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

Supporting information

Two-Dimensional MBene: a comparable catalyst to MXene for effective CO_2RR towards C_1 products

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Computational Methods

Computational hydrogen electrode model

The free energy diagrams of CO_2RR were calculated by referring to the computational hydrogen electrode (CHE) model proposed and developed by Norskov eta al. The $H^+(aq) + e^- \Leftrightarrow 1/2\ H_2(g)$ was equilibrated at 0 V versus the reversible hydrogen electrode (RHE).

The Gibbs reaction energy (ΔG) was defined as follows,

$$\Delta G = \Delta E + \Delta E_{ZPE} + \int C_p dT - T\Delta S + \Delta G_U$$

where ΔE was the DFT calculated electronic energy, ΔE_{ZPE}, $\int C_p dT$, and ΔS were the zero-point energy, enthalpic temperature correction, and the entropy difference between the products and the reactants, respectively, which were all calculated according to the vibration analysis at room temperature (T = 298.15 K). For the vibration analysis, frequencies were calculated by treating all 3N degrees of the adsorbates as vibrational in the harmonic oscillator approximation, in which the vibrations of the substrate surface were negligible. ΔG_U was the contribution of the applied electrode potential (U) to ΔG.

In this model, electrode potential correction to the free energy of each state is included by considering the electrochemical proton-electron transfer being a function of the applied electrical potential. The free energy of a proton-electron pair at 0 V versus RHE is defined to be equal to ½ of the H_2 free energy at 101,325 Pa. The free energy of each intermediate, calculated at 298.15 K, is then a function of the electrode potential (U) according to

$$G(U) = G(0V) + neU$$

where e is the elementary charge of an electron, n is the number of proton-electron pairs transferred to the investigated intermediate or final states. The application of this equation to the elementary reaction pathway results in the electrode potential corrected free energy pathway, therefore provides a venue to evaluate at which potential a certain CO_2 electroreduction pathway opens, as well as defining the potential dependent reaction step.

Quantifying Product Selectivity

The selectivity of the competing CO_2RR and HER is quantified by applying the model reported in reference [1]. For CO_2RR, four possible C_1 products, CO, HCOOH, CH_3OH, and CH_4, are taken into consideration. The ratio of the CO_2RR and HER current densities, j_{CO2RR}/j_{HER}, at 0 V is given by the equation,

$$\frac{j_{CO2RR}(U = 0\ V)}{j_{HER}} = Exp(\frac{G_{max\text{ - }HER}^{\#} - G_{max\text{ - }CO2RR}^{\#}}{k_BT})$$

In which, k_B denotes Boltzmann's constant, and T the absolute temperature in Kelvin (T = 298.15 K).

The CO_2RR selectivity relevant to HER is determined by the following equation:

$$CO2RR\ selectivity = \frac{Exp(\frac{G_{max\text{ - }HER}^{\#} - G_{max\text{ - }CO2RR}^{\#}}{k_BT})}{Exp(\frac{G_{max\text{ - }HER}^{\#} - G_{max\text{ - }CO2RR}^{\#}}{k_BT}) + 1}$$

The free-energy distance of the transition-state free energies, $G_{max\text{ - }HER}^{\#} - G_{max\text{ - }CO2RR}^{\#}$, is approximated by assuming a linear decrease of the free-energy spacing of the H intermediate and the CO_2RR intermediate along the reaction coordinate. Assuming that the activated complexes of the CO_2RR and HER are located in the middle of the electrochemical double layer (αCO_2RR = αHER = ½), the following relation holds true:

$$G_{max\text{ - }HER}^{\#} - G_{max\text{ - }CO2RR}^{\#} = 1/2(\Delta G_{max\text{ - }HER} - \Delta G_{max\text{ - }CO2RR})$$

