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

Electronic Supplementary Information

Enhancement of Selectivity of MXenes (M_2C, M=Ti, V, Nb, Mo) via Oxygen-functionalization: Promising Materials for Gas-sensing and -separation

Anchalee Junkaew[*a] *and Raymundo Arróyave*[b]

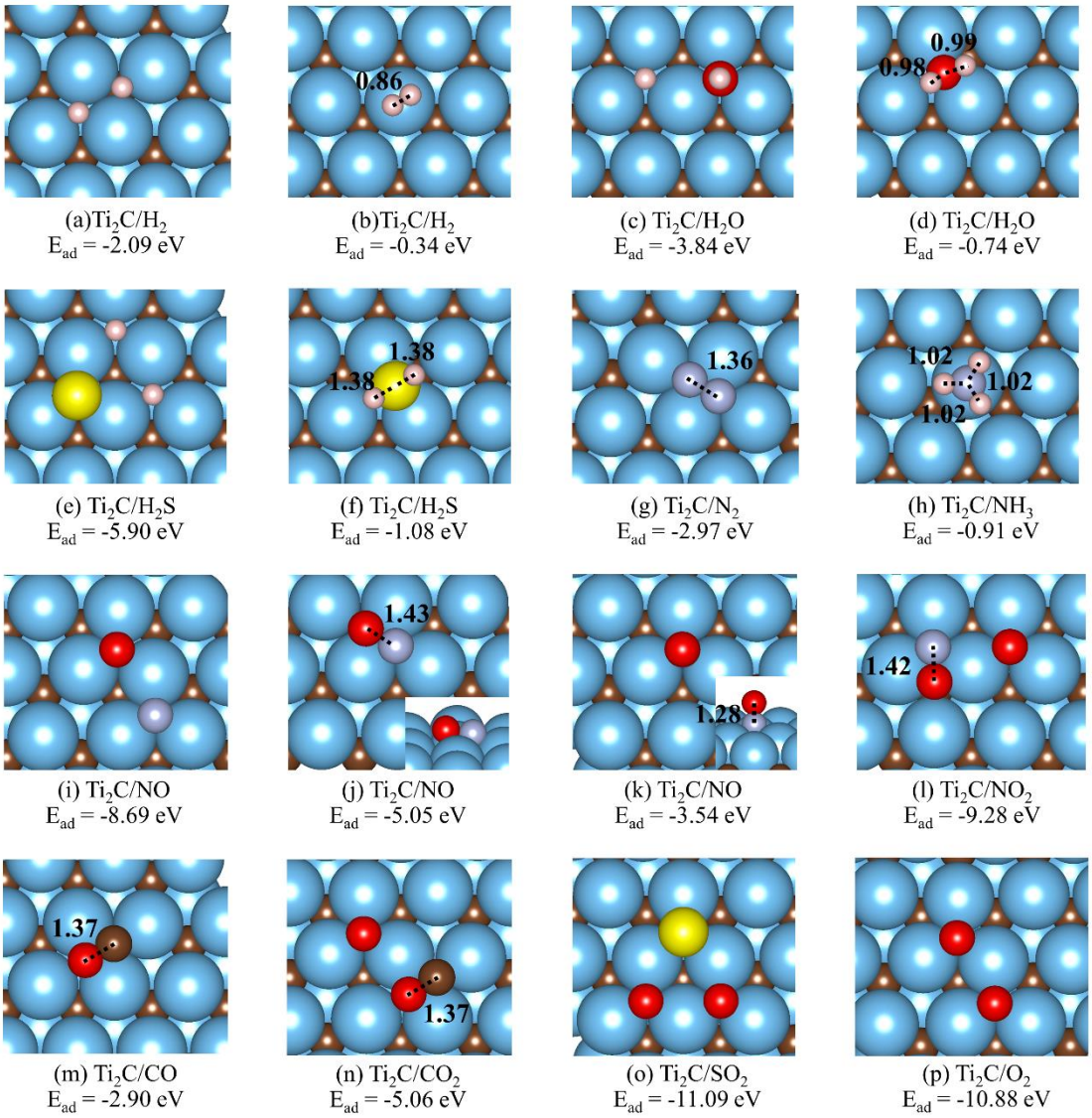
[a]*National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), 111 Thailand Science Park, Phahonyothin Road, Khlong Nueng, Khlong Luang, Pathum Thani 12120, Thailand*

