

ELECTRONIC SUPPLEMENTARY INFORMATION

Charge-orbital synergistic engineering of TM@Ti₃C₂O_{1-x}B_x for highly selective CO₂ electrochemical reduction

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This Supplementary Information contains:

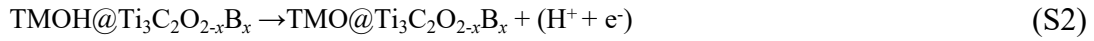
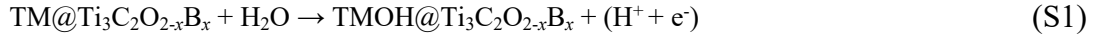
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Pourbaix diagrams of TM@Ti₂CT_x

For an electrochemical reaction, not only AIMD simulation but also the Pourbaix diagram is necessary to evaluate the stability of materials in aqueous solution. Composed by equilibrium lines that separate two different phases, Pourbaix diagrams^{1, 2} can serve as a useful tool to identify the stable state of catalysts in water as a function of pH and applied potential. To demonstrate the stability of MXene-based SACs, their oxidation reactions (Eq. S1-2) are considered as:



The free energy change (ΔG) of these reactions are computed as:

$$\Delta G = G_{\text{TMOH@Ti}_3\text{C}_2\text{O}_{2-x}\text{B}_x} + (G_{\text{H}^+} + G_{\text{e}^-}) - G_{\text{TM@Ti}_3\text{C}_2\text{O}_{2-x}\text{B}_x} - G_{\text{H}_2\text{O}} \quad (\text{S3})$$

$$\Delta G = G_{\text{TMO@Ti}_3\text{C}_2\text{O}_{2-x}\text{B}_x} + (G_{\text{H}^+} + G_{\text{e}^-}) - G_{\text{TMOH@Ti}_3\text{C}_2\text{O}_{2-x}\text{B}_x} \quad (\text{S4})$$

Where $G_{\text{TMOH@Ti}_3\text{C}_2\text{O}_{2-x}\text{B}_x}$, $G_{\text{TM@Ti}_3\text{C}_2\text{O}_{2-x}\text{B}_x}$, $G_{\text{TMO@Ti}_3\text{C}_2\text{O}_{2-x}\text{B}_x}$ and $G_{\text{H}_2\text{O}}$ are calculated with DFT. According to the CHE model, $G_{\text{H}^+} + G_{\text{e}^-}$ can be represented as $1/2 \text{H}_2$ on standard hydrogen electrode (SHE) scale:

$$G_{\text{H}^+} + G_{\text{e}^-} = 1/2 G_{\text{H}_2} - eU_{\text{SHE}} - 0.059\text{pH} \quad (\text{S5})$$

Then the effect of pH and U_{SHE} can be contained as:

$$\Delta G (U, \text{pH}) = \Delta G - U_{\text{SHE}} - 0.059\text{pH} \quad (\text{S6})$$

The equilibrium line represents the values of pH and U_{SHE} when $\Delta G (U, \text{pH}) = 0$.

