ELECTRONIC SUPPLEMENTARY INFORMATION

Promising prospects for 2D d^2-d^4 M_3C_2 transition metal carbides (MXenes) in N_2 capture and conversion into ammonia

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COMPUTATIONAL DETAILS

The mechanism for the electrochemical conversion of N_2 into NH_3 catalysed by d^2 (Ti, Zr, and Hf), d^3 (V, Nb, and Ta), and d^4 (Cr and Mo) 2D transition metal carbides, or MXenes, with formulae $M_{n+1}C_n$ (n = 2, M_3C_2 unit-cell), has been studied by means of density functional theory (DFT) through the generalised gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional,[1] using a plane-wave cut-off energy of 450 eV,[2, 3] and representative 2×2×1 $M_{12}C_8$ super-cells. Concerning the periodic boundary conditions, the Brillouin zone was sampled by 5×5×1 *k*-points using the Monkhorst-Pack scheme. In order to avoid interactions between periodic images, a vacuum distance of 20 Å was imposed between different layers. Optimisation calculations were done using energy and force convergence limits equal to 10^{-4} eV/atom and |0.02| eV/Å, respectively. Thermal and zero point energy (ZPE) corrections were calculated over Γ points. Also, explicit dispersion correction terms to the energy were employed through the use of the DFT-D3 method with the standard parameters programmed by Grimme and co-workers.[4, 5]

Since the d^3 V_3C_2 and Nb_3C_2 surfaces are demonstrated to be the most promising catalysts for the N_2 conversion into NH_3, due to the low reaction energies the exhibit, the nudge elastic band (NEB) method[6] has been applied to these materials to find the transition states (TS) through the minimum energy path. With exception of the force convergence limit (|0.05|, |0.075| eV/Å), similar computational settings have been applied as to the location of minima and intermediate states.

All optimisation calculations have been performed through the facilities provided by the Vienna *Ab-Initio* Simulation Package (VASP, version 5.3.5).[7-10]

THERMOCHEMISTRY†

The fundamental thermodynamic relation states that:

$$G^0 = H^0 - TS \qquad (1)$$

at temperatures greater than 0 K and constant pressure, enthalpy for a given temperature (here T = 298.15 K) can be expressed in terms of H^0 and the heat capacity, C_P:

$$H = H^0 + \int C_P \, dT \quad (2)$$

in addition, the entropy term can be expressed as the sum of the translational, rotational, vibrational, and electronic contributions as to:

$$S = S_t + S_r + S_v + S_e \quad (3)$$

and also, intrinsic zero point energy (ZPE) and extrinsic dispersion (D) corrections can be included to finally obtain:

$$G = H^0 + \int C_P \, dT - T(S_t + S_r + S_v + S_e) + ZPE + D \quad (4)$$

When computing the Gibbs free energy variation between two states named as 1 and 2, and applying eqn. (4), ΔG results in:

$$\Delta G_{21} = H^0_2 + \int C_{P,2} \, dT - T(S_{t,2} + S_{r,2} + S_{v,2} + S_{e,2}) + ZPE_2 + D_2 - \\ - H^0_1 - \int C_{P,1} \, dT + T(S_{t,1} + S_{r,1} + S_{v,1} + S_{e,1}) - ZPE_1 - D_1 \quad (5)$$

or simply:

$$\Delta G_{21} = \Delta H^0_{21} + \Delta \int (C_P)_{21} \, dT - T\Delta S_{21} + \Delta ZPE_{21} + \Delta D_{21} \quad (5)$$

Over this last equation, some approximations can be applied:

1. At the fundamental electronic level: $S_e \approx 0$
2. For gases, translational, rotational, and vibrational entropy terms have contributions that might not be neglected, and therefore: $S = S_t + S_r + S_v$
3. For solids and adsorbates, both $S_t \approx 0$ and $S_r \approx 0$, and therefore: $S = S_v$
4. Since $\int C_P \, dT$ is almost negligible and $\Delta \int C_P \, dT \approx 0$, no thermal corrections for the enthalpy have been taken into account for the ΔG calculation.

