Electronic Supplementary Information for

Functionalized MXenes for efficient electrocatalytic nitrate reduction to ammonia

Tao Hu,[†a] Mengting Wang,[†a] Chunxian Guo,[*a] and Chang Ming Li[*a,b]

a. Institute of Materials Science and Devices, School of Materials Science and Engineering, Suzhou University of Science and Technology, Suzhou 215009, China

b. Institute for Cross-field Science and College of Life Science, Qingdao University, Qingdao 200671, China

† These authors contributed equally. Email: cxguo@usts.edu.cn; cmli@usts.edu.cn.

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Part I Calculation Details

Table S1. Potential NRA pathways on MXene and the elementary steps

NRA1: NO_3^-→*NO_3→*NO_2→*NO→*N→*NH→*NH_2→*NH_3→NH_3(g)			
*+NO_3^-(l) → *NO_3+e^-	(r1)		
*NO_3 + $2H^+$ + $2e^-$ → *NO_2 + H_2O	(r2)	*NO_3→*NO_2+*O	(r2')
*NO_2 + $2H^+$ + $2e^-$ → *NO + H_2O	(r3)	*NO_2→*NO+*O	(r3')
*NO + $2H^+$ +$2e^-$ → *N + H_2O	(r4)	*NO→*N+*O	(r4')
*N + H^+ + e^- → *NH	(r5)	*N+*H→*NH	(r5')
*NH + H^+ + e^- → *NH_2	(r6)	*NH+*H→*NH_2	(r6')
*NH_2 + H^+ + e^- → *NH_3	(r7)	*NH_2+*H→*NH_2	(r7')
*NH_3 → * + NH_3	(r8)		
Total: r1→r2→r3→r4→r5→r6→r7→r8 NO_3^- + $9H^+$ + $8e^-$ → NH_3+ $3H_2O$			
NRA2: NO_3^-→*NO_3^-→*NO_2→*NO→*NOH →*NHOH→*NH→*NH_3→NH_3(g)			
*NO + H^+ +e^- → *NOH	(r9)	*NO+*H→*NOH	(r9')
*NOH + H^+ +e^- → *NHOH	(r10)	*NOH+*H→*NHOH	(r10')
*NHOH + H^+ +e^- → *NH+H_2O	(r11)	*NHOH+*H→*NH+H_2O	(r11')
Total: r1→r2→r3→r9→r10→r11→r6→r7→r8 NO_3^- + $9H^+$ + $8e^-$ → NH_3+ $3H_2O$			
NRA3: NO_3^-→*NO_3^-→*NO_2→*NO→*NOH→*NHOH→*NH_2OH→*NH_2→*NH_3→NH_3(g)			
*NHOH + H^+ +e^- → *NH_2OH	(r12)	*NHOH+*H→*NH_2OH	(r12')

$*NH_2OH + H^+ + e^- \rightarrow *NH_2 + H_2O$ (r13)	$*NH_2OH + *H \rightarrow *NH_2 + H_2O$ (r13')

Total : r1→r2→r3→r9→r10→r12→r13→r7→r8

$NO_3^- + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O$

Equations *r*1, *r*2, *r*3, *r*4, *r*5, *r*6, *r*7, *r*8, r9, r10, r11, r12, r13 were used for thermodynamics calculation. Equations *r*2', *r*3', *r*4', *r*5', *r*6', *r*7', r9', r10', r11', r12', r13' were used to calculate kinetics.

Table S2. NRA1 reaction steps and pH correction to Gibbs free energy

NRA1: $NO_3^- \rightarrow *NO_3^- \rightarrow *NO_2 \rightarrow *NO \rightarrow *N \rightarrow *NH \rightarrow *NH_2 \rightarrow *NH_3 \rightarrow NH_3(g)$

$* + NO_3^-(l) \rightarrow *NO_3 + e^-$ (r1)	$\Delta G_1 = \Delta G_1^0$
$*NO_3 + 2H^+ + 2e^- \rightarrow *NO_2 + H_2O$ (r2)	$\Delta G_2 = \Delta G_2^0 + 2k_B T \ln 10 \times pH$
$*NO_2 + 2H^+ + 2e^- \rightarrow *NO + H_2O$ (r3)	$\Delta G_3 = \Delta G_3^0 + 2k_B T \ln 10 \times pH$
$*NO + 2H^+ + 2e^- \rightarrow *N + H_2O$ (r4)	$\Delta G_4 = \Delta G_4^0 + 2k_B T \ln 10 \times pH$
$*N + H^+ + e^- \rightarrow *NH$ (r5)	$\Delta G_5 = \Delta G_5^0 + k_B T \ln 10 \times pH$
$*NH + H^+ + e^- \rightarrow *NH_2$ (r6)	$\Delta G_6 = \Delta G_6^0 + k_B T \ln 10 \times pH$
$*NH_2 + H^+ + e^- \rightarrow *NH_3$ (r7)	$\Delta G_7 = \Delta G_7^0 + k_B T \ln 10 \times pH$
$*NH_3 \rightarrow * + NH_3$ (r8)	$\Delta G_8 = \Delta G_8^0$

The elementary steps of competing hydrogen evolution reactions are described as:

$$* + H^+ \rightarrow *H \text{ (Volmer step)} \quad \text{(r14)}$$

$$*H + H^+ + e^- \rightarrow * + H_2 \text{ (Heyrovsky step)} \quad \text{(r15)}$$

$$2*H \rightarrow * + H_2 \text{ (Tafel step)} \quad \text{(r16)}$$

For Volmer-Heyrovsky process:

$$\Delta G = \Delta G_{max}^0 + k_B T \ln 10 \times pH$$

For Volmer-Tafel process:

$$\Delta G = 2\Delta G_{max}^0 + 2k_B T \ln 10 \times pH$$

Note that the ΔG_{max}^{0} is the maximum value of *H adsorption or desorption.

Part II Supplementary Tables and Figures

Table S3. Corrections of entropic contribution of gas for H_2O, H_2 and NH_3 used in the Gibbs free energy calculations

Species	TΔS (eV)	Literature(eV)
H_2	0.40	0.41[a]
H_2O(0.035bar)	0.67	0.67[a]
NH_3	0.60	0.60[b]

a Data from Norskov's work[1]

b Data from Lange's handbook,[2]Table 1.56, Page 1.238, TΔS (NH_3)=192.78 $Jdeg^{-1}mol^{-1}$ × 298.15 K = 0.60 eV

Table S4. The correction of zero-point energy of adsorption species and molecules involved in NRA reaction.

Species	ΔZPE (eV)	Literature(eV)[3]
*NO_3	0.39	0.42
*NO_2	0.22	0.28
*NO	0.16	0.17
*N	0.09	0.08
*NH	0.36	0.38
*NH_2	0.61	0.69
*NH_3	0.95	1.00
*H	0.17	0.17
H_2	0.28	0.27
H_2O	0.58	0.57
NH_3	0.93	0.91
HNO_3	0.70	-
*NOH	0.45	0.45
*NHOH	0.72	0.79

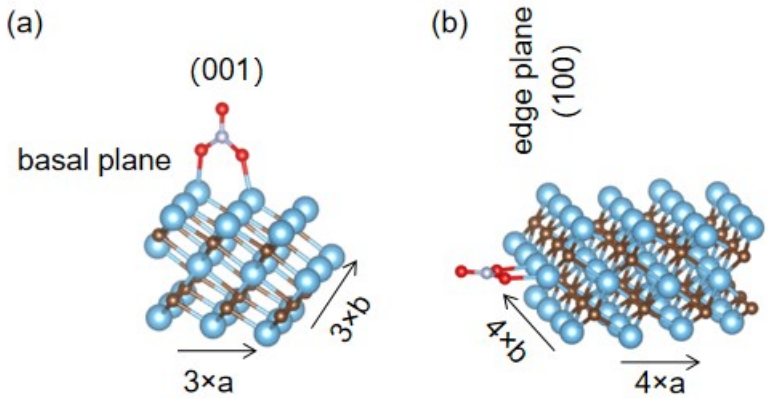

Fig. S1 Schematic of Ti_3C_2 basal plane and edge plane models used in the study.

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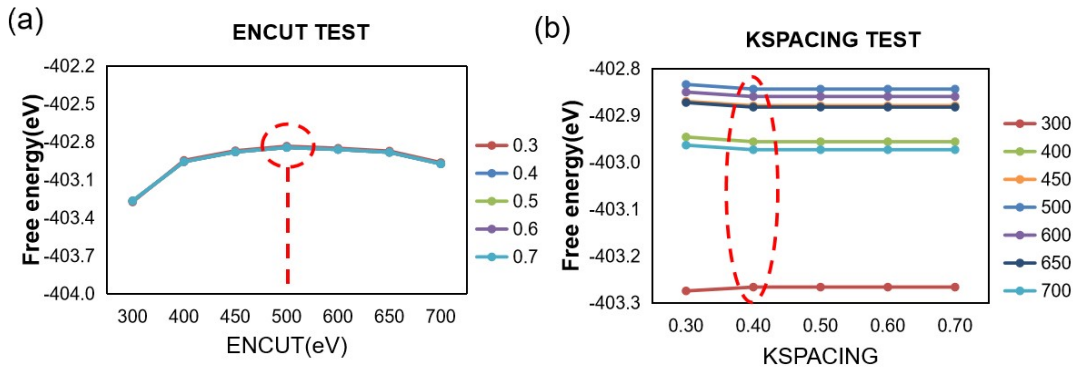

Fig. S2 (a) ENCUT test on Ti_3C_2, KSPACING is set to 0.3, 0.4, 0.5, 0.6, 0.7 $Å^{-1}$. The free energies at varied KSPACING are close. (b) KSPACING test on Ti_3C_2, ENCUT is set to 300, 400, 450, 500, 600, 650, 700 eV.

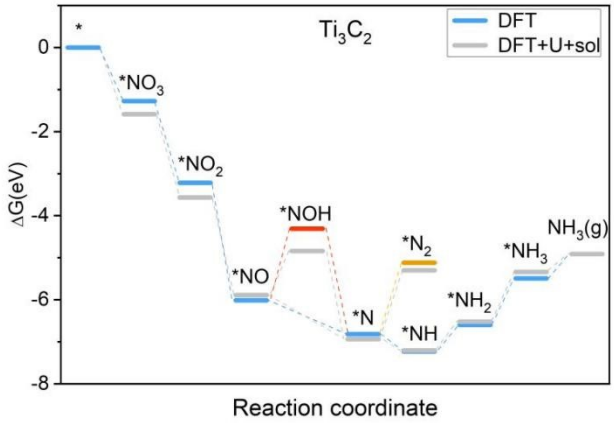

Fig. S3 Gibbs free energy diagram of NRA on Ti_3C_2 MXene calculated by DFT and DFT+U+sol. Though free energy change (ΔG) in each reaction step changes, the trend and RDS are same. NRA1: NO_3^- → $*NO_3$→ $*NO_2$ → *NO → *N → *NH → $*NH_2$ → $*NH_3$ → NH_3(g) is the most favorable reaction pathway, and RDS is still $*NH_2$ → $*NH_3$.

Table S5. Comparison of total energy calculated by DFT and DFT+U+sol

Substrate	DFT (eV)	DFT+U+sol (eV)	ΔE_{value} (eV)
Ti_3C_2	-402.98	-329.47	73.51
*NO_3	-430.69	-357.49	73.20
*NO_2	-425.04	-351.88	73.16
*NO	-420.35	-346.71	73.63
*N	-413.66	-340.27	73.39
*NH	-417.78	-344.25	73.53
*NH_2	-420.84	-347.25	73.59
*NH_3	-423.51	-349.85	73.66
*H	-407.51	-333.97	73.54
Mo_3C_2	-453.14	-354.93	98.21
*NO_3	-480.52	-381.40	99.12
*NO_2	-474.92	-375.68	99.24
*NO	-468.52	-368.78	99.74
*N	-463.22	-363.37	99.85
*NH	-467.19	-367.21	99.98
*NH_2	-470.71	-371.57	99.14
*NH_3	-474.25	-374.96	99.29
*H	-456.93	-358.23	98.71
V_3C_2	-419.30	-332.57	86.73
*NO_3	-446.65	-360.34	86.31
*NO_2	-441.10	-354.35	86.74
*NO	-435.77	-348.27	87.50
*N	-429.57	-342.74	86.82
*NH	-433.46	-346.78	86.68
*NH_2	-436.70	-349.80	86.89

*NH_3	-439.98	-353.10	86.88
*H	-422.52	-336.37	86.15
Cr_3C_2	-413.03	-345.07	67.96
*NO_3	-440.54	-374.04	66.50
*NO_2	-434.98	-367.73	67.25
*NO	-428.73	-362.30	66.43
*N	-422.97	-356.16	66.81
*NH	-427.20	-359.63	67.57
*NH_2	-430.48	-363.31	67.16
*NH_3	-433.97	-366.05	67.91
*H	-416.79	-349.94	66.85
Nb_3C_2	-454.72	-389.66	65.06
*NO_3	-482.22	-417.73	64.49
*NO_2	-476.67	-412.06	64.60
*NO	-471.61	-406.78	64.82
*N	-465.34	-400.62	64.72
*NH	-469.23	-404.27	64.96
*NH_2	-472.48	-407.45	65.03
*NH_3	-475.63	-410.54	65.10
*H	-458.13	-393.41	64.72

ΔE_{value} is the difference between total energies calculated by the two methods. For each substrate, the total energy values of different intermediates all shift to positive direction after considering U and solvation effect.

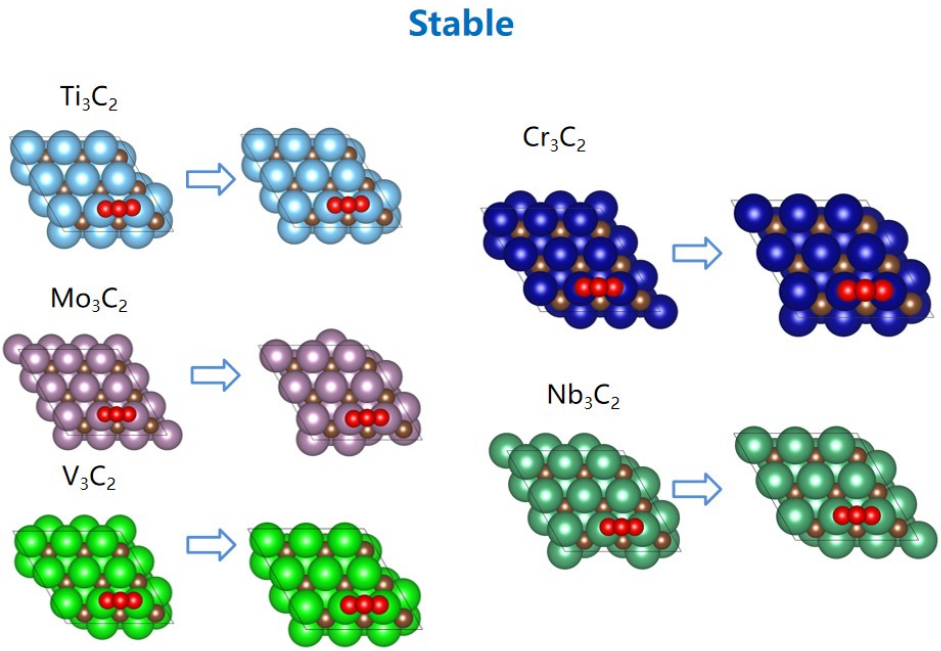

Fig. S4 Atomic structure of *NO_3 (* = M_3C_2, M=Ti, Mo, V, Cr, Nb) before and after optimization.

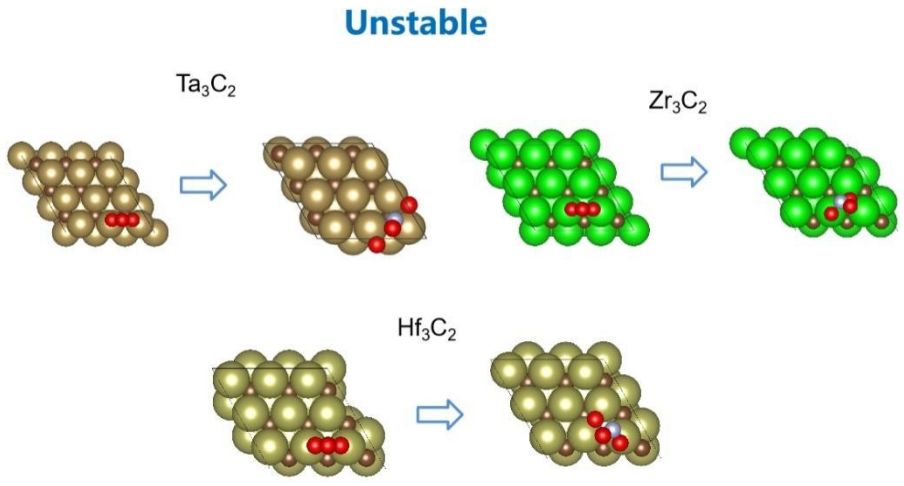

Fig. S5 The atomic structure of *NO_3 (*= M_3C_2, M=Ta, Zr, Hf) before and after optimization.

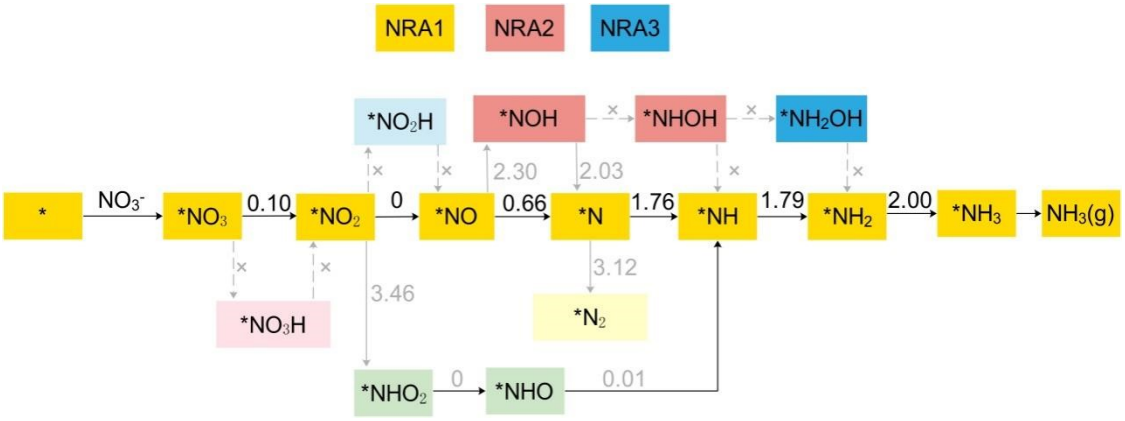

Fig. S6 The overview of reaction kinetics along different NRA pathways on pristine Ti_3C_2. "×" means that this intermediate decomposes on Ti_3C_2. The activation energy of each elementary step is given in eV.

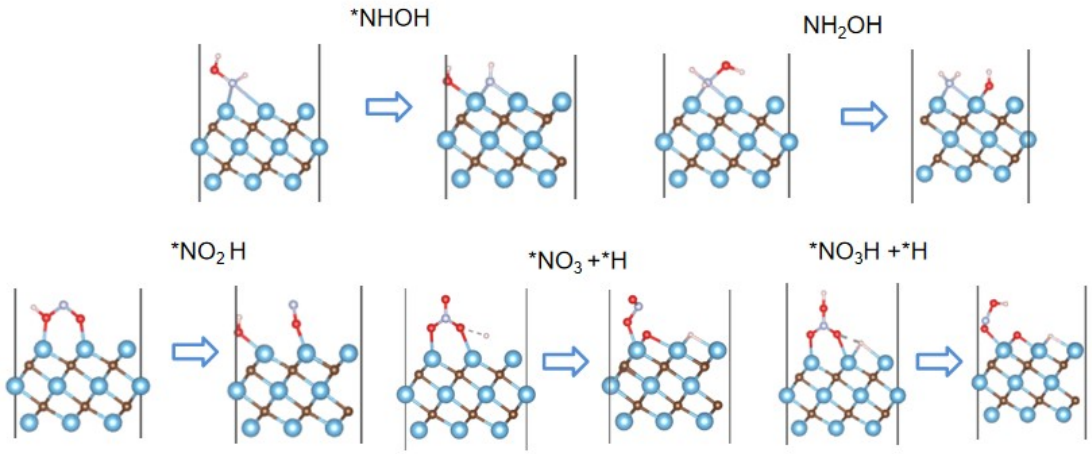

Fig. S7 Geometry of *NHOH, *NH_2OH, *NO_2H, *NO_3+*H and *NO_3H+*H on Ti_3C_2 before and after optimization.