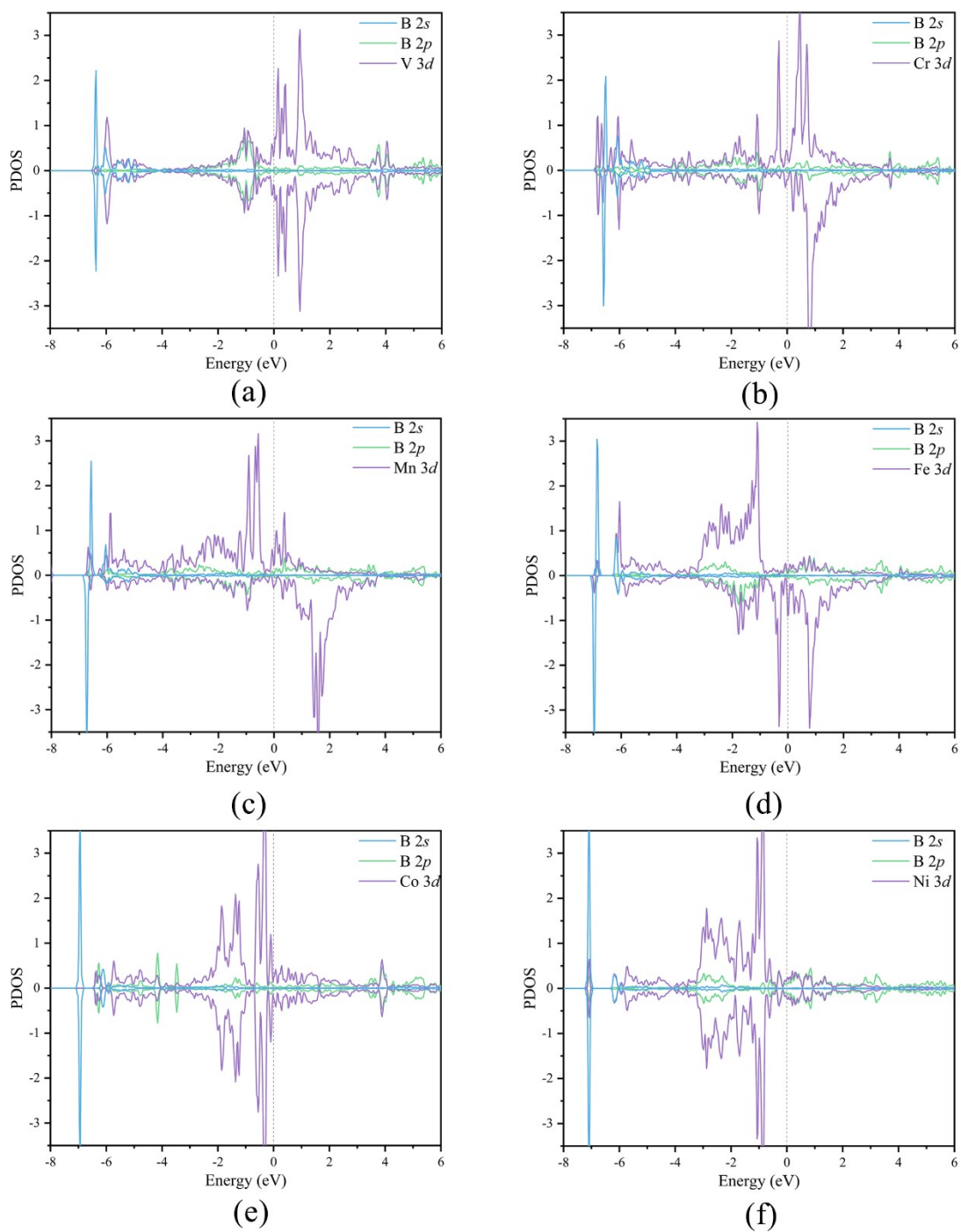


Fig. S1 DFT-calculated Projected densities of states (PDOSs) of $\text{TM@Ti}_3\text{C}_2\text{O}_{2-x}\text{B}_x$, where $\text{TM} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}$ and Ni . The Fermi level is set to zero in black dashed line.

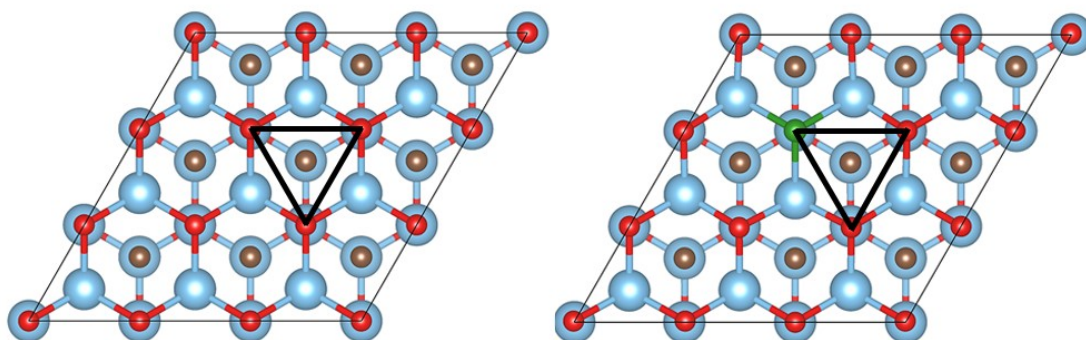


Fig. S2 The defined area of H1 sites on $\text{Ti}_3\text{C}_2\text{O}_2$ and $\text{Ti}_3\text{C}_2\text{O}_{2-x}\text{B}_x$ TM.

