Supplementary Information

for

Unlocking the Catalytic Potential of iMXenes: Selective Electrochemical CO_2 Reduction for Methane Production

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Supplementary Figures:

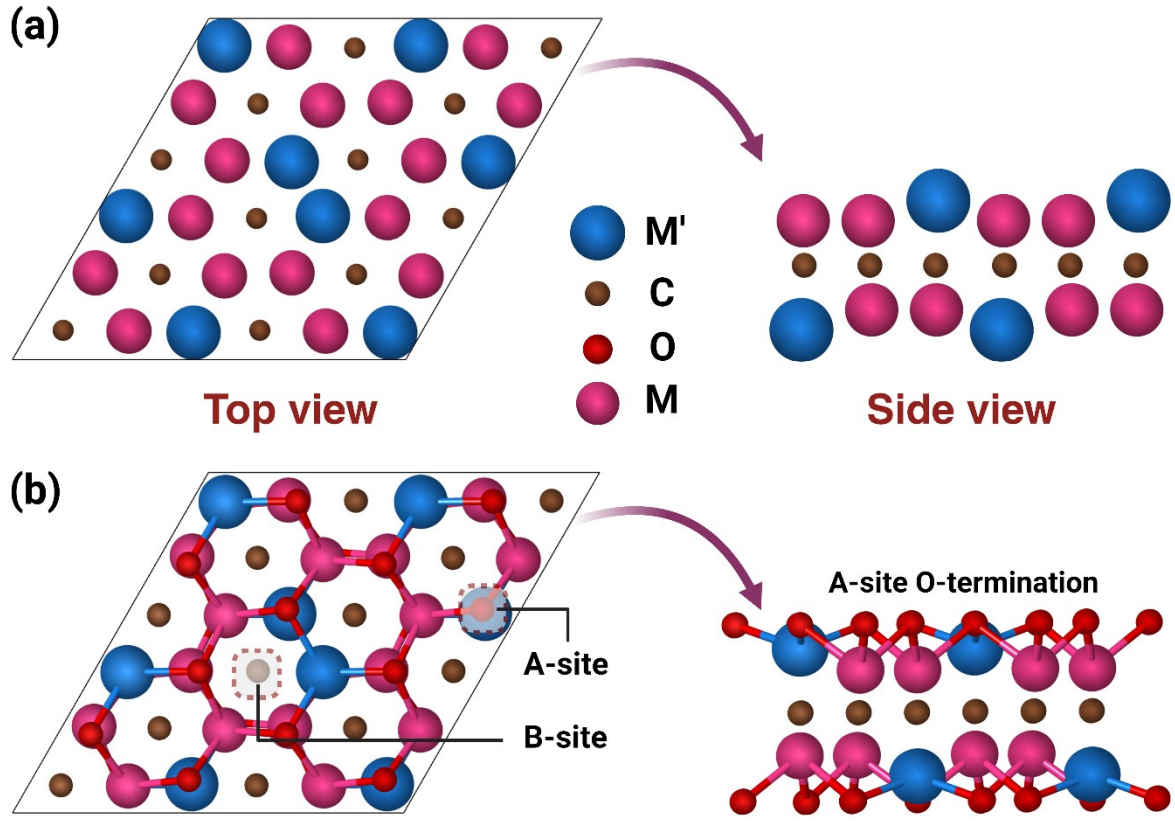

Fig. S1 Top and side view of **(a)** bare and **(b)** O-terminated iMXenes, with two different O-termination adsorption sites (A and B site).

