

Theoretical investigations of transition metal atom-doped MoSi₂N₄ monolayers as catalysts for electrochemical CO₂ reduction reactions

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1. Zero-point energy (ZPE) and entropy corrections (TS)

In our DFT calculations, we calculated the zero-point energy (ZPE) of each adsorbed intermediate and free molecule by substituting the following equation using the vibrational frequency¹:

$$E_{ZPE} = \sum_{i=1}^{3N} \frac{hv_i}{2}$$

Where ν_i is DFT-calculated normal-mode frequency for species of 3N degree of freedom (N=number of atoms) adsorbed on TM@MoSi₂N₄-N_v, h is the Planck's constant (6.626×10^{-34} J·s).

The entropies of the gaseous molecules were taken from the NIST Chemistry WebBook². As the adsorbates were stably adsorbed on the catalyst, only their vibrational contribution to entropy terms was considered, excluding their translational and rotational contributions. And the vibrational contribution to entropy terms was calculated by the following equation³:

$$\Delta S_{ads}(0 \rightarrow T, P^0) = S_{vib} = \sum_{i=1}^{3N} \left[\frac{N_A h \nu_i}{T(e^{\frac{h\nu_i}{k_B T}} - 1)} - R \ln \left(1 - e^{-\frac{h\nu_i}{k_B T}} \right) \right]$$

Where ν_i is DFT-calculated normal-mode frequency for species of 3N degree of freedom (N=number of atoms) adsorbed on TM@MoSi₂N₄-N_v, N_A is the Avogadro's constant (6.022×10^{23} mol⁻¹), h is the Planck's constant (6.626×10^{-34} J·s), and k_B is the Boltzmann constant (1.38×10^{-23} J·K⁻¹), R is the ideal gas constant (8.314 J·K⁻¹·mol⁻¹), and T is the system temperature, and T=298K in this work.

2. Phonon frequency calculation: theory and method

The phonon calculations are carried out using a finite differences approach. To compute the phonon modes and frequencies we start by Taylor expanding the total energy (E)

around the set of equilibrium positions of the nuclei ($\{R^0\}$):

$$E(\{R\}) = E(\{R^0\}) + \sum_{I\alpha} \frac{\partial E(\{R^0\})}{\partial R_{I\alpha}} (R_{I\alpha} - R_{I\alpha}^0) + \sum_{I\alpha} \frac{\partial^2 E(\{R^0\})}{\partial R_{I\alpha} \partial R_{J\beta}} (R_{I\alpha} - R_{I\alpha}^0) (R_{J\beta} - R_{J\beta}^0) + O(R^3) \quad (1)$$

where $\{R\}$ are the positions of the nuclei.

The first derivative of the total energy with respect to the nuclei corresponds to the forces

$$F_{I\alpha}(\{R^0\}) = - \left. \frac{\partial E(\{R\})}{\partial R_{I\alpha}} \right|_{R=R^0} \quad (2)$$

and the second derivative to the second-order force-constants

$$\Phi_{I\alpha J\beta}(\{R^0\}) = \left. \frac{\partial^2 E(\{R\})}{\partial R_{I\alpha} \partial R_{J\beta}} \right|_{R=R^0} = - \left. \frac{\partial F_{I\alpha}(\{R\})}{\partial R_{J\beta}} \right|_{R=R^0} \quad (3)$$

Changing variables in the Taylor expansion of the total energy with $u_{I\alpha} = R_{I\alpha} - R_{I\alpha}^0$ that corresponds to the displacement of the atoms with respect to their equilibrium position $R_{I\alpha}^0$ leads to

$$E(\{R\}) = E(\{R^0\}) + \sum_{I\alpha} -F_{I\alpha}(\{R^0\}) u_{I\alpha} + \sum_{I\alpha} \Phi_{I\alpha J\beta}(\{R^0\}) u_{I\alpha} u_{J\beta} + O(R^3) \quad (4)$$

If we take the system to be in equilibrium, the forces on the atoms are zero and then the Hamiltonian of the system is

$$H = \frac{1}{2} \sum_{I\alpha} M_I \dot{u}_{I\alpha}^2 + \frac{1}{2} \sum_{I\alpha J\beta} \Phi_{I\alpha J\beta} u_{I\alpha} u_{J\beta} \quad (5)$$

with M_I the mass of the I -th nucleus. The equation of motion is then given by

$$M_I \ddot{u}_{I\alpha} = - \Phi_{I\alpha J\beta} u_{J\beta} \quad (6)$$

We then look for solutions in the form of plane waves traveling parallel to the wave vector q

q , i.e.

$$u_{I\alpha,v}(q,t) = \frac{1}{2\sqrt{M_I}} \left\{ A^v(q) \varepsilon_{I\alpha,v}(q) e^{i[q \cdot R_I - \omega_v(q)t]} + A^{v*}(q) \varepsilon_{I\alpha,v}^*(q) e^{-i[q \cdot R_I - \omega_v(q)t]} \right\} \quad (7)$$

where $\varepsilon_{I\alpha,v}(q)$ are the phonon mode eigenvectors and $A^v(q)$ the amplitudes. Replacing it in the equation of motion we obtain the following eigenvalue problem

$$\sum_{j\beta} D_{I\alpha j\beta}(q) \varepsilon_{j\beta,v}(q) = \omega_v^2(q) \varepsilon_{I\alpha,v}(q) \quad (8)$$

with $D_{I\alpha j\beta}(q) = \frac{1}{\sqrt{M_I M_J}} \Phi_{I\alpha j\beta} e^{iq \cdot (R_J - R_I)}$ the dynamical matrix in the harmonic approximation. Now by solving the eigenvalue problem above we can obtain the phonon modes $\varepsilon_{I\alpha,v}(q)$ and frequencies $\omega_v(q)$ at any arbitrary q point.

We can write the positions of the atoms in the supercell R_I in terms of integer multiples of the lattice vectors of the unit cell I such that $R_I \rightarrow R_{li} = I + r_i$ with r_i being the position of the ion in the unit cell. The force constants then become $\Phi_{I\alpha j\beta} \rightarrow \Phi_{li\alpha, l'j\beta}$. The dynamical matrix is then given by

$$D_{i\alpha j\beta}(q) = \frac{1}{\sqrt{M_i M_j}} \sum_l \Phi_{li\alpha, 0j\beta} e^{-iq \cdot (l + r_i - r_j)} \quad (9)$$

With I chosen using the minimal image convention.

This allows us to compute the phonons in the unit cell using the following equation

$$\sum_{j\beta} D_{i\alpha j\beta}(q) \varepsilon_{j\beta,v}(q) = \omega_v^2(q) \varepsilon_{i\alpha,v}(q) \quad (10)$$

with the dynamical matrix having dimension $3n$ with n the number of atoms in the unit cell.

The second-order force constants are computed using finite differences of the forces when each ion is displaced in each independent direction. This is done by creating systems with finite ionic displacement of atom a in direction i with magnitude λ , computing the orbitals $\psi_{\lambda}^{u_{I\alpha}}$ and the forces for these systems. The second-order force constants are then computed using

$$\Phi_{I\alpha J\beta} = \frac{\partial^2 E}{\partial u_{I\alpha} \partial u_{J\beta}} = - \frac{\partial F_{I\alpha}}{\partial u_{J\beta}} \approx \frac{\left(F\left[\left\{\psi_{\lambda}^{u_{J\beta}}\right\}\right] - F\left[\left\{\psi_{-\lambda}^{u_{I\alpha}}\right\}\right] \right)_{I\alpha}}{2\lambda}$$

$$I=1, \dots, N_{\text{atoms}}, J=1, \dots, N_{\text{atoms}}, \alpha = x, y, z, \beta = x, y, z. \quad (11)$$

where $u_{I\alpha}$ corresponds to the displacement of atom I

in the cartesian direction α and $F[\psi]$ retrieves the set of forces acting on all the ions given the ψ_{nk} Kohn-Sham orbitals.