Thus, and in the present instance, the computing of the ΔG change for the NH_3 (g) chemisorption on a clean MXene surface (binding energy), can be expressed as:

$$\Delta G(NH_3 \cdots MXene) = G(NH_3 \cdots MXene) - G(MXene) - G(NH_3) \quad (6)$$

where:

$$G(NH_3\cdots MXene) = H^0(NH_3\cdots MXene) - TS_v(NH_3\cdots MXene) + \\ + ZPE(NH_3\cdots MXene) + D(NH_3\cdots MXene) \quad (6.1)$$

$$G(MXene) = H^0(MXene) - TS_v(MXene) + ZPE(MXene) + D(MXene) \quad (6.2)$$

$$G(NH_3) = H^0(NH_3) - TS_t(NH_3) - TS_r(NH_3) - TS_v(NH_3) + ZPE(NH_3) + \\ + D(NH_3) \quad (6.3)$$

Finally, this can be also extended to the calculation of the Gibbs free reaction energy, and therefore eqn. (7) has been applied to calculate ΔG_R, where n is the number of H^+/e^- pairs transferred and m the number of NH_3 molecules released, if applicable. In such a context, the chemical potential of the H^+/e^- pair has the half value of the chemical potential of the dihydrogen (H_2) molecule [see eqn. (8)],[11] when working at standard hydrogen electrode (SHE) conditions, i.e. pH = 0, $f(H_2)$ = 101,325 Pa, and U = 0 V, being $f(H_2)$ and U the fugacity of H_2 and the external potential applied, respectively:

$$\Delta G_R = G(N_{2-m}H_{n-3m}\cdots MXene) + m\ G(NH_3) - G(MXene) - G(N_2) - \\ - n/2\ G(H_2) \quad (7)$$

For $n = 0$, $\Delta G_R = \Delta G_b$, binding Gibbs free energy in $N_2\cdots MXene$ (7.1)

$$\mu(H^+/e^-) = \tfrac{1}{2}\ \mu(H_2) \quad (8)$$

†Note: see foundations at *Quantum Chemistry*, D. A. McQuarrie and M. Hanson, Macmillan Education, 2nd revised edition, 2007.

COMPUTATION OF ACTIVATION BARRIERS

The computation of electrochemical activation energies or barriers is a challenging topic in which important efforts have been recently reported by Janik and co-workers[12] in the development of a strong, founded methodology in which an inner-sphere Marcus mechanism is

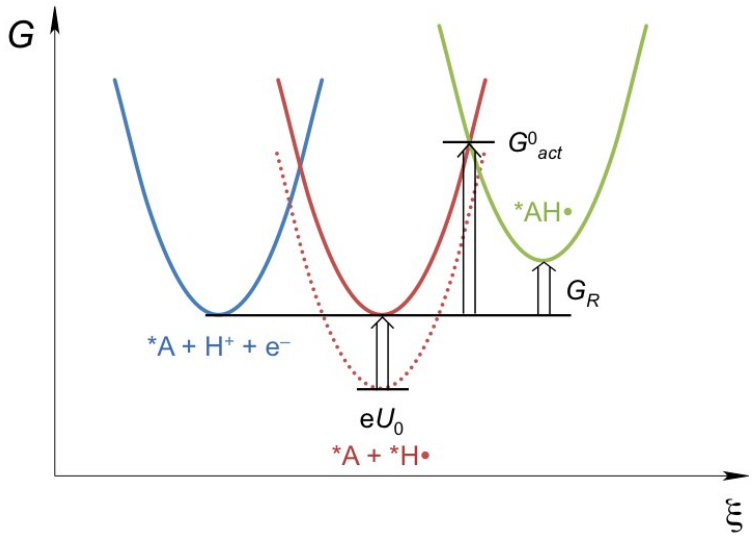
assumed. In classical chemical reactions, the TS is located with a zero charge-electron balance during the chemical process. In the case of elementary electrochemical reactions, a chemical species A, fixed on a catalytic surface (then, *A), gains one proton (H^+) from the bulk medium and one electron (e^-) motioning through the catalyst, in order to produce an adsorbed *AH• intermediate state:

$$*A + H^+ + e^- \rightarrow *AH\bullet \quad (9)$$

Given the obvious difficulties with the location of the TS in such elementary electrochemical reaction, Janik and co-workers propose the location of the analogous hydrogenation (chemical) reaction in which both, the *A and *H• species (see **Table S4** below), are fixed on the surface and react in order to produce the *AH• intermediate state:

$$*A + *H\bullet \rightarrow *AH\bullet \quad (10)$$

Once located, the TS for this chemical reaction and the TS for the electro-reduction of *A can be assumed as identical at one specific electrode potential, U_0, i.e. U_0 equates the energy of the *A + *H• reactants to *A + H^+ + e^-, as shown in the schematic parabolic curves approximated by the Marcus theory:



Finally and attending to Butler-Volmer theory, the Gibbs free activation barrier of the electro-reduction of *A (see **Table S5** below), G_{act}, can be approximated as:

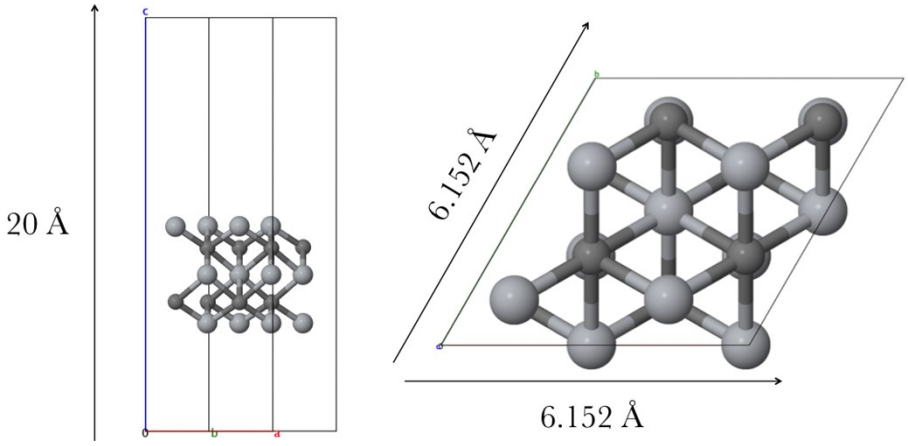
$$G_{act}(U) = G^0_{act} + \beta F(U - U_0) \quad (11)$$

where G^0_{act} is the activation barrier for the hydrogenation reaction of *A, β the symmetry coefficient (and approximated to 0.5), F the Faraday constant, and U the applied electrode potential.

OPTIMISATION OF LATTICE PARAMETERS IN MXENES

DFT optimisation, GGA with PBE functional.[1] Plane-wave cut-off energy of 400 eV.[2, 3] Energy and force convergence limits equal to 10^{-4} eV/atom and |0.05| eV/Å, respectively. Brillouin zone sampled by 3×3×1 *k*-points using the Monkhorst-Pack scheme. Inclusion of dispersion corrections through the DFT-D2 method developed by Grimme and co-workers.[13] 2×2×1 $M_{12}C_8$ super-cells.

Initial $M_{12}C_8$ structures, being $|\boldsymbol{a}| = |\boldsymbol{b}| = 6.152$ Å, and $|\boldsymbol{c}| = 20$ Å, in order to avoid interactions between periodic images:



Optimised lattice parameters, in Å, for the referred settings. (In all cases, $|\boldsymbol{c}| = 20$ Å):

	Ti_3C_2	Zr_3C_2	Hf_3C_2	V_3C_2	Nb_3C_2	Ta_3C_2	Cr_3C_2	Mo_3C_2
$\|\boldsymbol{a}\| = \|\boldsymbol{b}\|$	6.213	6.644	6.582	5.906	6.336	6.152	5.660	6.090

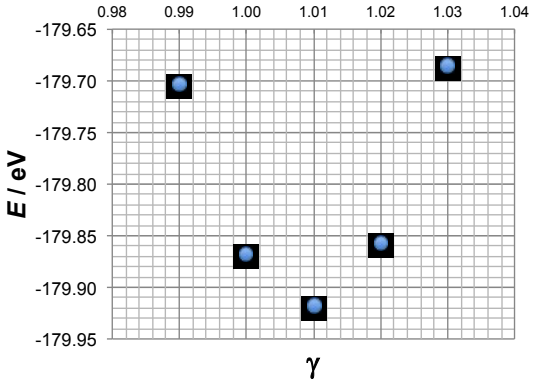
The γ scaling factor is applied for the searching of the optimised lattice parameters, so that:

$$\gamma\boldsymbol{a} = \gamma\boldsymbol{a}_x + \gamma\boldsymbol{a}_y + \gamma\boldsymbol{a}_z = \gamma \cdot 6.125\boldsymbol{i} \quad (12)$$