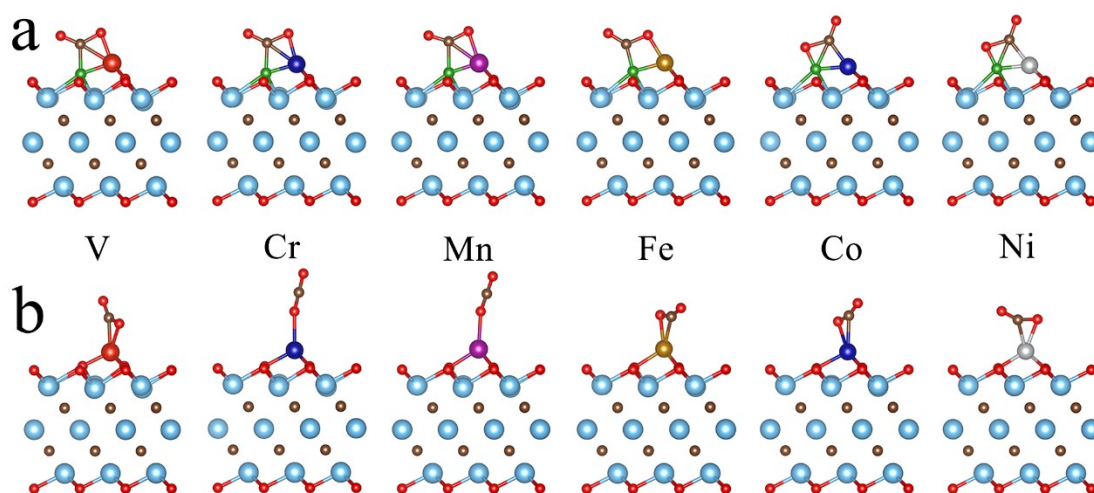


Fig. S3 Optimized geometric structures of CO_2 adsorbed on $\text{TM}@\text{Ti}_3\text{C}_2\text{O}_{2-x}\text{B}_x$ (a) and $\text{TM}@\text{Ti}_3\text{C}_2\text{O}_2$ (b).

