2$. Red, brown, green, blue, cyan, gray and purple balls represent oxygen, carbon, boron, tantalum, zirconium and hafnium atoms, respectively.

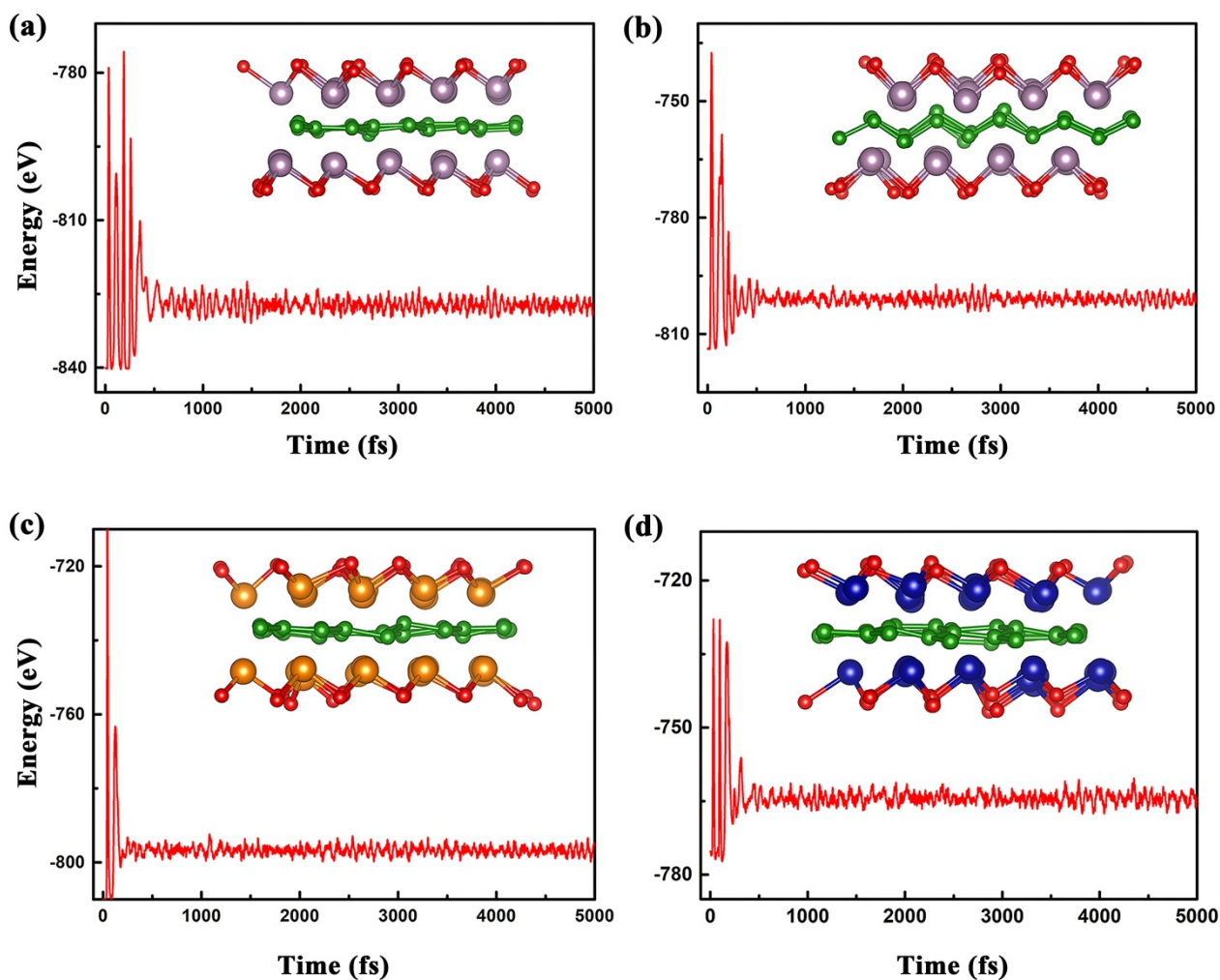**Fig. S4** AIMD simulations of energy versus time of (a) hex-$Mo_2B_2O_2$, (b) orth-$Mo_2B_2O_2$, (c) hex-$V_2B_2O_2$ and (d) hex-$Cr_2B_2O_2$ for 10 ps under 1000 K. The insets represent the corresponding structures.
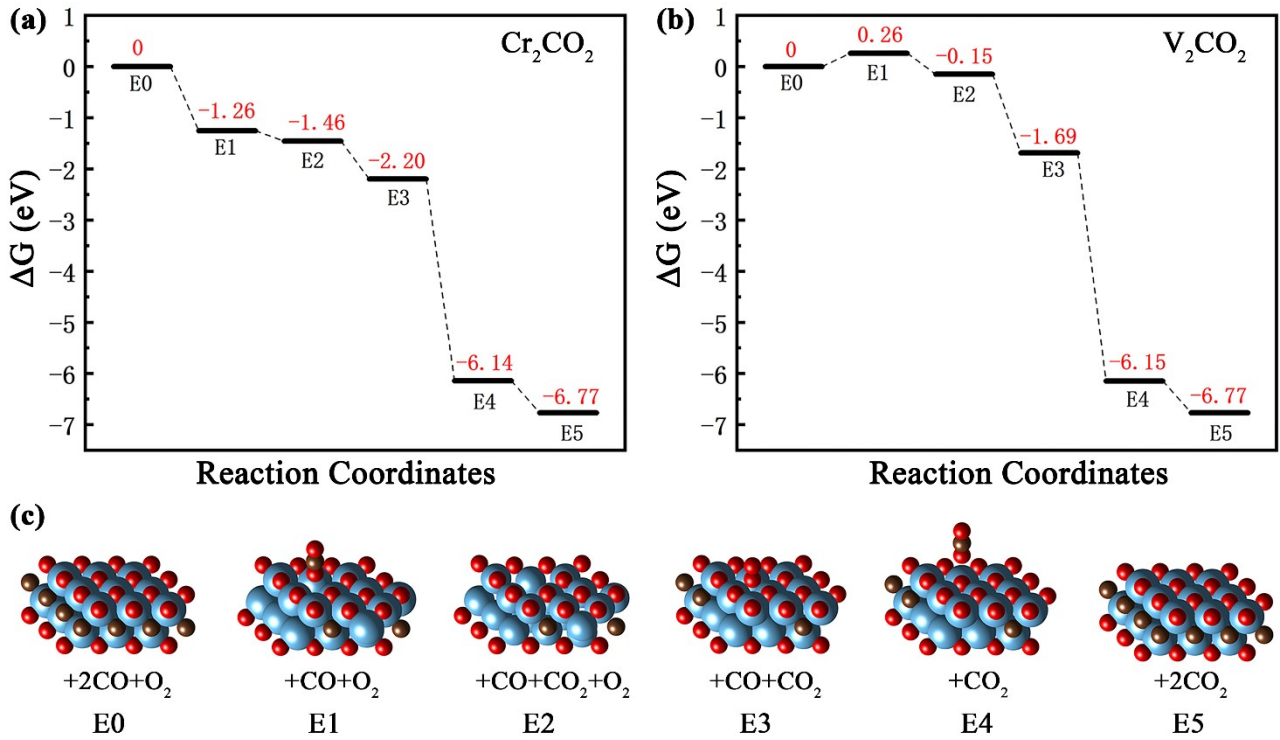
Fig. S5 Gibbs free energy change for COOR catalysis on (a) Cr_2CO_2 and (b) V_2CO_2. (c) Structures of the reaction systems at states E0 to E5.