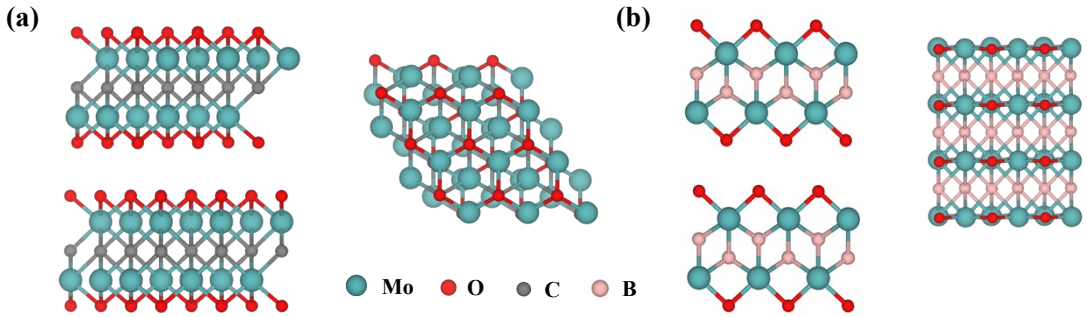

Figure S1. Optimized structural model of (a) Mo_2CO_2 and (b) $MoBO_2$.

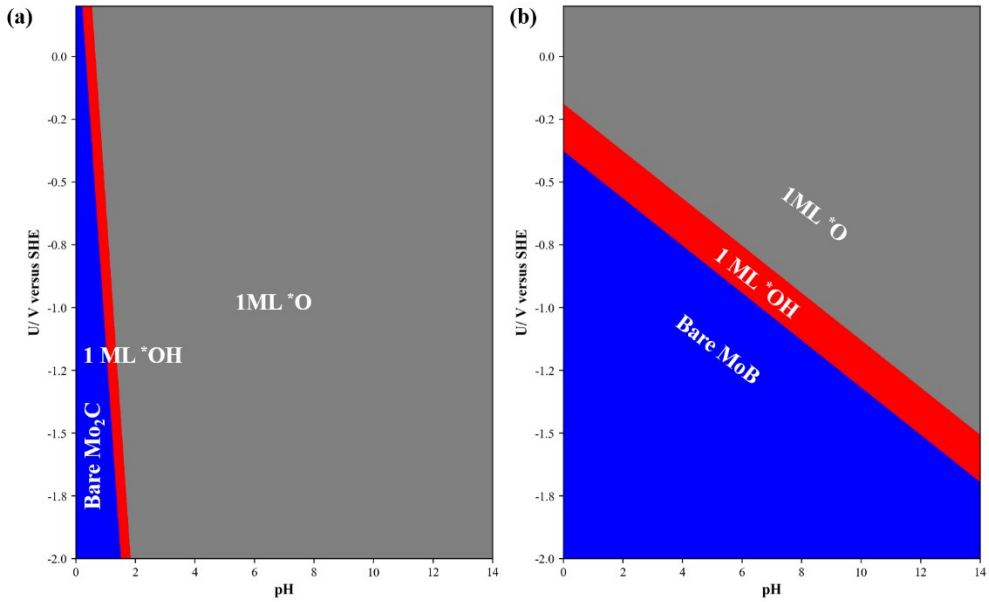

Figure S2. The calculated surface Pourbaix diagrams for (a) Mo_2C and (b) MoB.

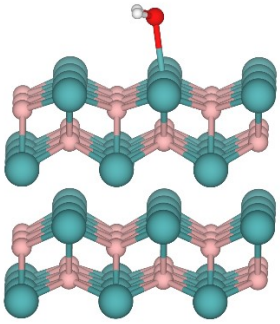

Figure S3. Optimized configuration of H_2O adsorbed on MoB.