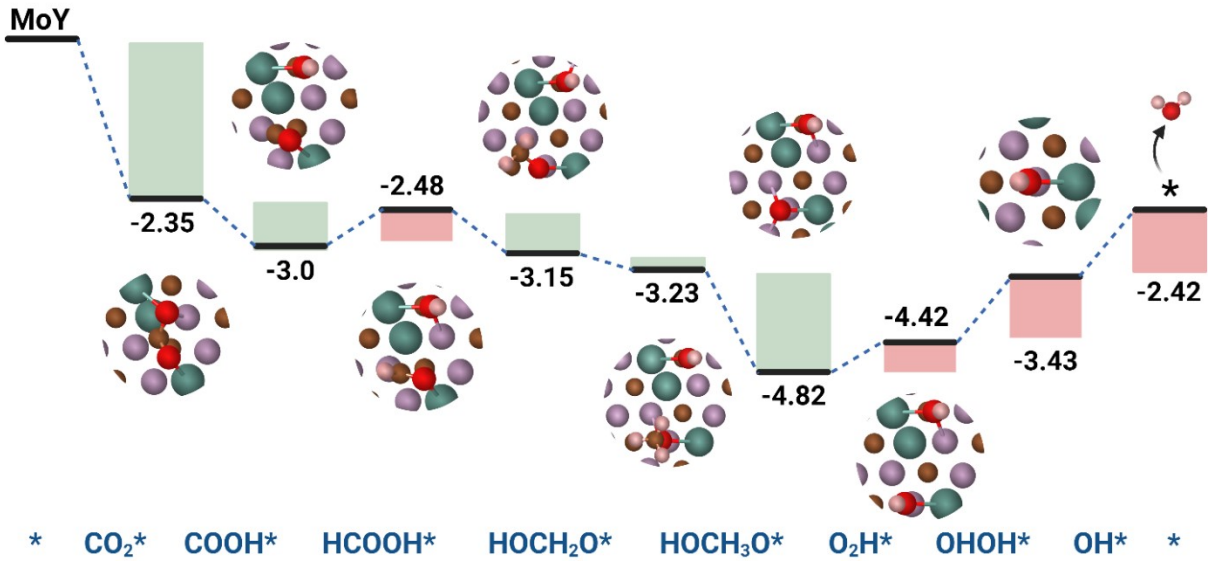

Fig. S2 Reaction free energy diagram with minimum energy path for CO_2 reduction to CH_4 catalyzed by MoY, at zero applied potential (*vs*. RHE). The Gibbs free energies values are in eV. The green and red color shadings indicate the spontaneous and non-spontaneous reactions.