In density-functional theory, we solve the Kohn-Sham (KS) equations

$$H(k)|\psi_{nk}\rangle = e_{nk}S(k)|\psi_{nk}\rangle \quad (12)$$

where $H(k)$ is the DFT Hamiltonian, $S(k)$ is the overlap operator, $|\psi_{nk}\rangle$ and e_{nk} are the Kohn-Sham (K-S) eigenstates and eigen energies..

Taking the derivative with respect to the ionic displacements $u_{I\alpha}$, we obtain the Sternheimer equations

$$[H(k) - e_{nk}S(k)]|\partial_{u_{I\alpha}} \psi_{nk}\rangle = - \partial_{u_{I\alpha}} [H(k) - e_{nk}S(k)]|\psi_{nk}\rangle \quad (13)$$

Once the derivative of the KS orbitals is computed, we can write

$$|\psi_{\lambda}^{u_{I\alpha}}\rangle = |\psi\rangle + |\partial_{u_{I\alpha}} \psi\rangle \quad (14)$$

where λ is a small numeric value to use in the finite differences formulas below.

The second-order response to ionic displacement, i.e., the force constants or Hessian matrix can be computed using the same equation used in the case of the finite

differences approach

$$\Phi_{I\alpha J\beta} = \frac{\partial^2 E}{\partial u_{I\alpha} \partial u_{J\beta}} = - \frac{\partial F_{I\alpha}}{\partial u_{J\beta}} \approx \frac{\left(F\left[\left\{\psi_{\lambda}^{u_{J\beta}}\right\}\right] - F\left[\left\{\psi_{-\lambda}^{u_{I\alpha}}\right\}\right] \right)_{I\alpha}}{2\lambda}$$

$$I=1, \dots, N_{\text{atoms}}, J=1, \dots, N_{\text{atoms}}, \alpha = x, y, z, \beta = x, y, z. \quad (15)$$

where again $F[\{\psi\}]$ yields the forces for a given set of ψ_{nk} K-S orbitals.

The widely used first principle software, including Vienna Ab initio Simulation Package (VASP), Material Studio, DS-PAW, Quantum Espresso and others, can solve K-S equation to obtain the total energy of supercell configurations with atomic displacement. With the help of Phonopy, the calculated atomic displacement and total energy, can be further used to construct phonon Hamiltonian. The phonon frequency can be solved from phonon Hamiltonian (whose main part is known as the force constants or Hessian matrix).

Usually, there are several steps to complete phonon frequency calculations. The VASP and Phonopy are used to demonstrate how to calculate phonon frequency step by step.

- (1) The supercell structures with (or without) displacements are created from a unit cell fully considering crystal symmetry.

To obtain supercells ($3 \times 3 \times 1$) with displacements, run phonopy using

`phonopy -d --dim 3 3 1`

then the following files SPOSCAR, phonopy_disp.yaml, and POSCAR-{number} can be generated:

```
phonopy_disp.yaml POSCAR POSCAR-001 POSCAR-002 POSCAR-003
POSCAR-004 POSCAR-005 POSCAR-006 SPOSCAR
```

Here SPOSCAR is the perfect supercell structure, phonopy_disp.yaml contains the information on displacements, and POSCAR-{number} are the supercells with atomic displacements. POSCAR-{number} corresponds to the different atomic displacements written in phonopy_disp.yaml. The primitive POSCAR will be copied and renamed as POSCAR-unitcell.

- (2) The total energy, the force of these structures with displacements are calculated

by DFT software. Usually, atomic structure, pseudopotentials and control parameters play important roles in DFT calculations. This process requires the high accuracy of total energy calculations.

In the case of VASP, the calculations for the finite displacement method can be proceeded just using the POSCAR-`{number}` files as POSCAR of VASP calculations. An example of the INCAR for VASP is as follows:

```
PREC = Accurate
IBRION = -1
ENCUT = 500
EDIFF = 1.0e-08
ISMEAR = 0; SIGMA = 0.01
IALGO = 38
LREAL = .FALSE.
LWAVE = .FALSE.
LCHARG = .FALSE.
```

- (3) The relation between displacement and total energy can be found and the force constant and dynamical matrix can be calculated.

Force constants are calculated using the structure files POSCAR-`{number}` (from forces on atoms) or using the SPOSCAR file

The FORCE_SETS file is created using VASP interface:

```
phonopy -f disp-{001..006}/vasprun.xml
```

A band.conf file should be created with following setting:

```
ATOM_NAME = Ga N
DIM = 5 5 1
BAND = 0.0 0.0 0.0 0.333 0.333 0.0 0.5 0.0 0.0 0.0 0.0 0.0
BAND_LABELS = G K M G
FORCE_CONSTANTS = WRITE
FC_SYMMETRY = .TRUE.
Then run the task as following
phonopy --dim='3 3 1' -c POSCAR-unitcell band.conf
```

The second order force constant matrix FORCE_CONSTANTS will be obtained now.

- (4) The dynamical matrix in the harmonic approximation, which is an eigenvalue

problem, can be solved to obtain the phonon modes and frequencies at any arbitrary q point.

phonopy-bandplot –gnuplot > 331.dat

The dynamical matrix is built from the force constants. Phonon frequencies and eigenvectors are calculated from the dynamical matrices with the specified q-points.

In our present work, the phonon frequency calculations were done using DS-PAW code with two input files contains frequency.in and structure.as. An example of the frequency.in is as follows:

```
task = frequency
sys.structure = structure.as
sys.functional = PBE
sys.spin = collinear
sys.symmetry = false
cal.ksampling = MP
cal.kpoints = [3,3,1]
cal.cutoffFactor = 1.0
cal.cutoff = 500
cal.smearing = 1
cal.sigma = 0.05

scf.convergence = 1e-6
scf.max = 60
scf.min = 2

frequency.dispOrder = 1
frequency.dispRange = 0.01

corr.VDW = true
corr.VDWType = D3G
corr.dftu = true
corr.dftuElements = [Mo,Ni]
corr.dftuOrbital = [d,d]
corr.dftuU = [2.18,3.4]
corr.dftuJ = [0,0]

io.charge = false
```

where the setting parameter task = frequency: This calculation is frequency

calculation.

Frequency.dispOrder: It indicates the way atoms vibrate during frequency calculation. Frequency.dispOrder=1 corresponds to the central difference method, so there are two atomic vibration modes: the displacement of the atom in each Cartesian direction is \pm frequency.dispRange; Frequency.dispOrder=2 corresponds to four modes of atomic vibration: the displacement of the atom in each Cartesian direction is \pm frequency.dispRange and $\pm 2 * \text{frequency.dispRange}$;

Frequency.dispRange: It indicates the range of atomic displacement during frequency calculation.

The file structure.as contains the crystal structure information, including lattice constant, the number of atoms, atomic name, atomic positions in Direct or Cartesian coordinations, and so on. This file structure.as is similar to the POSCAR file in VASP.