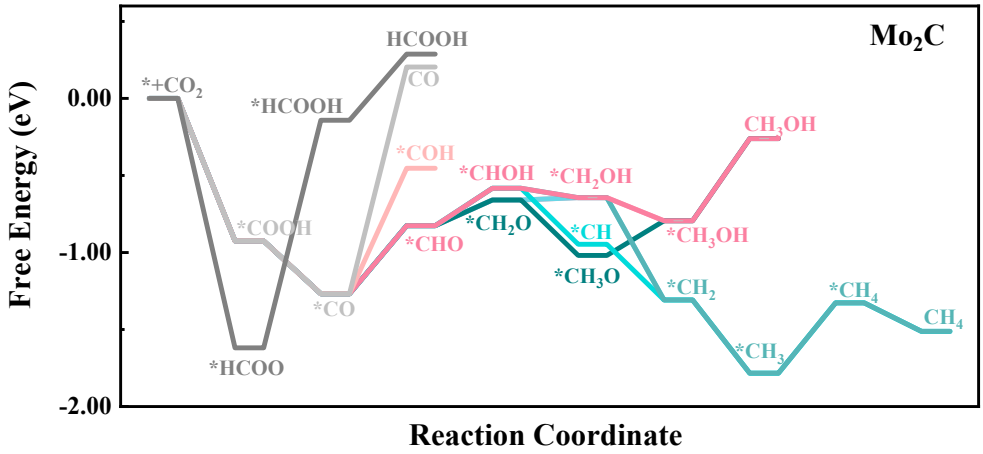

Figure S4. The CO_2RR pathways to CO, HCOOH, CH_3OH, and CH_4 on Mo_2C at 0 V versus RHE.

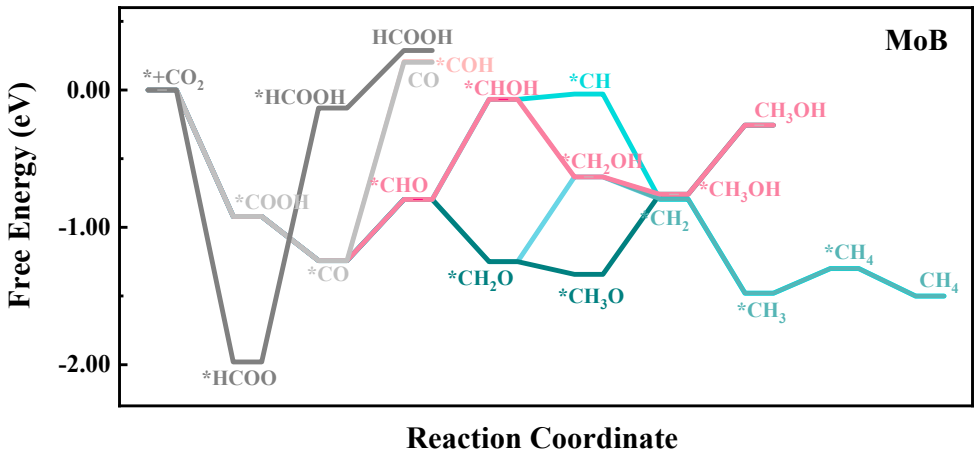

Figure S5. The CO_2RR pathways to CO, HCOOH, CH_3OH, and CH_4 on MoB at 0 V versus RHE.