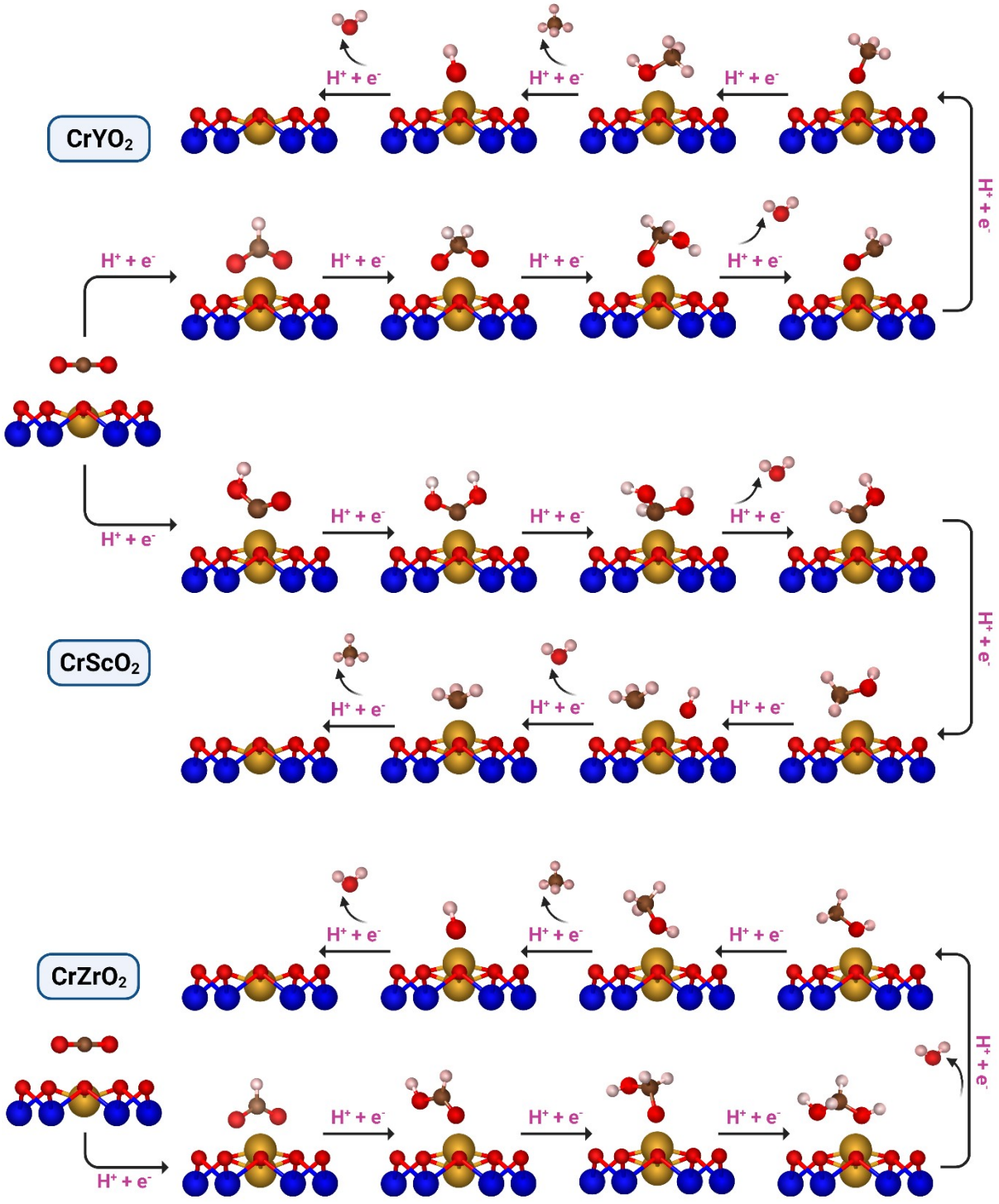

Fig. S3 The intermediate species for minimum energy path and their corresponding mechanisms for $CrScO_2$, $CrYO_2$, and $CrZrO_2$.