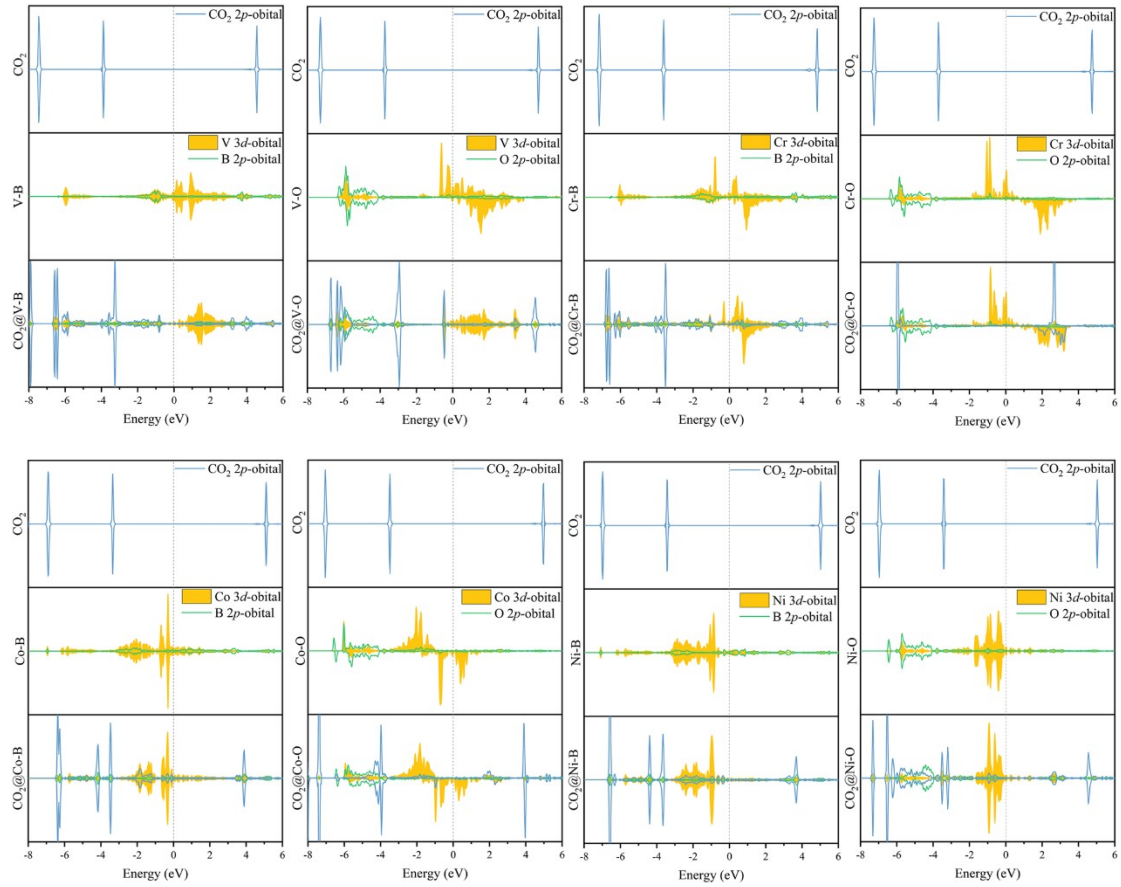


Fig. S4 The PDOS of CO_2 2p, TM 3d and coordination atoms 2p orbital before and after CO_2 adsorption on $\text{TM}@\text{Ti}_3\text{C}_2\text{O}_{2-x}\text{B}_x$ and $\text{TM}@\text{Ti}_3\text{C}_2\text{O}_2$.

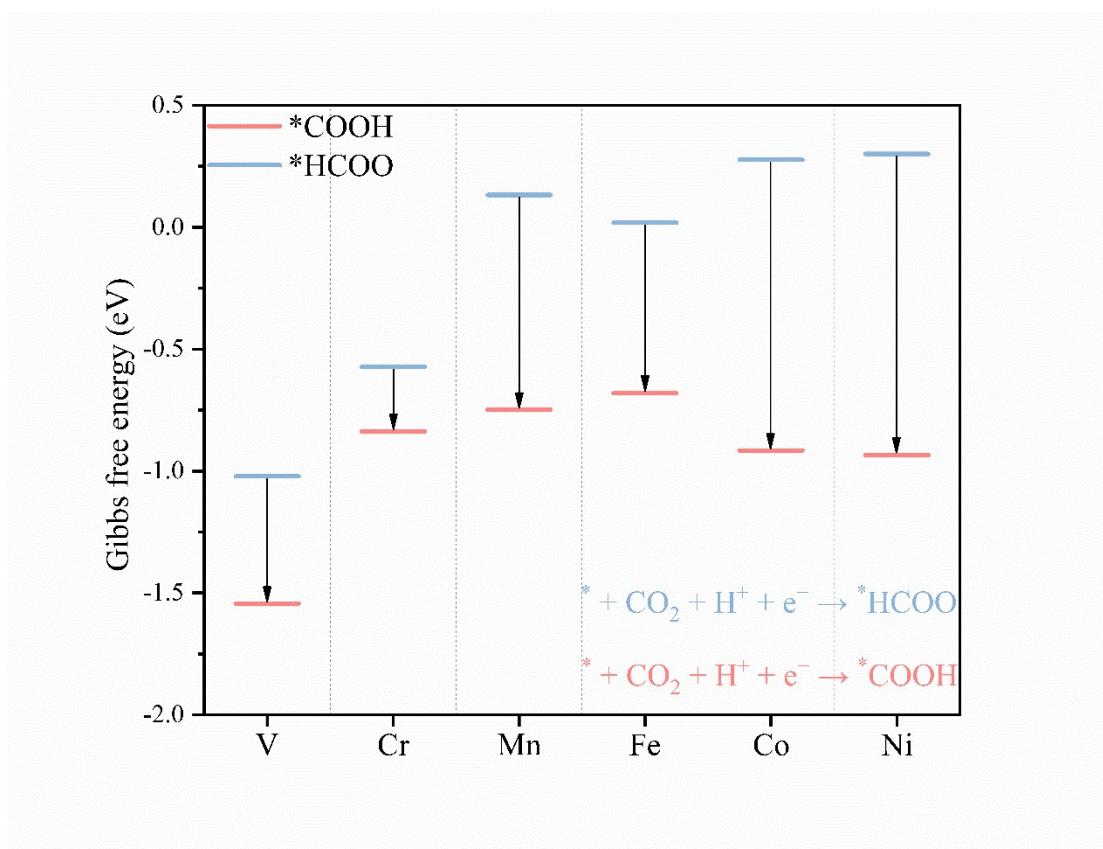


Fig. S5 Gibbs free energy changes of the 1st hydrogenation reaction for the CO₂ reduction on TM@Ti₃C₂O_{2-x}B_x.