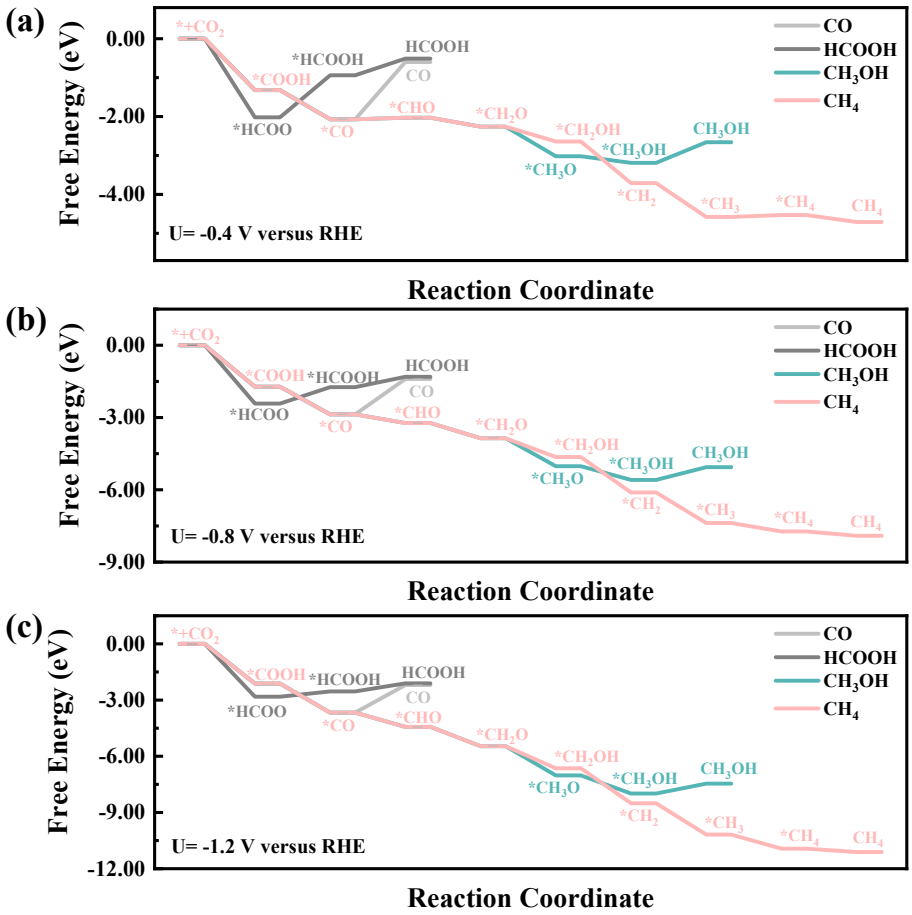

Figure S6. Free energy diagrams of CO_2RR to CO, HCOOH, CH_3OH, and CH_4 on Mo_2C at different applied potentials, (a) U = -0.4 V, (b) U= -0.8 V, and (c) U = -1.2 V versus RHE.