[b]*Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843-3003, USA*

*E-mail: anchalee@nanotec.or.th Phone: +6625647100 ext. 6661

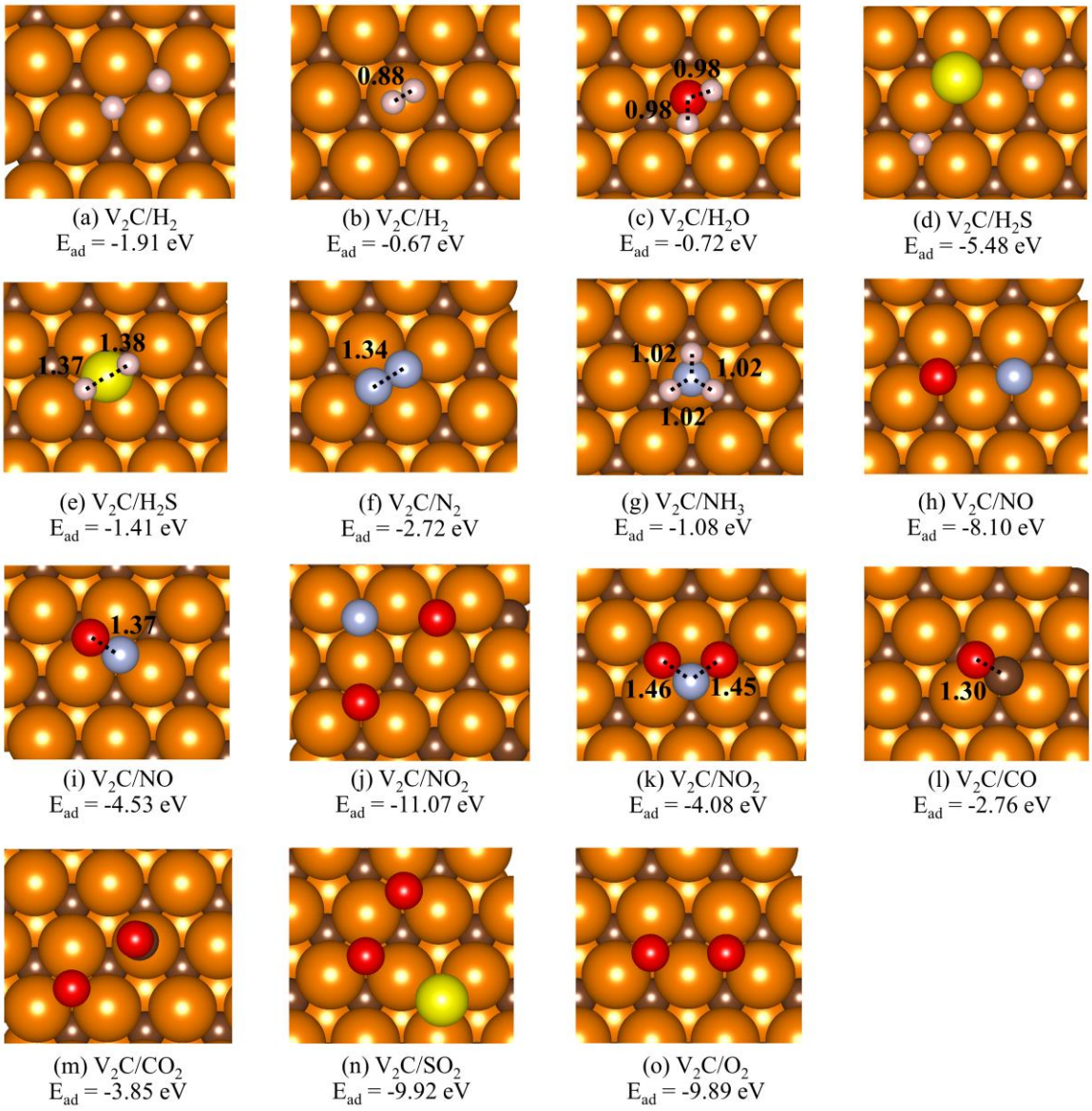
Table S1. Calculated E_{ad} (in eV/adsorbate) of gas adsorbed MXenes and O-MXenes

Gas	Ti_2C	Ti_2CO_2		V_2C	V_2CO_2		Nb_2C	Nb_2CO_2		Mo_2C	Mo_2CO_2	
	PBE	PBE	PBE-D3	PBE	PBE	PBE-D3	PBE	PBE	PBE-D3	PBE	PBE	PBE-D3
H_2	-2.09	-0.01	-0.07	-1.91	-0.01	-0.09	-1.91	-0.01	-0.06	-1.41	-0.01	-0.07
H_2O	-3.84	-0.04	-0.21	-0.72	-0.31	-0.45	-0.72	-0.05	-0.20	-0.73	-0.06	-0.21
H_2S	-5.90	-0.02	-0.24	-5.48	-0.31	-0.51	-5.57	-0.03	-0.24	-4.53	-0.16	-0.39
N_2	-2.97	0.00	-0.13	-2.72	-0.28	-0.36	-2.19	-0.01	-0.12	-1.40	-0.01	-0.12
NH_3	-0.91	-0.09	-0.37	-1.08	-0.33	-0.48	-1.07	-0.29	-0.50	-1.23	-0.20	-0.40
NO	-8.69	-0.10	-0.25	-8.10	-0.57	-0.73	-6.95	-0.07	-0.21	-3.43	-0.56	-0.80
NO_2	-9.28	-0.01	-0.17	-11.07	-0.02	-0.18	-10.15	-0.01	-0.18	-8.93	-0.08	-0.26
CO	-2.90	0.00	-0.13	-2.76	0.00	-0.14	-2.60	-0.01	-0.12	-2.21	0.00	-0.12
CO_2	-5.06	-0.01	-0.20	-3.85	-0.28	-0.36	-1.72	-0.02	-0.20	-1.15	-0.01	-0.21
SO_2	-11.09	-0.02	-0.26	-9.92	-0.03	-0.27	-10.08	-0.04	-0.29	-7.98	-0.03	-0.28
O_2	-10.88			-9.89			-9.83			-7.94		