The structure of CO₂ on Ni@MoSi₂N₄-N_v is taken as an example, and written as a structure.as file in the following:

```
Total number of atoms
66
Lattice
8.61279964 0.00000000 0.00000000
-4.30664001 7.45871836 0.00000000
0.00000000 0.00000000 30.00000000
Cartesian Fix_x Fix_y Fix_z
C 3.05792669 1.48801427 11.06099992 F F F
Mo 1.43572707 0.82791774 3.48299994 T T T
Mo 0.00592219 3.31465452 3.48900005 T T T
Mo -1.43206479 5.80512039 3.48600000 T T T
Mo 4.30809541 0.83090123 3.48299994 T T T
Mo 2.87441499 3.31390852 3.48299994 T T T
Mo 1.43685882 5.80064531 3.48299994 T T T
Mo 7.17831114 0.82866363 3.48299994 T T T
Mo 5.74290799 3.31465452 3.48299994 T T T
Mo 4.30750489 5.80064531 3.48299994 T T T
N 0.00123854 1.65807302 29.95800017 T T T
```

N -1.43416454 4.14406382 29.95800017 T T T
N -2.87085965 6.63080060 29.95800017 T T T
N 2.87188454 1.65807302 29.95800017 T T T
N 1.43562028 4.14406382 29.95800017 T T T
N 0.00021720 6.63005461 29.95800017 T T T
N 5.74339204 1.65807302 29.95800017 T T T
N 4.30755821 4.14480981 29.95800017 T T T
N 2.87086352 6.63005461 29.95800017 T T T
N 4.30615965 7.45722661 2.21399992 T T T
N -1.43195808 2.48897432 2.21699996 T T T
N -2.86606923 4.97272757 2.21699996 T T T
N 2.87279942 0.00074587 2.21699996 T T T
N 1.43782699 2.48599077 2.21699996 T T T
N 0.00070131 4.97198156 2.21699996 T T T
N 5.74258431 0.00074587 2.21699996 T T T
N 4.30976492 2.48673678 2.21699996 T T T
N 2.87263954 4.97123557 2.21699996 T T T
N 4.30486778 7.45648073 4.74899992 T T T
N -1.43195816 2.49046609 4.74299981 T T T
N -2.86434649 4.97123557 4.74299981 T T T
N 2.86892269 0.02386789 4.76100012 T T T
N 1.45634475 2.47032754 4.76400017 T T T
N 0.00199316 4.97272757 4.74899992 T T T
N 5.74086148 0.00074587 4.74599987 T T T
N 4.29641499 2.48002393 4.76400017 T T T
N 2.87177791 4.96974403 4.74899992 T T T
N -0.04268633 1.64464744 7.01699987 T T T
N -1.43588714 4.14257228 7.00500011 T T T
N -2.90487903 6.59574458 7.01699987 T T T
N 1.42657685 4.13735120 7.00500011 T T T
N -0.01011813 6.62408797 7.00500011 T T T
N 5.77482902 1.65285195 7.00500011 T T T
N 4.32047649 4.17613629 7.00500011 T T T
N 2.85191564 6.61961245 7.00800015 T T T
Ni 2.88308116 1.66105656 7.87800014 T T T
O 2.91538283 1.54992168 9.88200007 F F F
O 3.20262328 1.43431159 12.23100005 F F F
Si 1.42663147 2.44123860 6.50100006 T T T
Si 0.00000000 0.00000000 0.47700002 T T T
Si -1.43411126 2.48673678 0.47700002 T T T
Si -2.86994508 4.97347356 0.47700002 T T T
Si 2.87193799 0.00074587 0.48000002 T T T
Si 1.43653483 2.48673678 0.48000002 T T T
Si 0.00113174 4.97272757 0.48000002 T T T

Si 5.74301498 0.00000000 0.47700002 T T T
Si 4.30804206 2.48673678 0.47700002 T T T
Si 2.87177807 4.97272757 0.47700002 T T T
Si 4.29108754 7.44902202 6.49199991 T T T
Si -1.43583382 2.48972009 6.47700010 T T T
Si -2.86822220 4.96899802 6.47700010 T T T
Si 2.82499790 0.00895046 6.50100006 T T T
Si -0.00274407 4.97049001 6.48899986 T T T
Si 5.72966502 0.00074587 6.48599982 T T T
Si 4.32354486 2.49867070 6.51299983 T T T
Si 2.86618021 4.96153941 6.48899986 T T T

After the input files frequency.in and structure.as have been prepared, DS-PAW should be run, and three files DS-PAW.log, frequency.json, and frequency.txt will be generated. The calculated frequencies can be found in the frequency.txt file.

Table S1 The values of U–J parameter for DFT+U calculations

Metal	U-J
Sc	2.11
Ti	2.58
V	2.72
Cr	2.79
Mn	3.06
Fe	3.29
Co	3.42
Ni	3.4
Cu	3.87
Zn	4.12
Mo	2.18

Table S2 Calculated Zero-point energy and entropy corrections of the *COOH species during the CO₂ reduction process.

Metal	ZPE (eV) (298 K)	TS (eV)
Sc	0.60	0.25
Ti	0.61	0.24
V	0.61	0.17
Cr	0.62	0.22
Mn	0.60	0.23
Fe	0.60	0.14
Co	0.60	0.14
Ni	0.60	0.08
Cu	0.59	0.09

Table S3 Calculated Zero-point energy and entropy corrections of the *CO species during the CO₂ reduction process.

Metal	ZPE (eV) (298 K)	TS (eV)
Sc	0.18	0.06
Ti	0.18	0.12
V	0.19	0.17
Cr	0.18	0.19
Mn	0.19	0.11
Fe	0.20	0.04
Co	0.20	0.05
Ni	0.18	0.07
Cu	0.19	0.07

Table S4 The bond length (Å) between the TM atom and Si atom in the TM@MoSi₂N₄-N_v monolayers.

Metal	d(TM-Si1)	d(TM-Si2)	d(TM-Si3)	Bulk d(TM-Si)	Ref.
Sc	2.65	2.43	2.40	2.99	a
Ti	2.67	2.32	2.32	2.475	b
V	2.41	2.41	2.44	2.433	b
Cr	2.34	2.34	2.34	2.52	c
Mn	2.46	2.46	2.46	2.90	d
Fe	2.19	2.16	2.16	2.46	e
Co	2.09	2.09	2.09	2.31	f
Ni	2.16	2.16	2.15	2.39	g
Cu	2.39	2.34	2.34	2.36	h
Zn	3.23	3.33	3.33	2.45	i

- a. The Materials Project. Materials Data on Sc₂Nb₃Si₄ by Materials Project. United States: N. p., 2020. Web. doi:10.17188/1696485.
- b. J. Chem. Phys. 147, 084301 (2017)
- c. The Materials Project. Materials Data on U₄Cr₇Si by Materials Project. United States: N. p., 2020. Web. doi:10.17188/1759229.
- d. The Materials Project. Materials Data on Mn₄Si₇ by Materials Project. United States: N. p., 2020. Web. doi:10.17188/1274254.
- e. J. Phys.: Condens. Matter 26,355005(2014).
- f. The Materials Project. Materials Data on Yb₅(Co₂Si₇)₂ by Materials Project. United States: N. p., 2020. Web. doi:10.17188/1757482.

- g. The Materials Project. Materials Data on Sm6Si3Ni2 by Materials Project. United States: N. p., 2020. Web. doi:10.17188/1759804.
- h. The Materials Project. Materials Data on Li22(Cu3Si2)7 by Materials Project. United States: N. p., 2020. Web. doi:10.17188/1758821.
- i. Phys. Chem. Chem. Phys.,15, 3702-3705 (2013)

Table S5 Bond lengths (Å) between C, O, and TM atoms, bond angle (°) of CO₂ of *CO₂_2 configuration in the TM@MoSi₂N₄-Nv monolayers and charge (e) gained by the adsorbed CO₂ molecule.