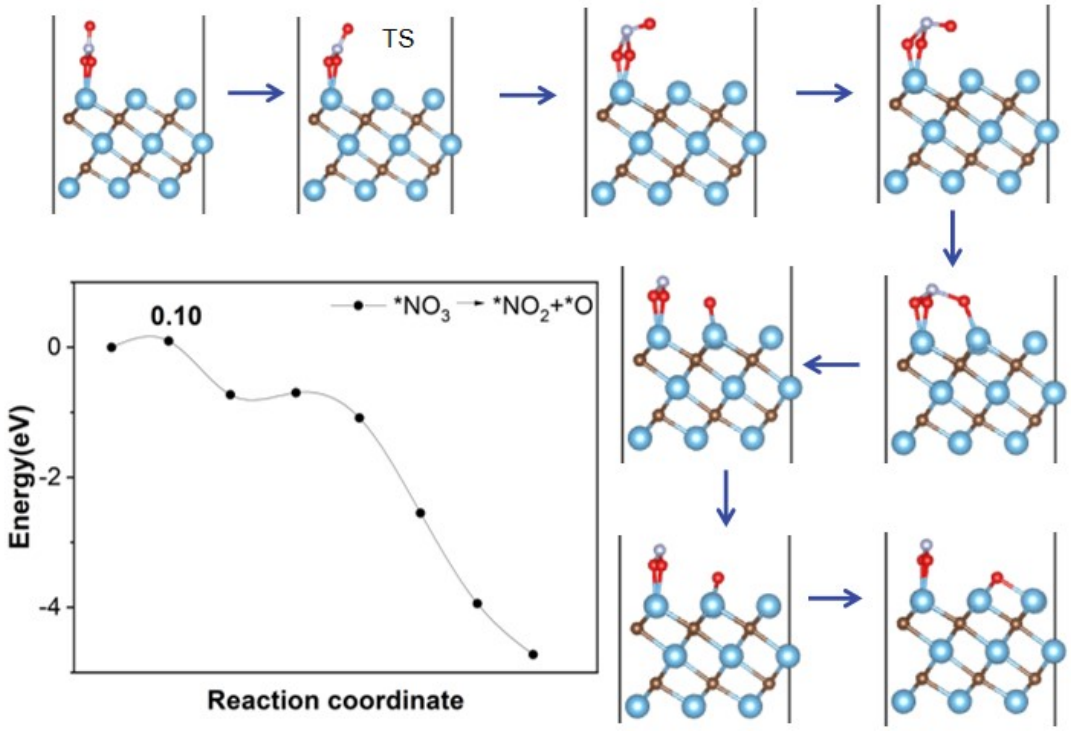

Fig. S8 Minimum energy path and activation barrier of elementary step $*NO_3 \rightarrow *NO_2 + *O$. TS stands for transition state.

Table S6. Calculated frequencies of TS in reaction $*NO_3 \rightarrow *NO_2 + *O$. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	189.98 meV
2f =	132.84 meV
3f =	112.08 meV
4f =	88.36 meV
5f =	79.46 meV
6f =	64.10 meV
7f =	34.89 meV
8f =	28.53 meV
9f =	19.97 meV
10f =	12.21 meV
11f =	1.62 meV
12f/i =	-6.24 meV

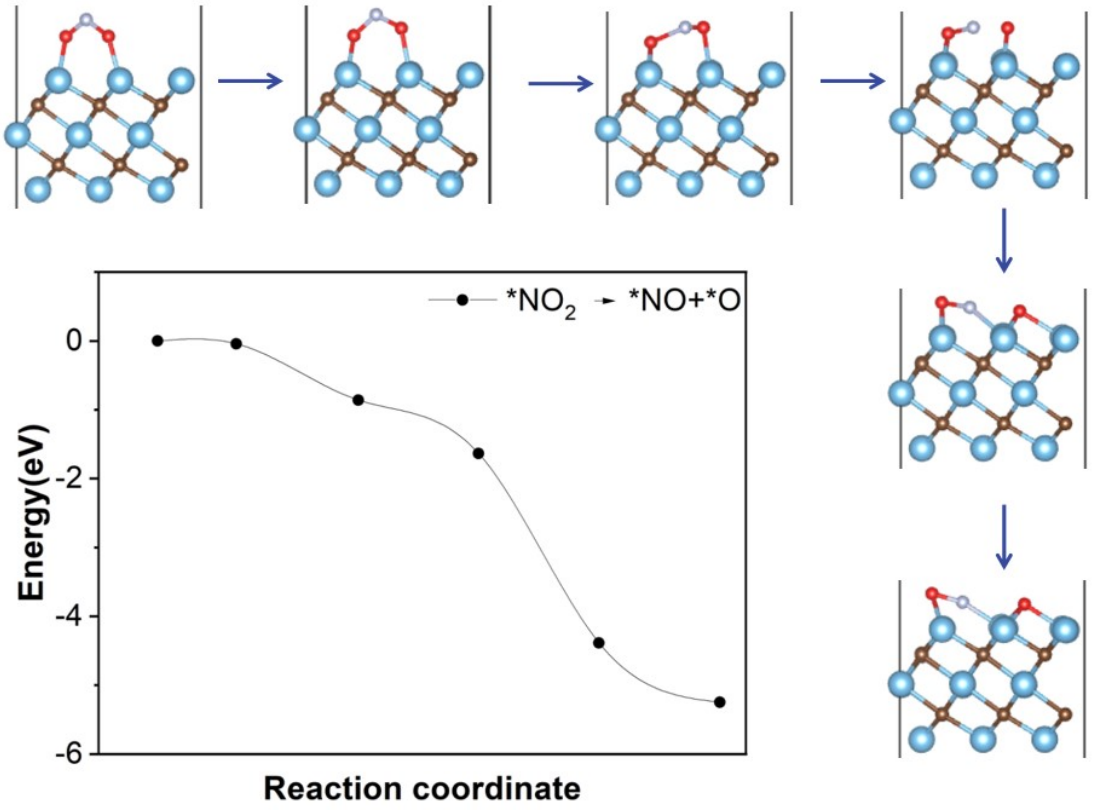

Fig. S9 Minimum energy path of elementary step $*NO_2 \rightarrow *NO+*O$. This step proceeds without barrier.

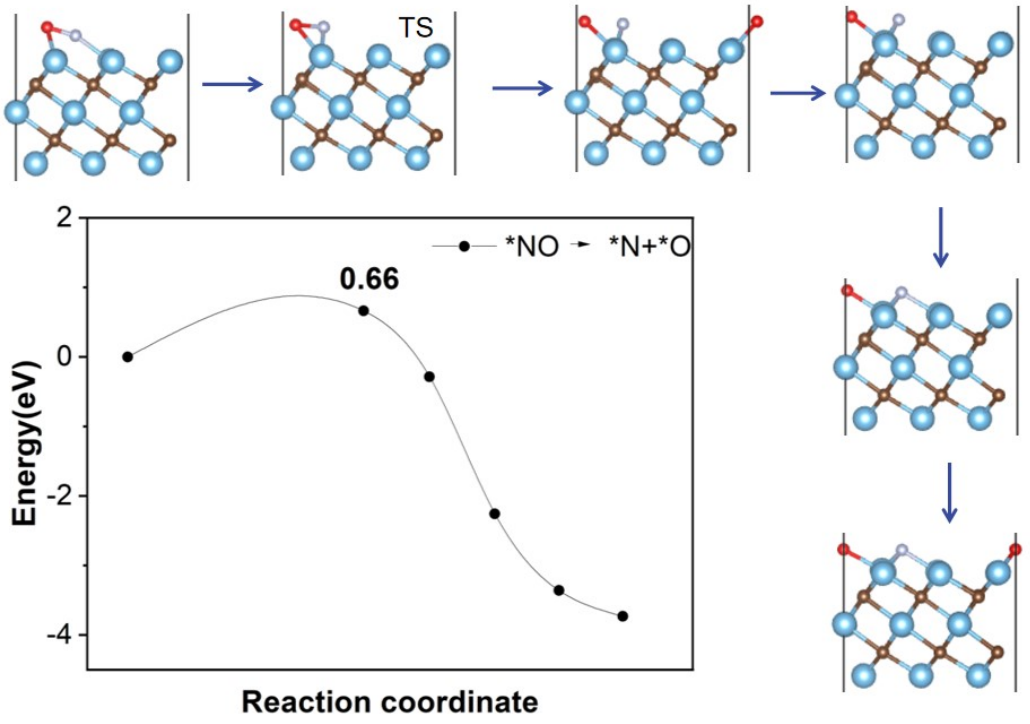

Fig. S10 Minimum energy path and activation barrier of elementary step *NO→*N+*O. TS stands for transition state.

Table S7. Calculated frequencies of TS in reaction *NO→*N+*O. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	79.90 meV
2f =	58.94 meV
3f =	51.04 meV
4f =	39.40 meV
5f =	32.24 meV
6f/i =	-1.69 meV

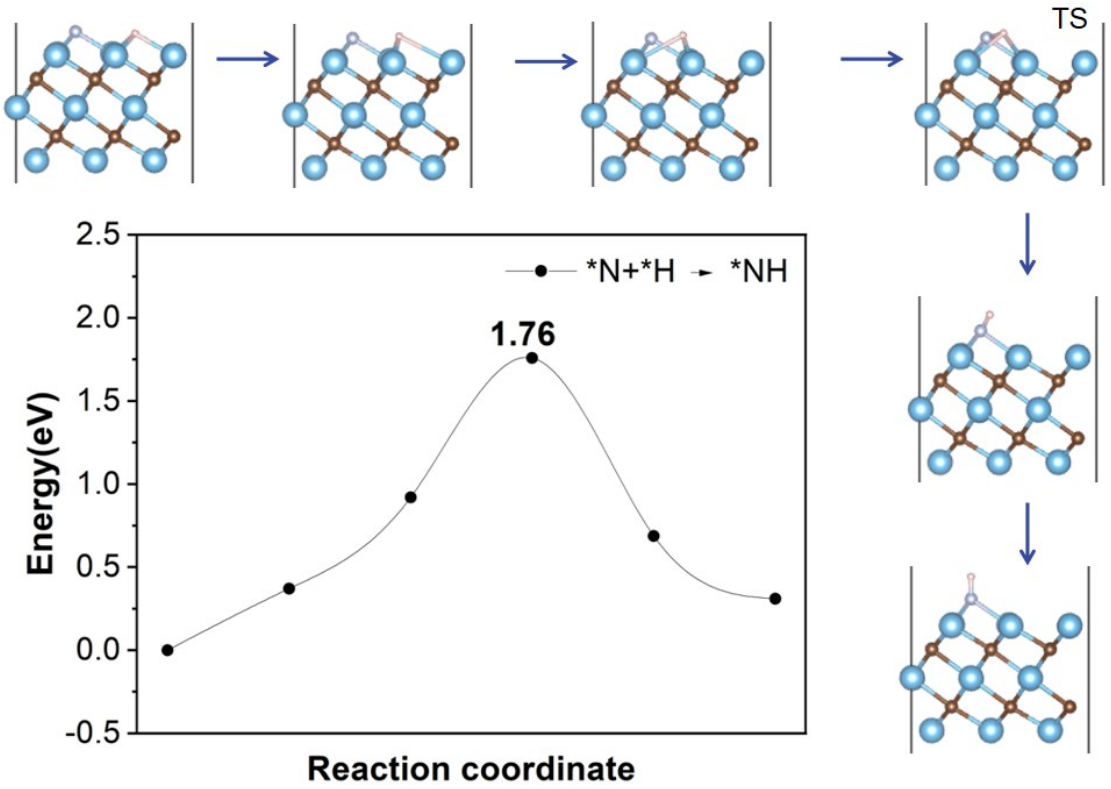

Fig. S11 Minimum energy path and activation barrier of elementary step *N+*H→*NH. TS stands for transition state.

Table S8. Calculated frequencies of TS in reaction *N+*H→*NH. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	130.81 meV

2f =	78.84 meV
3f =	63.43 meV
4f =	49.81 meV
5f =	47.36 meV
6f/i =	-169.25 meV

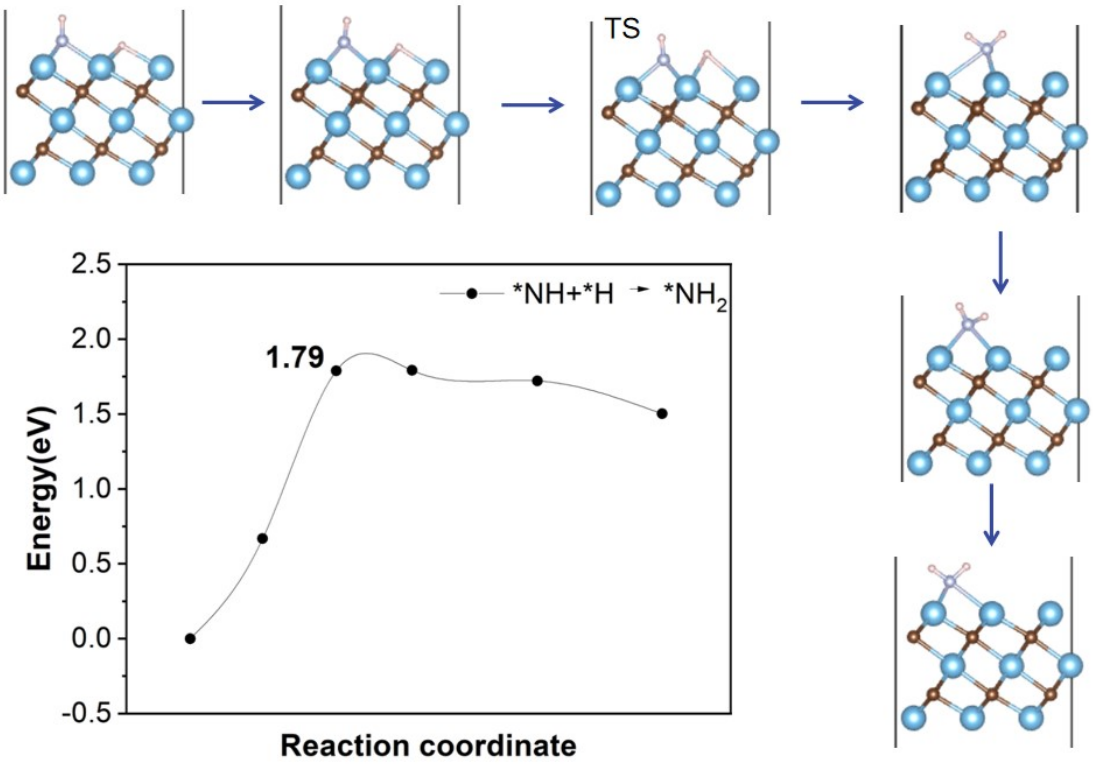

Fig. S12 Minimum energy path and activation barrier of elementary step *NH+*H→*NH_2. TS stands for transition state.

Table S9. Calculated frequencies of TS in reaction *NH+*H→*NH_2. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	457.02 meV
2f =	394.10 meV
3f =	188.98 meV
4f =	81.29 meV
5f =	50.59 meV

6f =	41.34 meV
7f =	30.11 meV
8f =	12.08 meV
9f/i =	-34.94 meV

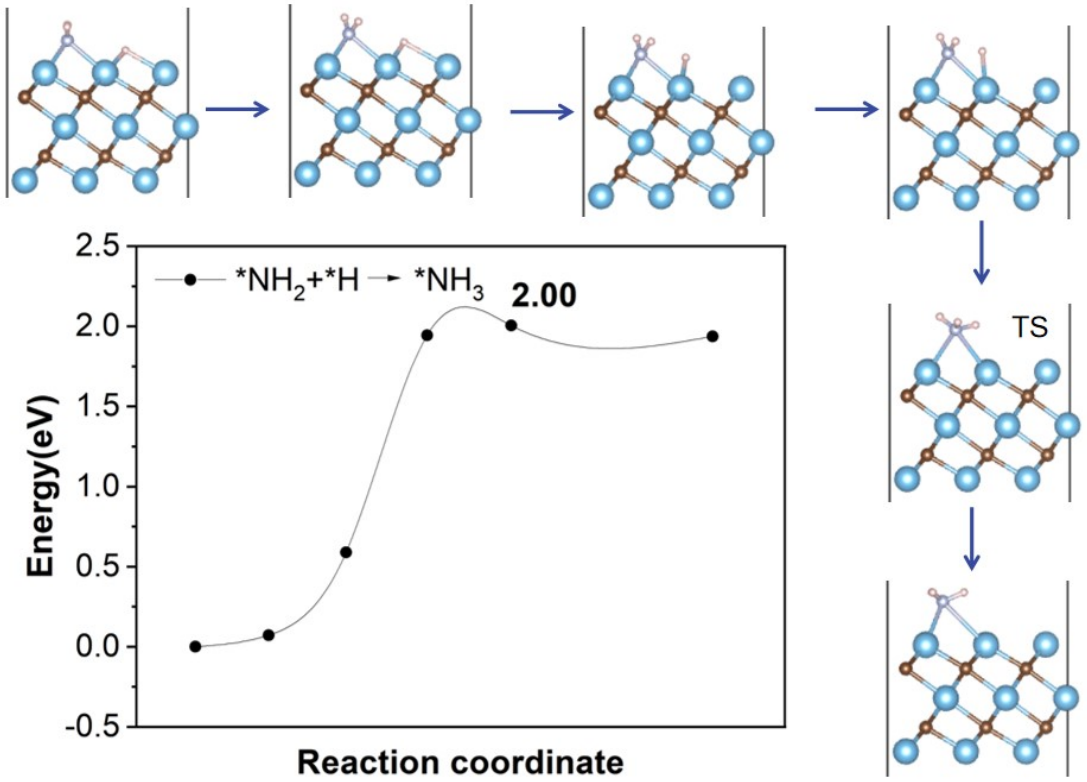

Fig. S13 Minimum energy path and activation barrier of elementary step $*NH_2+*H \rightarrow *NH_3$. TS stands for transition state.

Table S10. Calculated frequencies of TS in reaction $*NH_2+*H \rightarrow *NH_3$. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	412.14 meV
2f =	396.08 meV
3f =	373.88 meV
4f =	188.59 meV
5f =	185.62 meV

6f =	143.25 meV
7f =	60.48 meV
8f =	46.82 meV
9f =	29.11 meV
10f =	22.92 meV
11f =	8.28 meV
12f/i =	-11.36 meV

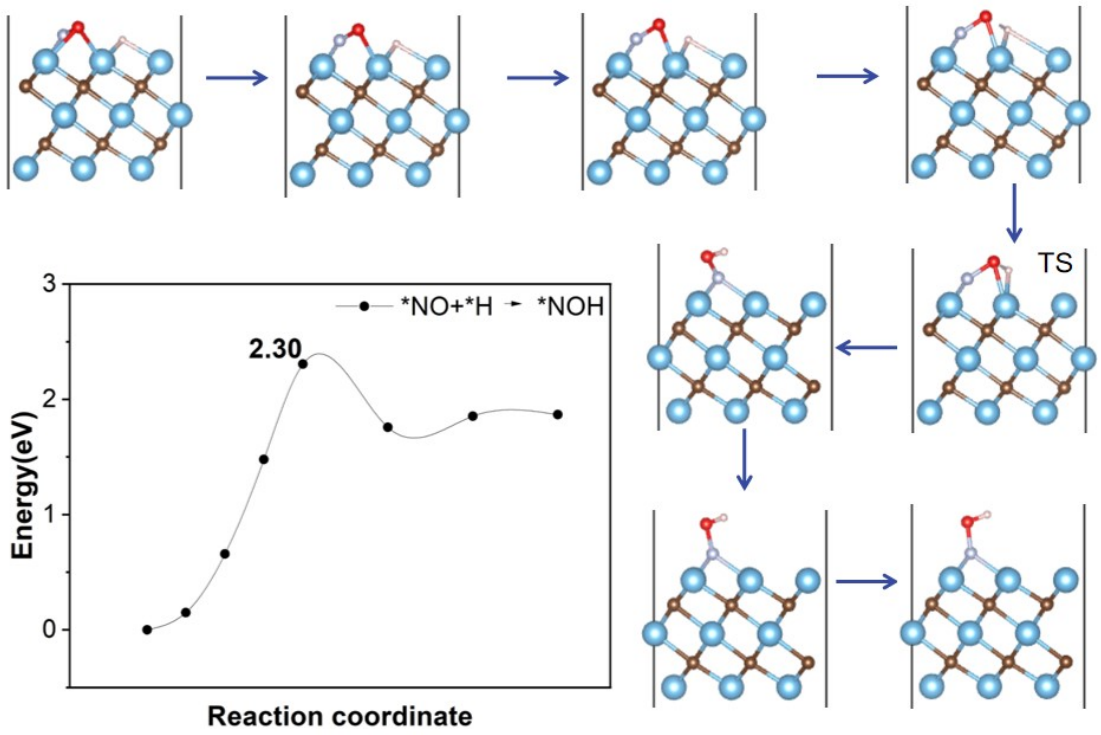

Fig. S14 Minimum energy path and activation barrier of elementary step *NO+*H→*NOH. TS stands for transition state.