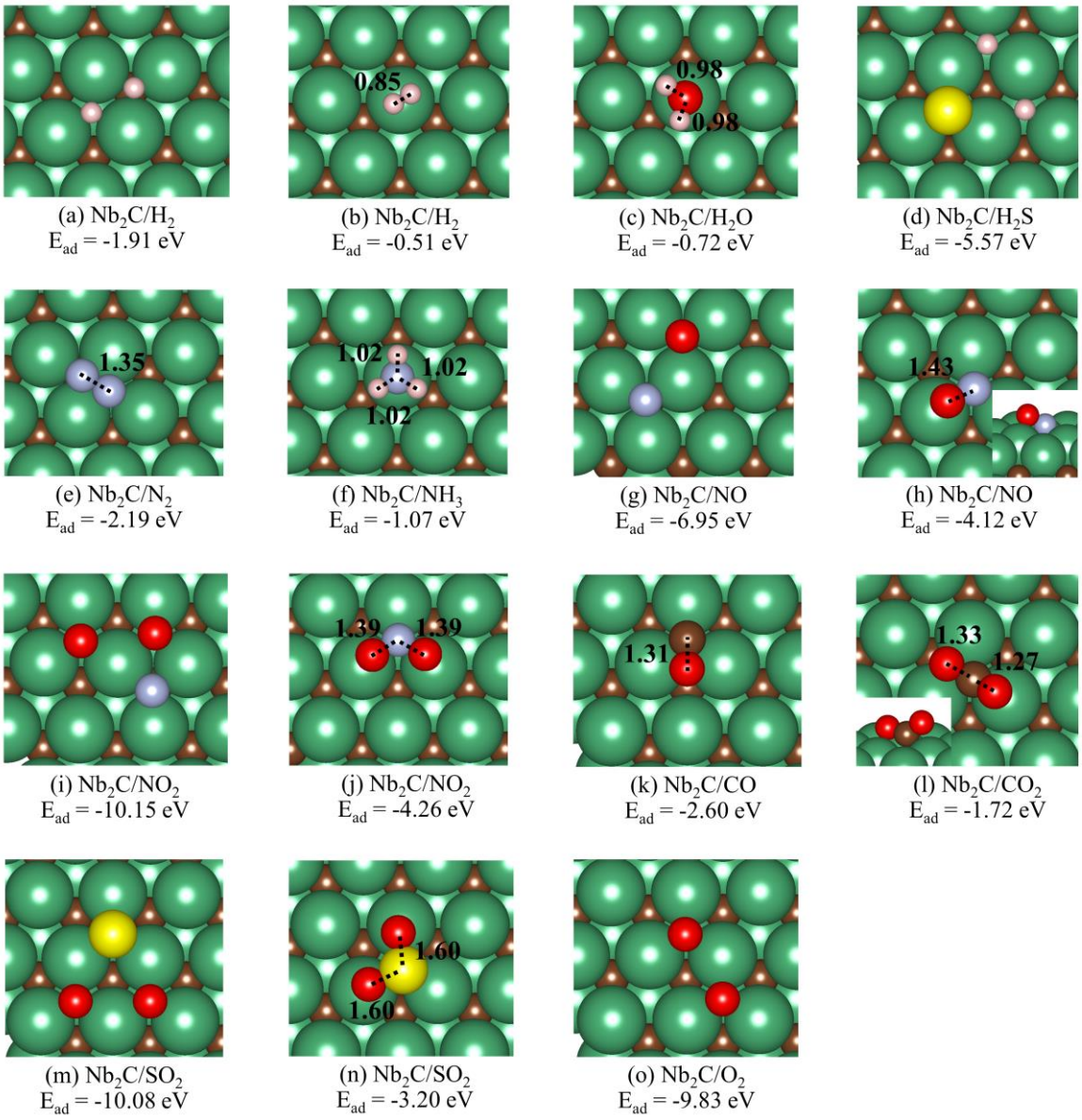
(a)Ti_2C/H_2 E_{ad} = -2.09 eV
(b)Ti_2C/H_2 E_{ad} = -0.34 eV
(c) Ti_2C/H_2O E_{ad} = -3.84 eV
(d) Ti_2C/H_2O E_{ad} = -0.74 eV
(e) Ti_2C/H_2S E_{ad} = -5.90 eV
(f) Ti_2C/H_2S E_{ad} = -1.08 eV
(g) Ti_2C/N_2 E_{ad} = -2.97 eV
(h) Ti_2C/NH_3 E_{ad} = -0.91 eV
(i) Ti_2C/NO E_{ad} = -8.69 eV
(j) Ti_2C/NO E_{ad} = -5.05 eV
(k) Ti_2C/NO E_{ad} = -3.54 eV
(l) Ti_2C/NO_2 E_{ad} = -9.28 eV
(m) Ti_2C/CO E_{ad} = -2.90 eV
(n) Ti_2C/CO_2 E_{ad} = -5.06 eV
(o) Ti_2C/SO_2 E_{ad} = -11.09 eV
(p) Ti_2C/O_2 E_{ad} = -10.88 eV