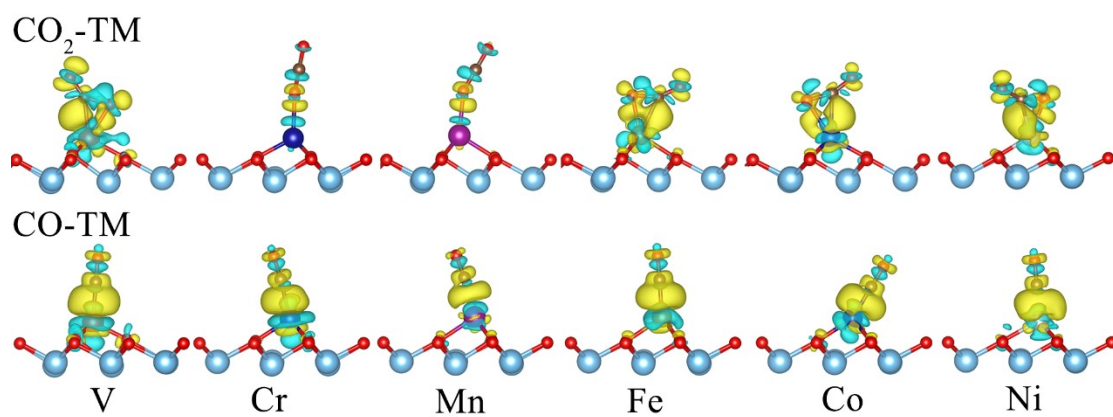


Fig. S6 The charge density differences of TM@Ti₃C₂O₂ with CO₂ and CO adsorption configurations.

