

Supporting Information

Mechanistic insights for electrochemical reduction of CO₂ into hydrocarbon fuels over O-terminated MXenes

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Table S1: The adsorption configuration and bond distance (Å) between adsorbed intermediate and the M_2XO_2 ($M = \text{Ti}$ and Zr ; $X = \text{C}, \text{N}$ and B) MXenes.

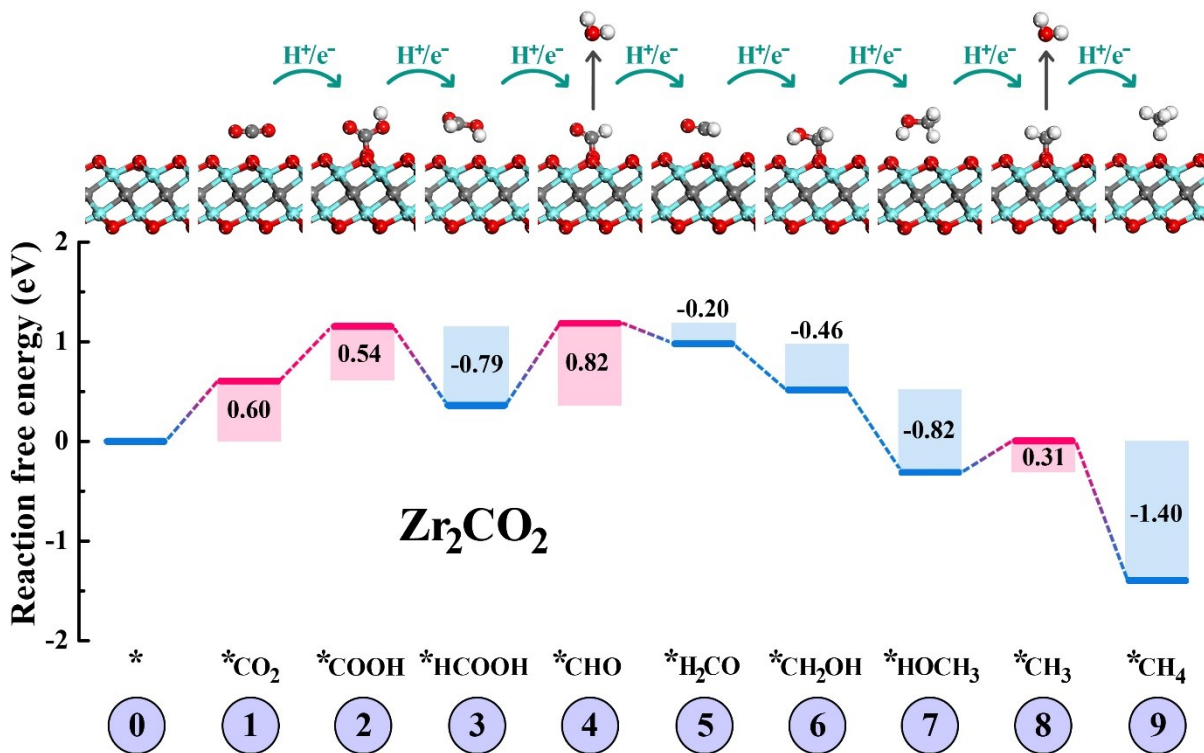
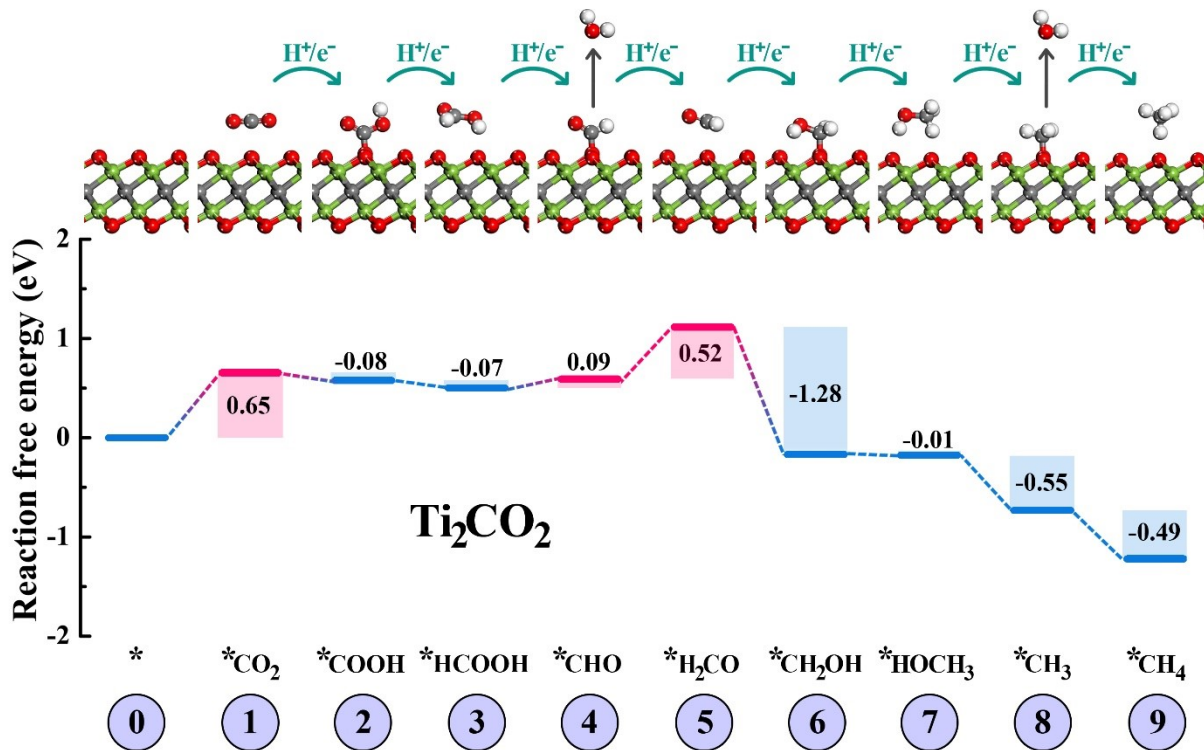
	Ti_2CO_2	Zr_2CO_2	Ti_2NO_2	Zr_2NO_2	Ti_2BO_2	Zr_2BO_2	
	* CO_2	2.469	2.325	2.507	2.372	2.348	2.365
	* COOH	1.374	1.363	1.387	1.371	1.370	1.359
	* HCOOH	1.925	1.864	1.956	1.872	1.933	1.827
	* CHO	1.405	1.387	1.411	1.389	1.414	1.382
	* H_2CO	2.384	2.280	2.479	2.370	2.357	2.290
	* CH_2OH	1.475	1.451	1.491	1.466	1.510	1.460
	* HOCH_3	1.981	1.997	1.987	2.003	1.951	1.939
	* CH_3	1.446	1.444	1.444	1.457	1.463	1.444
	* CH_4	1.916	1.943	1.926	1.965	1.911	1.927