Fig. S1 The structures of gas adsorption on Ti_2C and E_{ad} calculated by PBE



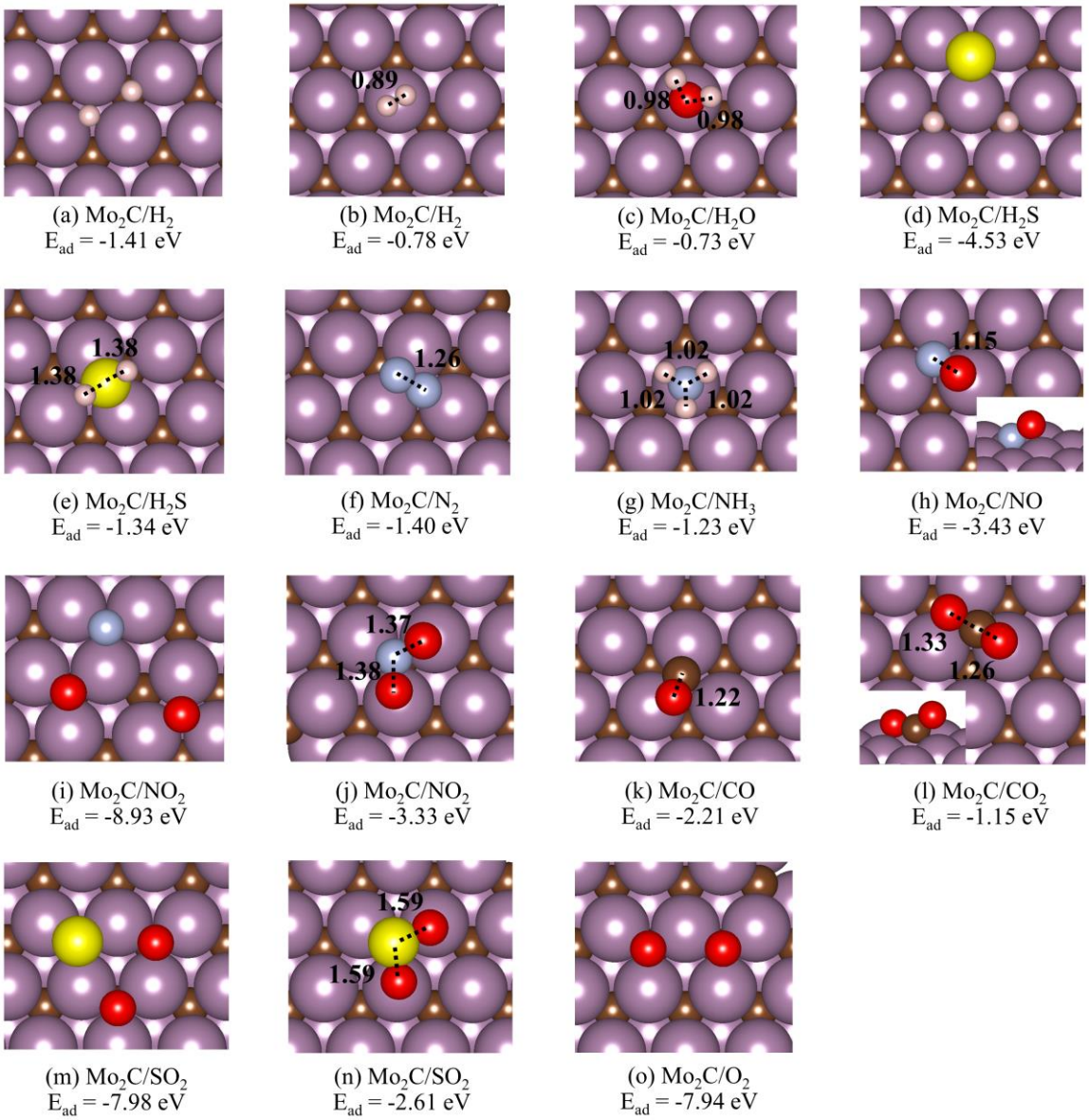
(a) V_2C/H_2 E_{ad} = -1.91 eV
(b) V_2C/H_2 E_{ad} = -0.67 eV
(c) V_2C/H_2O E_{ad} = -0.72 eV
(d) V_2C/H_2S E_{ad} = -5.48 eV
(e) V_2C/H_2S E_{ad} = -1.41 eV
(f) V_2C/N_2 E_{ad} = -2.72 eV
(g) V_2C/NH_3 E_{ad} = -1.08 eV
(h) V_2C/NO E_{ad} = -8.10 eV
(i) V_2C/NO E_{ad} = -4.53 eV
(j) V_2C/NO_2 E_{ad} = -11.07 eV
(k) V_2C/NO_2 E_{ad} = -4.08 eV
(l) V_2C/CO E_{ad} = -2.76 eV
(m) V_2C/CO_2 E_{ad} = -3.85 eV
(n) V_2C/SO_2 E_{ad} = -9.92 eV
(o) V_2C/O_2 E_{ad} = -9.89 eV

Fig. S2 The structures of gas adsorption on V_2C and E_{ad} calculated by PBE



(a) Nb_2C/H_2 E_{ad} = -1.91 eV
(b) Nb_2C/H_2 E_{ad} = -0.51 eV
(c) Nb_2C/H_2O E_{ad} = -0.72 eV
(d) Nb_2C/H_2S E_{ad} = -5.57 eV
(e) Nb_2C/N_2 E_{ad} = -2.19 eV
(f) Nb_2C/NH_3 E_{ad} = -1.07 eV
(g) Nb_2C/NO E_{ad} = -6.95 eV
(h) Nb_2C/NO E_{ad} = -4.12 eV
(i) Nb_2C/NO_2 E_{ad} = -10.15 eV
(j) Nb_2C/NO_2 E_{ad} = -4.26 eV
(k) Nb_2C/CO E_{ad} = -2.60 eV
(l) Nb_2C/CO_2 E_{ad} = -1.72 eV
(m) Nb_2C/SO_2 E_{ad} = -10.08 eV
(n) Nb_2C/SO_2 E_{ad} = -3.20 eV
(o) Nb_2C/O_2 E_{ad} = -9.83 eV