Metal	d(TM-C)	d(TM-O)	∠O-C-O	Bader charge
Sc	2.34	2.01	132.6	0.88
Ti	2.17	1.99	137.1	0.75
V	2.05	1.92	137.9	0.66
Cr	2.24	1.99	146.4	0.43
Mn	2.09	1.94	143.5	0.52
Fe	2.07	1.89	146.3	0.39
Co	2.16	1.90	155.5	0.19
Ni	2.06	1.96	149.7	0.32
Cu	2.03	1.97	148.9	0.33

Table S6 The Binding energy E_b (in eV) at 0 K, Binding free energy G_b (in eV) at 298 K and bond lengths $d(\text{TM-C})$ and $d(\text{TM-O})$ (in Å) of the *COOH intermediate in the CO generation process.

Metal	Binding energy E_b(*COOH) at 0K	Binding free energy G_b(*COOH) at 298.15 K	$d(\text{TM-C})$	$d(\text{TM-O})$
Sc	-0.85	-0.11	2.19	2.16
Ti	-1.01	-0.25	2.12	2.08
V	-1.04	-0.21	2.05	2.06
Cr	-0.15	0.64	2.01	2.06
Mn	-0.60	0.16	2.00	2.13
Fe	-0.53	0.32	1.96	2.10
Co	-0.14	0.71	1.88	2.06
Ni	-0.93	-0.01	1.88	2.17
Cu	-0.56	0.34	1.94	2.73

Table S7 The Binding energy E_b (in eV) at 0 K, Binding free energy G_b (in eV) at 298 K, and bond lengths (in Å) of the *CO intermediate in the CO generation process.

Metal	Binding energy $E_b(*CO)$ at 0K	Binding Free energy $G_b(*CO)$ at 298.15 K	d(TM-C)	d(TM-O)
Sc	-0.21	0.27	2.25	3.40
Ti	-0.24	0.19	2.14	3.29
V	-0.67	-0.29	2.02	3.17
Cr	-0.19	0.16	2.05	3.20
Mn	-0.19	0.26	1.91	3.06
Fe	-0.87	-0.35	1.82	2.98
Co	-0.69	-0.18	1.81	2.96
Ni	-0.72	-0.25	1.83	2.99
Cu	-0.69	-0.20	1.83	2.98

Table S8 The electrode potential (U vs. RHE), and DFT calculated theoretical limiting potential (U vs. RHE) of catalyst in previous studies.

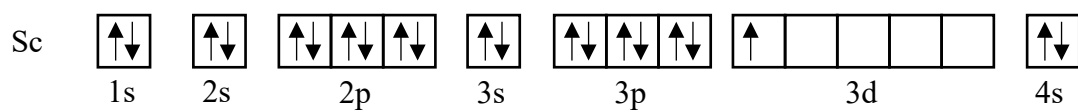
Catalyst	Electrode Potential	Theoretical Limiting potential	Reference
Co-N ₅	-0.73	-0.83	<i>J. Am. Chem. Soc.</i> 2018 , 140, 4218
Co-PMOF	-0.80	-0.34	<i>Nat. Commun.</i> 2018 , 9, 4466
Co-N ₂ -C	-0.68	~-0.80	<i>Angew. Chem.</i> 2018 , 57, 1944
Ni-N-C	-0.80	-1.09	<i>Adv. Energy Mater.</i> 2019 , 1903068
Bi-N ₄ -C	-0.50	-0.58	<i>J. Am. Chem. Soc.</i> 2019 , 141, 16569
Ni-N ₂ -C	--	-0.84	<i>Nat. Commun.</i> 2020 , 11, 2256
Ni-N ₃ -C	--	-0.92	<i>Nat. Commun.</i> 2020 , 11, 2256
Ni-N ₄ -C	--	-1.03	<i>Nat. Commun.</i> 2020 , 11, 2256
Mn-N ₃ -C	-0.55	-0.24	<i>Nat. Commun.</i> 2020 , 11, 4341
Edge-hosted Fe-N ₄	-0.58	-0.30	<i>ACS Catal.</i> 2020 , 10, 10803
Ni-N ₄ B ₂ -C _x	-1.20	-0.20	<i>Mater. Today</i> 2022 , 54, 63
Cr-NN-Ti ₃ C ₂ O ₂	--	-0.20	<i>CEJ.</i> 2023 , 461,141936
Co-NN-	--	-0.23	<i>CEJ.</i> 2023 , 461,141936

$\text{Ti}_3\text{C}_2\text{O}_2$

Table S9 The magnetic moments for single TM atoms and total magnetic moments for TM @ MoSi₂N₄-N_v

Metal	Single TM	TM @ MoSi ₂ N ₄ -N _v
Sc	1.001	0.002
Ti	4.000	1.693
V	5.000	4.294
Cr	6.000	4.736
Mn	5.087	4.865
Fe	4.090	2.664
Co	3.000	0.013
Ni	1.990	1.040
Cu	1.089	2.072
Zn	0.002	1.448

The electronic configurations for TMs are given as following:



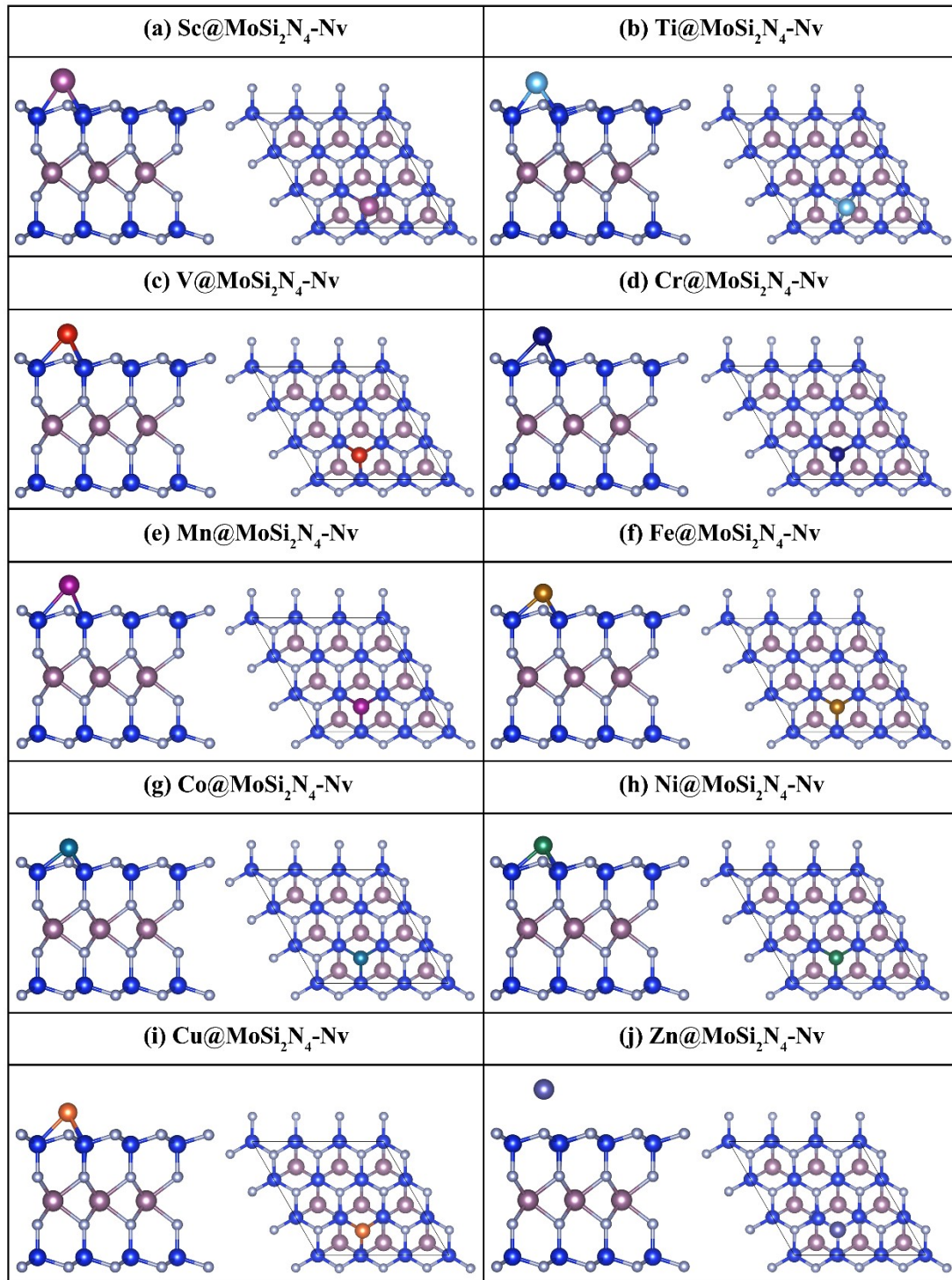


Figure S1 All TM@MoSi₂N₄-N_v monolayers optimized geometry structures for side view and top view: (a) Sc@MoSi₂N₄-N_v, (b) Ti@MoSi₂N₄-N_v, (c) V@MoSi₂N₄-N_v, (d) Cr@MoSi₂N₄-N_v, (e) Mn@MoSi₂N₄-N_v, (f) Fe@MoSi₂N₄-N_v, (g) Co@MoSi₂N₄-N_v, (h) Ni@MoSi₂N₄-N_v, (i) Cu@MoSi₂N₄-N_v and (j) Zn@MoSi₂N₄-N_v.

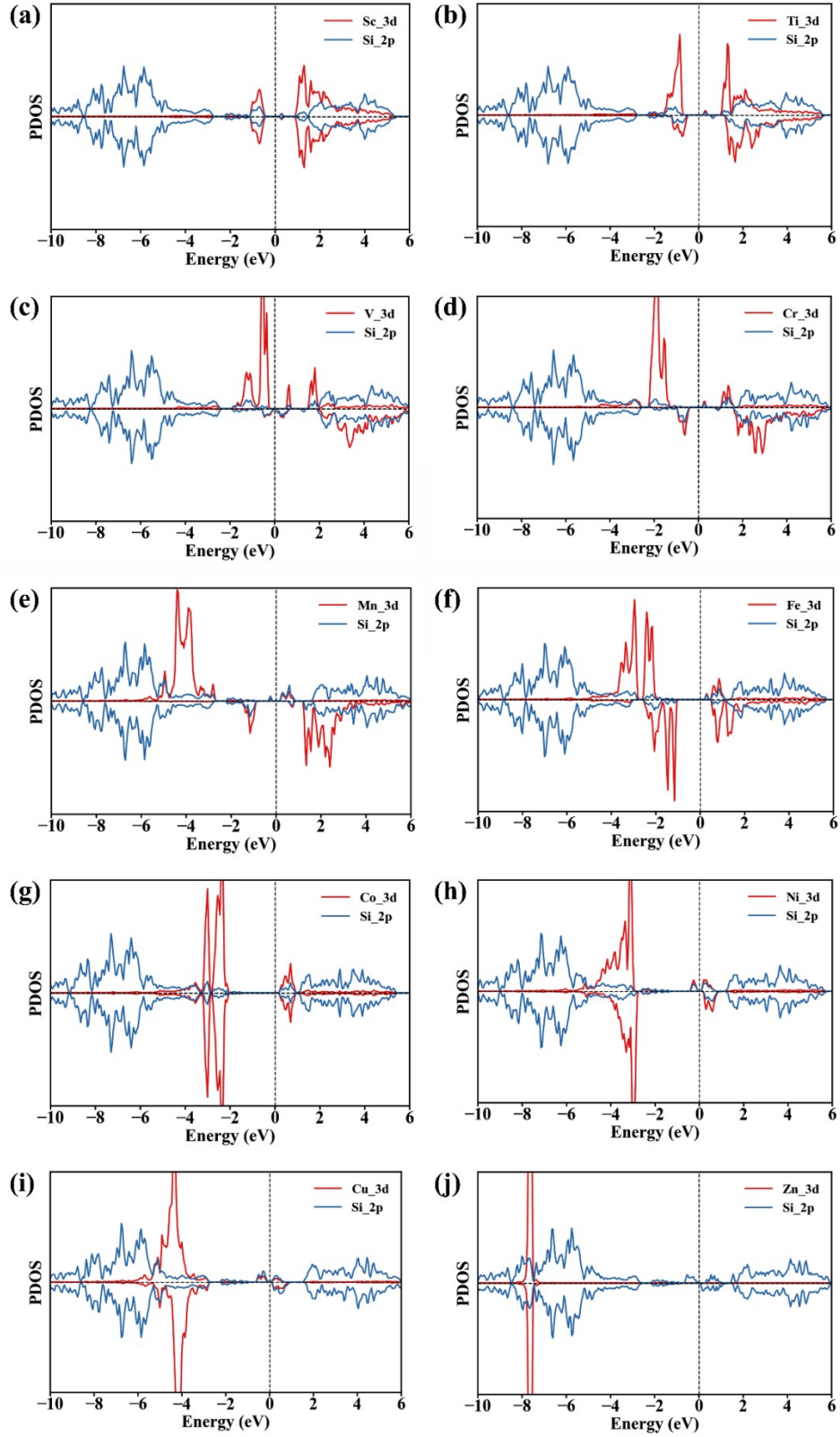


Figure S2 The partial density of states (PDOS) of TM-3d and Si-2p of TM@MoSi₂N₄-N_v (TM=Sc~Zn) monolayers.

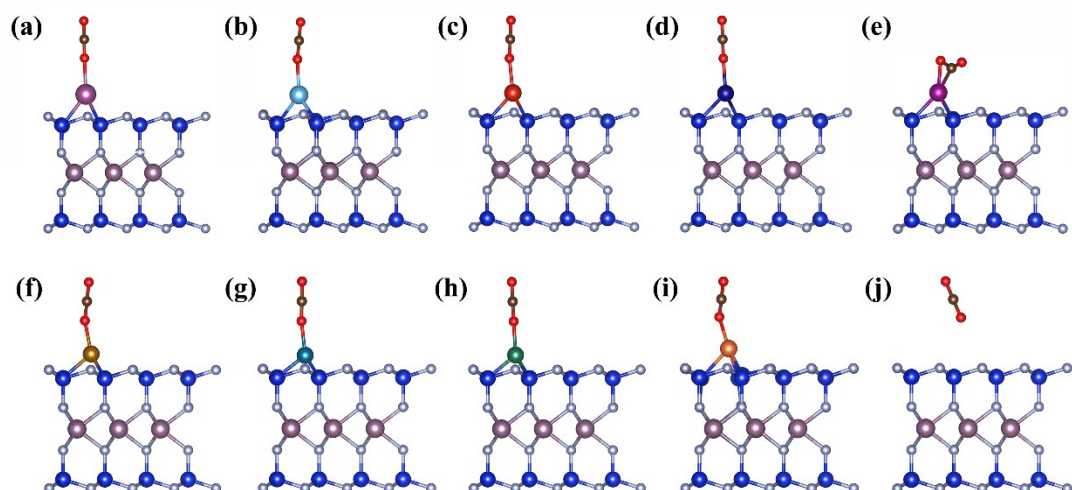


Figure S3 *CO_2_1 optimized configurations of $TM@MoSi_2N_4-N_v$ ($TM=Sc\sim Cu$) monolayers and pristine $MoSi_2N_4$ monolayer.