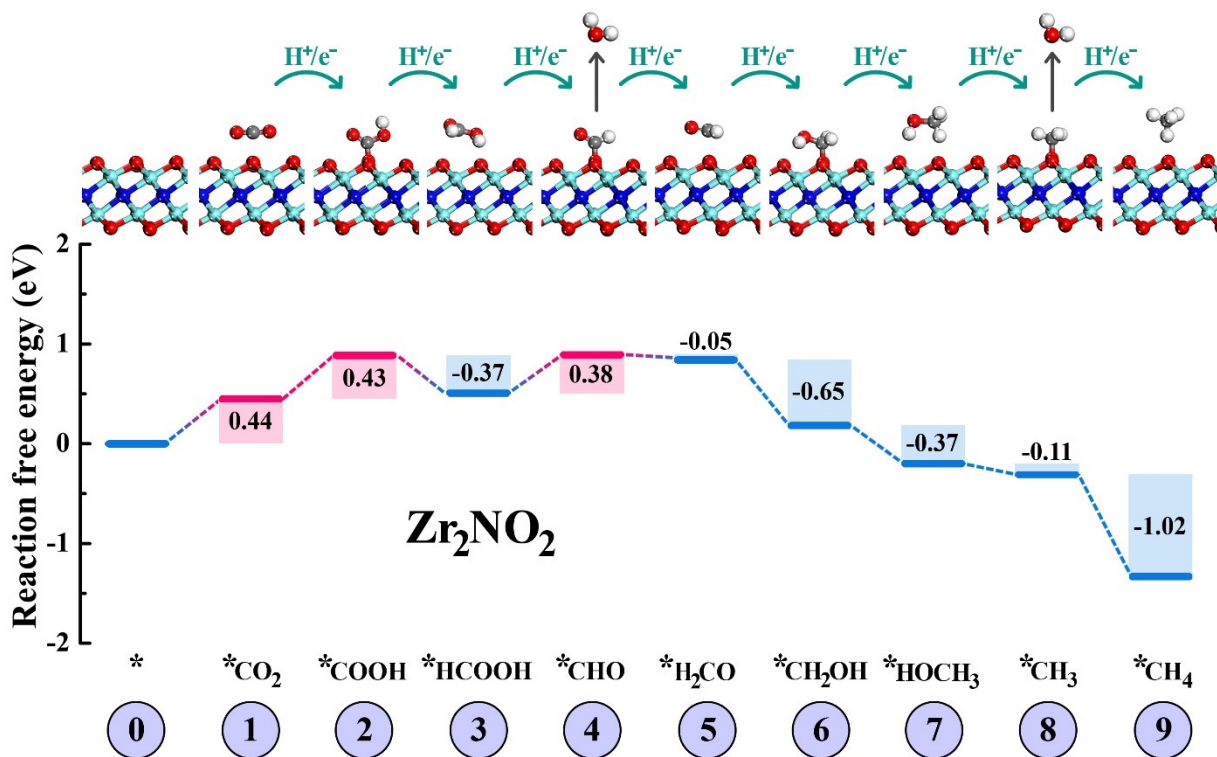
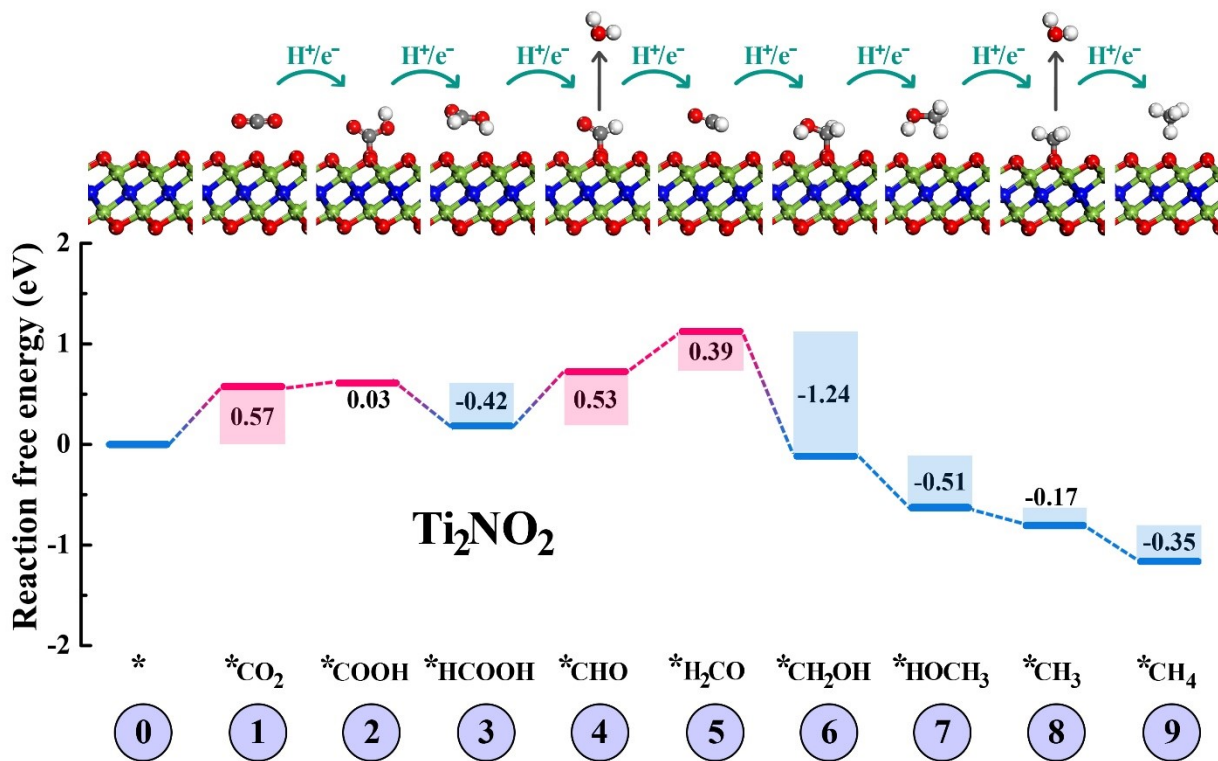
Table S2: Gibbs free energies (in eV) corresponding to various intermediates along the CO₂ conversion pathway catalysed by M₂XO₂ (M = Ti and Zr; X = C, N and B) MXenes.