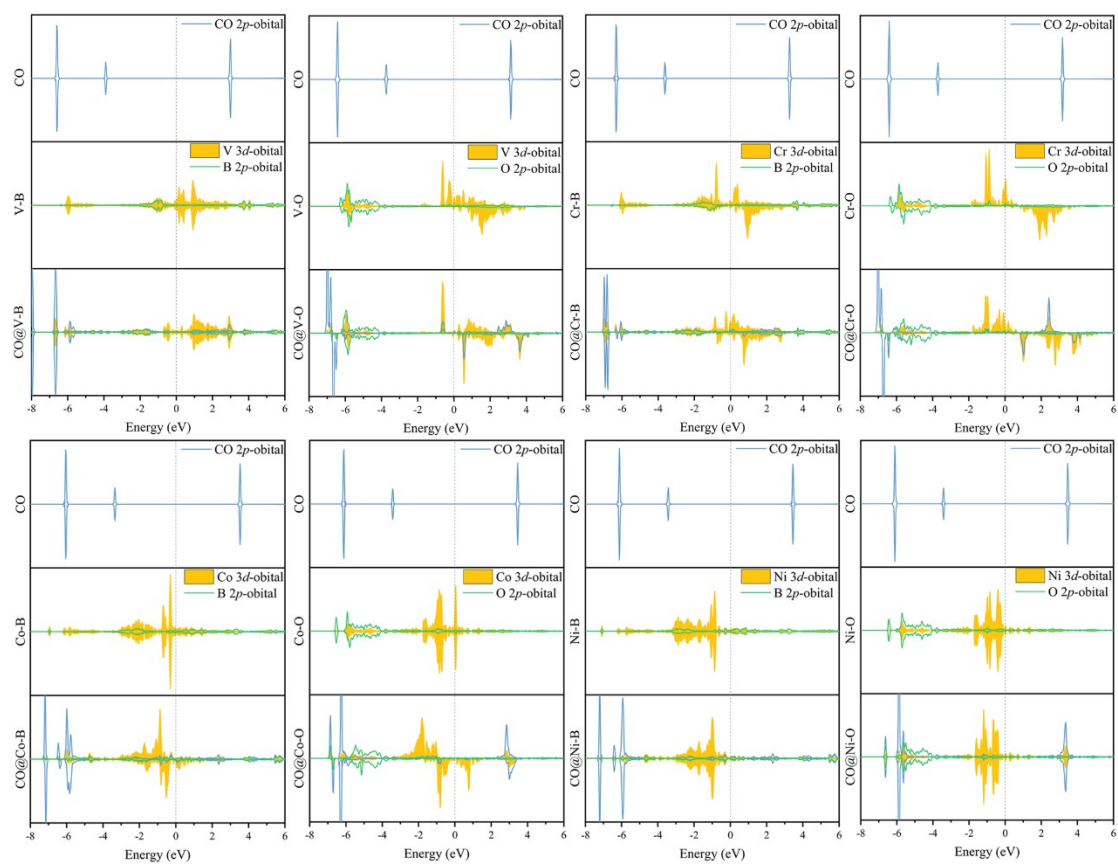


Fig. S7 The PDOS of CO $2p$, TM $3d$ and coordination atoms $2p$ orbital before and after CO adsorption on $\text{TM}@\text{Ti}_3\text{C}_2\text{O}_{2-x}\text{B}_x$ and $\text{TM}@\text{Ti}_3\text{C}_2\text{O}_2$.

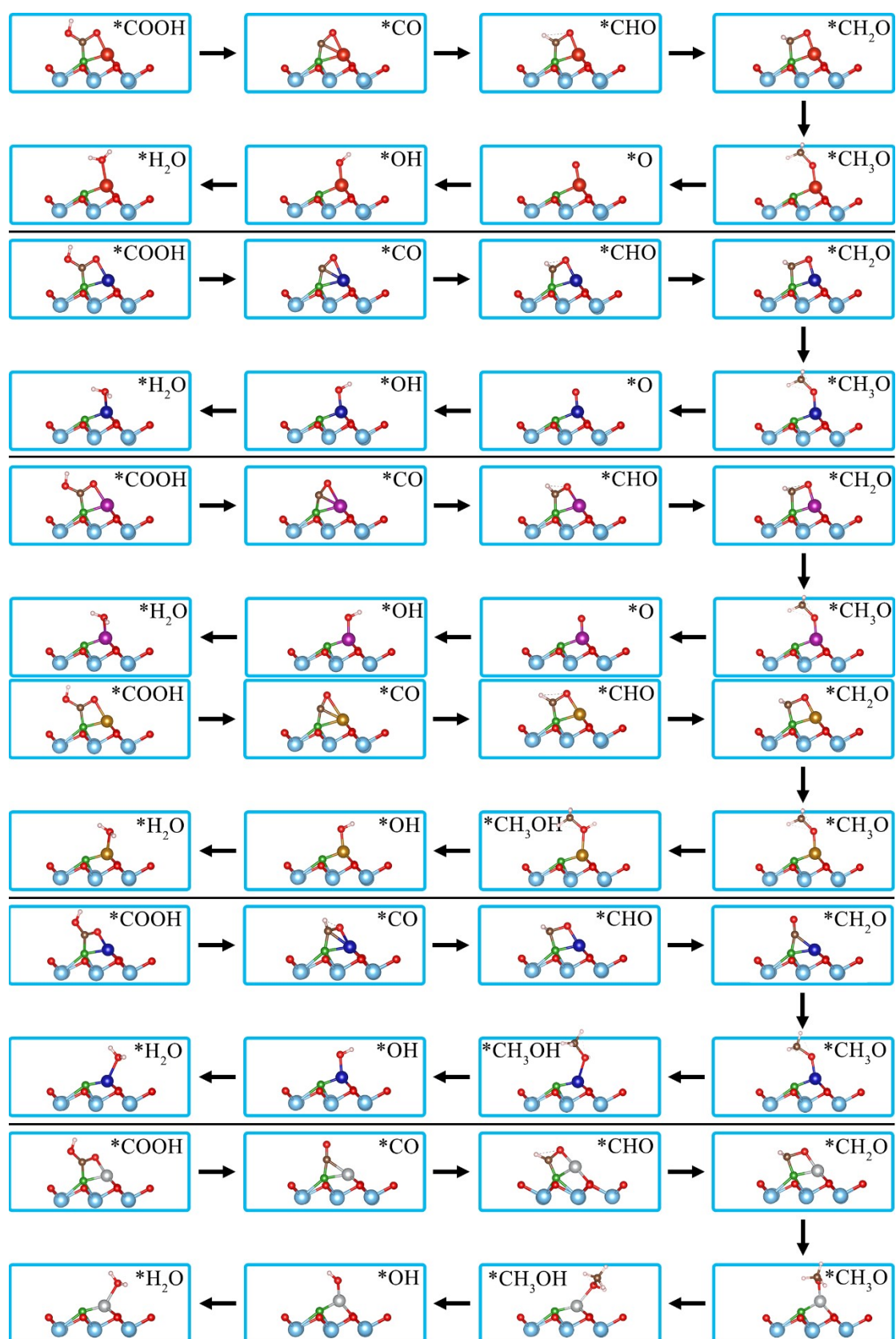


Fig. S8 DFT-optimized structures along the reaction pathway of CO₂RR.