Table S11. Calculated frequencies of TS in reaction *NO+*H→*NOH. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	152.51 meV
2f =	108.48 meV
3f =	94.16 meV
4f =	55.84 meV

5f =	47.82 meV
6f =	44.11 meV
7f =	27.14 meV
8f =	12.43 meV
9f/i =	-168.49 meV

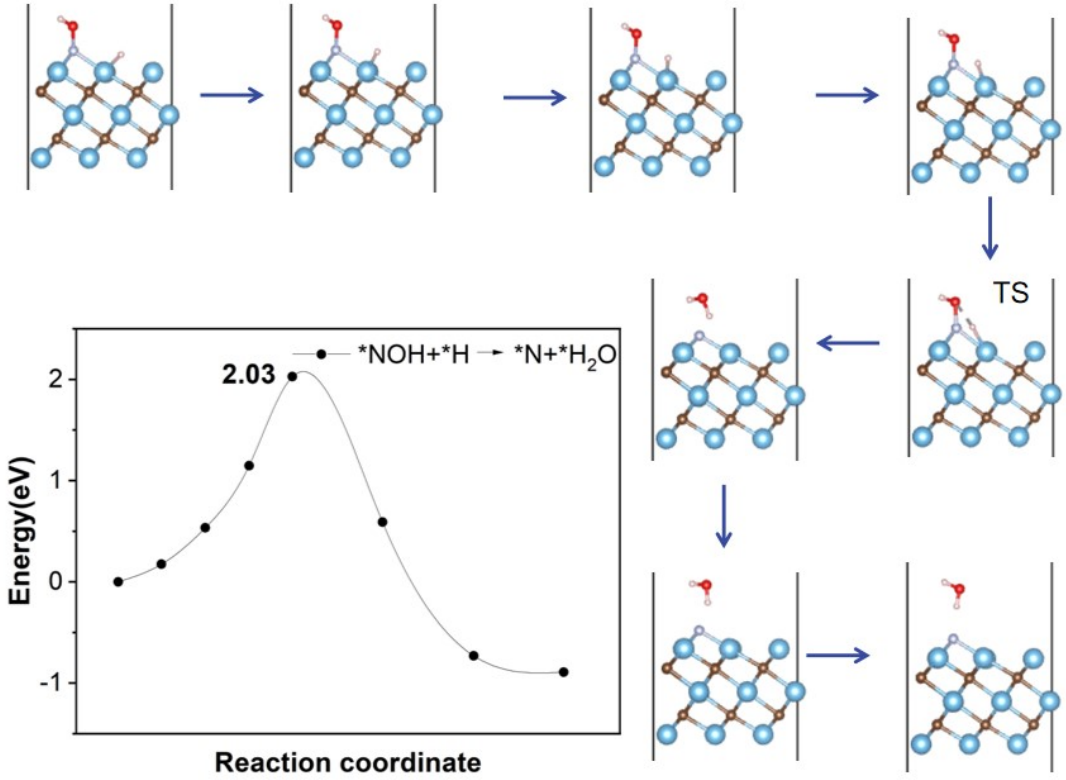

Fig. S15 Minimum energy path and activation barrier of elementary step *NOH+*H→*N+H_2O.TS stands for transition state.

Table S12. Calculated frequencies of TS in reaction *NOH+*H→*N+H_2O. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	448.65 meV
2f =	192.33 meV
3f =	156.04 meV
4f =	96.11 meV
5f =	71.40 meV

6f =	50.27 meV
7f =	40.32 meV
8f =	36.85 meV
9f =	34.69 meV
10f =	28.40 meV
11f =	19.73 meV
12f/i =	-151.36 meV

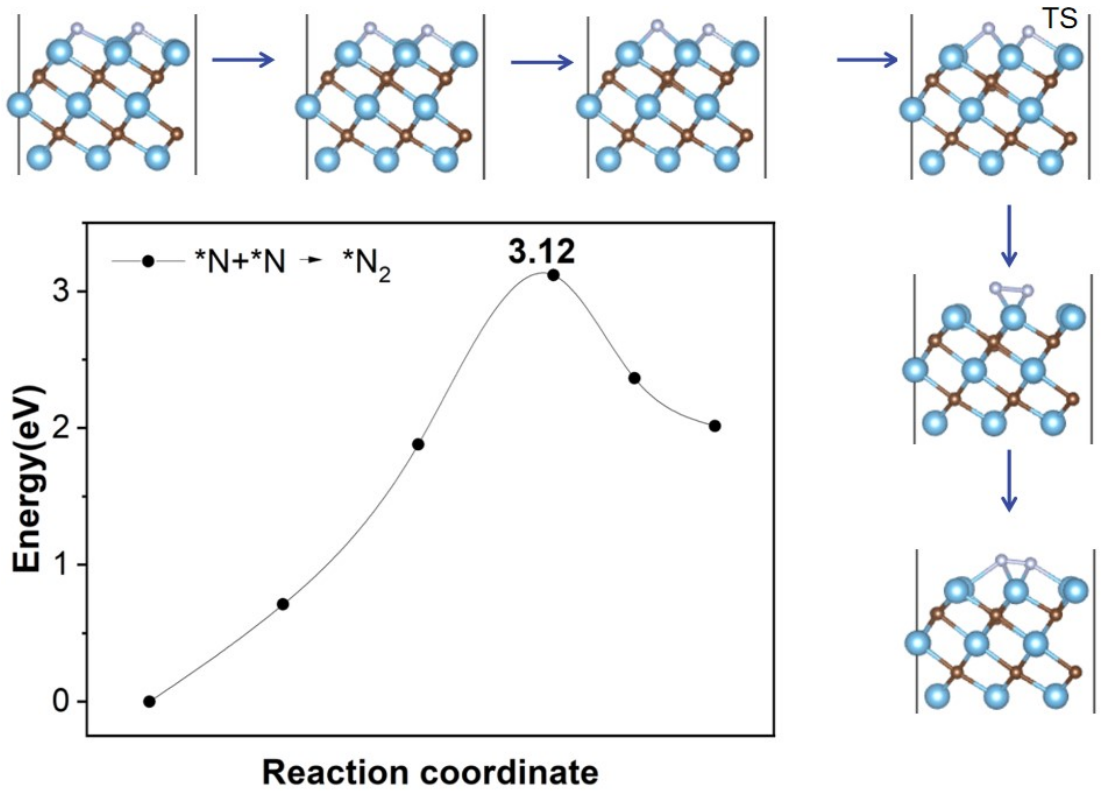

Fig. S16 Minimum energy path and activation barrier of elementary step *N+*N→*N_2. TS stands for transition state.

Table S13. Calculated frequencies of TS in reaction *N+*N→*N_2. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	66.19 meV
2f =	63.91 meV
3f =	50.38 meV

4f =	43.45 meV
5f =	34.97 meV
6f/i =	-74.81 meV

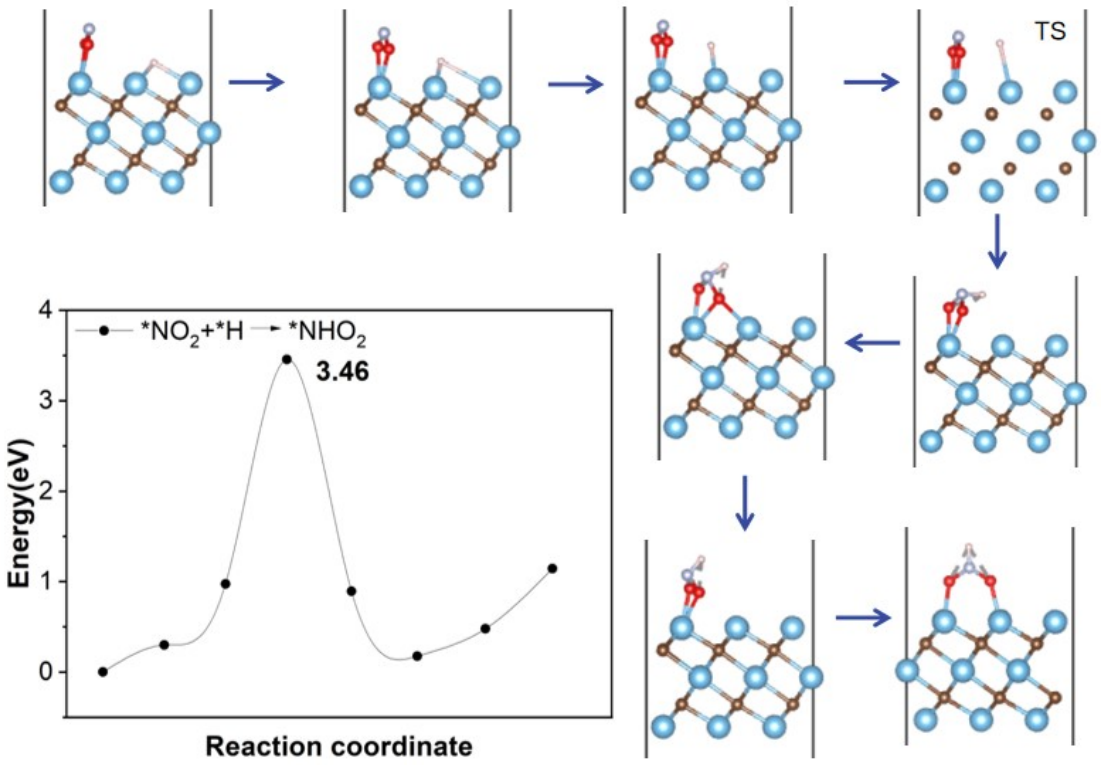

Fig. S17 Minimum energy path and activation barrier of elementary step $*NO_2+*H \rightarrow *NHO_2$. TS stands for transition state.

Table S14. Calculated frequencies of TS~~3~~ in reaction step $*NO_2+*H \rightarrow *NHO_2$. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	120.85 meV
2f =	113.78 meV
3f =	88.47 meV
4f =	82.50 meV
5f =	51.09 meV
6f =	42.53 meV
7f =	40.52 meV

8f =	37.35 meV
9f =	16.51 meV
10f =	8.54 meV
11f =	2.93 meV
12f/i =	-63.91 meV

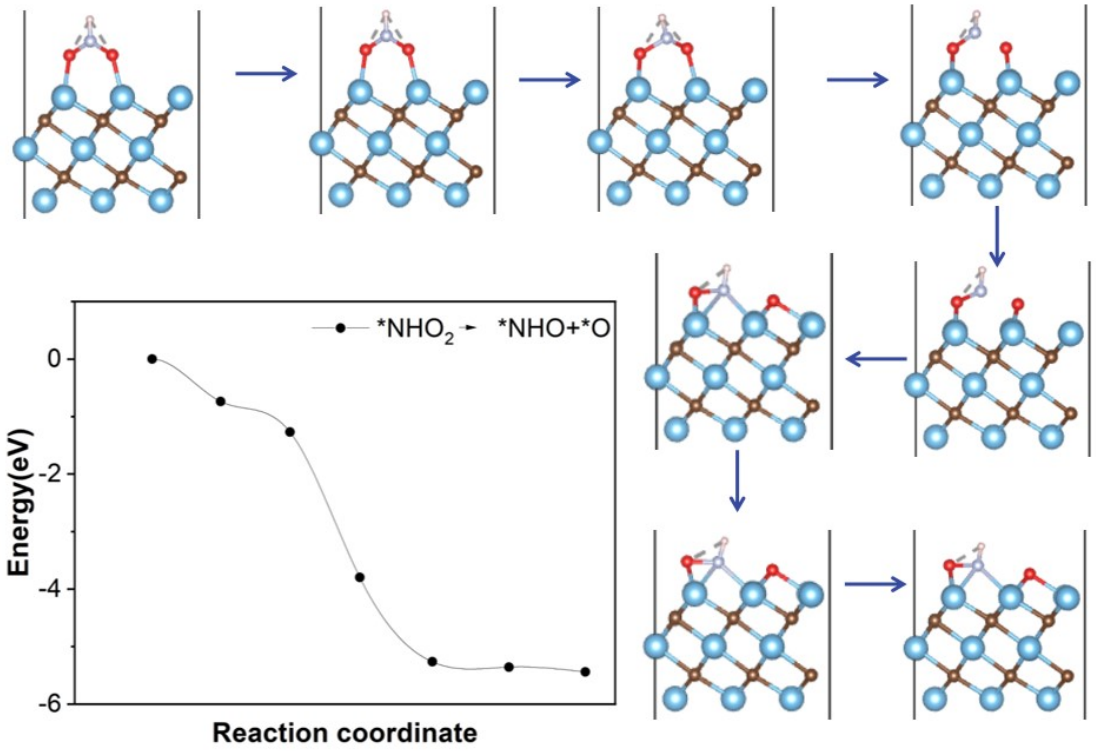

Fig. S18 Minimum energy path and activation barrier of elementary step $*NHO_2 \rightarrow *NHO+*O$. This step proceeds without barrier.

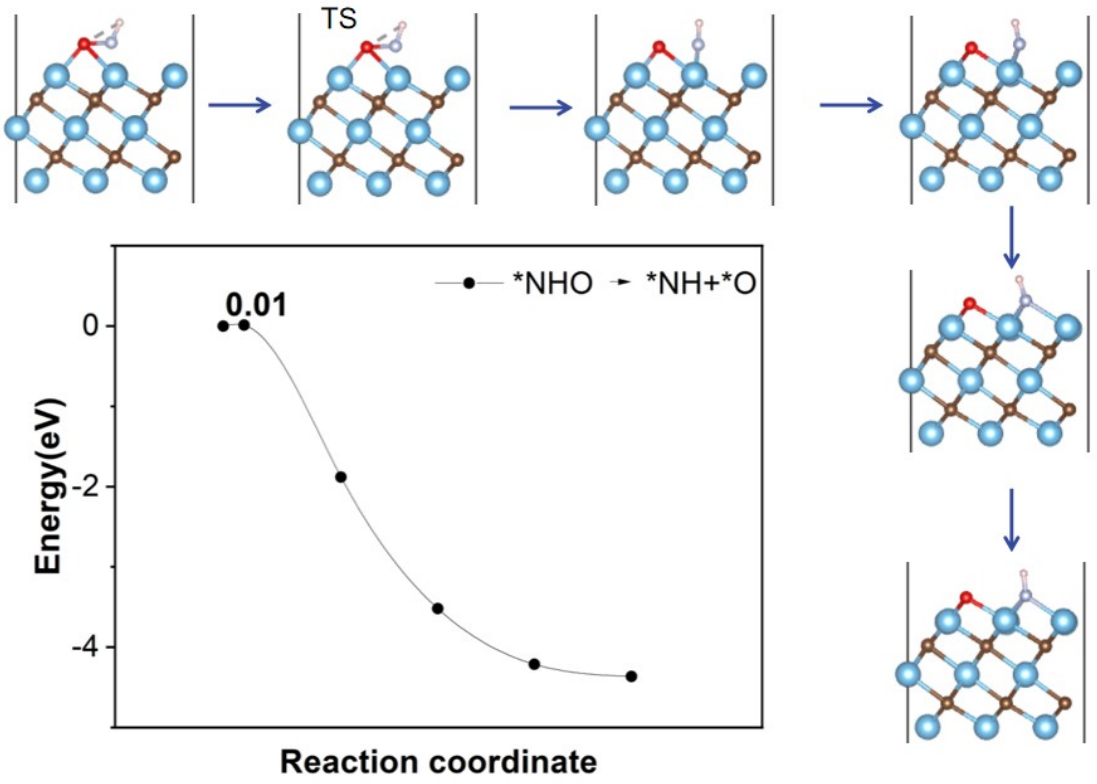

Fig. S19 Minimum energy path and activation barrier of elementary step *NHO→*NH+*O. This step proceeds without barrier.

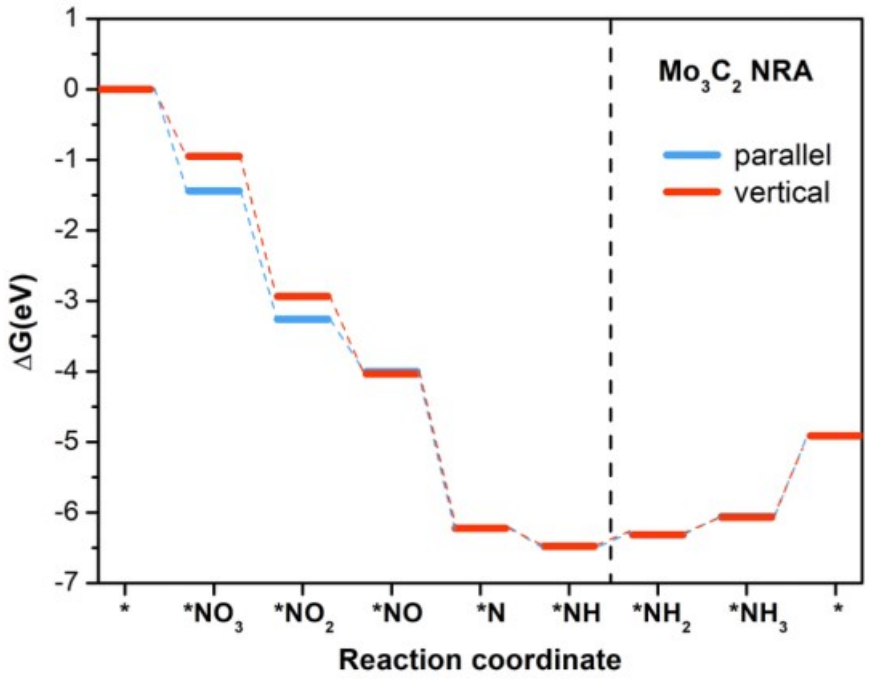

Fig. S20 Gibbs free energy diagram of NRA on Mo_3C_2 by vertical and parallel *NO_3 adsorption modes.

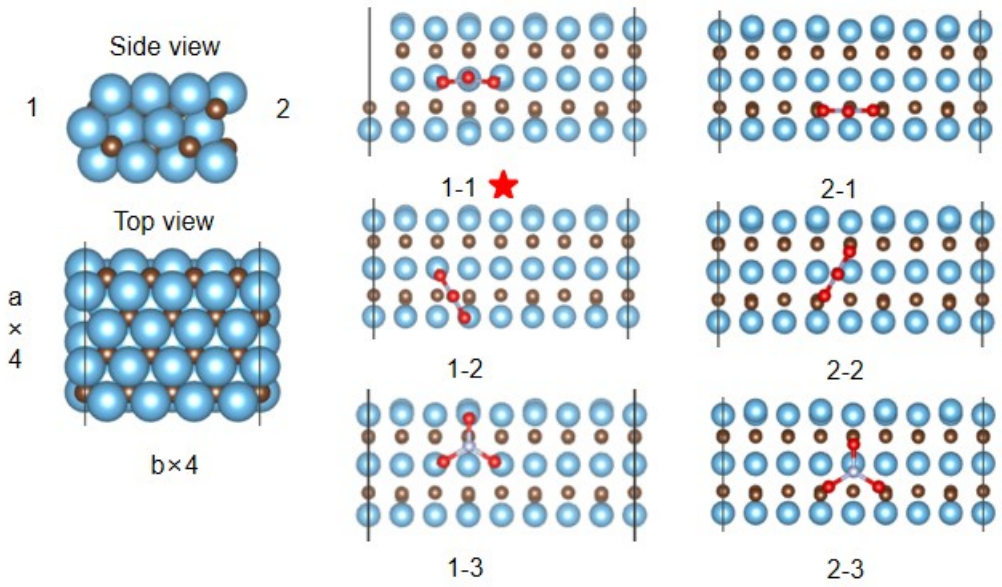

Fig. S21 Absorption sites on Ti_3C_2 edge plane. "1", "2" represent two inequivalent sites on edge plane, and "3" means intermediates are parallel with edge plane.

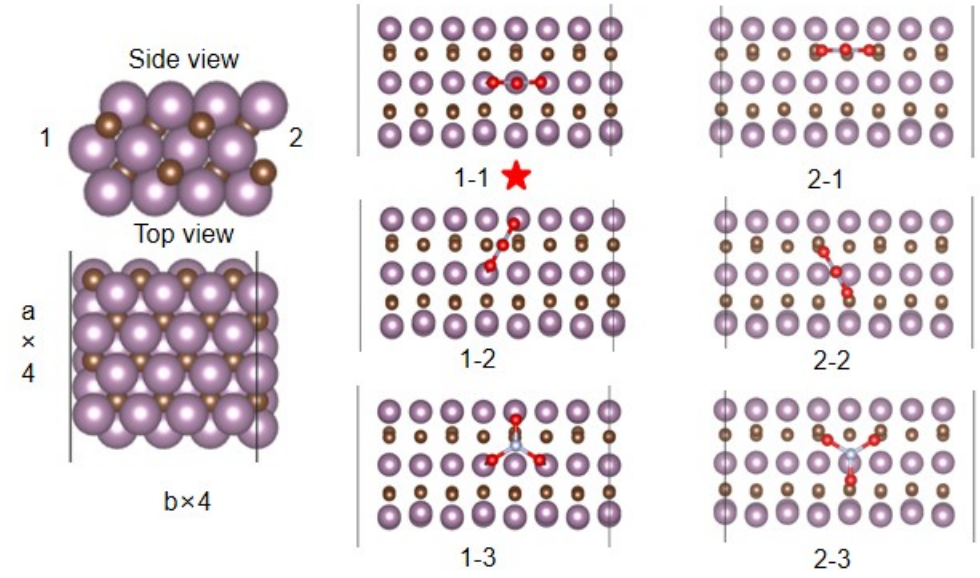

Fig. S22 Absorption sites on Mo_3C_2 edge plane. "1"," 2" represent two inequivalent sites on edge plane, and "3" means intermediates are parallel with edge plane.