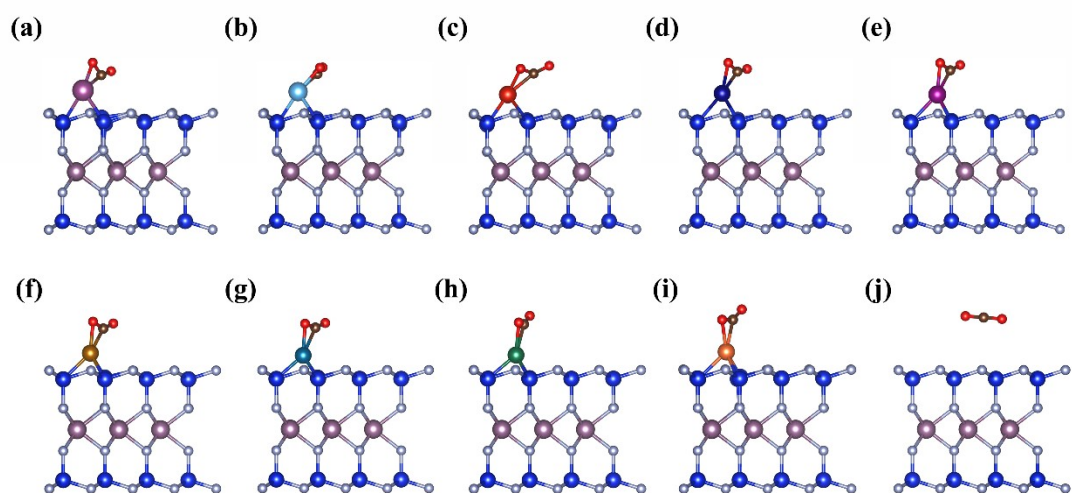


Figure S4 *CO_2_2 optimized configurations of $TM@MoSi_2N_4-N_v$ ($TM=Sc\sim Cu$) monolayers and pristine $MoSi_2N_4$ monolayer.

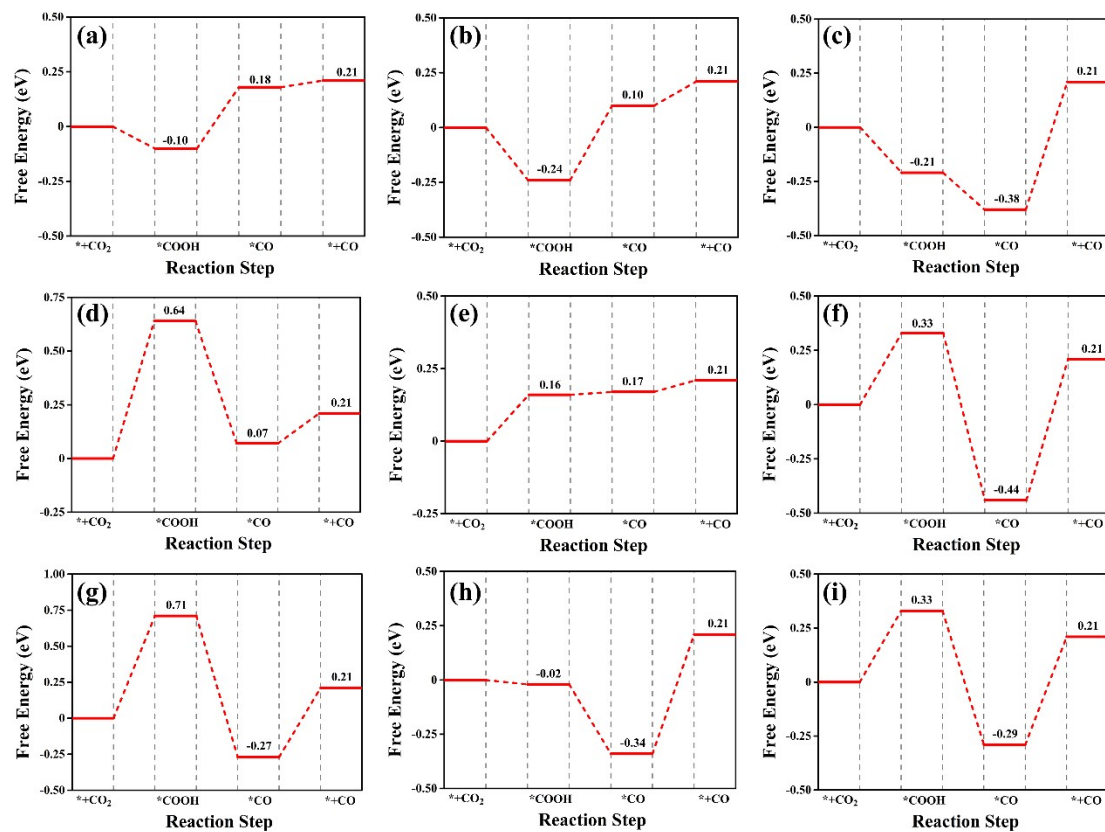


Figure S5 The Gibbs free energy diagrams of CO₂ to CO on (a) Sc@MoSi₂N₄-N_v, (b) Ti@MoSi₂N₄-N_v, (c) V@MoSi₂N₄-N_v, (d) Cr@MoSi₂N₄-N_v, (e) Mn@MoSi₂N₄-N_v, (f) Fe@MoSi₂N₄-N_v, (g) Co@MoSi₂N₄-N_v, (h) Ni@MoSi₂N₄-N_v and (i) Cu@MoSi₂N₄-N_v monolayer ($U^{\text{RHE}} = 0$ V).