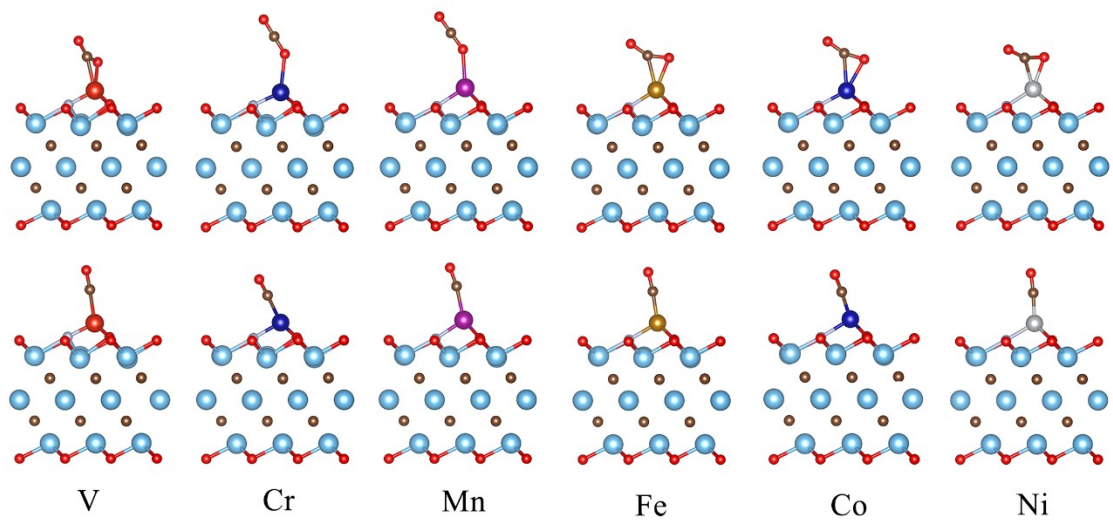


Fig. S9 Optimized geometric structures of CO₂ and CO adsorbed on TM@Ti₃C₂O_{2-x}B_x.

Table S1. Calculated cohesive energies (E_c) of metals and calculated binding energy - cohesive energy ($E_b - E_c$) of metal at H site.

		$Ti_3C_2O_{2-x}B_x$	$Ti_3C_2O_2$	$Ti_3C_2O_{2-x}B_x$	$Ti_3C_2O_2$
Metal	E_c (eV/atom) ^a	E_b (eV/atom)		$E_b - E_c$ (eV/atom)	
V	-5.62	-7.62	-5.48	-2.00	0.14
Cr	-4.04	-5.79	-3.41	-1.75	0.63
Mn	-3.49	-5.50	-3.51	-2.01	-0.02
Fe	-4.73	-5.99	-3.56	-1.26	1.17
Co	-5.01	-5.98	-3.60	-0.97	1.41
Ni	-4.85	-5.85	-3.51	-1.00	1.34

^a E_c is the intrinsic characteristic of metal and the E_c data retrieved from reference³

Table S2. Adsorption Gibbs free energy (G_{ads}/eV) of *CO, *CH₂O and *CH₃OH reduction products on TM@ $Ti_3C_2O_{2-x}B_x$

	CO	CH ₂ O	CH ₃ OH
V@ $Ti_3C_2O_{2-x}B_x$	-1.8	-3.17	-1.03
Cr@ $Ti_3C_2O_{2-x}B_x$	-0.93	-2.28	-0.47
Mn@ $Ti_3C_2O_{2-x}B_x$	-1.10	-1.45	-0.36
Fe@ $Ti_3C_2O_{2-x}B_x$	-0.92	-1.56	-0.58
Co@ $Ti_3C_2O_{2-x}B_x$	-1.15	-1.54	-0.43
Ni@ $Ti_3C_2O_{2-x}B_x$	-1.3	-1.24	-0.47

Table S3 The Gibbs free energy differences ($\Delta G/eV$) for the possible elementary hydrogenation steps of subsequent *CO reduction on TM/Ti₃C₂O_{2-x}B_x. The intermediate with red is more energetically preferred.