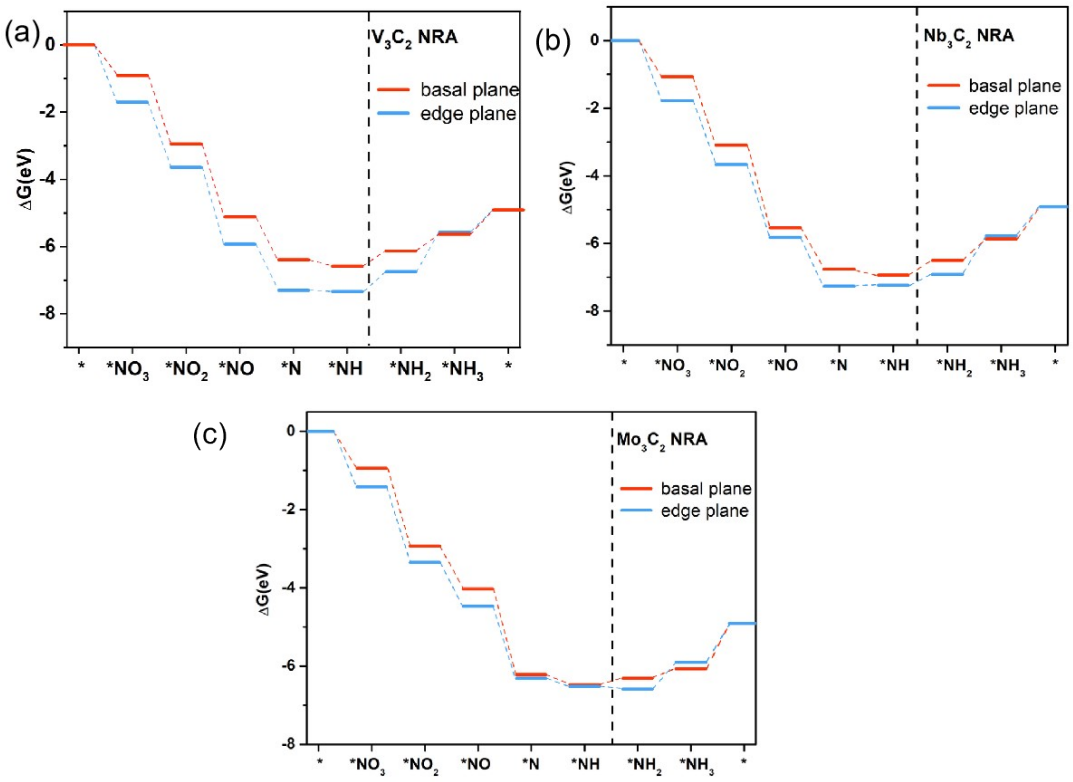

Fig. S23 NRA pathway on (a) V_3C_2, (b)Nb_3C_2, (c)Mo_3C_2 basal plane and edge plane.

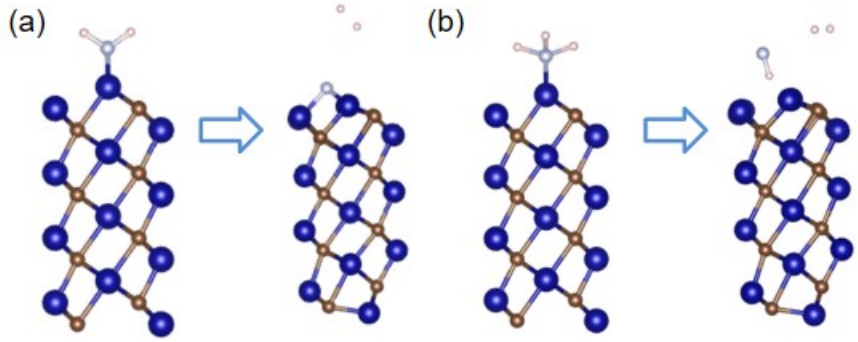

Fig. S24 Geometric configuration of (a) *NH_2 and (b) *NH_3 on Cr_3C_2 edge plane. Left represents initial structure, and right represents structure after optimization,

Pristine M_3C_2 MXene

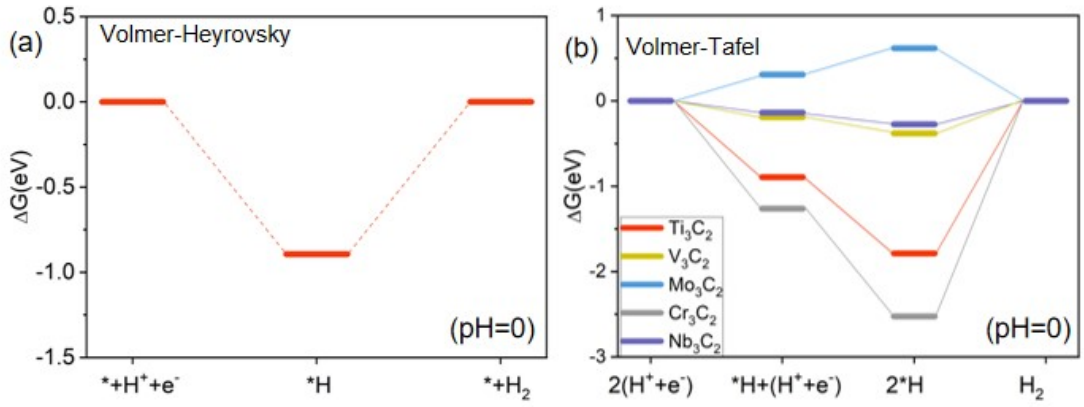

Fig. S25 Gibbs free energy diagram of (a) HER (Volmer-Heyrovsky) on Ti_3C_2 at pH = 0 and (b) HER (Volmer-Tafel) on M_3C_2 MXene at pH = 0.

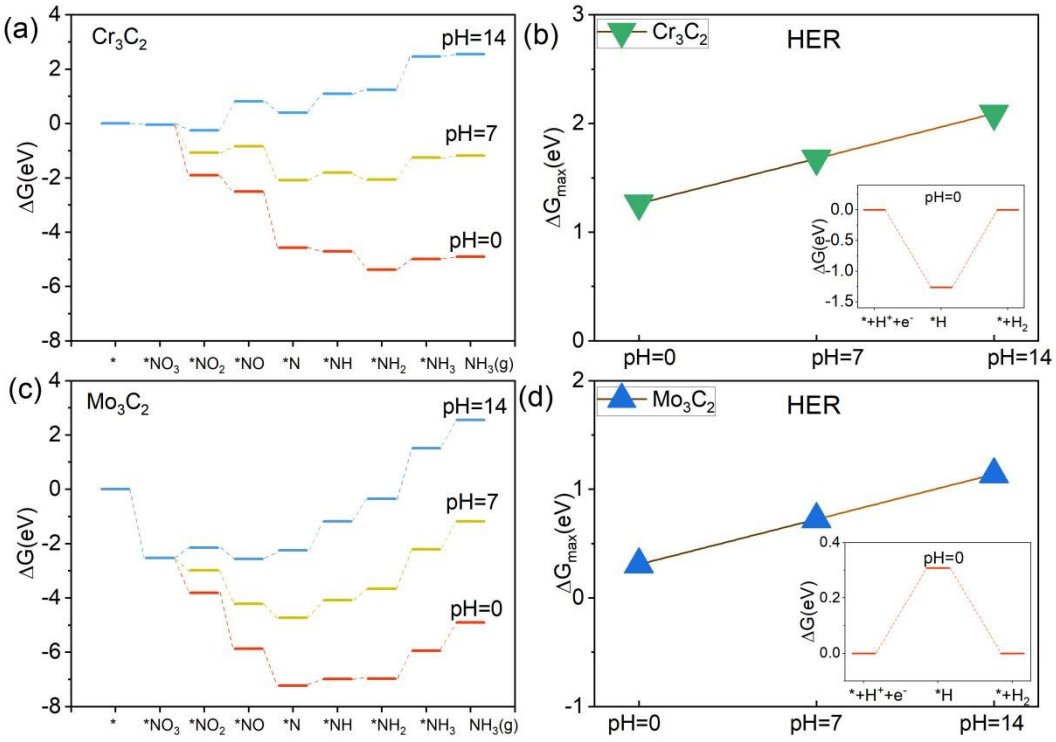

Fig. S26 (a) Gibbs free energy diagram of NRA and (b) ΔG_{max} of HER on Cr_3C_2 at pH = 0, 7, 14, inset: ΔG_{*H} on Cr_3C_2 at pH = 0. (c) Gibbs free energy diagram of NRA and (d) ΔG_{max} of HER on Mo_3C_2 at pH = 0, 7, 14, inset: ΔG_{*H} on Mo_3C_2 at pH = 0.

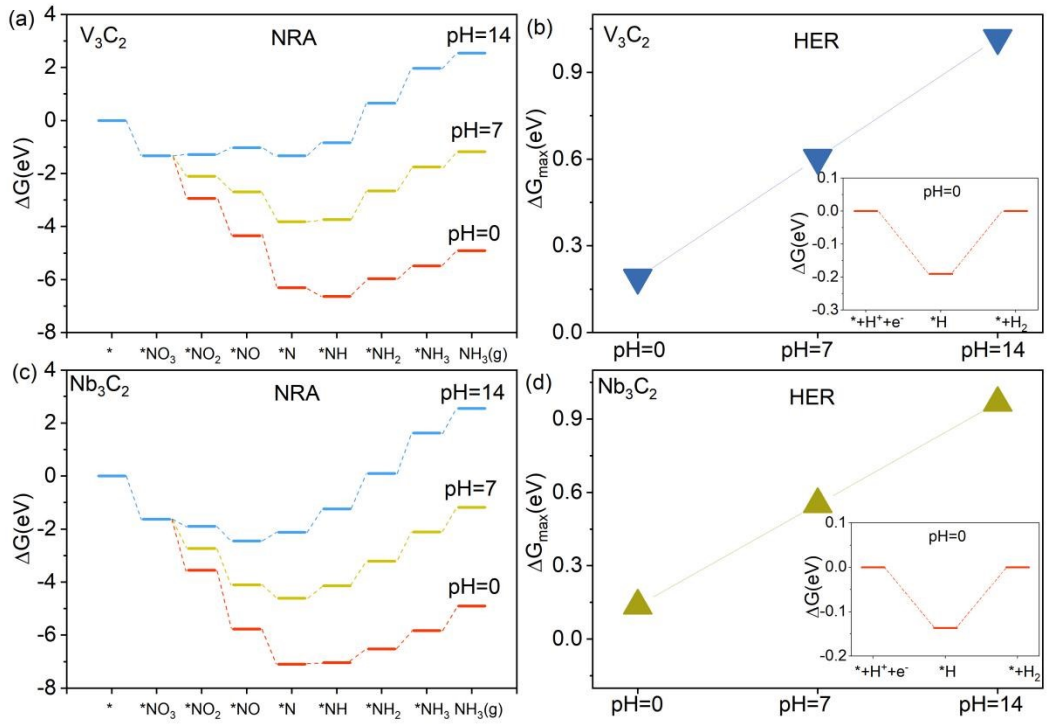

Fig. S27 (a) Gibbs free energy diagram of NRA and (b) ΔG_{max} of HER on V_3C_2 at pH = 0, 7, 14, inset: ΔG_{*H} on V_3C_2 at pH = 0. (c) Gibbs free energy diagram of NRA and (d) ΔG_{max} of HER on Nb_3C_2 at pH = 0, 7, 14, inset: ΔG_{*H} on Nb_3C_2 at pH = 0.

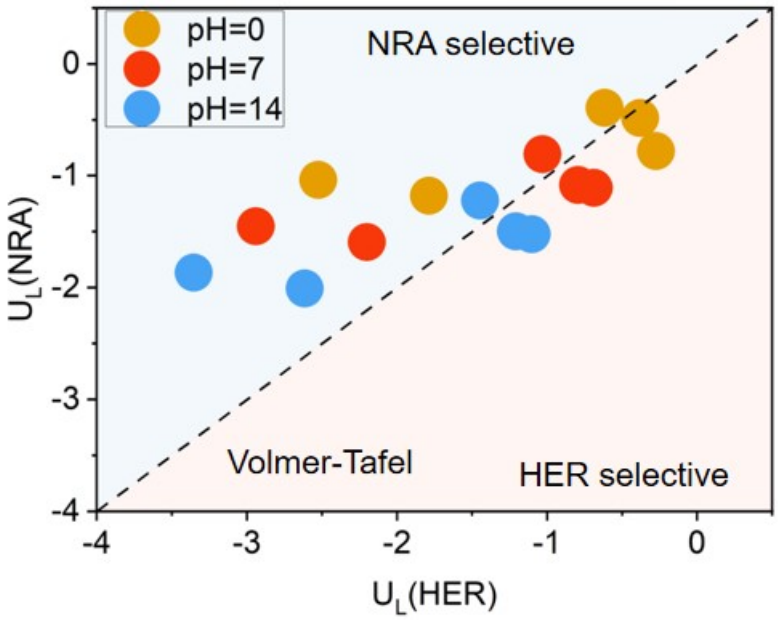

Fig. S28 Calculated limiting potentials for HER (U_L(HER)) and NRA (U_L(NRA)) on the surfaces of six M_3C_2 candidates by Volmer-Tafel pathway at pH=0, 7, and 14.

M@Ti_3C_2

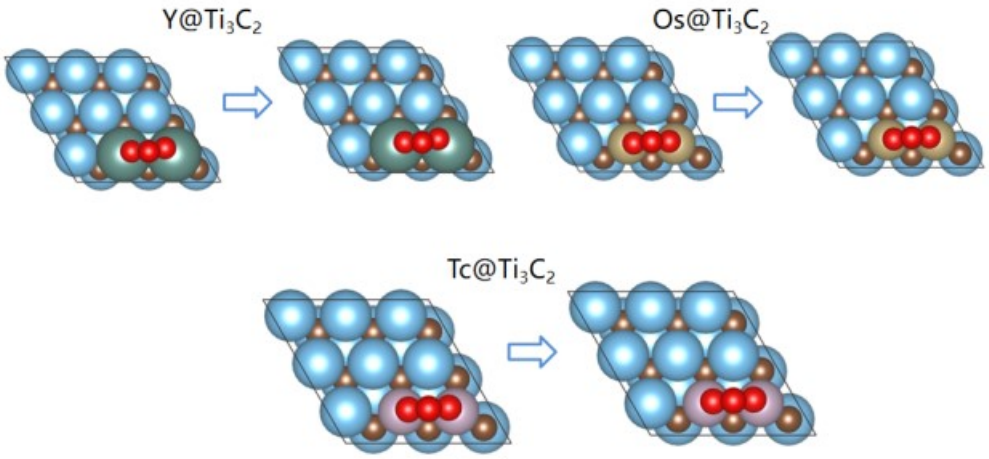

Fig. S29 Geometric configuration of *M*@Ti_3C_2 MXene (*M*=Y, Os, Tc), left represents initial structure, right structure represents optimized structure.

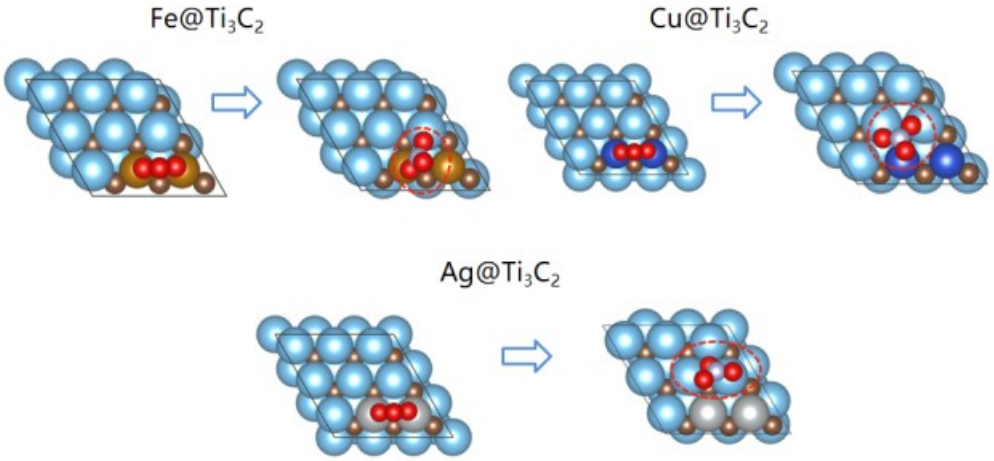

Fig. S30 Geometric configuration of *M*@Ti_3C_2 MXene (*M*=Fe, Cu, Ag), left represents initial structure, right structure represents optimized structure, *M*@Ti_3C_2M MXene (M=Sc, Au, Co, Ni, Zn, Sr, Ru, Rh, Pd, Re, Ir, Pt, Hg) remain same results.

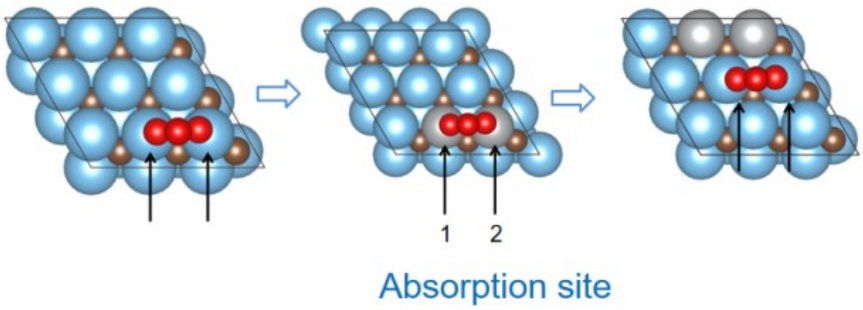

Fig. S31 Graphic of NO_3 absorption site on *M*@Ti_3C_2.

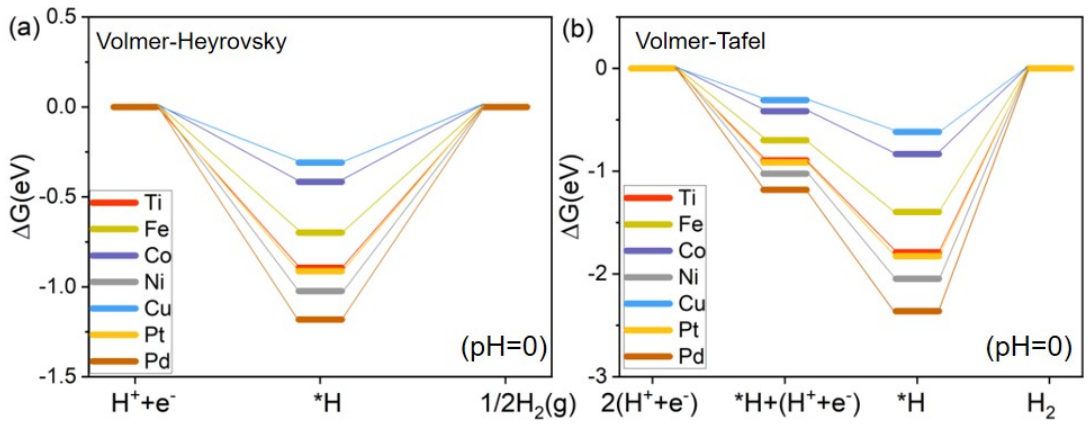

Fig. S32 Gibbs free energy of hydrogen adsorption and desorption on *M*@Ti_3C_2 (*M*=Ti, Fe, Co, Ni, Cu, Pt, Pd) basal plane at pH=0, (a) Vomer-Heyrovsky pathway, (b) Volmer-Tafel pathway.

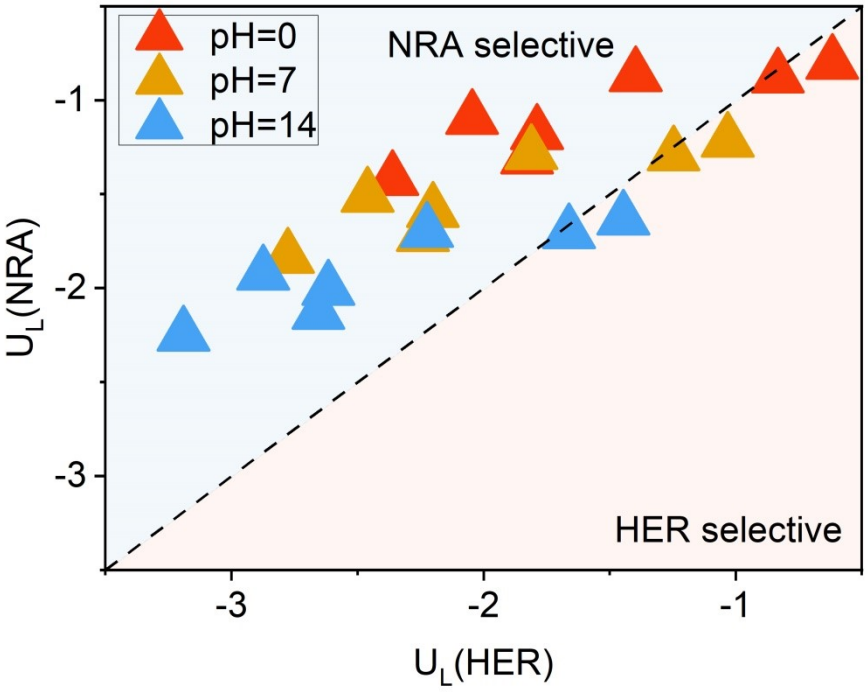

Fig. S33 Calculated limiting potentials for HER (U_L(HER)) and NRA (U_L(NRA)) on the surfaces of seven *M*@M_3C_2 candidates by Volmer-Tafel pathway at pH=0, 7, and 14.