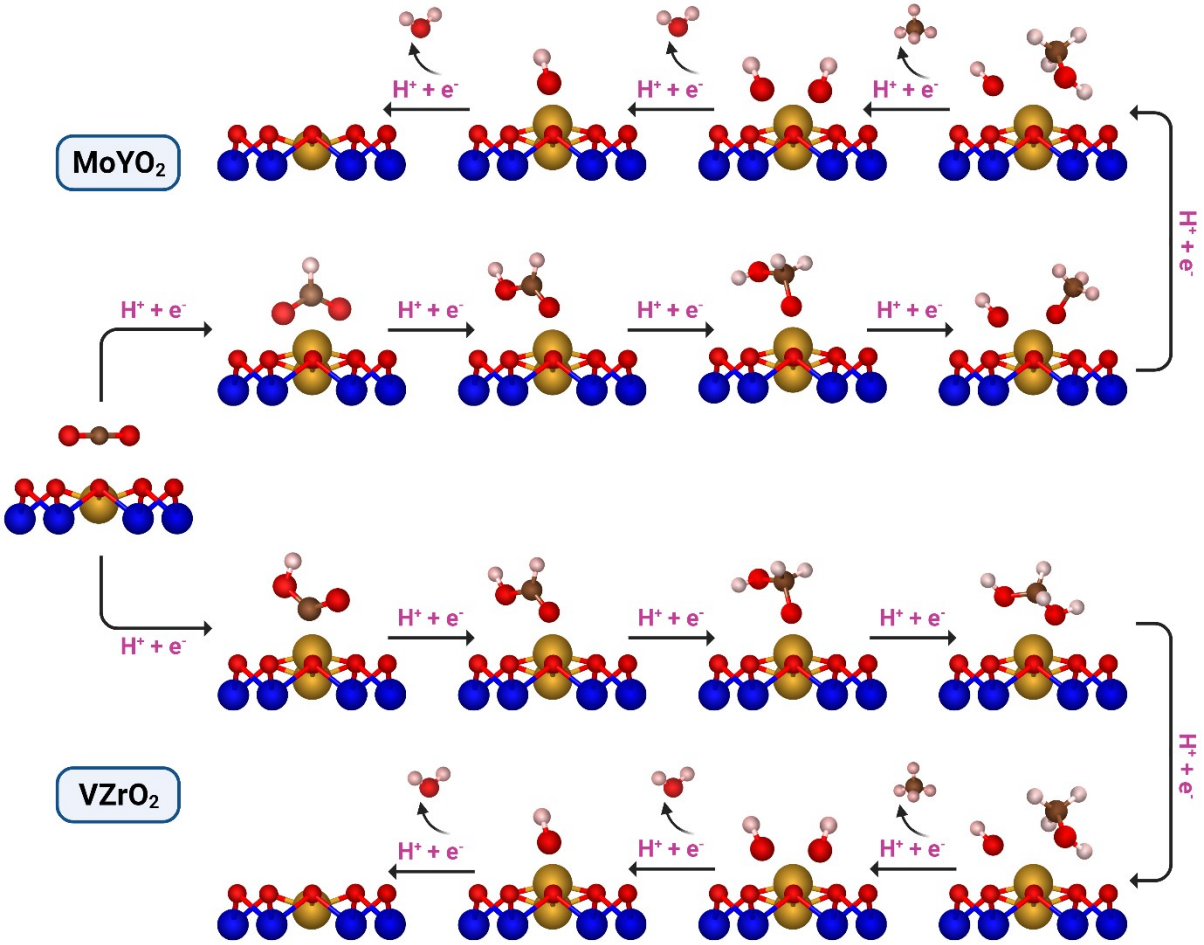

Fig. S4 The intermediate species for minimum energy path and their corresponding mechanisms for $MoYO_2$ and $VZrO_2$.

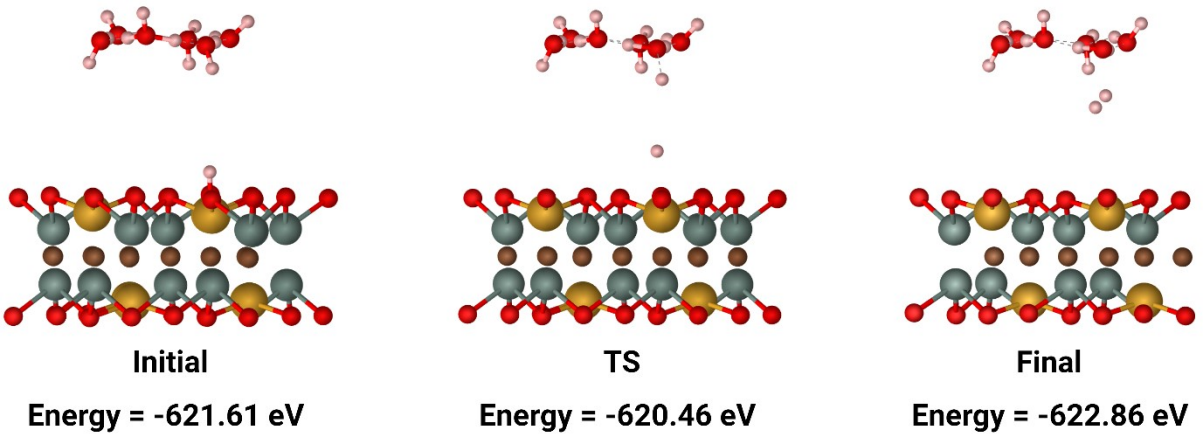

Fig. S5 The initial, transition state (TS), and final configuration from the CI-NEB calculation performed using the explicit solvation model for H_2 production on the $MoScO_2$ surface.