Hydrogenation steps	3	4	5	6	7	8
V/Ti ₃ C ₂ O _{2-x} B _x	*CHO	*CH ₂ O	*CH ₃ O	*O + CH ₄	*OH	*H ₂ O
	-0.29	-0.69	0.60	-0.24	-1.63	1.47
	*COH	*CHOH	*CH ₂ OH	*CH ₃ OH		
	2.00	0.46	2.15	0.79		
Cr/Ti ₃ C ₂ O _{2-x} B _x	*CHO	*CH ₂ O	*CH ₃ O	*O + CH ₄	*OH	*H ₂ O
	-0.30	-0.66	0.16	-0.43	-0.34	0.96
	*COH	*CHOH	*CH ₂ OH	*CH ₃ OH		
	0.73	0.67	1.55	0.91		
Mn/Ti ₃ C ₂ O _{2-x} B _x	*CHO	*CH ₂ O	*CH ₃ O	*O + CH ₄	*OH	*H ₂ O
	0.13	-0.1	0.10	-0.37	-0.41	0.23
	*COH	*CHOH	*CH ₂ OH	*CH ₃ OH		
	0.94	0.63	1.43	0.28		
Fe/Ti ₃ C ₂ O _{2-x} B _x	*CHO	*CH ₂ O	*CH ₃ O	*O + CH ₄	*OH	*H ₂ O
	0.15	-0.40	0.30	0.22	-0.96	0.15
	*COH	*CHOH	*CH ₂ OH	*CH ₃ OH		
	0.78	0.24	1.95	0.15		
Co/Ti ₃ C ₂ O _{2-x} B _x	*CHO	*CH ₂ O	*CH ₃ O	*O + CH ₄	*OH	*H ₂ O
	0.11	-0.11	0.55	0.38	-0.58	-0.18
	*COH	*CHOH	*CH ₂ OH	*CH ₃ OH		
	0.74	0.42	1.72	-0.17		
Ni/Ti ₃ C ₂ O _{2-x} B _x	*CHO	*CH ₂ O	*CH ₃ O	*O + CH ₄	*OH	*H ₂ O
	0.52	-0.08	0.68	0.85	-0.34	-0.37
	*COH	*CHOH	*CH ₂ OH	*CH ₃ OH		
	0.87	0.06	2.47	-0.64		

Table S4. DFT-predicted potential determining steps (PDS), limiting potentials (U_L) and active sites for production of CH_4 on bimetal electrocatalysts. Data of CO_2RR on other bimetal electrocatalysts were retrieved from literature.

Active site	PDS	U_L (V)	Ref.
Fe@Ti ₃ C ₂ O _{2-x} B _x	*CH ₂ O+H ⁺ +e ⁻ =*CH ₃ O	0.40	This work
Mn@Ti ₃ C ₂ O _{2-x} B _x	*CO+H ⁺ +e ⁻ =*CHO	0.51	This work
MnCu@2SV	*CO+H ⁺ +e ⁻ =*CHO	0.61	4
NiCu@2SV	*CO+H ⁺ +e ⁻ =*CHO	0.70	4
NiCo@C ₂ N	*CHO+H ⁺ +e ⁻ =*CHOH	0.25	5
Ni ₂ @C ₂ N	*CO+H ⁺ +e ⁻ =*CHO	0.67	5
CuMn@BN	*HCOOH+H ⁺ +e ⁻ =*CHO + H ₂ O	0.61	6
Fe ₂ @BN	*CO+H ⁺ +e ⁻ =*CHO	0.47	6
RuFe@g-C ₃ N ₄	*HCOO+H ⁺ +e ⁻ =*HCOOH	0.58	7
RuCu@g-C ₃ N ₄	*HCOO+H ⁺ +e ⁻ =*HCOOH	0.40	7
Mn ₂ @PC ₆	*CO+H ⁺ +e ⁻ =*CHO	0.31	8
CrPd@PC ₆	*CO+H ⁺ +e ⁻ =*CHO	0.41	8
AgCr@N6V4	*CO ₂ +H ⁺ +e ⁻ =*COOH	0.38	9

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