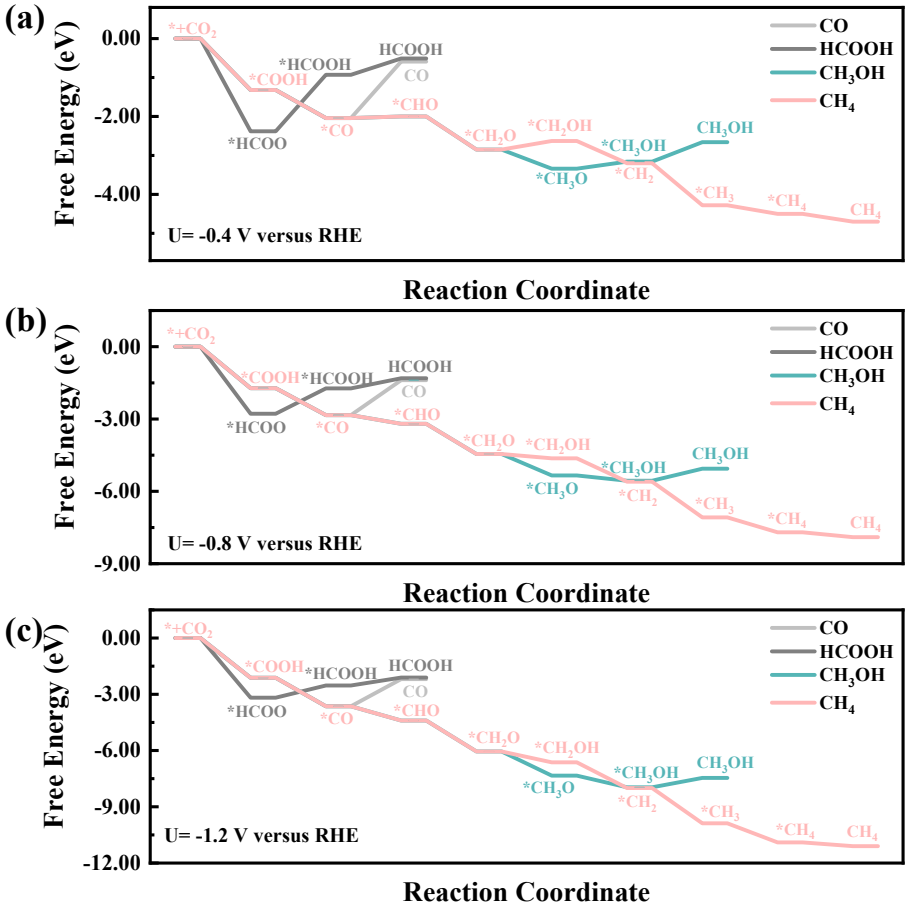

Figure S7. Free energy diagrams of CO_2RR to CO, HCOOH, CH_3OH, and CH_4 on MoB at different applied potentials, (a) U = -0.4 V, (b) U= -0.8 V, and (c) U = -1.2 V versus RHE.

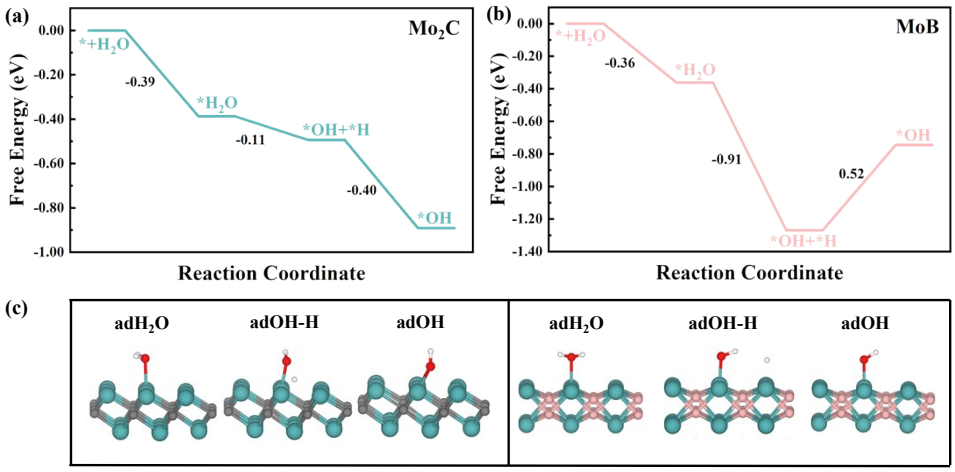

Figure S8. Hydrogen evolution reaction mechanisms in the alkaline electrolyte on (a) Mo_2C and (b) MoB and (c) corresponding structural configurations.

Table S1. The Calculated (eV) and the experimental (eV) values of reaction potential at pH = 6.8 vs. RHE for CO_2RR.

Half reaction	Calculated	Experimental
$CO_{2(g)}+2(H^+_{(aq)} + e^-) \rightarrow CO_{(g)} + H_2O_{(l)}$	-0.12	-0.12
$CO_{2(g)}+2(H^+_{(aq)} + e^-) \rightarrow HCOOH_{(l)}$	-0.20	-0.20
$CO_{2(g)}+4(H^+_{(aq)} + e^-) \rightarrow HCHO_{(aq)} + H_2O_{(l)}$	-0.07	-0.07
$CO_{2(g)}+6(H^+_{(aq)} + e^-) \rightarrow CH_3OH_{(aq)} + H_2O_{(l)}$	0.03	0.03
$CO_{2(g)}+8(H^+_{(aq)} + e^-) \rightarrow CH_{4(g)} + 2H_2O_{(l)}$	0.17	0.17

Table S2. Formation energy of Mo_2C, Mo_2CO_2, and MoB.