Fig. S3 The structures of gas adsorption on Nb_2C and E_{ad} calculated by PBE



(a) Mo_2C/H_2 E_{ad} = -1.41 eV
(b) Mo_2C/H_2 E_{ad} = -0.78 eV
(c) Mo_2C/H_2O E_{ad} = -0.73 eV
(d) Mo_2C/H_2S E_{ad} = -4.53 eV
(e) Mo_2C/H_2S E_{ad} = -1.34 eV
(f) Mo_2C/N_2 E_{ad} = -1.40 eV
(g) Mo_2C/NH_3 E_{ad} = -1.23 eV
(h) Mo_2C/NO E_{ad} = -3.43 eV
(i) Mo_2C/NO_2 E_{ad} = -8.93 eV
(j) Mo_2C/NO_2 E_{ad} = -3.33 eV
(k) Mo_2C/CO E_{ad} = -2.21 eV
(l) Mo_2C/CO_2 E_{ad} = -1.15 eV
(m) Mo_2C/SO_2 E_{ad} = -7.98 eV
(n) Mo_2C/SO_2 E_{ad} = -2.61 eV
(o) Mo_2C/O_2 E_{ad} = -7.94 eV

Fig. S4 The structures of gas adsorption on Mo_2C and E_{ad} calculated by PBE

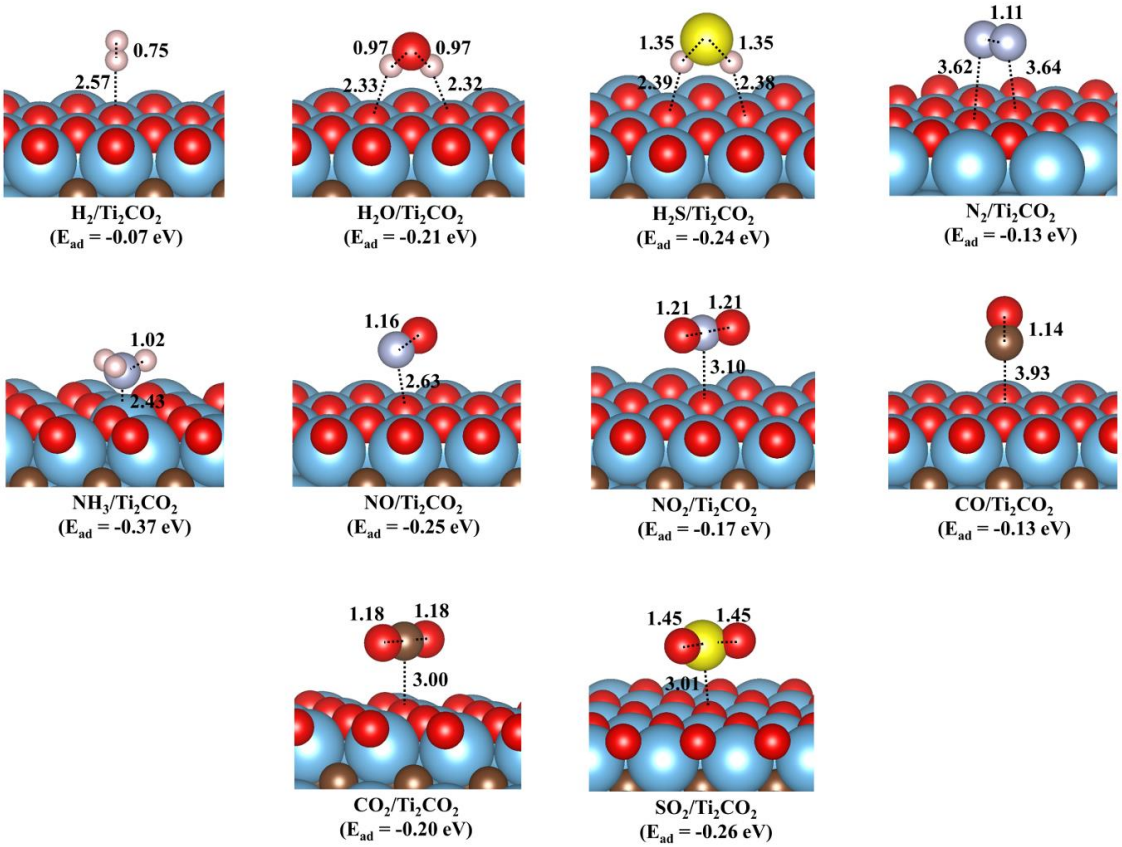


Fig. S5 The most preferable structures of gas on Ti_2CO_2 and E_{ad} calculated by PBE-D3