$Ti_3C_2O_2$-O_v

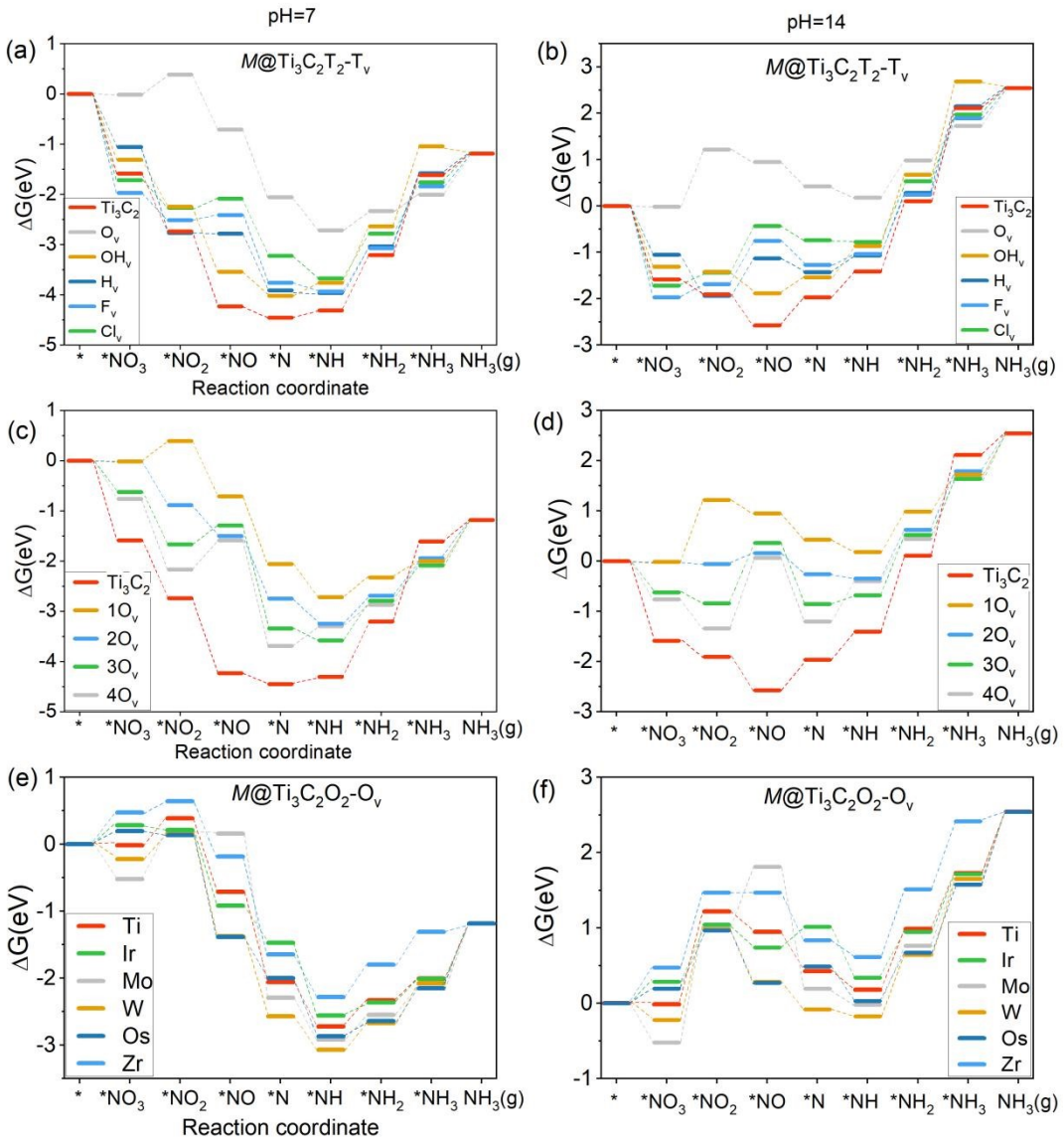

Fig. S34 Gibbs free energy diagram of NRA on $Ti_3C_2T_2$-T_v at (a) pH=7, (b) pH=14. Gibbs free energy diagram of NRA on $Ti_3C_2O_2$-nO_v at (c) pH=7, (d) pH=14. Gibbs free energy diagram of NRA on *M*@$Ti_3C_2O_2$-O_v at (e) pH=7, (f) pH=14.

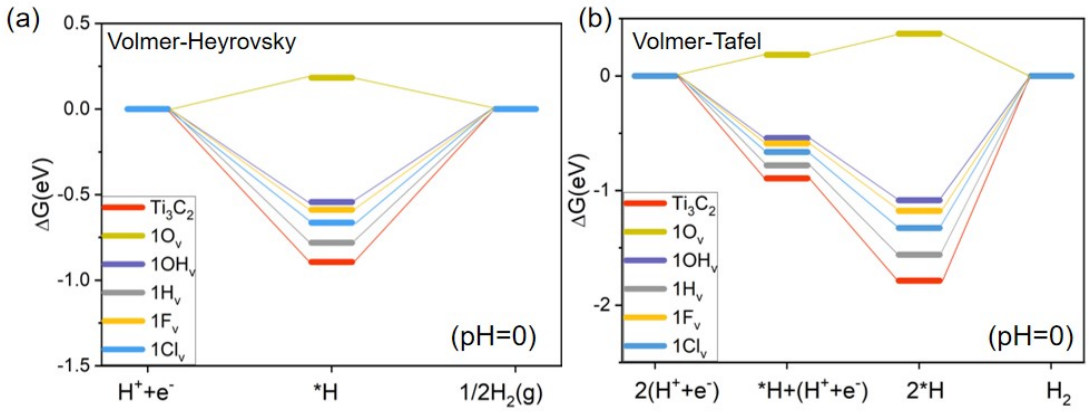

Fig. S35 Gibbs free energy of hydrogen adsorption and desorption on $Ti_3C_2T_2$-T_v (T=O, OH, H, F, Cl) basal plane at pH=0, (a) Vomer-Heyrovsky pathway, (b) Volmer-Tafel pathway.

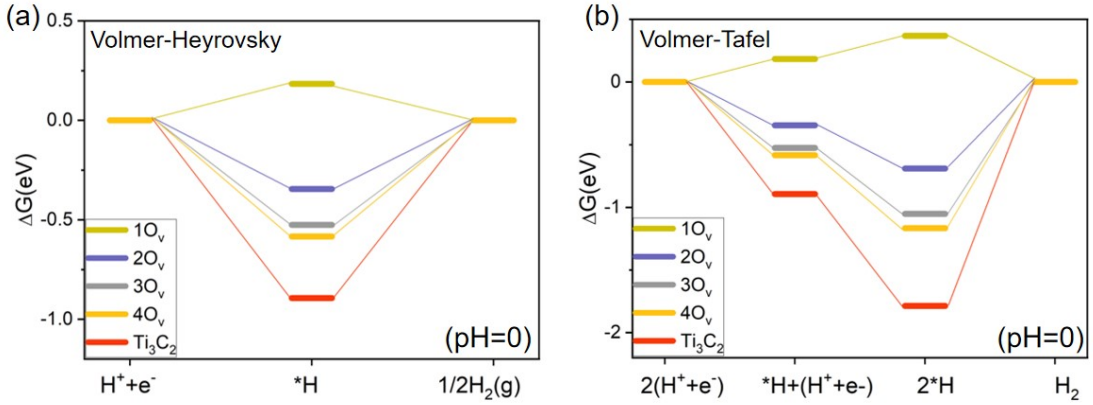

Fig. S36 Gibbs free energy of hydrogen adsorption and desorption on $Ti_3C_2O_2$-nO_v basal plane at pH=0, (a) Vomer-Heyrovsky pathway, (b) Volmer-Tafel pathway.

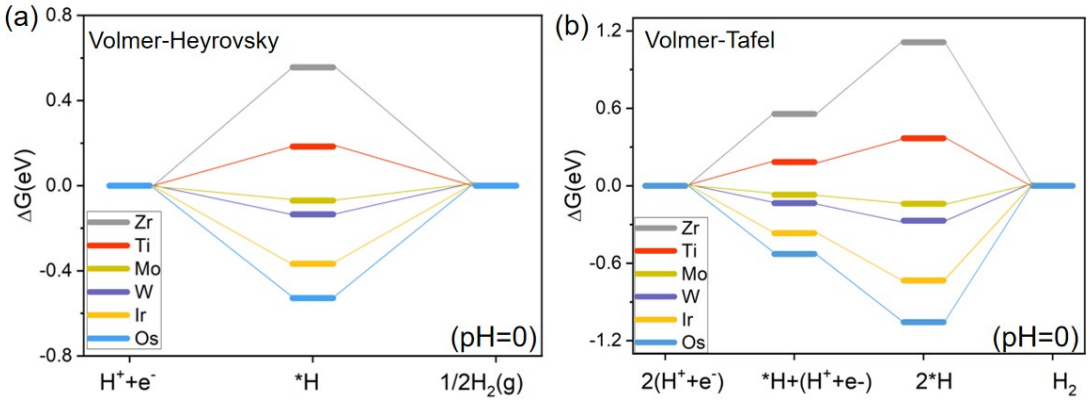

Fig. S37 Gibbs free energy of hydrogen adsorption and desorption on M@$Ti_3C_2O_2$-O_v basal plane at pH=0, (a) Vomer-Heyrovsky pathway, (b) Volmer-Tafel pathway.

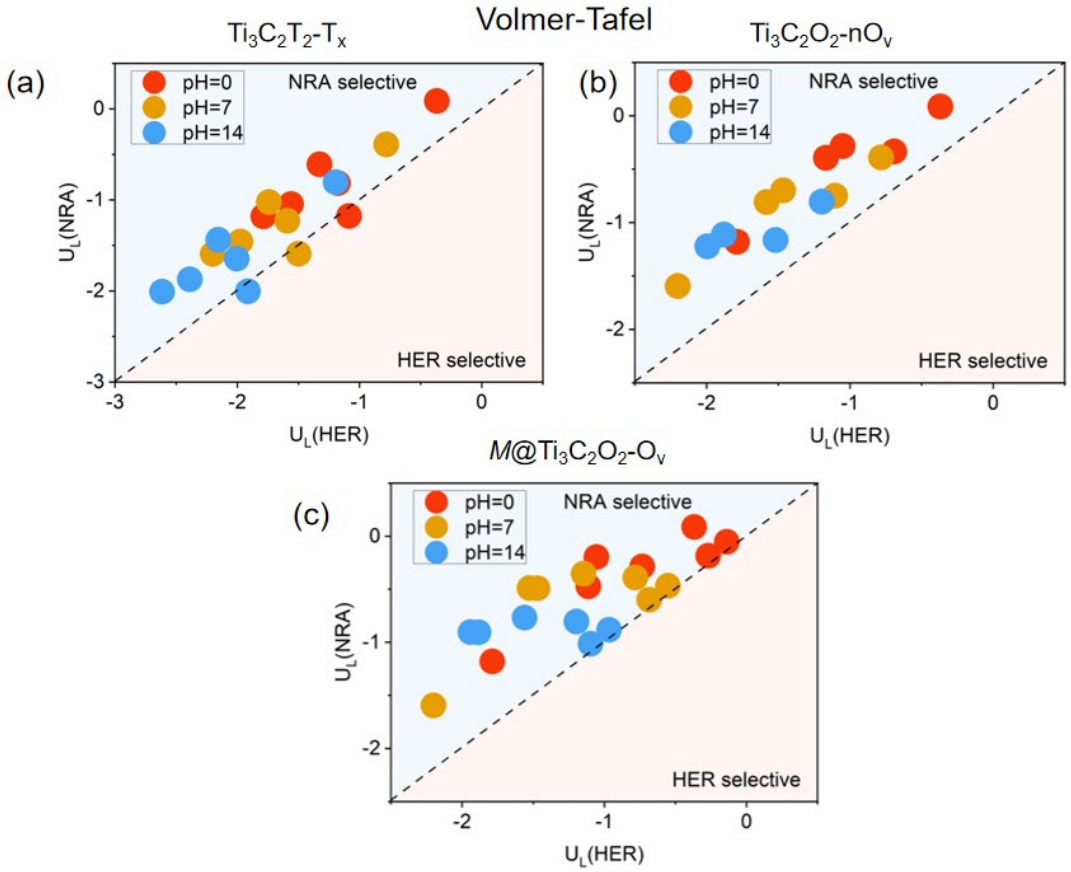

Fig. S38 Calculated limiting potentials for HER (U_L(HER)) and NRA (U_L(NR(A)) on the surfaces of (a) $Ti_3C_2T_2$-T_v, (b) $Ti_3C_2O_2$-nO_v, (c) *M*@$Ti_3C_2O_2$-O_v by Volmer-Tafel pathway at pH=0, 7, and 14.

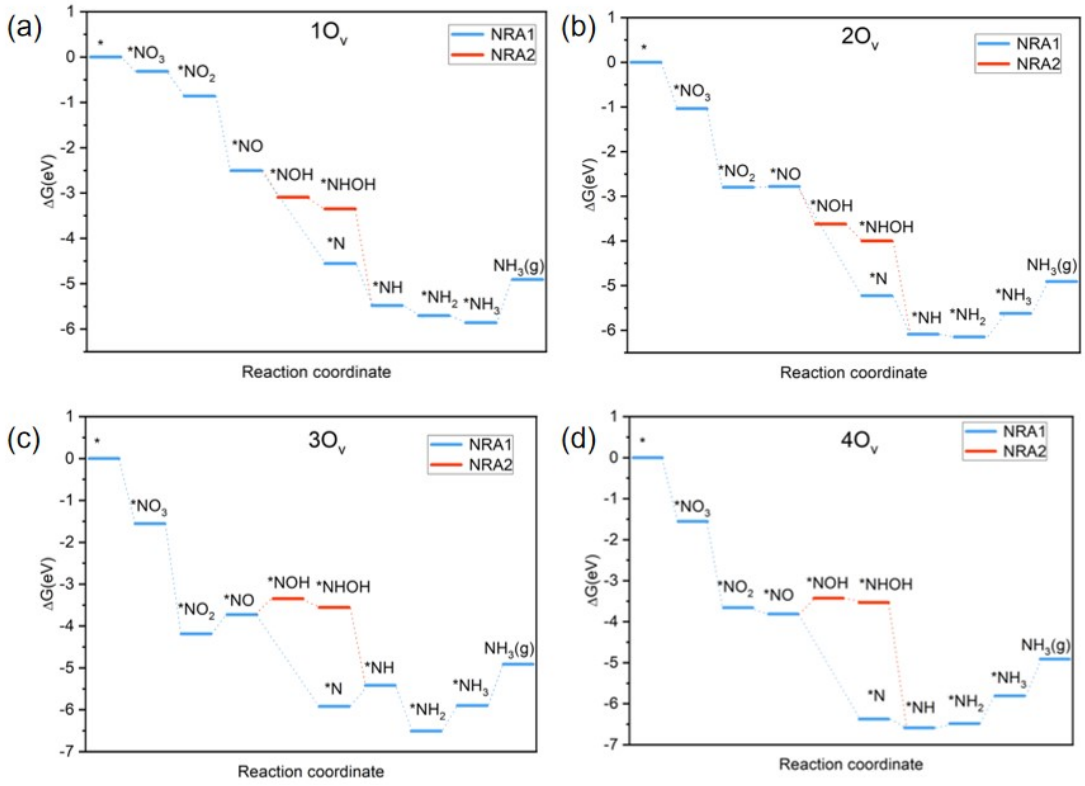

Fig. S39 NRA reaction pathway identification on $Ti_3C_2O_2$-nO_v. (a) 1O_v, (b)2O_v, (c) 3O_v, (d) 4O_v.

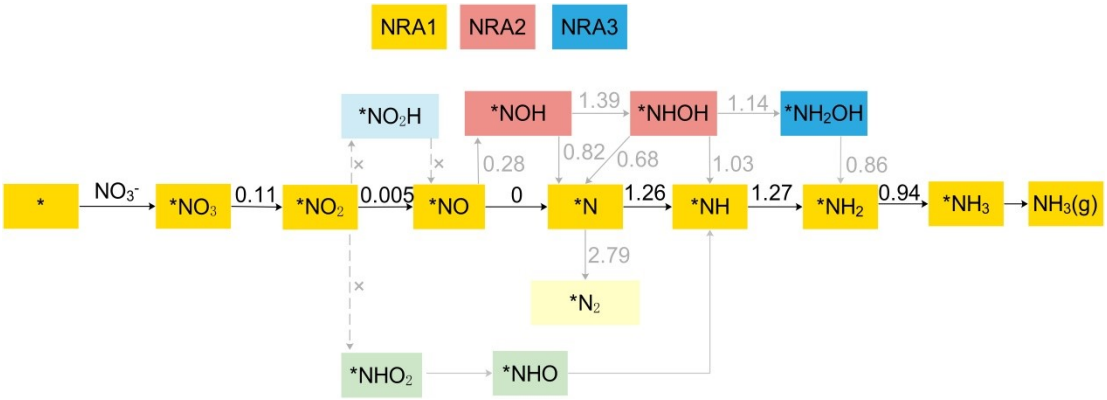

Fig. S40 The overview reaction kinetics for different intermediates on $Ti_3C_2O_2$-O_v for NRA, "×" means this intermediate decomposes. The Activation energy of each elementary step is given in eV. Combined the thermodynamic and kinetics data, NRA1 is the most favorable pathway for NRA.

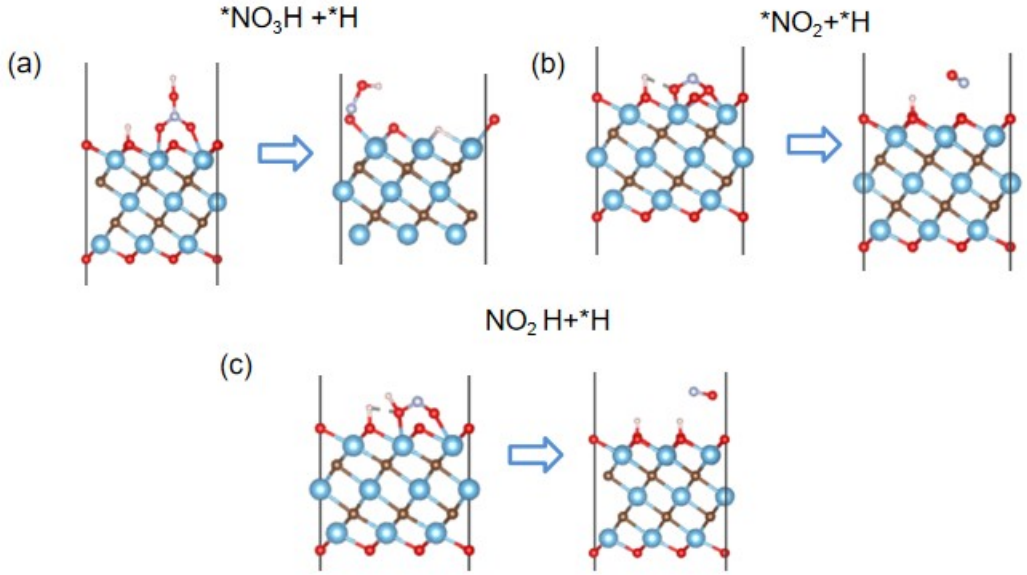

Fig. S41 Geometry of (a) $*NO_3+*H$, (b) $*NO_2+*H$, (c) $*NO_2H+*H$ on $Ti_3C_2O_2$-$1O_v$ before and after optimization.

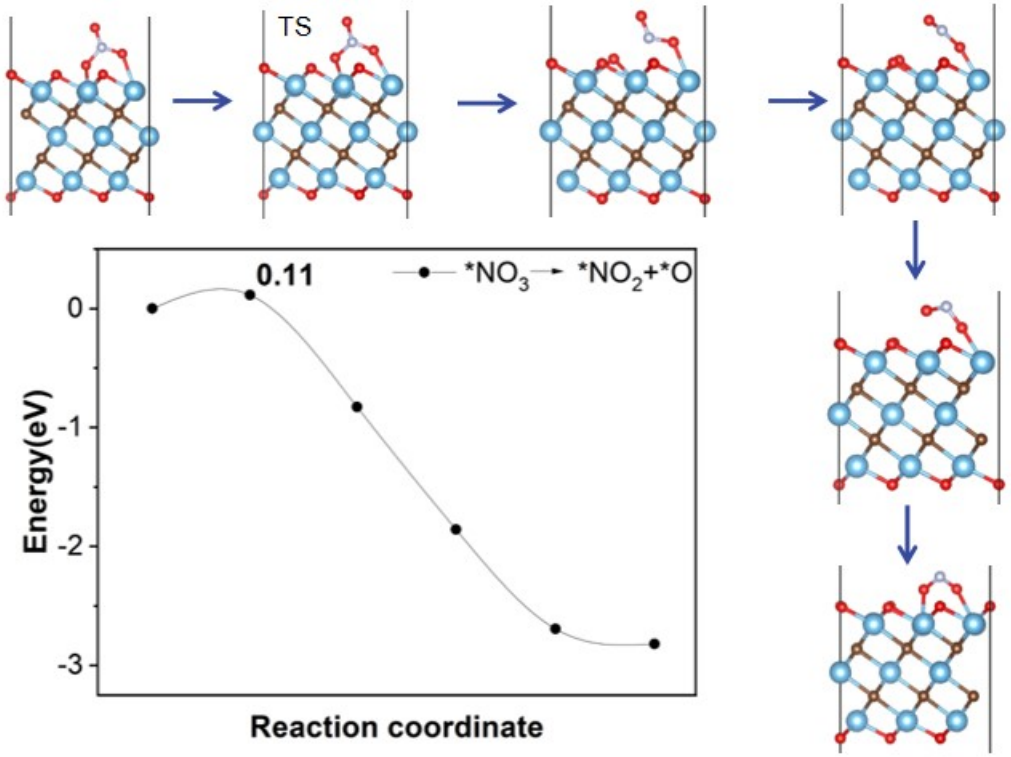

Fig. S42 Minimum energy path and activation barrier of elementary step $*NO_3 \rightarrow *NO_2+*O$. TS stands for transition state.