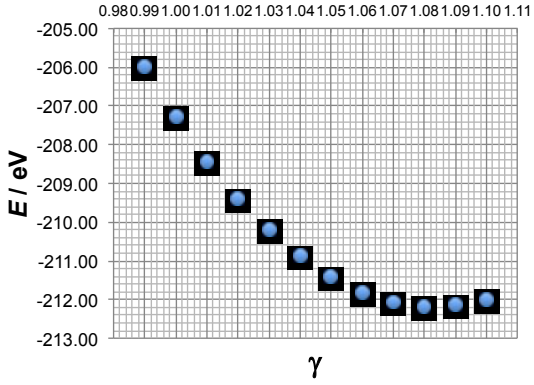
$$\gamma\boldsymbol{b} = \gamma\boldsymbol{b}_x + \gamma\boldsymbol{b}_y + \gamma\boldsymbol{b}_z = \gamma \cdot 3.076\boldsymbol{i} + \gamma \cdot 5.328\boldsymbol{j} \quad (13)$$

$$\gamma\boldsymbol{a} = \gamma\boldsymbol{a}_x + \gamma\boldsymbol{a}_y + \gamma\boldsymbol{a}_z = \gamma\boldsymbol{a}_z = 20\boldsymbol{k}, \text{ in all cases} \quad (14)$$

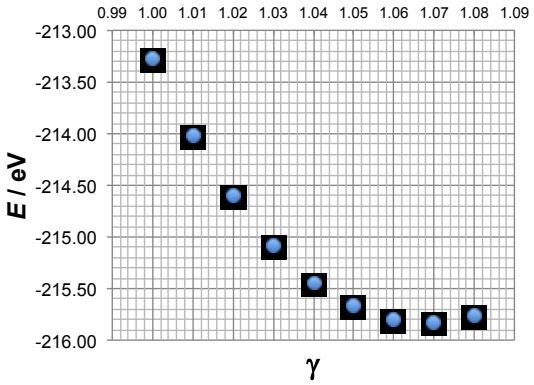
In each case, representing the electronic energy, *E*, *vs*. γ:



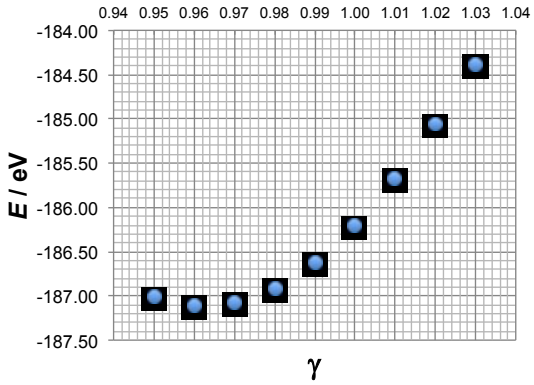
Ti_3C_2, $\gamma_{\square\square\square} = 1.01$



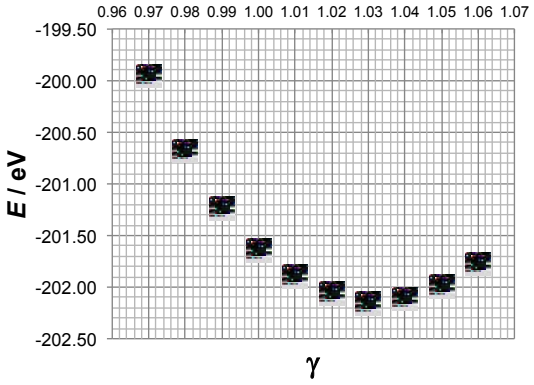
Zr_3C_2, $\gamma_{\square\square\square} = 1.08$