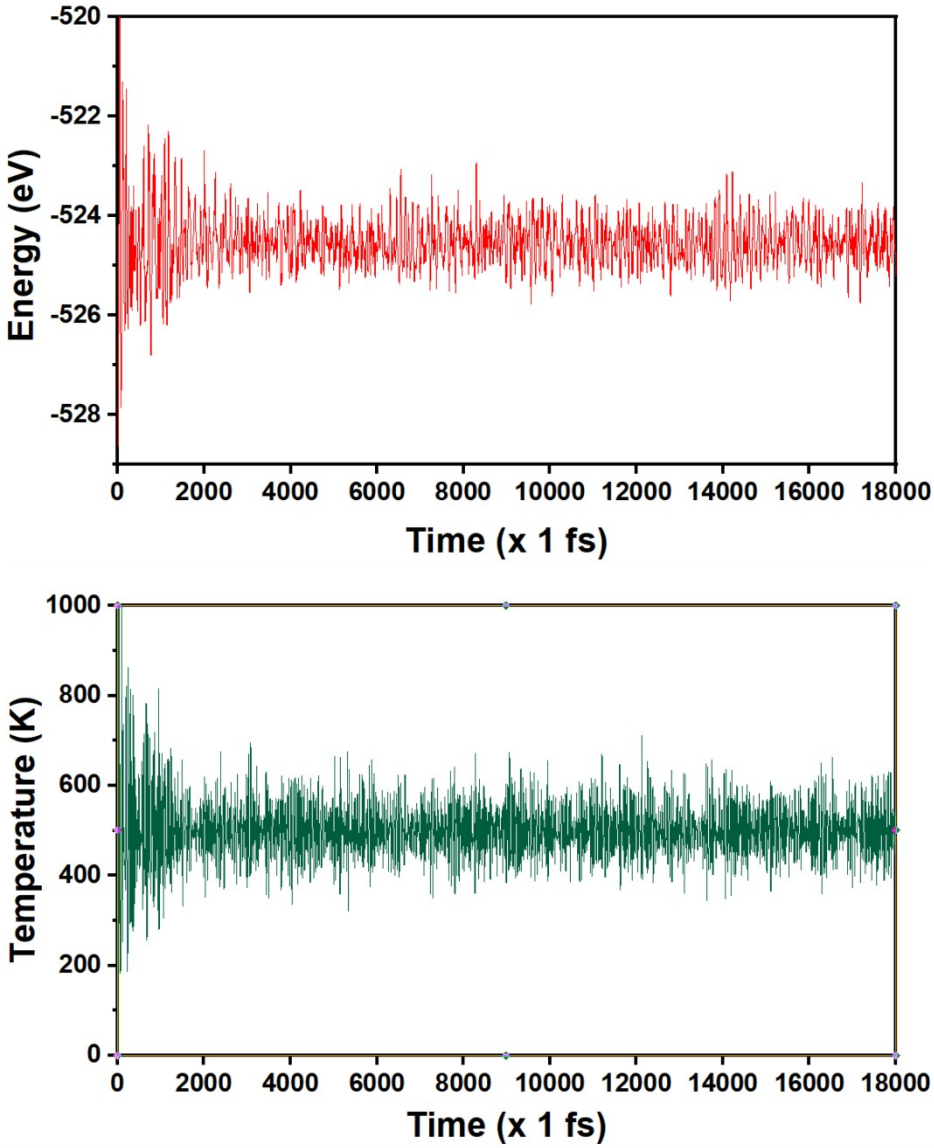

Fig. S6 The energy and temperature changes along time in MD simulatiuons for $MoScO_2$. The machine learning potential are generated using on-the-fly sampling and sparse Gaussian regression (SGPR) algorithm as implemented in AUTOFORCE. The MD simulations are conducted at T=500K.

Supplementary Tables:

Table S1 Geometrical parameters after CO_2 adsorption on both bare and O-terminated iMXenes, bond angle O-C-O, distance between surface and CO_2 ($d^{surf\text{-}CO2}$), distance between carbon and two oxygen atoms of CO_2* ($d^{C\text{-}O}$).