Table S15. Calculated frequencies of TS in reaction step $*NO_3 \rightarrow *NO_2 + *O$. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	197.61 meV
2f =	143.21 meV
3f =	113.90 meV
4f =	90.51 meV
5f =	86.10 meV
6f =	83.91 meV
7f =	36.61 meV
8f =	26.01 meV
9f =	17.73 meV
10f =	16.53 meV
11f =	3.64 meV
12f/i =	-12.64 meV

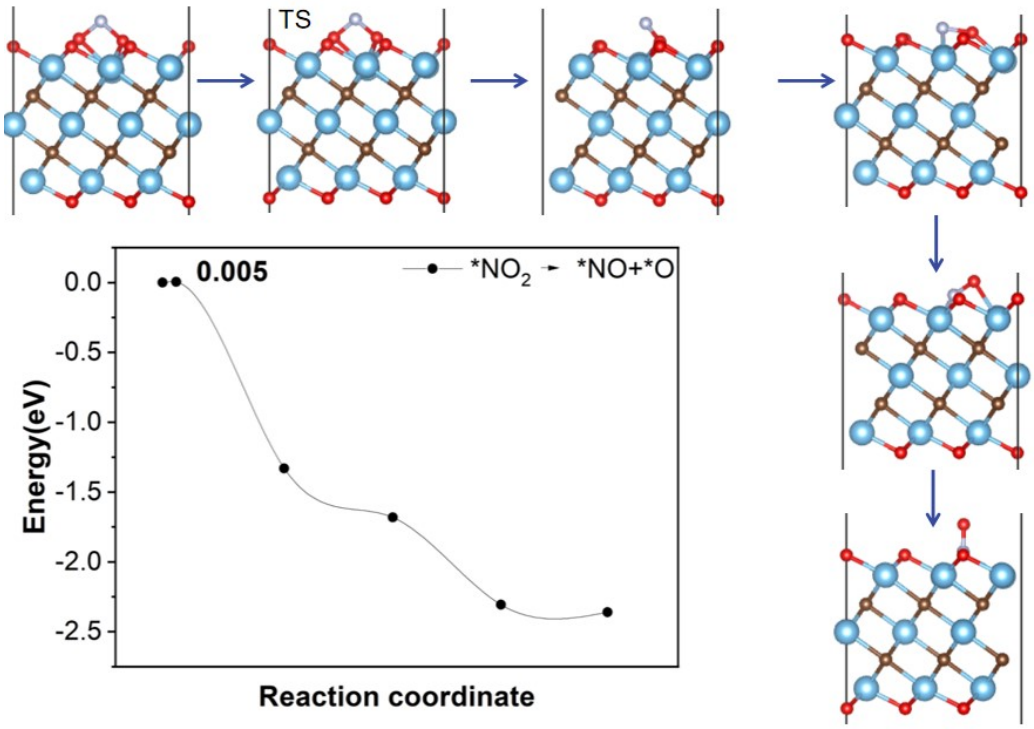

Fig. S43 Minimum energy path and activation barrier of elementary step $*NO_2 \rightarrow *NO + *O$. This step proceeds without barrier.

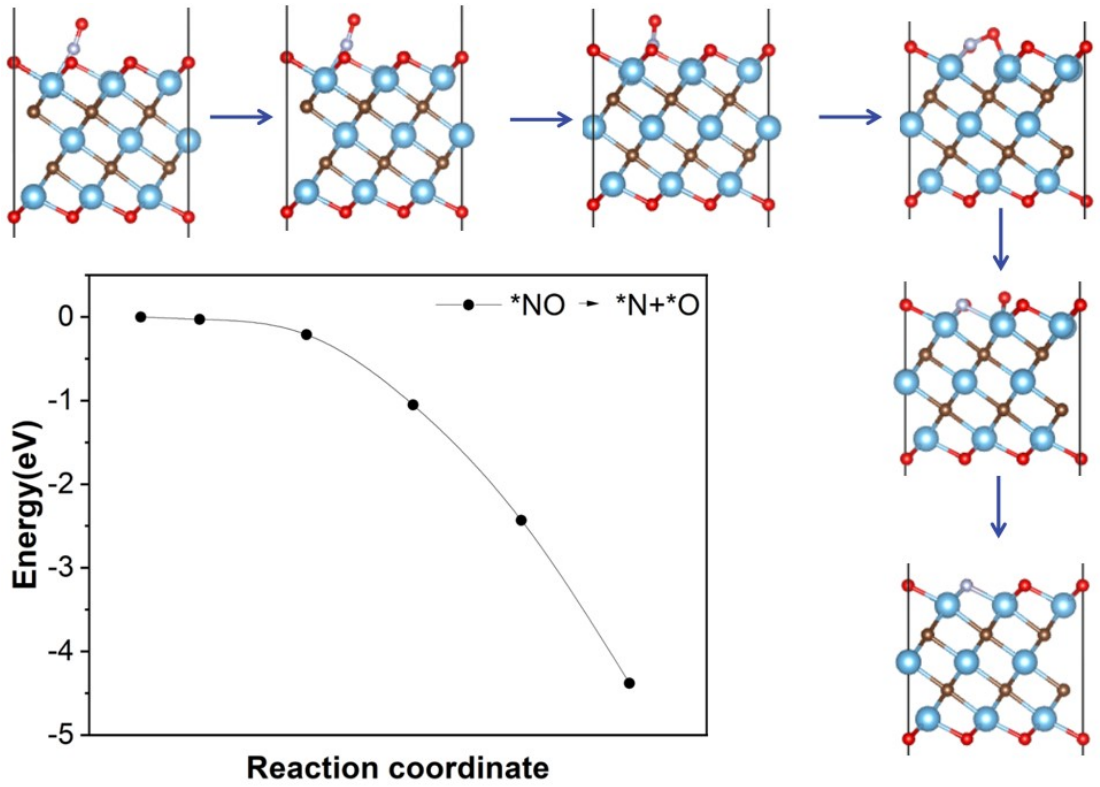

Fig. S44 Minimum energy path and activation barrier of elementary step *NO→*N+*O. This step proceeds without barrier.

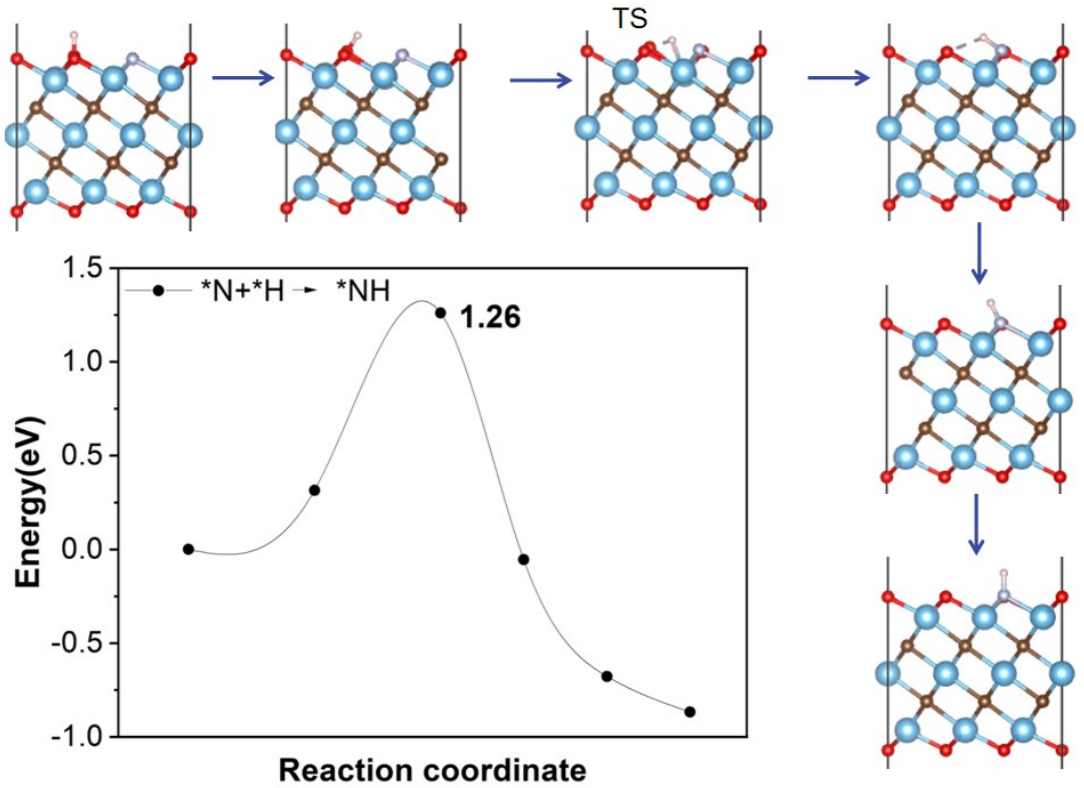

Fig. S45 Minimum energy path and activation barrier of elementary step *N+*H→*NH. TS stands for transition state.

Table S16. Calculated frequencies of TS in reaction *N+*H→*NH. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	193.91 meV
2f =	141.38 meV
3f =	66.43 meV
4f =	64.26 meV
5f =	59.74 meV
6f/i =	-204.95 meV

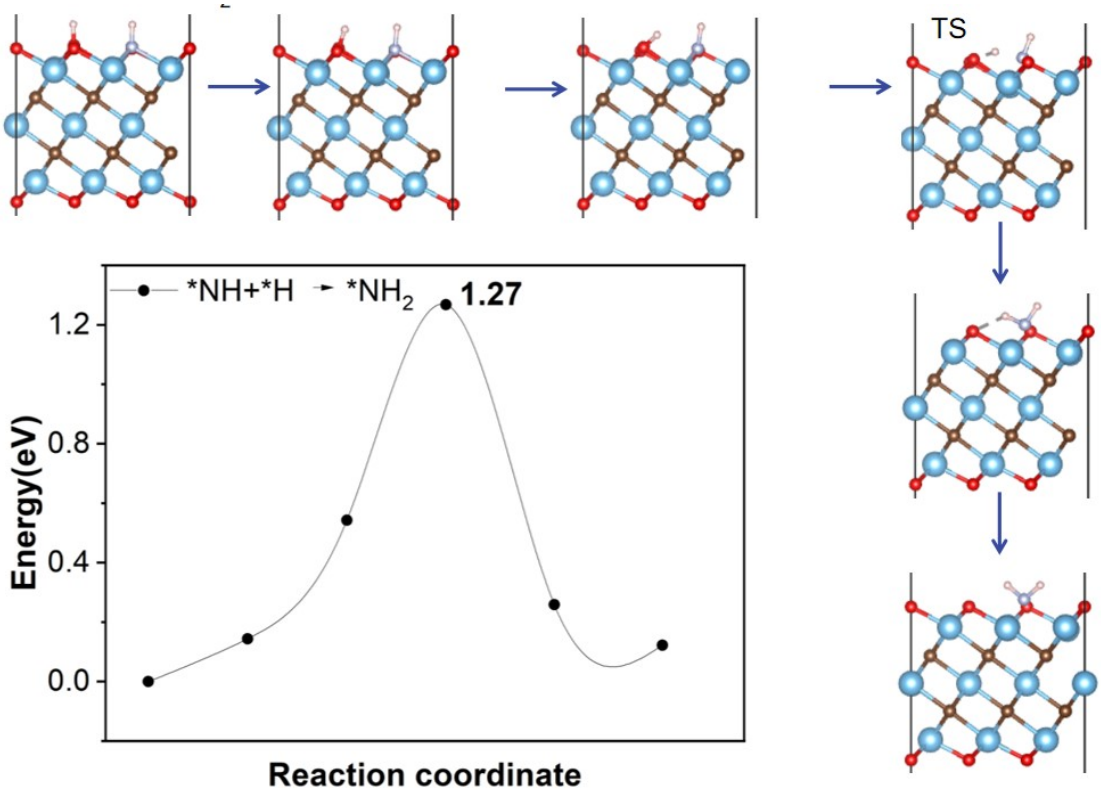

Fig. S46 Minimum energy path and activation barrier of elementary step *NH+*H→*NH_2. TS stands for transition state.

Table S17. Calculated frequencies of TS in reaction *NH+*H→*NH_2. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	425.81 meV

2f =	201.94 meV
3f =	148.86 meV
4f =	94.60 meV
5f =	74.36 meV
6f =	63.25 meV
7f =	51.50 meV
8f =	44.55 meV
9f/i =	-193.44 meV

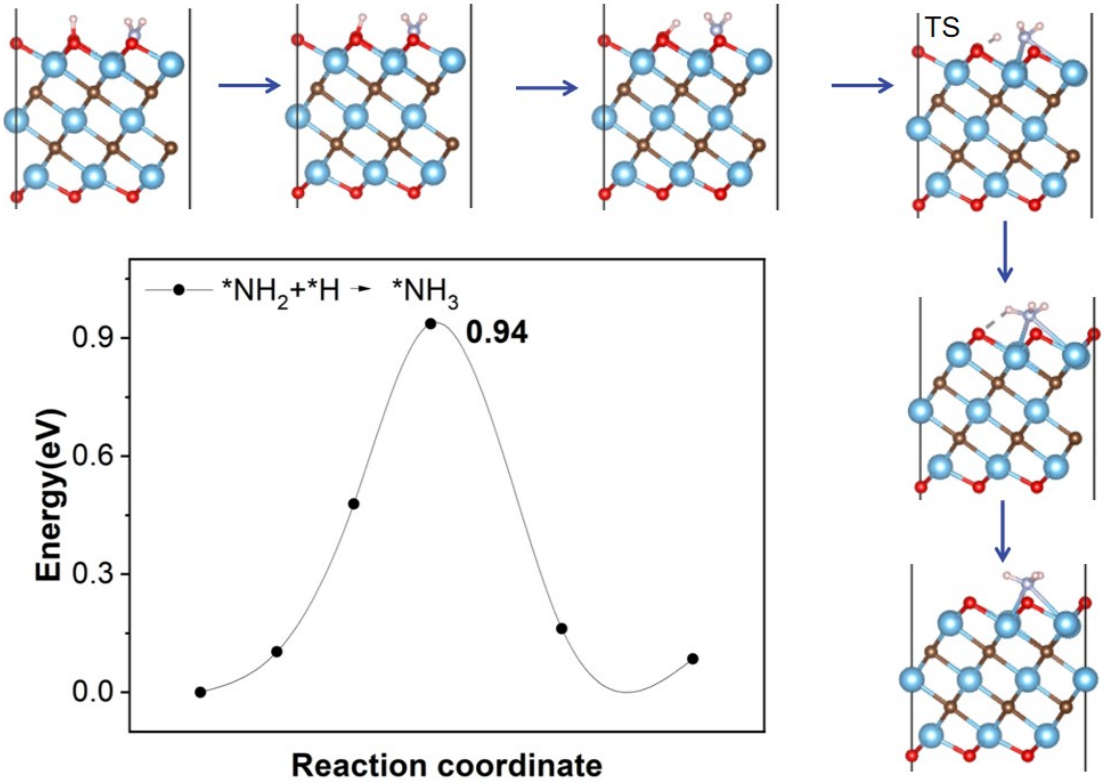

Fig. S47 Minimum energy path and activation barrier of elementary step $*NH_2+*H \rightarrow *NH_3$. TS stands for transition state.

Table S18. Calculated frequencies of TS in reaction $*NH_2+*H \rightarrow *NH_3$. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	427.91 meV
2f =	418.55 meV
3f =	197.62 meV

4f =	187.52 meV
5f =	165.50 meV
6f =	92.33 meV
7f =	79.39 meV
8f =	64.23 meV
9f=	53.14 meV
10f =	37.09 meV
11f =	23.49 meV
12f/i =	-152.83 meV

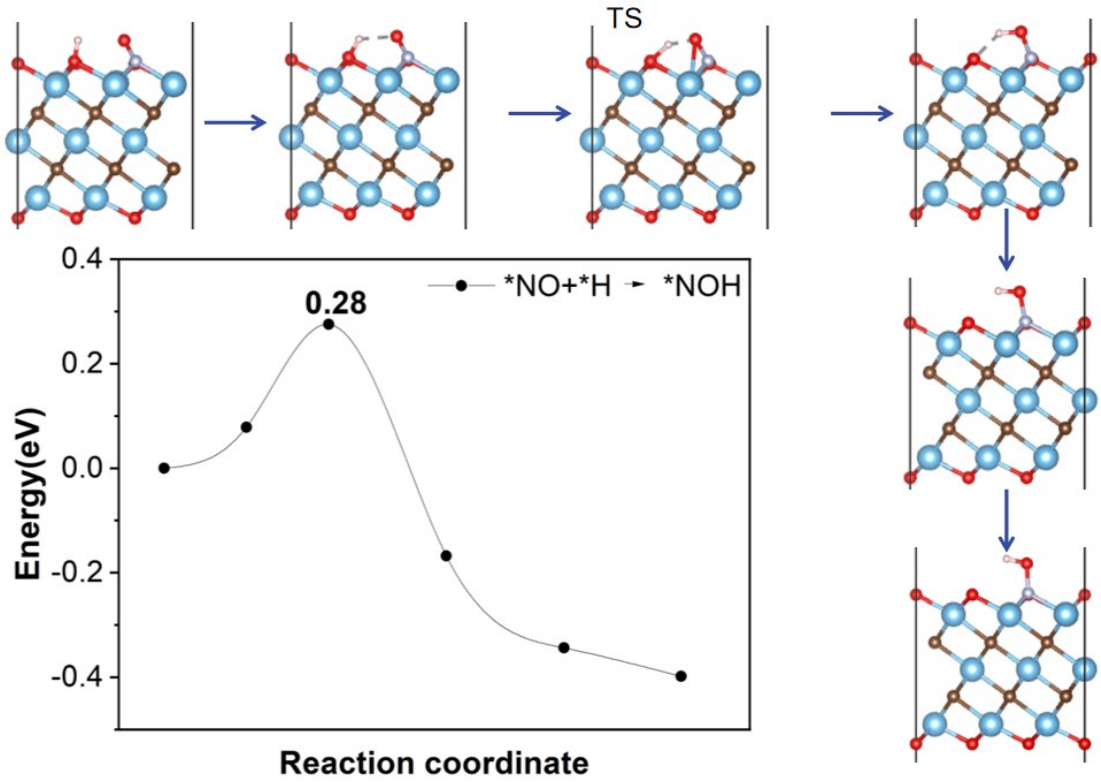

Fig. S48 Minimum energy path and activation barrier of elementary step *NO+*H→*NOH. TS stands for transition state.

Table S19. Calculated frequencies of TS in reaction *NO+*H→*NOH. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	194.02 meV

2f =	151.43 meV
3f =	127.74 meV
4f =	57.51 meV
5f =	56.78 meV
6f =	49.55 meV
7f =	39.86 meV
8f =	28.25 meV
9f/i =	-136.13 meV

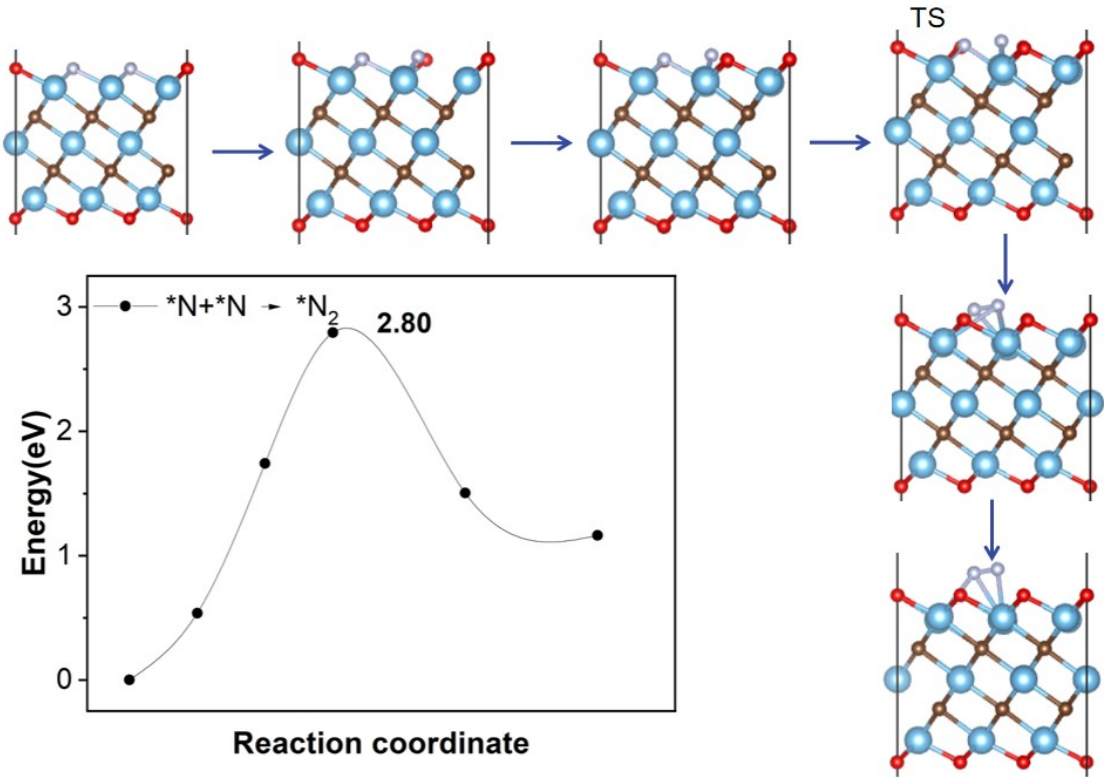

Fig. S49 Minimum energy path and activation barrier of elementary step *N+*N→*N_2. TS stands for transition state.