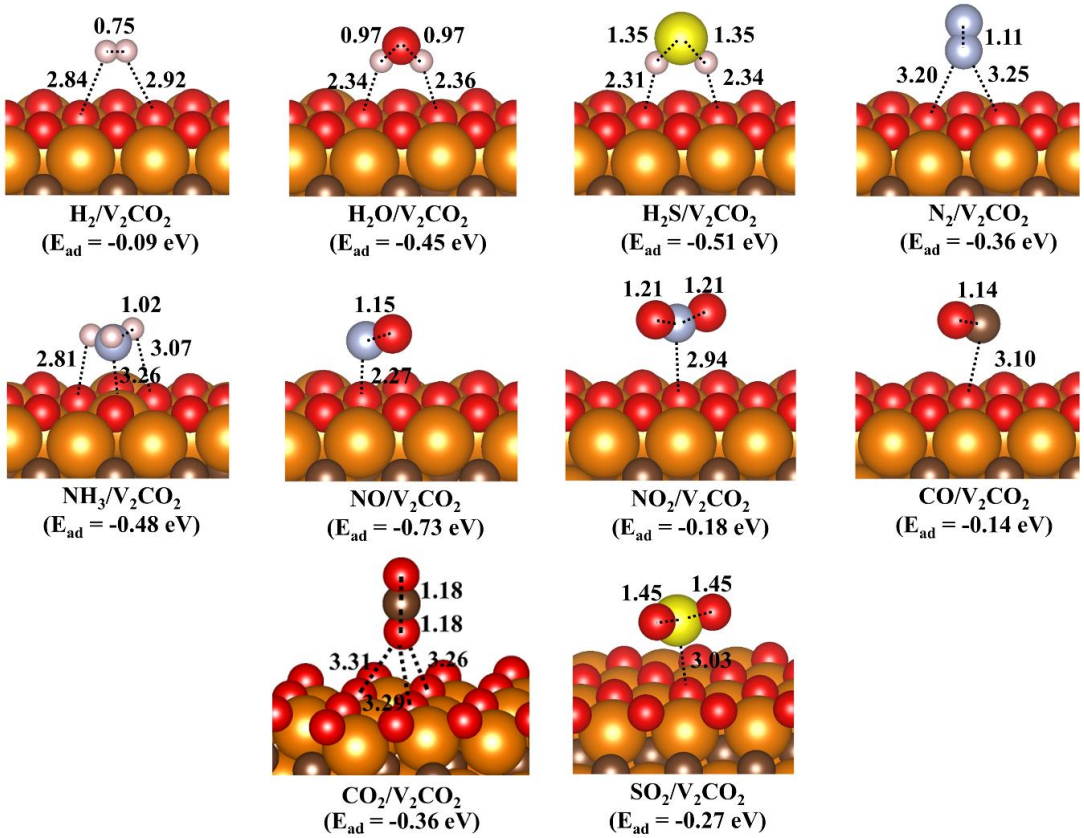


Fig. S6 The most preferable structures of gas on V_2CO_2 and E_{ad} calculated by PBE-D3

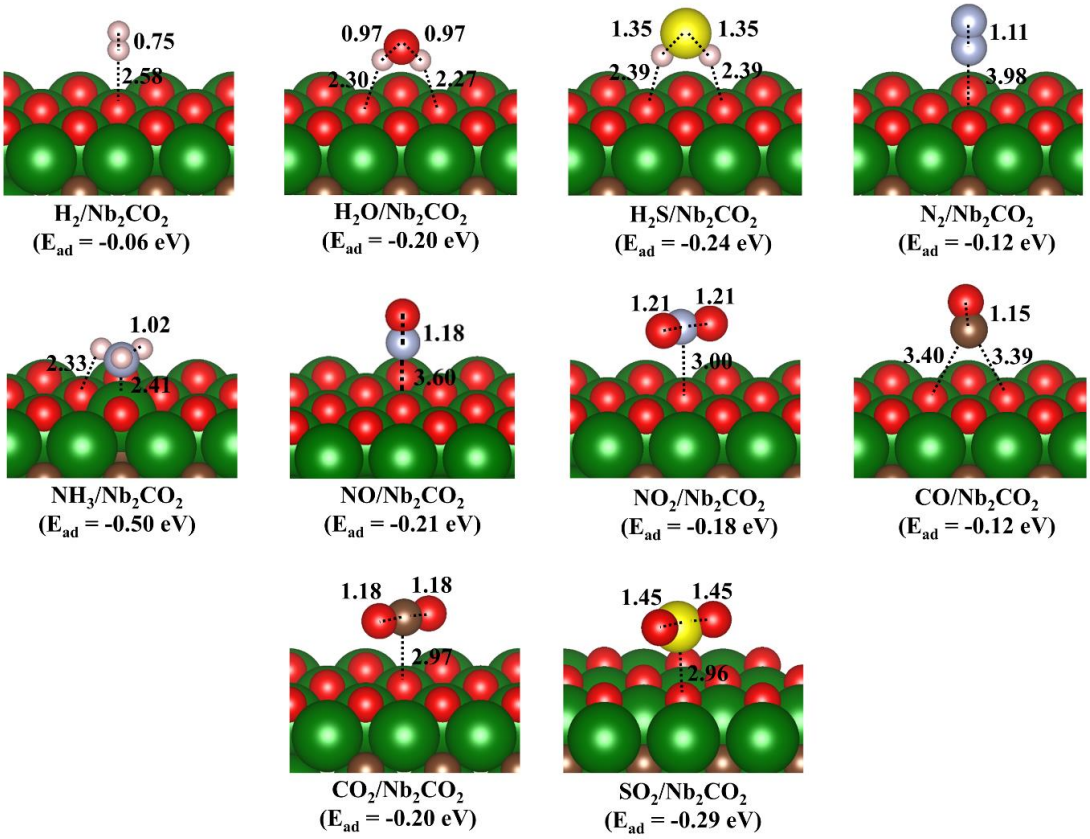


Fig. S7 The most preferable structures of gas on Nb_2CO_2 and E_{ad} calculated by PBE-D3