iMXenes	O-C-O (deg.)	$d^{surf\text{-}CO2}$ (Å)	$d^{C\text{-}O}$ (Å)	
			$C\text{-}O_1$	$C\text{-}O_2$
CrSc	116.72	2.06	1.31	1.38
CrY	122.93	2.29	1.33	1.29
CrZr	116.07	2.24	1.38	1.33
MoSc	118.50	1.38	1.39	1.31
MoY	121.10	1.38	1.38	1.31
VZr	116.27	1.41	1.41	1.33
WSc	131.77	2.23	1.29	1.27
WY	127.00	2.30	1.26	1.34
$CrScO_2$	178.00	2.73	1.18	1.18
$CrYO_2$	177.00	2.79	1.17	1.19
$CrZrO_2$	179.00	2.96	1.18	1.18
$MoScO_2$	178.60	2.64	1.18	1.19
$MoYO_2$	176.80	2.75	1.19	1.17
$VZrO_2$	179.20	2.96	1.18	1.18
$WScO_2$	179.50	3.00	1.18	1.18
WYO_2	178.00	2.80	1.19	1.17

Table S2 Bader charge analysis of CO_2 adsorbed intermediate bare and O-terminated iMXenes. C, O_1, and O_2 are adsorbed CO_2 atoms. The net charge transferred to CO_2 is also provided.

iMXenes	C	O_1	O_2	Net charge on CO_2
CrSc	0.71	-1.17	-1.16	-1.62
CrY	0.96	-1.20	-1.20	-1.44
CrZr	0.71	-1.16	-1.16	-1.61
MoSc	0.76	-1.14	-1.18	-1.56
MoY	0.79	-1.16	-1.21	-2.02
VZr	0.54	-1.15	-1.17	-1.78
WSc	0.76	-1.15	-1.12	-1.51
WY	0.76	-1.20	-1.15	-1.59
$CrScO_2$	2.13	-1.10	-1.07	-0.04
$CrYO_2$	2.17	-1.12	-1.12	-0.07
$CrZrO_2$	2.13	-1.07	-1.09	-0.03
$MoScO_2$	2.06	-1.12	-1.04	-0.10
$MoYO_2$	2.11	-1.10	-1.05	-0.04
$VZrO_2$	2.14	-1.08	-1.09	-0.03
$WScO_2$	2.12	-1.07	-1.08	-0.03
WYO_2	2.14	-1.12	-1.07	-0.05

Table S3 DFT based calculated electronic energies (E_{elec}), zero-point energies (ZPE), and entropy contributions (TS) for the gaseous molecules in eV.

Species	E_{elec} (eV)	ZPE (eV)	-TS (eV)
CO_2	-22.26	0.30	-0.21
CO	-14.42	0.13	-0.62
HCOOH	-29.20	0.90	-0.48
CH_3OH	-29.92	1.34	-0.82
CH_4	-24.04	1.31	-0.46
H_2O	-14.22	0.55	-0.62
0.5 H_2	-3.38	0.14	-0.20

Table S4 The adsorption Gibbs free energies change (ΔG_{ad}) for CO_2 and H_2O adsorption on both bare and O-terminated iMXenes in eV.

iMXenes	ΔG_{CO2*}	ΔG_{H2O*}
CrSc	-3.63	-1.59
CrY	-2.77	-0.75
CrZr	-3.23	-0.63
MoSc	-2.19	-0.31
MoY	-2.36	-0.29
VZr	-2.77	-0.42
WSc	-1.77	-0.28
WY	-2.19	-0.27
$CrScO_2$	-1.10	-0.38
$CrYO_2$	-1.23	-0.90
$CrZrO_2$	-0.33	-0.08
$MoScO_2$	-0.25	-0.09
$MoYO_2$	-0.45	-0.12
$VZrO_2$	-0.33	-0.10
$WScO_2$	-0.81	-1.01

WYO_2	-0.40	-0.09

Table S5 The Gibbs free energies change (ΔG) for each hydrogenation step for CO_2 reduction to CH_4. The potential determining step (PDS) are represented in bold for both bare and O-terminated iMXenes in eV. The 1st, 2nd and so on to 8th represents the hydrogenation steps.