Table S20. Calculated frequencies of TS in reaction *N+*N→*N_2. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	74.81 meV
2f =	65.88 meV

3f =	59.35 meV
4f =	52.77 meV
5f =	28.38 meV
6f/i =	-66.89 meV

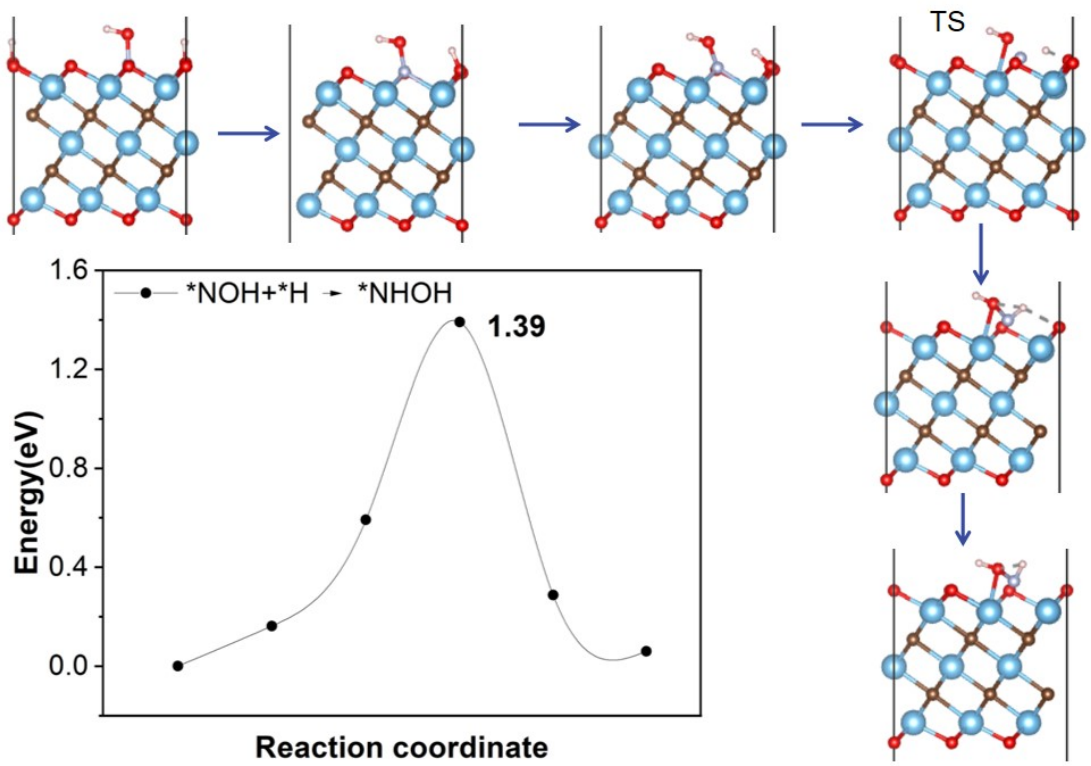

Fig. S50 Minimum energy path and activation barrier of elementary step *NOH+*H→*NHOH. TS stands for transition state.

Table S21. Calculated frequencies of TS in reaction *NOH+*H→*NHOH. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	442.01 meV
2f =	191.98 meV
3f =	156.79 meV
4f =	148.70 meV
5f =	112.99 meV
6f =	76.16 meV

7f =	57.78 meV
8f =	45.84 meV
9f =	34.26 meV
10f =	25.39 meV
11f =	22.80 meV
12f/ i=	-193.49 meV

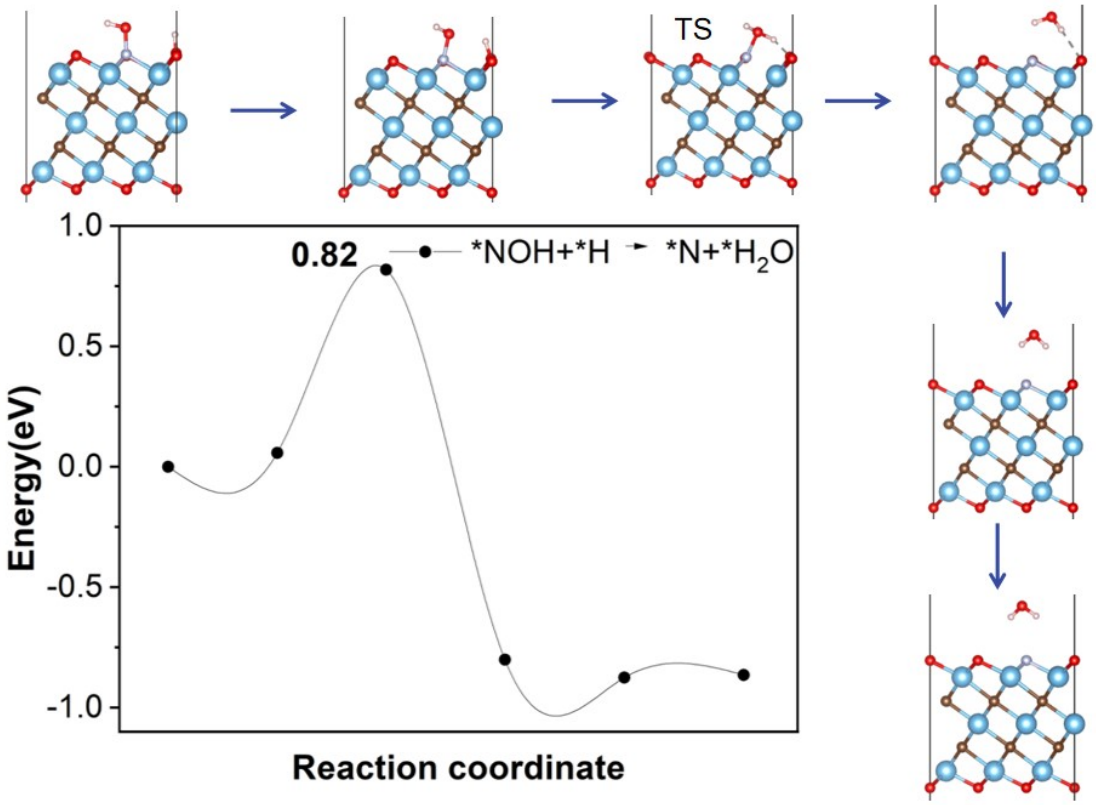

Fig. S51 Minimum energy path and activation barrier of elementary step *NOH+*H→*N+H_2O. TS stands for transition state.

Table S22. Calculated frequencies of TS in reaction *NOH+*H→*N+H_2O. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	446.36 meV
2f =	200.66 meV
3f =	166.01 meV
4f =	126.84 meV

5f =	114.78 meV
6f =	67.15 meV
7f =	61.24 meV
8f =	59.50 meV
9f =	46.74 meV
10f =	32.70 meV
11f =	20.17 meV
12f/ i=	-68.53 meV

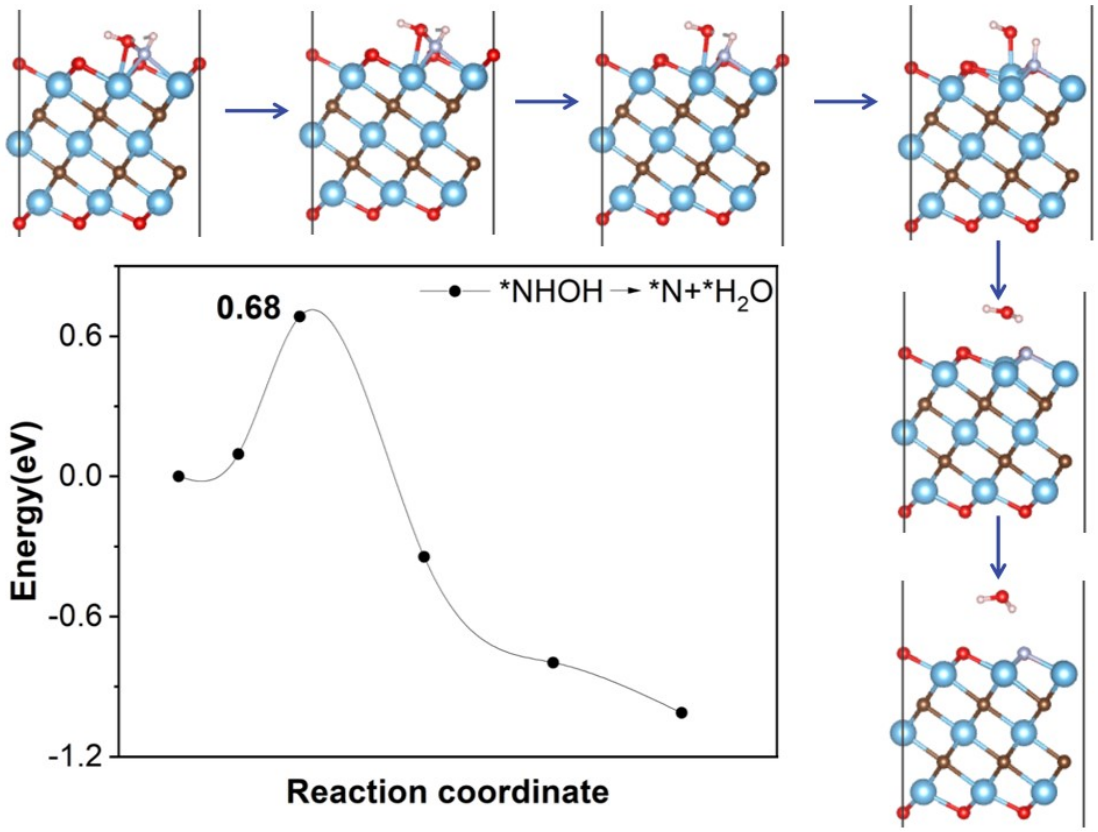

Fig. S52 Minimum energy path and activation barrier of elementary step *NHOH→*N+*H_2O. TS stands for transition state.

Table S23. Calculated frequencies of TS in reaction *NHOH→*N+*H_2O. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	451.79 meV
2f =	423.45 meV

3f =	114.31 meV
4f =	108.25 meV
5f =	77.12 meV
6f =	72.87 meV
7f =	53.21 meV
8f =	49.86 meV
9f =	39.90 meV
10f =	35.12 meV
11f =	28.12 meV
12f/ i=	-62.45 meV

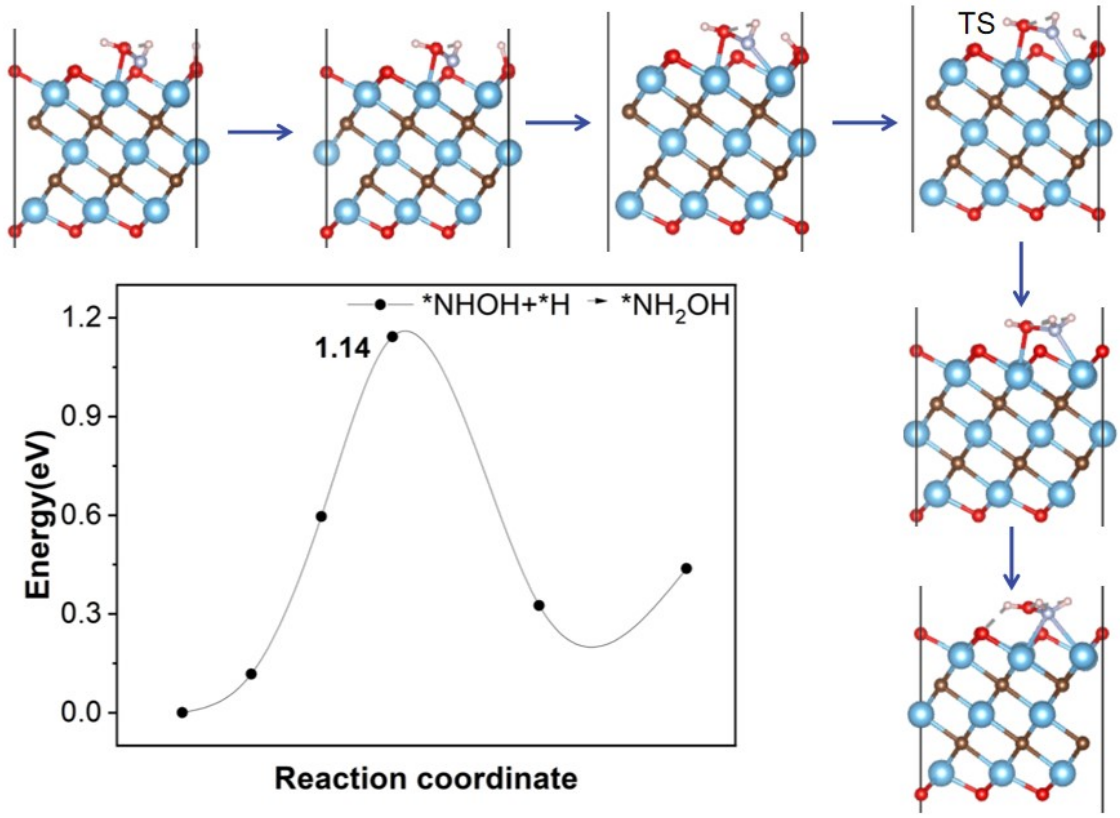

Fig. S53 Minimum energy path and activation barrier of elementary step *NHOH+*H→*NH_2OH. TS stands for transition state.

Table S24. Calculated frequencies of TS in reaction *NHOH+*H→*NH_2OH. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	434.74 meV
2f =	424.47 meV
3f =	193.11 meV
4f =	170.52 meV
5f =	165.80 meV
6f =	150.45 meV
7f =	112.66 meV
8f =	84.27 meV
9f =	75.03 meV
10f =	55.34 meV
11f =	37.88 meV
12f =	35.89 meV
13f =	27.66 meV
14f =	24.25 meV
15f/ i=	-155.09 meV

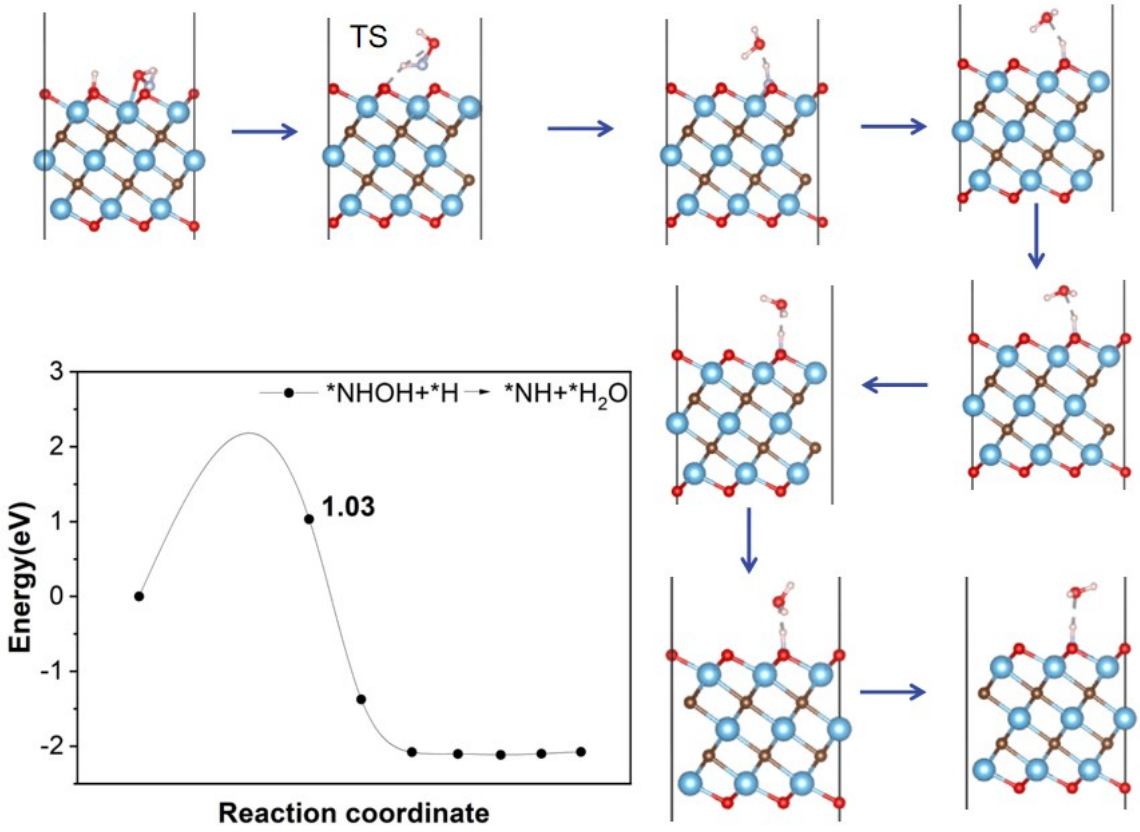

Fig. S54 Minimum energy path and activation barrier of elementary step *NHOH+*H→*NH+H_2O. TS stands for transition state.

Table S25. Calculated frequencies of TS in reaction *NHOH+*H→*NH+H_2O. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	445.75 meV
2f =	422.54 meV
3f =	399.00 meV
4f =	193.78 meV
5f =	173.35 meV
6f =	163.81 meV
7f =	155.87 meV
8f =	112.52 meV
9f =	57.26 meV
10f =	30.76 meV

11f =	25.86 meV
12f =	23.88 meV
13f =	13.09 meV
14f =	4.53 meV
15f/ i=	-11.94 meV

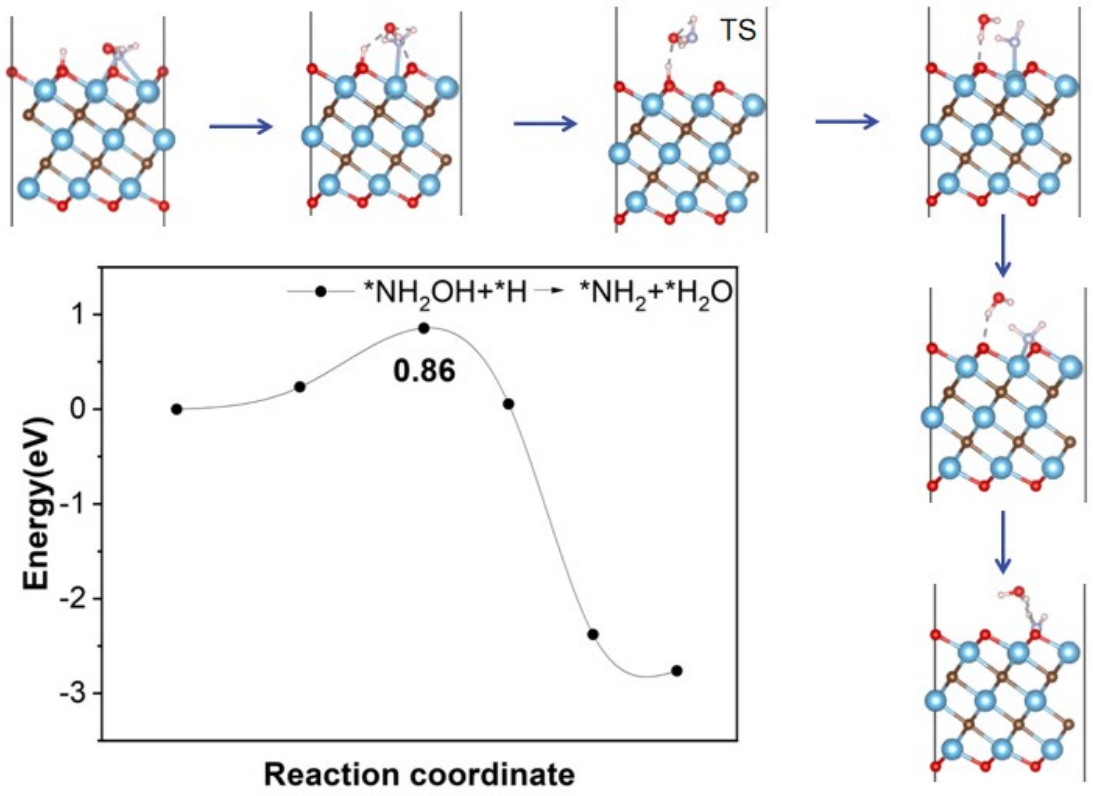

Fig. S55 Minimum energy path and activation barrier of elementary step $*NH_2OH+*H \rightarrow *NH_2+H_2O$. TS stands for transition state.