	e ⁻ transferred	Ti ₂ CO ₂	Zr ₂ CO ₂	Ti ₂ NO ₂	Zr ₂ NO ₂	Ti ₂ BO ₂	Zr ₂ BO ₂
Surface	0	0	0	0	0	0	0
CO₂	1	0.65	0.61	0.58	0.45	0.65	0.61
COOH	2	0.58	1.15	0.61	0.89	0.32	0.43
HCOOH	3	0.5	0.36	0.19	0.51	0.15	0.51
CHO	4	0.59	1.19	0.72	0.89	0.43	0.47
H₂CO	5	1.12	0.98	1.12	0.84	1.12	1.07
CH₂OH	6	-0.17	0.52	-0.12	0.18	-0.54	-0.44
HOCH₃	7	-0.18	-0.31	-0.63	-0.2	-0.17	-0.33
CH₃	8	-0.73	0.01	-0.81	-0.31	-0.85	-1.14
CH₄	9	-1.22	-1.4	-1.16	-1.33	-1.01	-1.71

Table S3: Computed U_L(CO₂), U_L(H₂) and U_L(CO₂) - U_L(H₂).

System	U _L (CO ₂) (V)	U _L (H ₂) (V)	U _L (CO ₂) - U _L (H ₂) (V)
Ti₂CO₂	-0.653	-0.466	-0.187
Zr₂CO₂	-0.606	-0.162	-0.444
Ti₂NO₂	-0.575	-0.454	-0.121
Zr₂NO₂	-0.446	-0.509	0.063
Ti₂BO₂	-0.646	-0.384	-0.261
Zr₂BO₂	-0.608	0.201	-0.809





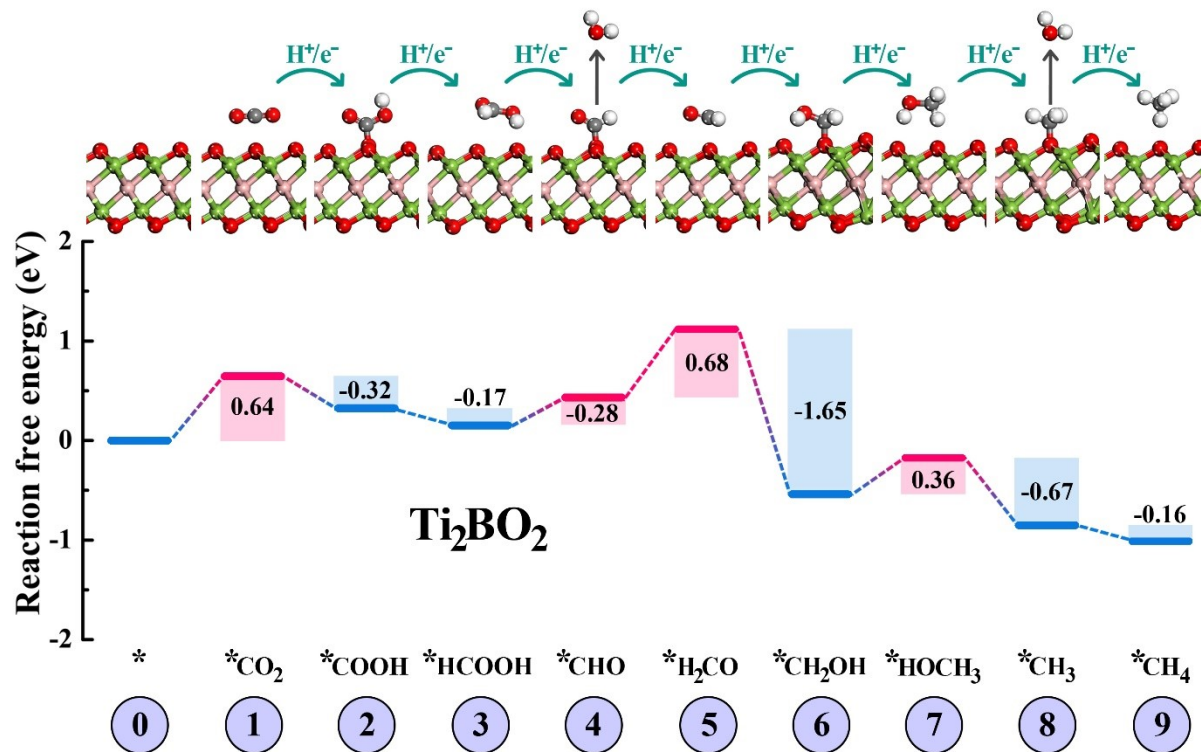


Figure S1: Free energy diagrams of the overall CO₂RR for M₂XO₂ (M = Ti and Zr; X = C, N and B) MXenes. Arrow represents the transfer of (H⁺+e⁻) pair in the CO₂ reduction pathway. Here white, red, gray, blue, pink, green and cyan spheres refer to H, O, C, N, B, Ti and Zr atoms, respectively.