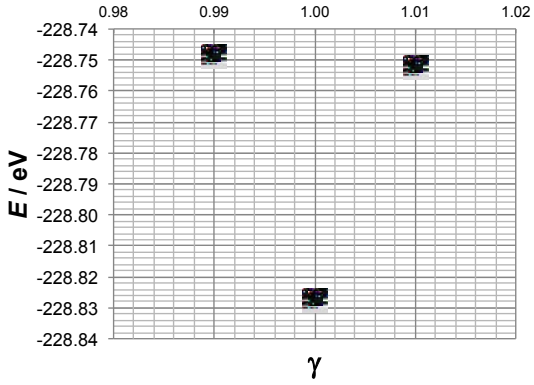
Hf_3C_2, $\gamma_{\square\square\square} = 1.07$



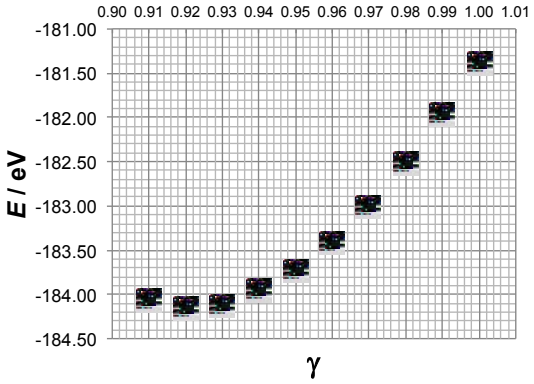
V_3C_2, $\gamma_{\square\square\square} = 0.96$



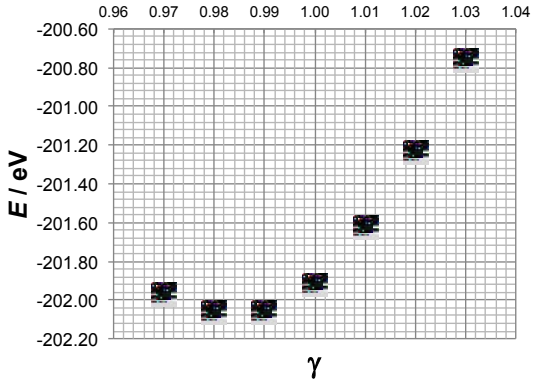
Nb_3C_2, $\gamma_{□□□} = 1.03$



Ta_3C_2, $\gamma_{□□□} = 1.00$



Cr_3C_2, $\gamma_{□□□} = 0.92$



Mo_3C_2, $\gamma_{□□□} = 0.99$

Starting geometry 2×2×1 $M_{12}C_8$ super-cell, $\gamma = 1$:

a	6.15180016	0.00000000	0.00000000
b	3.07590008	5.32761521	0.00000000
c	0.00000000	0.00000000	20.00000000
M	6.07456776	0.01439335	7.56729778
M	2.99888805	1.79037091	5.11470004
M	2.99868780	0.01436766	7.56730216
M	6.07469131	1.79037837	5.11473081
M	7.61253247	2.67823860	7.56735586
M	4.53679295	4.45410237	5.11467368
M	4.53658237	2.67817067	7.56717284
M	7.61269262	4.45416133	5.11471321
M	1.46059508	0.90206131	10.02006145
M	4.53648978	0.90201163	10.01999590

M	2.99849559	3.56587332	10.01998955
M	6.07449396	3.56586832	10.01999635
C	2.99856492	1.79009700	8.90183698
C	1.46087886	0.90250290	6.23292953
C	6.07436363	1.79010582	8.90182083
C	4.53676904	0.90244681	6.23306926
C	4.53646569	4.45384988	8.90186354
C	2.99877127	3.56631689	6.23298490
C	7.61235866	4.45389820	8.90165859
C	6.07477970	3.56631959	6.23304764

COMPUTATIONAL SETTINGS

Settings DFT/DFT-D2 optimisation

M_3C_2 lattice parameters optimisation

```
PREC = Medium
ENCUT = 400
EDIFF = 1E-4
EDIFFG = -0.05
IBRION = 1
ISIF = 2
ISMEAR = 0
SIGMA = 0.02
POTIM = 0.2
LREAL = Auto
ALGO = Fast

LVDW = .TRUE.
```

Settings DFT+*U*/DFT-D3 optimisation

N_2 conversion into NH_3 mechanism

```
PREC = Medium
ENCUT = 450
EDIFF = 1E-4
EDIFFG = -0.02
IBRION = 2
ISIF = 2
ISMEAR = 0
SIGMA = 0.02
POTIM = 0.2

IVDW = 11
  VDW_RADIUS = 50.2
  VDW_CNRADIUS = 20.0
  VDW_S6 = 14.0
  VDW_S8 = 16.0
  VDW_SR = 1.0
```