Table S26. Calculated frequencies of TS in reaction $*NH_2OH+*H \rightarrow *NH_2+H_2O$. The only one imaginary frequency is highlighted in grey

No.	Frequency
1f =	450.41 meV
2f =	425.08 meV
3f =	413.17 meV
4f =	339.61 meV
5f =	201.49 meV
6f =	170.31 meV

7f =	155.39 meV
8f =	144.39 meV
9f =	140.46 meV
10f =	127.33 meV
11f =	107.15 meV
12f =	68.42 meV
13f =	34.86 meV
14f =	25.84 meV
15f=	19.11 meV
16f =	5.23 meV
17f =	4.80 meV
18f/ i=	-12.83 meV

Activity origin

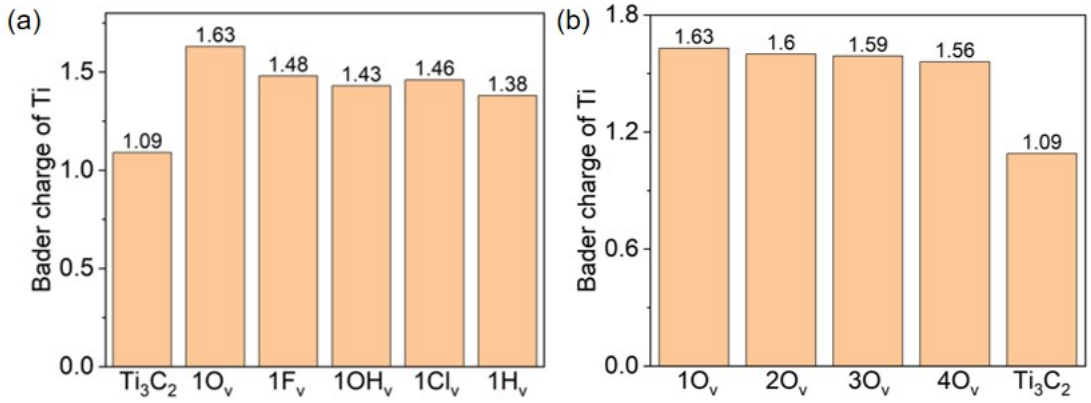

Fig. S56 Bader charge of Ti on Ti_3C_2 and (a) $Ti_3C_2T_2$-T_v, (b) $Ti_3C_2T_2$-nO_v.

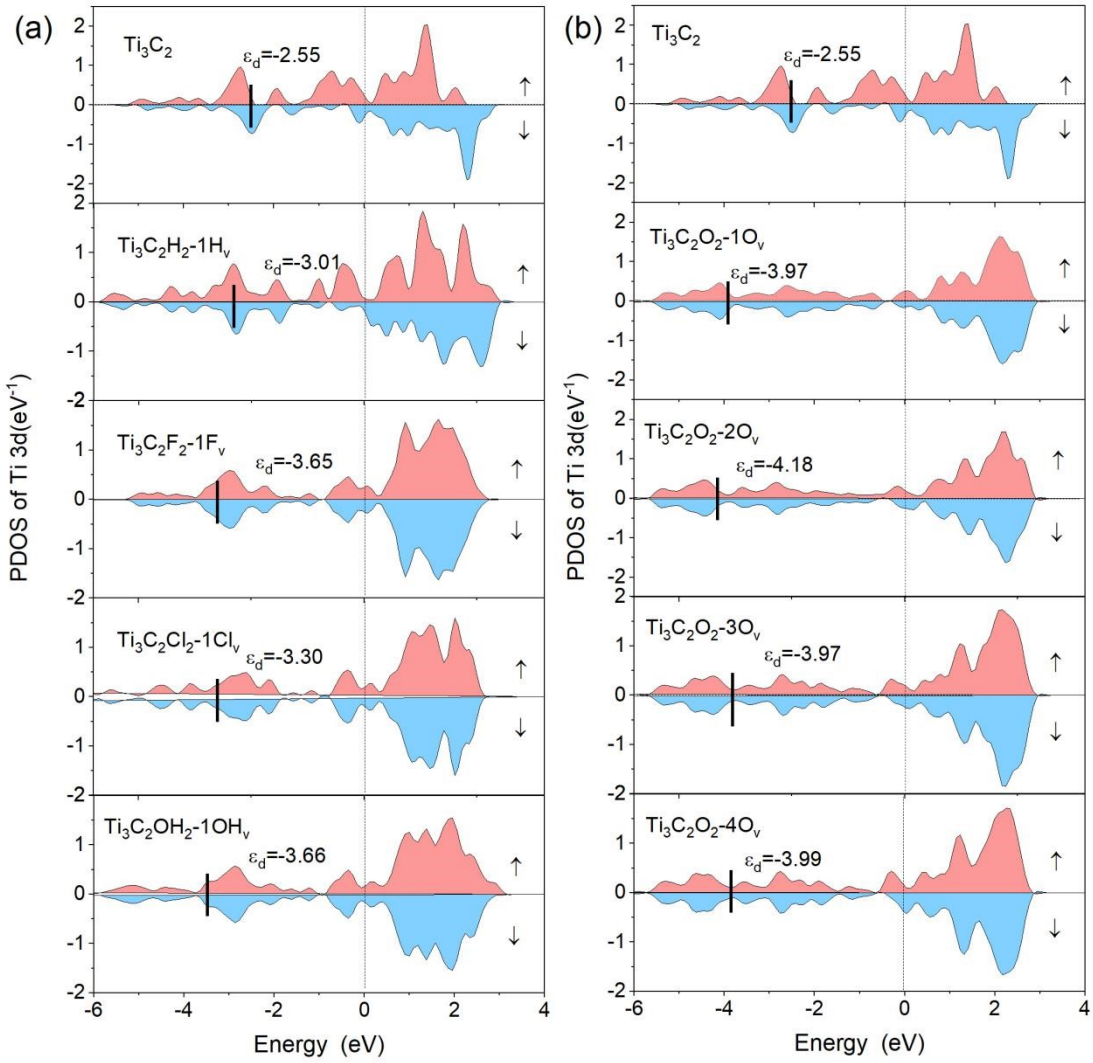

Fig. S57 d-band centers and projected density of states (PDOSs) of Ti 3d on Ti_3C_2 and (a) $Ti_3C_2T_2$-1T_v, (b) $Ti_3C_2T_2$-nO_v.

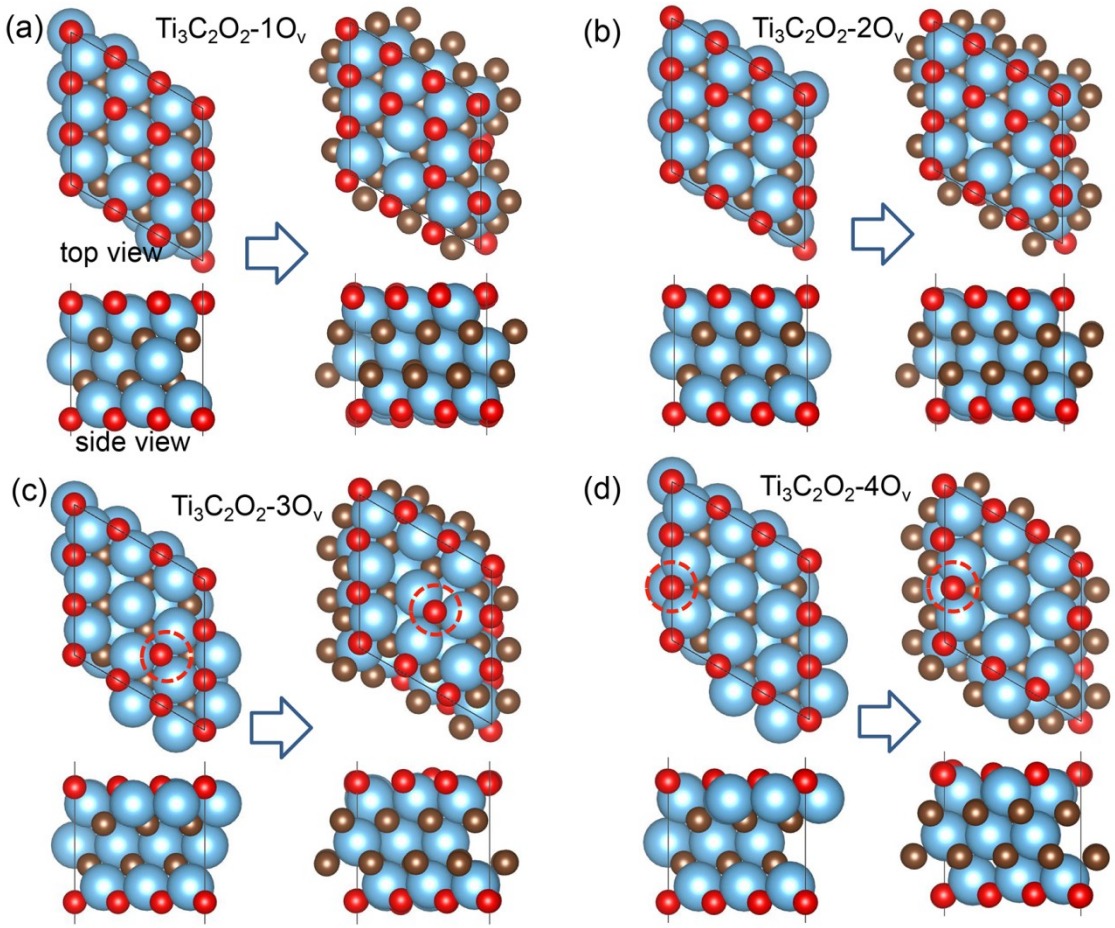

Fig. S58 Room temperature stability of partially O-vacant $Ti_3C_2O_2$ MXene. Snapshot of $Ti_3C_2O_2$ with (a) $1O_v$, (b) $2O_v$, (c) $3O_v$, (3) $4O_v$ endure 1000 fs AIMD at 300K. Except for some surface O atoms migration, no structure collapse or reconstruction of Ti_3C_2 layer was found.

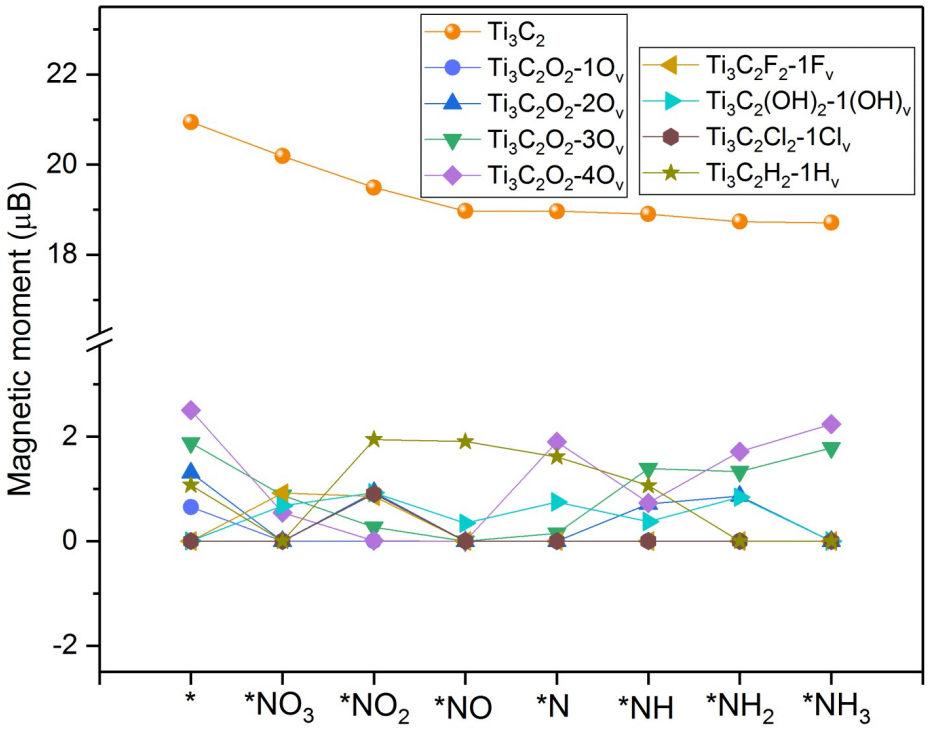

Fig. S59 Magnetic moments change of Ti_3C_2 MXene–based catalysts with the presence of NRA intermediates.

Tables

Table S27. The overpotential and RDS of NRA on Ti_3C_2 at pH=0

Ti_3C_2	ΔG_{max}(eV)	Overpotential(V)	Rate determining step
vertical	1.18	-1.18	$*NH_2+H^++e^-\rightarrow *NH_3$
parallel	1.18	-1.18	$*NH_2+H^++e^-\rightarrow *NH_3$
basal plane	1.18	-1.18	$*NH_2+H^++e^-\rightarrow *NH_3$
edge plane	1.69	-1.69	$*NH+H^++e^-\rightarrow *NH_2$

Table S28. The overpotential and RDS of NRA on M_3C_2 at pH=0

M_3C_2	ΔG_{max}(eV)	Overpotential(V)	Rate determining step
Ti_3C_2	1.18	-1.18	$*NH_2+H^++e^-\rightarrow *NH_3$
Mo_3C_2	0.39	-0.39	$*NH_2+H^++e^-\rightarrow *NH_3$
V_3C_2	0.67	-0.67	$*NH+H^++e^-\rightarrow *NH_2$
Cr_3C_2	1.04	-1.04	$*NH_2+H^++e^-\rightarrow *NH_3$
Nb_3C_2	0.70	-0.70	$*NH_2+H^++e^-\rightarrow *NH_3$

Table S29. The overpotential and RDS of NRA on *M*@Ti_3C_2 at pH=0

M@Ti_3C_2	ΔG_{max}(eV)	Overpotential(V)	Rate determining step
Ti	1.18	-1.18	$*NH_2+H^++e^-\rightarrow *NH_3$
Fe	0.87	-0.87	$*NH_2+H^++e^-\rightarrow *NH_3$
Co	0.88	-0.88	$*NH_2+H^++e^-\rightarrow *NH_3$
Ni	1.10	-1.10	$*NH_2+H^++e^-\rightarrow *NH_3$
Cu	0.81	-0.81	$*NH_2+H^++e^-\rightarrow *NH_3$
Pt	1.31	-1.31	$*NH_2+H^++e^-\rightarrow *NH_3$
Pd	1.42	-1.42	$*NH_2+H^++e^-\rightarrow *NH_3$

Table S30. The overpotential and RDS of NRA on $Ti_3C_2T_2$-T_v at pH=0

Substrate	ΔG_{max}(eV)	Overpotential(V)	Rate determining step
Ti_3C_2	1.18	-1.18	$*NH_2+H^++e^-\rightarrow *NH_3$
$Ti_3C_2O_2$-O_v	-0.09	0	$*NH_2+H^++e^-\rightarrow *NH_3$
$Ti_3C_2OH_2$-OH_v	1.18	-1.18	$*NH_2+H^++e^-\rightarrow *NH_3$
$Ti_3C_2H_2$-H_v	1.04	-1.04	$*NH_2+H^++e^-\rightarrow *NH_3$
$Ti_3C_2F_2$-F_v	0.82	-0.82	$*NH_2+H^++e^-\rightarrow *NH_3$
$Ti_3C_2Cl_2$-Cl_v	0.61	-0.61	$*NH_2+H^++e^-\rightarrow *NH_3$

Table S31. The overpotential and RDS of NRA reaction on $Ti_3C_2O_2$-nO_v at pH=0

$Ti_3C_2O_2$-nO_v	ΔG_{max}(eV)	Overpotential(V)	Rate determining step
Ti_3C_2	1.18	-1.18	$*NH_2+H^++e^-\rightarrow *NH_3$
$1O_v$	-0.09	0	$*NH_2+H^++e^-\rightarrow *NH_3$
$2O_v$	0.34	-0.34	$*NH+H^++e^-\rightarrow *NH_2$
$3O_v$	0.38	-0.38	$*NH_2+H^++e^-\rightarrow *NH_3$
$4O_v$	0.39	-0.39	$*NH_2+H^++e^-\rightarrow *NH_3$

Table S32. The overpotential and RDS of NRA reaction on *M*@$Ti_3C_2O_2$-O_v at pH=0

***M*@$Ti_3C_2O_2$-O_v**	ΔG_{max}(eV)	Overpotential(V)	Rate determining step
Ti	-0.09	0	$*NH_2+H^++e^-\rightarrow *NH_3$
Ir	0.28	-0.28	$*+NO_3^-\rightarrow *NO_3+e^-$

Mo	0.05	-0.05	$*NH_2+H^++e^-\rightarrow *NH_3$
W	0.18	-0.18	$*NH_2+H^++e^-\rightarrow *NH_3$
Os	0.20	-0.20	$*+NO_3^-\rightarrow *NO_3+e^-$
Zr	0.47	-0.47	$*+NO_3^-\rightarrow *NO_3+e^-$

Table S33. Gibbs free energy change of each elementary step of NRA on Ti_3C_2 MXene basal plane. Vertical and parallel absorption modes of NO_3^- are considered. ΔG_{total} is the sum of all ΔG. The unit of ΔG is eV

	Vertical	**Parallel**
ΔG_1	-1.59	-2.28
ΔG_2	-1.98	-2.64
ΔG_3	-2.32	-0.97
ΔG_4	-1.05	-1.05
ΔG_5	-0.27	-0.27
ΔG_6	0.69	0.69
ΔG_7	1.18	1.18
ΔG_8	0.43	0.43
ΔG_{total}	-4.91	-4.91

Table S34. Free energy change of each elementary step of NRA on M_3C_2 MXene (M=Ti, Mo, V, Cr, Nb) basal plane. The unit of ΔG is eV

pH		Ti	Mo	V	Nb	Cr
0	ΔG_1	-1.59	-0.04	-1.33	-1.63	-2.53
	ΔG_2	-1.98	-1.87	-1.60	-1.92	-1.28
	ΔG_3	-2.32	-0.59	-1.41	-2.21	-2.07
	ΔG_4	-1.05	-2.08	-1.96	-1.33	-1.35
	ΔG_5	-0.27	-0.13	-0.34	0.06	0.24
	ΔG_6	0.69	-0.67	0.67	0.51	0.01
	ΔG_7	1.18	0.39	0.49	0.70	1.04
	ΔG_8	0.43	0.08	0.57	0.92	1.03
	ΔG_{total}	-4.91	-4.91	-4.91	-4.91	-4.91
7	ΔG_1	-1.59	-0.04	-1.33	-1.63	-2.53
	ΔG_2	-1.15	-1.04	-0.78	-1.10	-0.45
	ΔG_3	-1.50	0.23	-0.58	-1.38	-1.24
	ΔG_4	-0.22	-1.25	-1.13	-0.50	-0.52
	ΔG_5	0.14	0.28	0.08	0.47	0.65
	ΔG_6	1.10	-0.26	1.08	0.92	0.42
	ΔG_7	1.59	0.81	0.90	1.11	1.45
	ΔG_8	0.43	0.08	0.57	0.92	1.03
	ΔG_{total}	-1.18	-1.18	-1.18	-1.18	-1.18
14	ΔG_1	-1.59	-0.04	-1.33	-1.63	-2.53
	ΔG_2	-0.32	-0.21	0.05	-0.27	0.38
	ΔG_3	-0.67	1.06	0.25	-0.55	-0.41
	ΔG_4	0.61	-0.42	-0.30	0.33	0.31
	ΔG_5	0.56	0.70	0.49	0.89	1.07
	ΔG_6	1.52	0.16	1.50	1.34	0.84
	ΔG_7	2.01	1.22	1.31	1.52	1.87
	ΔG_8	0.43	0.08	0.57	0.92	1.03
	ΔG_{total}	2.54	2.54	2.54	2.54	2.54

Table S35. Free energy change of each elementary step of NRA on M_3C_2 MXene (M=Ti, Mo, V, Nb) edge plane. ΔG_{total} is the sum of all ΔG. The unit of ΔG is eV

pH		Ti	Mo	V	Nb
0	ΔG_1	-1.72	-1.43	-1.71	-1.78
	ΔG_2	-1.79	-1.93	-1.93	-1.88
	ΔG_3	-2.45	-1.12	-2.28	-2.15
	ΔG_4	-0.24	-1.84	-1.38	-1.44
	ΔG_5	-0.80	-0.21	-0.04	0.02
	ΔG_6	1.69	-0.06	0.58	0.33
	ΔG_7	0.22	0.68	1.18	1.13
	ΔG_8	0.18	1.00	0.67	0.87
	ΔG_{total}	-4.91	-4.91	-4.91	-4.91
7	ΔG_1	-1.72	-1.43	-1.71	-1.78
	ΔG_2	-0.96	-1.10	-1.10	-1.06
	ΔG_3	-1.62	-0.29	-1.46	-1.32
	ΔG_4	0.59	-1.02	-0.55	-0.62
	ΔG_5	-0.38	0.20	0.37	0.44
	ΔG_6	2.10	0.35	1.00	0.74
	ΔG_7	0.63	1.10	1.59	1.55
	ΔG_8	0.18	1.00	0.67	0.87
	ΔG_{total}	-1.18	-1.18	-1.18	-1.18
14	ΔG_1	-1.72	-1.43	-1.71	-1.78
	ΔG_2	-0.13	-0.27	-0.27	-0.23
	ΔG_3	-0.80	0.54	-0.63	-0.50
	ΔG_4	1.42	-0.19	0.28	0.21
	ΔG_5	0.03	0.61	0.79	0.85
	ΔG_6	2.52	0.77	1.41	1.16
	ΔG_7	1.04	1.51	2.01	1.96
	ΔG_8	0.18	1.00	0.67	0.87
	ΔG_{total}	2.54	2.54	2.54	2.54

Table S36. Free energy change of each elementary step of HER on M_3C_2 MXene (M= Mo, V, Cr, Nb) basal plane. The unit of ΔG is eV

		Ti	Mo	V	Cr	Nb
pH=0	ΔG_1	-0.89	0.31	-0.19	-1.26	-0.14
	ΔG_2	0.89	-0.31	0.19	1.26	0.14
pH=7	ΔG_1	-1.31	0.72	-0.60	-1.68	-0.55
	ΔG_2	1.31	-0.72	0.60	1.68	0.55
pH=14	ΔG_1	-1.72	1.14	-1.02	-2.09	-0.97
	ΔG_2	1.72	-1.14	1.02	2.09	0.97

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