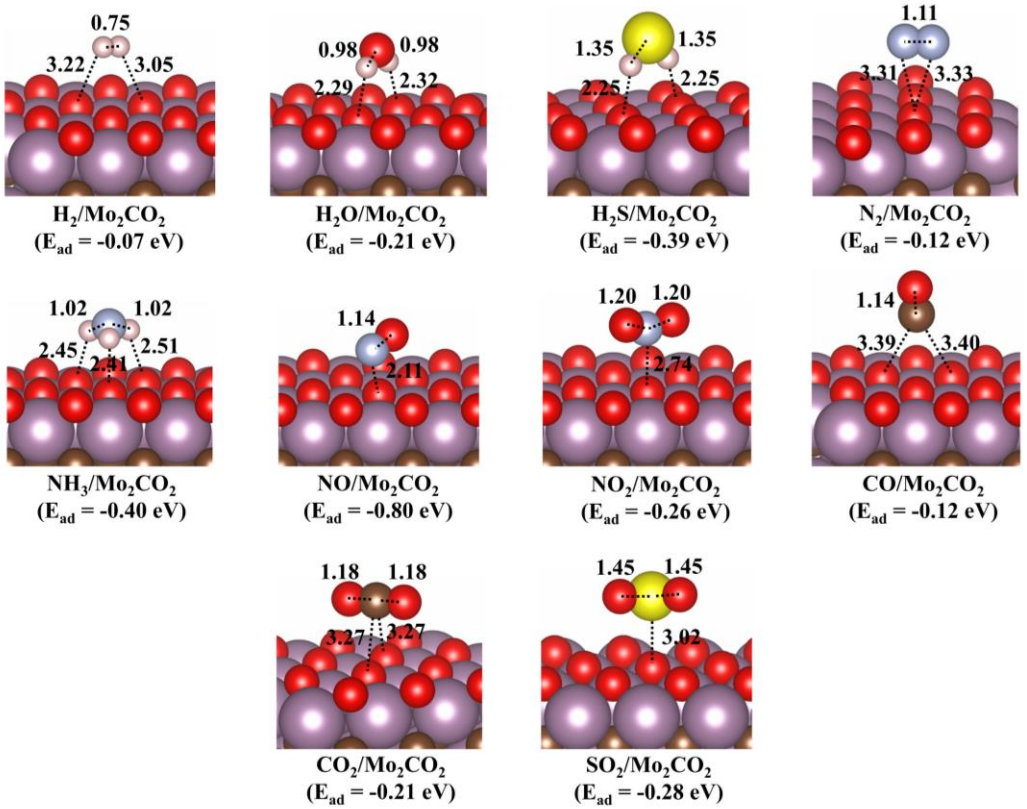


Fig. S8 The most preferable structures of gas on Mo_2CO_2 and E_{ad} calculated by PBE-D3

Table S2 E_{ad} in eV and atomic distance (r) in Å between atoms regarding Fig. S9 from PBE and PBE-D3 calculations. Prime (') represents an atom of O-MXene.

System	PBE			PBE-D3		
	E_{ad} (eV)	r (Å)		E_{ad} (eV)	r (Å)	
NH_3/Ti_2CO_2	-0.09	Ti'—N	2.46	-0.37	Ti'—N	2.43
		$O^{1'}$-H^1	3.38		$O^{1'}$-H^1	3.34
		$O^{2'}$-H^2	3.39		$O^{2'}$-H^2	3.34
		$O^{3'}$-H^3	3.38		$O^{3'}$-H^3	3.35
		Ti'-$O^{1'}$	1.94		Ti'-$O^{1'}$	1.95
		Ti'-$O^{2'}$	1.94		Ti'-$O^{2'}$	1.95
		Ti'-$O^{3'}$	1.94		Ti'-O^3	1.95
		Ti'-$C^{1'}$	2.38		Ti'-$C^{1'}$	2.36
		Ti'-$C^{2'}$	2.38		Ti'-$C^{2'}$	2.37
		Ti'-$C^{3'}$	2.38		Ti'-$C^{3'}$	2.36
		N-H (g)	1.02		N-H	1.02
NH_3/Nb_2CO_2	-0.29	Nb'—N	2.41	-0.50	Nb'—N	2.41
		$O^{1'}$-H^1	2.35		$O^{1'}$-H^1	2.34
		$O^{2'}$-H^2	2.35		$O^{2'}$-H^2	2.33
		$O^{3'}$-H^3	2.35		$O^{3'}$-H^3	2.33
		Nb'-O^1	1.98		Nb'-O^1	1.99
		Nb'-O^2	1.98		Nb'-O^2	1.99
		Nb'-O^3	1.98		Nb'-O^3	1.99
		Nb'-$C^{1'}$	2.43		Nb'-$C^{1'}$	2.42
		Nb'-$C^{2'}$	2.43		Nb'-$C^{2'}$	2.41
		Nb'-$C^{3'}$	2.43		Nb'-$C^{3'}$	2.42
		N-H (g)	1.02		N-H (g)	1.02
NO/V_2CO_2	-0.57	O'—N	2.31	-0.73	O'—N	2.27
		O'-$V^{1'}$	1.96		O'-$V^{1'}$	1.96
		O'-$V^{2'}$	2.01		O'-$V^{2'}$	2.02
		O'-$V^{3'}$	1.97		O'-$V^{3'}$	1.97
		$V^{1'}$-$C^{1'}$	1.99		$V^{1'}$-$C^{1'}$	2.00
		$V^{1'}$-$C^{2'}$	2.21		$V^{1'}$-$C^{2'}$	2.21
		$V^{2'}$-$C^{2'}$	1.97		$V^{2'}$-$C^{2'}$	1.97
		$V^{2'}$-$C^{3'}$	1.96		$V^{2'}$-$C^{3'}$	1.96
		$V^{3'}$-$C^{3'}$	2.19		$V^{3'}$-$C^{3'}$	2.18
		$V^{3'}$-$C^{1'}$	1.99		$V^{3'}$-$C^{1'}$	1.98
		N-O (g)	1.15		N-O (g)	1.15
NO/Mo_2CO_2	-0.56	O'—N	2.02	-0.80	O'—N	2.11
		O'-Mo^1	2.09		O'-Mo^1	2.08
		O'-Mo^2	2.15		O'-Mo^2	2.08
		O'-Mo^3	2.09		O'-Mo^3	2.08
		Mo^1-$C^{1'}$	2.16		Mo^1-$C^{1'}$	2.16
		Mo^2-$C^{1'}$	2.16		Mo^2-$C^{1'}$	2.16
		Mo^3-$C^{1'}$	2.16		Mo^3-$C^{1'}$	2.16
		N-O(g)	1.14		N-O	1.14