Catalyst	Mo_2C	Mo_2CO_2	MoB	$MoBO_2$
Formation energy (eV/atom)	0.34	-1.13	-0.11	0.78

Table S3. Proposed elementary steps and free energy changes for CO_2RR pathways on Mo_2C and MoB at 0 V versus RHE.

Elementary steps	ΔG/eV	
	Mo_2C	MoB
$H^+ + e^- \rightarrow *H$	-0.21	-0.50
$CO_2 + H^+ + e^- \rightarrow *COOH$	-0.92	-0.92
$CO_2 + H^+ + e^- \rightarrow *HCOO$	-1.44	-1.98
$*HCOO + H^+ + e^- \rightarrow *HCOOH$	1.30	1.85
$*HCOOH \rightarrow * + HCOOH$	0.43	0.42
$*COOH + H^+ + e^- \rightarrow *CO + H_2O$	-0.34	-0.32
$*CO \rightarrow * + CO$	1.47	1.45
$*CO + H+ + e^- \rightarrow *COH$	0.82	1.44
$*CO + H^+ + e^- \rightarrow *CHO$	0.44	0.45
$*CHO + H^+ + e^- \rightarrow *CHOH$	0.24	0.73
$*CHO + H^+ + e^- \rightarrow *CH_2O$	0.17	-0.45
$*CHOH + H^+ + e^- \rightarrow *CH_2OH$	-0.06	-0.57
$*CHOH + H^+ + e^- \rightarrow *CH + H_2O$	-0.36	0.04
$*CH_2O + H^+ + e^- \rightarrow *CH_3O$	-0.36	-0.09
$*CH_2O + H^+ + e^- \rightarrow *CH_2OH$	0.02	0.62
$*CH_3O + H^+ + e^- \rightarrow *O + CH_4$	-1.48	-1.07
$*O + CH_4 + H^+ + e^- \rightarrow *OH + CH_4$	0.10	0.18
$*OH + CH_4 + H^+ + e^- \rightarrow *H_2O + CH_4$	0.49	0.39
$*H_2O \rightarrow * + H_2O$	0.40	0.362
$*CH_2OH + H^+ + e^- \rightarrow *CH_2 + H_2O$	-0.66	-0.16
$*CH_2OH + H^+ + e^- \rightarrow *CH_3OH$	-0.15	-0.13
$*CH_3OH \rightarrow * + CH_3OH$	0.49	0.50
$*CH + H^+ + e^- \rightarrow *CH_2$	-0.36	-0.77
$*CH_2 + H^+ + e^- \rightarrow *CH_3$	-0.47	-0.68
$*CH_3 + H^+ + e^- \rightarrow *CH_4$	0.46	0.18
$*CH_4 \rightarrow * + CH_4$	-0.18	-0.20

Table S4. CO_2RR products selectivity relevant to HER, all the CO_2RR products selectivity are calculated by taking HER activity as a reference.

	Mo_2C				MoB			
	0 V	-0.4 V	-0.8 V	-1.2 V	0 V	-0.4 V	-0.8 V	-1.2 V
CO	0	0	0.01%	23.76%	0	0	6.16%	99.37%
HCOOH	0	0.01%	99.84%	100%	0	0	99.37%	100%
CH_3OH	0.43%	82.58%	99.99%	100%	17.42%	99.81%	100%	100%
CH_4	0.77%	99.99%	100%	100%	8.83%	99.99%	100%	100%

Reference

[1] K.S. Exner, Design criteria for the competing chlorine and oxygen evolution reactions: avoid the OCl adsorbate to enhance chlorine selectivity, *Phys. Chem. Chem. Phys*., 2020, **2**, 22451-22458.