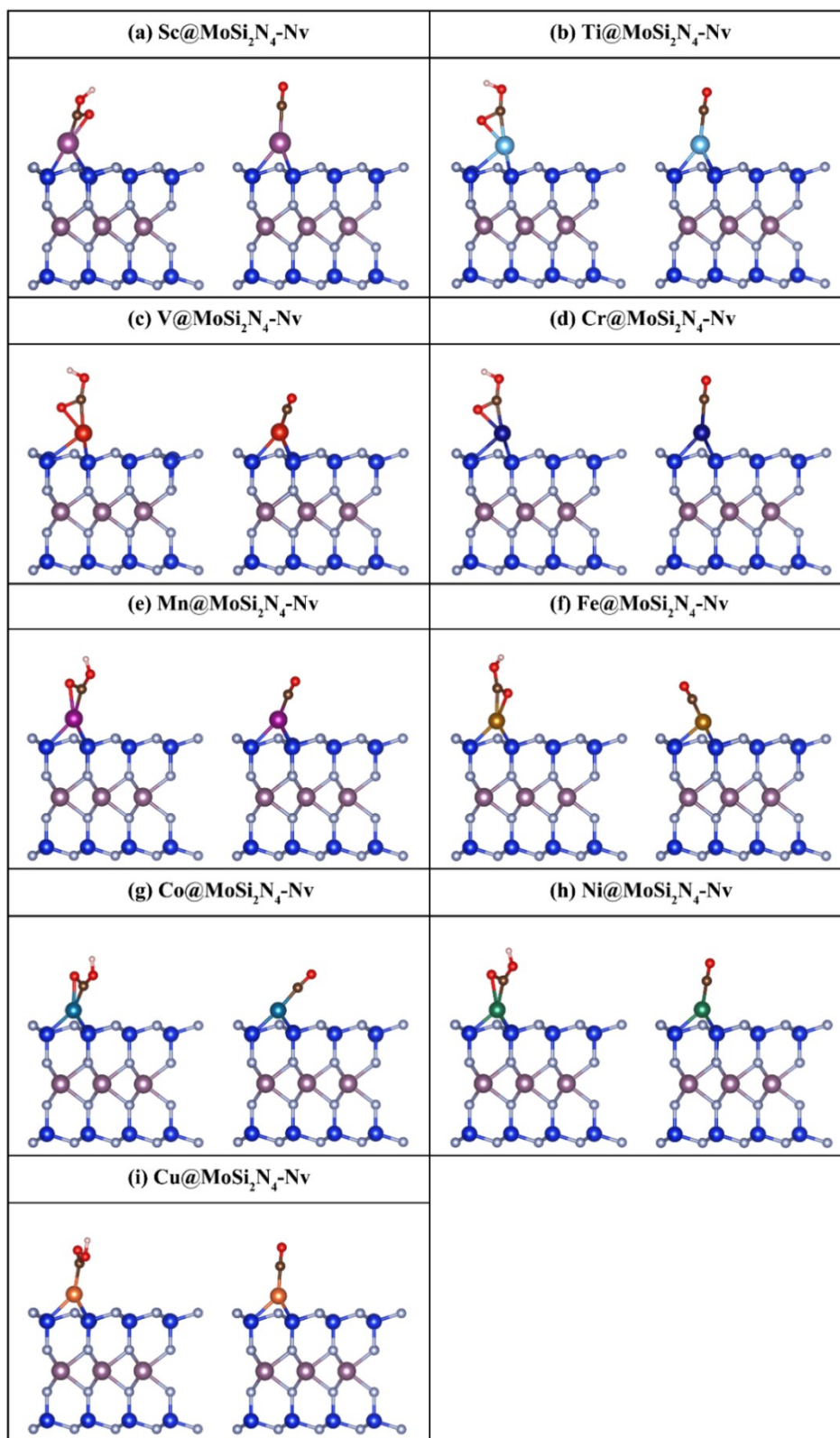


Figure S6 Optimized structures of the process of CO₂ to CO involved intermediate species on TM@MoSi₂N₄-N_v (TM=Sc~Cu) monolayers.

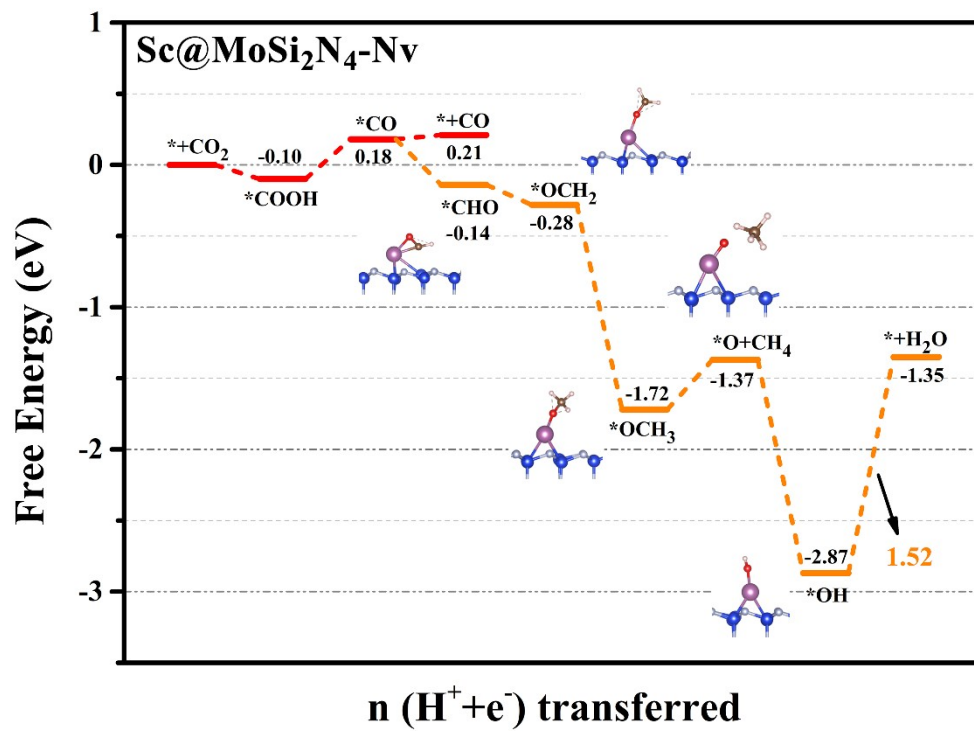


Figure S7 Free energy diagram for CO and CH₄ production from Sc@MoSi₂N₄-N_v monolayer ($U^{\text{RHE}} = 0$ V). The insets show the optimized configurations of the intermediates.

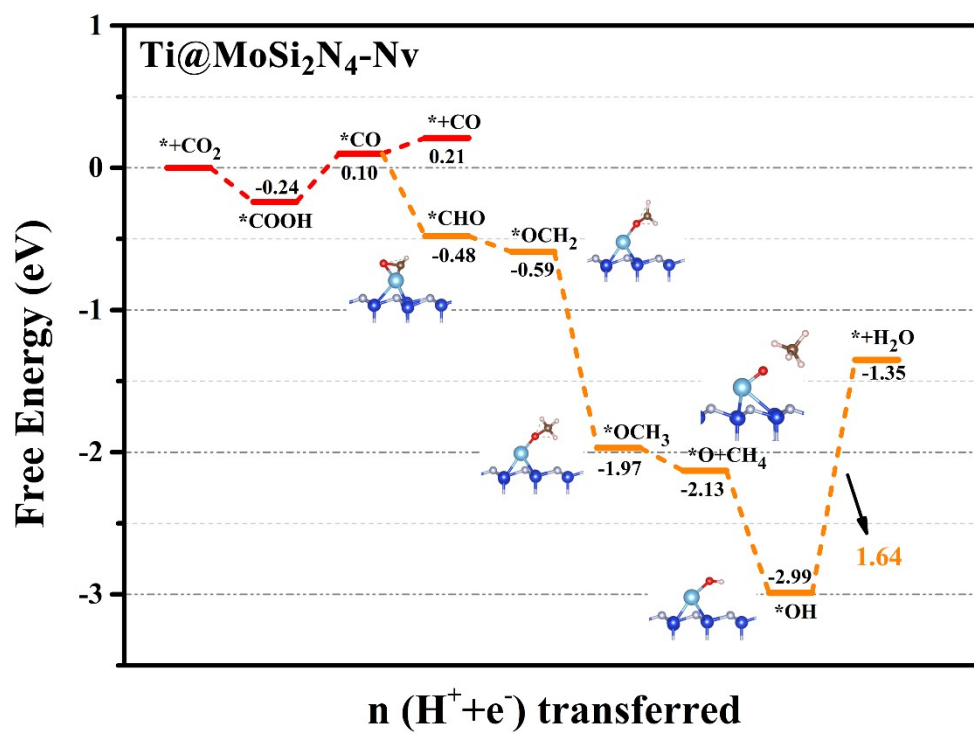


Figure S8 Free energy diagram for CO and CH₄ production from Ti@MoSi₂N₄-N_v monolayer ($U^{\text{RHE}} = 0$ V). The insets show the optimized configurations of the intermediates.