iMXenes	1st	2nd	3rd	4th	5th	6th	7th	8th
CrSc	-0.46	1.29	-0.27	-1.91	0.19	-2.46	1.49	**1.92**
CrY	0.17	-0.41	0.45	-0.09	-0.07	-1.78	0.45	**1.85**
CrZr	-0.36	0.32	-0.04	-0.06	-2.14	0.57	0.83	**1.78**
MoSc	-0.89	0.33	-0.31	-0.83	-1.61	0.51	1.15	**1.52**
MoY	-0.64	0.52	-0.67	-0.08	-1.59	0.40	0.99	**1.01**
VZr	-0.84	-0.02	-0.19	-0.55	-1.80	0.24	1.98	**1.63**
WSc	-0.43	-1.29	-1.98	0.35	0.02	0.59	0.96	**1.37**
WY	-0.76	-0.25	0.15	-0.86	-0.09	-0.38	**1.04**	1.00
$CrScO_2$	-0.66	0.54	-0.13	-0.37	-0.32	**0.77**	-0.35	0.24
$CrYO_2$	-0.75	1.36	-0.63	-2.03	**1.6**	0.04	-1.19	0.26
$CrZrO_2$	**0.53**	-0.12	0.26	-0.5	-0.31	-1.34	-0.03	-0.28
$MoScO_2$	-0.09	0.21	**0.27**	-0.41	-0.5	-0.31	-0.8	-0.23
$MoYO_2$	-0.23	0.68	0.07	-0.62	-0.23	-0.94	-0.13	**0.75**
$VZrO_2$	0.44	-0.55	**0.61**	-0.26	-0.76	-0.6	-0.51	-0.16
$WScO_2$	-0.14	**0.89**	0.01	-0.11	-0.8	-0.04	-1.13	-0.02
WYO_2	-0.79	**1.21**	-0.12	0.01	-0.9	-0.09	-1.13	0.09

Table S6 The Gibbs free energies change (ΔG) for CO_2 reduction to CO. The 1st and 2nd represents the first and second hydrogenation step for bare iMXenes in eV. The PDS of the reaction is shown in bold. All values are in eV.

iMXenes	1st	2nd	$CO^{desorption}$
CrSc	-0.46	1.29	**2.66**
CrY	0.17	-0.41	**2.89**
CrZr	-0.36	-	**2.25**
MoSc	-0.89	-	**2.00**
MoY	-0.64	-	**2.35**
VZr	-0.84	-	**2.42**
WY	-0.76	-	**1.01**

Table S7 The Gibbs free energies change (ΔG) for CO_2 reduction to HCOOH. The 1st and 2nd represent the first and second hydrogenation step for the O-terminated iMXenes which form HCOOH* intermediate. The PDS of the reaction is shown in bold. All values are in eV.

iMXenes	1st	2nd (HCOOH*)	HCOOH desorption
$CrZrO_2$	**0.53**	-0.12	0.19
$MoScO_2$	-0.09	0.21	**0.51**
$MoYO_2$	-0.23	**0.68**	0.28
$VZrO_2$	0.44	-0.55	**0.70**
$WScO_2$	-0.14	**0.89**	0.33
WYO_2	-0.79	**1.21**	0.25

Table S8 The Gibbs free energies change (ΔG) for CO_2 reduction to CH_3OH. The 5^{th} and 6^{th} represent the fifth and sixth hydrogenation step for the O-terminated iMXenes which form CH_3OH* intermediate. The PDS of the reaction is shown in bold. All values are in eV.

iMXenes	**5^{th}**	**6^{th} (CH_3OH*)**	**CH_3OH desorption**	**PDS**
$CrYO_2$	1.6	0.04	0.74	5^{th} (1.6)
$CrZrO_2$	-0.31	-1.34	0.88	desorp (0.88)
$MoScO_2$	-0.5	-0.31	0.37	desorp (0.37)
$WScO_2$	-0.8	-0.04	0.08	2^{nd} (0.89)
WYO_2	-0.9	-0.09	0.16	2^{nd} (1.21)
	5^{th}	**CH_3OH desorption**	**6^{th}**	**PDS**
$MoYO_2$	-0.23	-0.05	-0.94	2^{nd} (0.68)
$VZrO_2$	-0.76	-0.09	-0.60	3^{rd} (0.61)

Table S9 Hydrogen adsorption free energies (ΔG_{H^*} in eV) for both bare and O-terminated iMXenes.