■ **Tables**

Table S1. Entropy of O_2, CO and CO_2 gas at 298 K and 1 bar

	O_2	CO	CO_2
S (J/mol * K)	205.15	197.66	213.79

Table S2. Oxygen termination formation energy (ΔG_f^O) and oxygen vacancy formation energy (ΔG_f^{Va})

		Ti	V	Cr	Zr	Nb	Mo	Hf	Ta	W
ΔG_f^O	Orth	-9.41	-7.79	-6.71	-9.82	-9.03	-7.47	-10.36	-9.74	-8.38
(eV)	Hex	-11.40	-9.92	-6.28	-11.68	-10.86	-9.00	-12.22	-11.07	-9.19

ΔG_f^{Va}	Orth	4.62	2.90	2.55	5.00	4.12	2.99	5.36	4.75	3.60
(eV)	Hex	4.70	3.75	2.32	5.22	4.79	4.03	5.59	5.04	4.34

Table S3. O-O bond length (Δd) and the number of electrons that O_2 molecule obtains from the substrates (N_e).

		Ti	V	Cr	Zr	Nb	Mo	Hf	Ta	W
Δd (Å)	Orth	1.36	1.29	1.35	1.39	1.34	1.30	1.40	1.49	1.32
	Hex	1.37	1.33	1.32	1.45	1.37	1.34	3.19	1.40	1.36
N_e	Orth	0.89	0.54	0.82	1.03	0.77	0.57	1.05	1.12	0.69
	Hex	0.96	0.72	0.67	1.23	0.93	0.77	2.31	1.03	0.86

Table S4. Gibbs free energy change for the formation of the first CO_2 ($\Delta G_2 + \Delta G_3$).

		Ti	V	Cr	Zr	Nb	Mo	Hf	Ta	W
$\Delta G_2 + \Delta G_3$ (eV)	Orth	-5.51	-4.46	-4.49	-5.72	-5.46	-4.52	-5.88	-4.30	-4.95
	Hex	-5.07	-5.02	-4.67	-4.20	-5.48	-5.24	-1.63	-5.71	-5.68

Table S5. Gibbs free energy change for the adsorption of the second CO (ΔG_4) and the desorption of the second CO_2 (ΔG_5). The bold figures represent the largest Gibbs free energy for COOR (ΔG_{max}).

		Ti	V	Cr	Zr	Nb	Mo	Hf	Ta	W
ΔG_4 (eV)	Orth	**1.32**	-0.59	-0.56	**1.53**	**0.58**	-0.60	**1.89**	**1.25**	**0.27**
	Hex	**1.22**	**0.39**	-0.87	**1.83**	**1.50**	**0.85**	**2.35**	**1.96**	**1.06**
ΔG_5 (eV)	Orth	-0.08	**0.10**	**-0.28**	0.08	0.15	**0.20**	0.08	0.12	-0.06
	Hex	0.09	-0.02	**-0.20**	0.01	-0.09	-0.21	-0.14	-0.30	-0.10