NH_3(g)		N-H (g)	1.02		N-H (g)	1.02
NO (g)		N-O (g)	1.17		N-O (g)	1.17

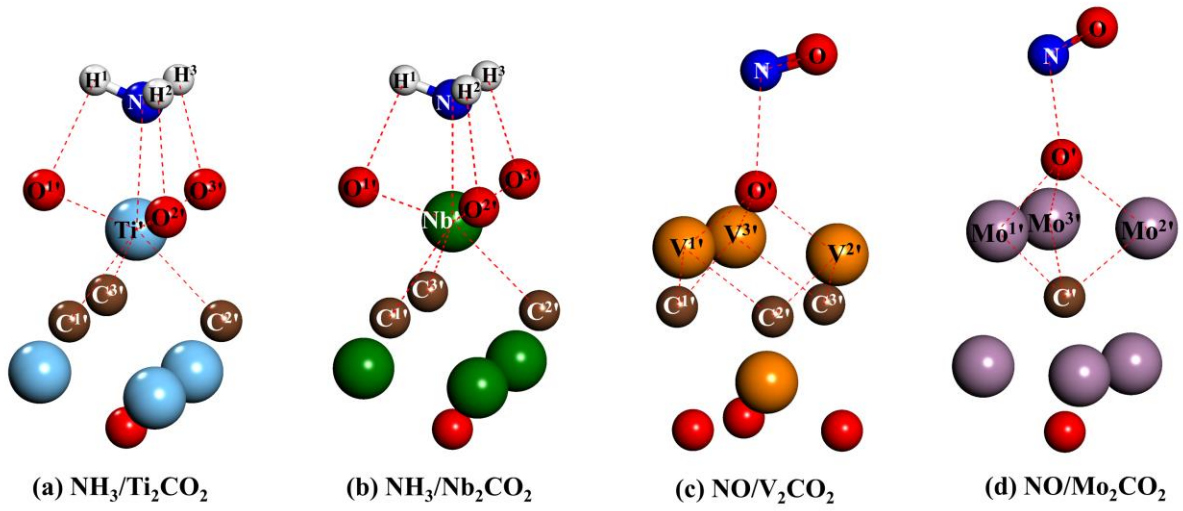


Fig. S9 Structures of (a) NH_3/Ti_2CO_2, (b) NH_3/Ti_2CO_2, (c) NO/V_2CO_2 and (d) NO/Mo_2CO_2

Table S3. The calculated E_{ad} difference (ΔE_{ad}) in eV between the results from PBE and PBE-D3 calculations. Each atomic distance difference (Δr) in Å is selected from the closest interacting points between a substrate and an adsorbate, where prime (') represents an atom of O-MXene.

Gas	Ti_2CO_2			Nb_2CO_2			V_2CO_2			Mo_2CO_2		
	ΔE_{ad} (eV)	bond	Δr (Å)	ΔE_{ad} (eV)	bond	Δr (Å)	ΔE_{ad} (eV)	bond	Δr (Å)	ΔE_{ad} (eV)	bond	Δr (Å)
H_2	-0.07	O'-H	-0.12	-0.06	O'-H	0.00	-0.08	O'-H	-0.21	-0.06	O'-H	-0.03
H_2O	-0.17	O'-H	-0.03	-0.15	O'-H	0.00	-0.14	O'-H	-0.01	-0.16	O'-H	-0.01
H_2S	-0.22	O'-H	-0.36	-0.21	O1'-H	-0.12	-0.19	O'-H	-0.36	-0.23	O'-H	-0.16
NH_3	-0.27	O'-H* (Ti'-N)**	-0.05 (-0.03)	-0.21	O'-H* (Nb'-N)**	-0.02 (-0.00)	-0.15	O'-H* (V'-N)**	-0.25 (-0.20)	-0.20	O'-H*	-0.14
N_2	-0.12	O'-N	-0.04	-0.11	O'-N	-0.02	-0.08	O'-N	-0.27	-0.12	O'-N	-0.04
NO	-0.14	O'-N	-0.02	-0.14	O'-N	0.00	-0.15	O'-N	0.06	-0.24	O'-N	0.09
NO_2	-0.15	O'-N	-0.04	-0.17	O'-N	0.00	-0.16	O'-N	-0.02	-0.19	O'-N	-0.02
CO	-0.12	O'-C	0.00	-0.11	O'-C	0.00	-0.14	O'-C	-0.01	-0.12	O'-C	0.00
CO_2	-0.19	O'-C	0.00	-0.19	O'-C	0.00	-0.08	O'-O	-0.00	-0.20	O'-O	-0.01
SO_2	-0.24	O'-S	-0.10	-0.25	O'-S	-0.12	-0.23	O'-S	-0.16	-0.25	O'-S	-0.19

*Δr of H of NH_3 and a metal atom of a substrate **Δr of N of NH_3 and a metal atom of a substrate