iMXenes	ΔG_{H^*}
CrSc	-0.95
CrY	0.98
CrZr	0.43
MoSc	-0.92
MoY	-0.91
VZr	-1.04
WSc	-0.87
WY	-0.87
$CrScO_2$	-0.93
$CrYO_2$	-1.40
$CrZrO_2$	-0.21
$MoScO_2$	-0.29
$MoYO_2$	-0.35
$VZrO_2$	-0.39
$WScO_2$	0.35
WYO_2	0.48

Table S10 First hydrogen adsorption energies (ΔE_{ad} in eV). $\Delta E_{ad\text{-}CO2H*}$ represents H-adsorption on adsorbed CO_2 and $\Delta G_{ad\text{-}surf*}$ represents H-adsorption on the surface with CO_2*.

iMXenes	$\Delta E_{ad\text{-}CO2H*}$	$\Delta E_{ad\text{-}surf*}$
$CrScO_2$	-1.28	-1.21
$CrYO_2$	-1.08	-0.79
$CrZrO_2$	0.20	-0.62
$MoScO_2$	-0.66	-0.43
$MoYO_2$	-0.57	-0.39
$VZrO_2$	-0.06	-0.75
$WScO_2$	-0.48	-0.15
WYO_2	-1.13	-0.45

Table S11 Adsorption free energies for H_2O adsorption (* + H_2O → H_2O*) and OH adsorption (H_2O* → OH* + H^+ + e^-) on O-terminated iMXenes, depicted as ΔG_{H2O*} and ΔG_{OH*} (in eV), respectively.

iMXenes	ΔG_{H2O*}	ΔG_{OH*}
$CrScO_2$	-0.38	0.83
$CrYO_2$	-0.90	0.18
$CrZrO_2$	-0.08	0.40
$MoScO_2$	-0.09	0.36
$MoYO_2$	-0.12	0.39
$VZrO_2$	-0.10	0.18
$WScO_2$	-1.01	0.05
WYO_2	-0.09	0.06

Table S12 The free energies (eV) of each reaction step for MoY and $MoScO_2$ incorporating the solvation corrections using the implicit solvent model.

Hydrogenation Step	MoY	$MoScO_2$
1	-0.74	-0.65
2	0.61	0.26
3	-0.49	0.29
4	-0.07	-0.75
5	-0.11	-0.82
6	0.58	0.03
7	0.87	-1.08
8	0.96	-0.08

Table S13 The adsorption energy (E_{ad} in eV) per terminated O-atom for both possible O-termination configurations (A and B site).

iMXenes	A-site	B-site
$CrScO_2$	-2.55	-2.14
$CrYO_2$	-3.97	-3.55
$CrZrO_2$	-3.81	-3.59
$MoScO_2$	-4.38	-3.72
$MoYO_2$	-4.74	-4.27
$VZrO_2$	-2.88	-2.48
$WScO_2$	-4.34	-4.00
WYO_2	-4.73	-4.42

Table S14 The electronic energies (eV) for CO_2RR of each stable intermediate for MoY and $MoScO_2$, with corresponding images provided in the above figures. To calculate the free energies of each step, the energies of gaseous molecules from Table S3 should be included or subtracted accordingly.

Hydrogenation Step	MoY	$MoScO_2$
Pristine	-320.18	-530.65
***CO_2**	-344.78	-553.15
1	-349.13	-556.96
2	-352.27	-560.56
3	-356.53	-563.99
4	-360.35	-568.17
5	-341.11	-572.19
6	-344.42	-561.52
7	-332.36	-541.42
8	-335.23	-544.87

Table S15 The electronic energies (eV) of both pristine and *H adsorbed intermediate for both bare and O-terminated iMXenes.

iMXenes	Bare		O-terminated	
	pris	*H	Pris	*H
CrSc	-311.23	-315.82	-520.76	-525.33
CrY	-299.10	-301.75	-500.25	-505.28
CrZr	-313.93	-317.14	-520.23	-524.07
MoSc	-318.02	-322.58	-530.65	-534.57
MoY	-320.18	-324.72	-531.28	-535.26
VZr	-313.60	-318.27	-531.62	-535.64
WSc	-345.11	-349.61	-563.64	-566.92

WY	-346.63	-351.13	-564.43	-567.58