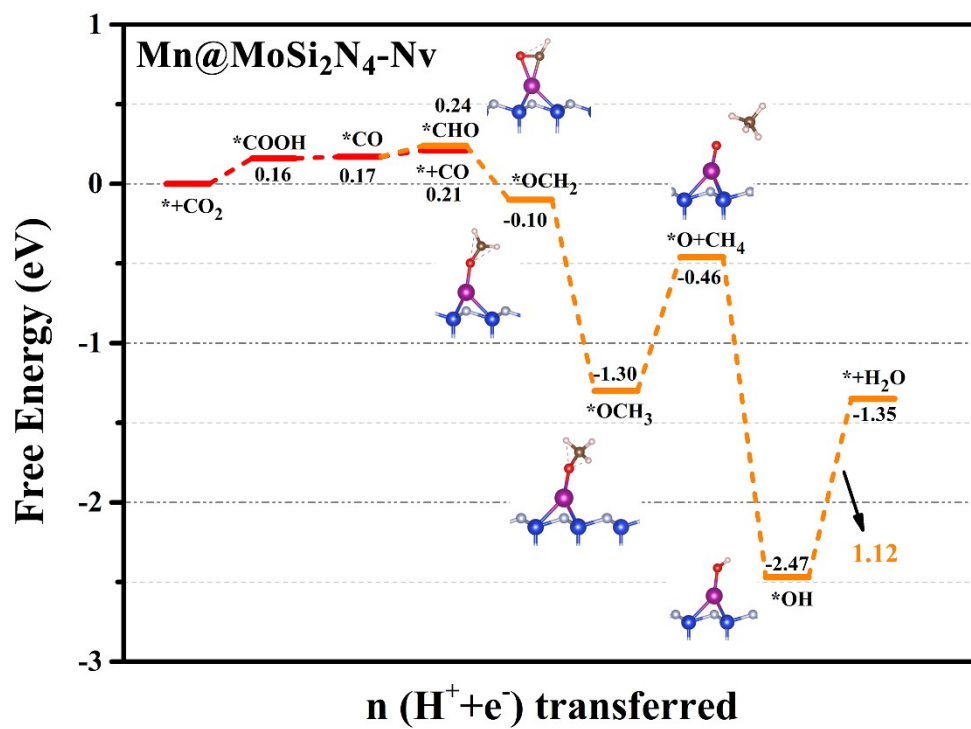


Figure S9 Free energy diagram for CO and CH₄ production from Mn@MoSi₂N₄-N_v monolayer ($U^{\text{RHE}} = 0$ V). The insets show the optimized configurations of the intermediates.

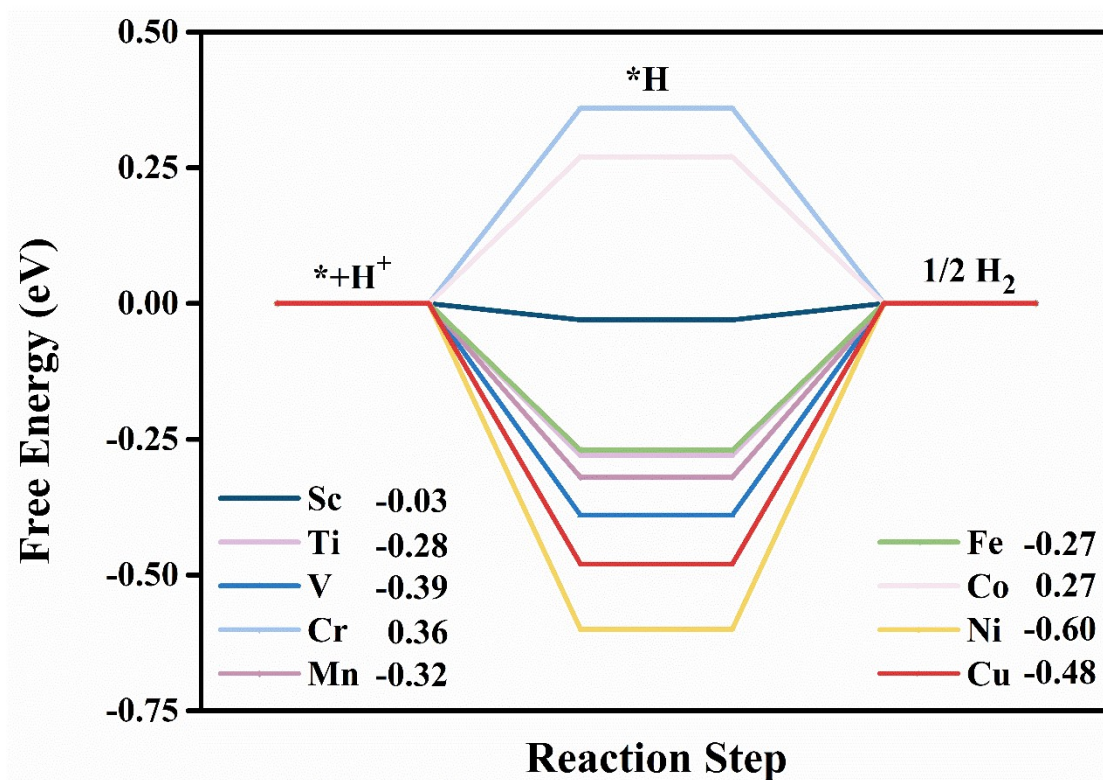


Figure S10 Gibbs free energy diagram of HER on TM@MoSi₂N₄-N_v (TM=Sc~Cu) monolayers ($U^{\text{RHE}} = 0$ V).

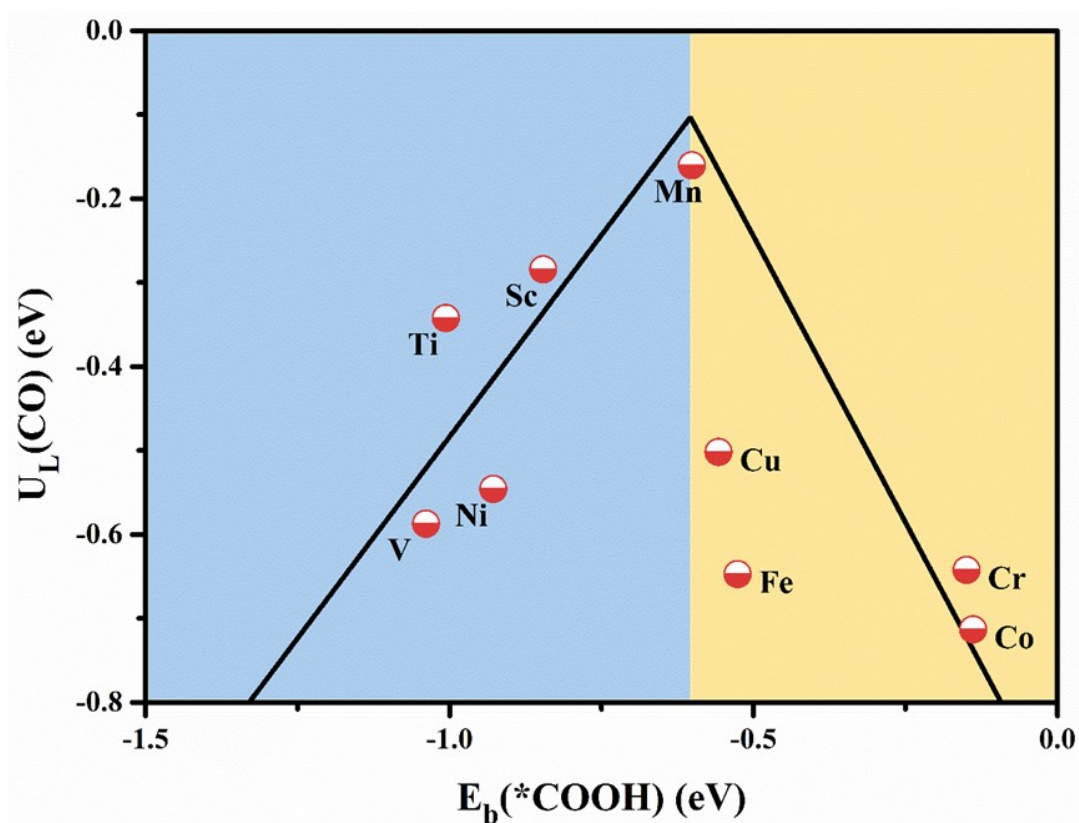


Figure S11 The activity volcano plot for two-electron reduction of CO₂ to CO, the relationship is the binding energy at 0 K $E_b(*COOH)$ and U_L .

Referernces

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