Pseudo-potentials applied:

Nitrogen: PAW_PBE N 08Apr2002

Hydrogen: PAW_PBE H 15Jun2001

Oxygen: PAW_PBE O 08Apr2002

Titanium: PAW_PBE Ti_pv 07Sep2000

Zirconium: PAW Zr_sv_GW 07Apr2010

Hafnium: PAW_PBE Hf_pv 06Sep2000

Vanadium: PAW_PBE V_pv 07Sep2000

Niobium: PAW_PBE Nb_pv 08Apr2002

Tantalum: PAW_PBE Ta_pv 07Sep2000

Chromium: PAW_PBE Cr_pv 02Aug2007

Molybdenum: PAW_PBE Mo_pv 04Feb2005

GIBBS FREE ENERGIES

Table S1. Thermodynamic quantities, in eV, for the isolated N_2, CO_2, H_2O, H_2, and NH_3 species in the gas phase. (T= 298.15 K and f= 101,325 Pa).

Species	$H^0 + D$	$-TS_t$	$-TS_r$	$-TS_v$	ZPE	G
N_2 $(g)^a$	–16.61	–0.45	–0.13	0.00(0)	0.15	–17.04
CO_2 $(g)^a$	–22.92	–0.47	–0.17	–0.00(5)	0.27	–23.29
H_2O $(g)^a$	–14.16	–0.43	–0.12	0.00(0)	0.56	–14.16
H_2 $(g)^a$	–6.77	–0.35	–0.04	0.00(0)	0.27	–6.89
NH_3 $(g)^a$	–19.50	–0.43	–0.13	–0.00(2)	0.58	–19.49

[a]Experimental values from NIST database (http://cccbdb.nist.gov):

N_2 (g): d_{NN} = 1.098 Å, ν_1 (Σ_g) = 2,359 cm^{-1}

CO_2 (g): d_{CO} = 1.162 Å, A_{OCO} = 180.0º, ν_1 (Σ_g) = 1,333 cm^{-1}, ν_2 (Σ_u) = 2,349 cm^{-1}, ν_3 (Π_u) = 667 cm^{-1}

H_2O (g): d_{OH} = 0.958 Å, A_{HOH} = 104.5º, ν_1 (A_1) = 3,657 cm^{-1}, ν_2 (A_1) = 1,595 cm^{-1}, ν_3 (B_2) = 3,756 cm^{-1}

H_2 (g): d_{HH} = 0.741 Å, ν_1 (Σ_g) = 4,401 cm^{-1}

NH_3 (g): d_{NH} = 1.012 Å, A_{HNH} = 106.67º, A_{XNH} = 112.15º, ν_1 (A_1) = 3,337 cm^{-1}, ν_2 (A_1) = 950 cm^{-1}, ν_3 (E) = 3,444 cm^{-1}, ν_4 (E) = 1,627 cm^{-1}

Table S2. Gibbs free energies at 298.15 K (ZPE and D3 corrections applied), in eV, corresponding to the chemisorbed CO_2 and H_2O species on the M_3C_2 MXene (M = Ti, Zr, Hf, V, Nb, Ta, Cr, and Mo) surfaces.

$M_{12}C_8$ super-cell	d^2			d^3			d^4	
Species	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo
CO_2	–205.69	–236.24	–231.26	–207.37	–219.94	—[a]	–198.48	–213.44
H_2O	–194.89	–225.68	–220.75	–197.66	–209.71	–232.21	–189.03	–204.00

[a]For Ta_3C_2, no chemisorbed CO_2 minimum was obtained.

Table S3. Gibbs free energies at 298.15 K (ZPE and D3 corrections applied), in eV, corresponding to the different states along the N_2 conversion mechanism (Schemes 1 and Fig 2) catalysed by M_3C_2 MXenes (M = Ti, Zr, Hf, V, Nb, Ta, Cr, and Mo).

$M_{12}C_8$ super-cell	d^2			d^3			d^4	
Species	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo
clean surface	–179.38	–209.85	–205.39	–182.54	–194.58	–217.03	–174.08	–189.29
N_2	–198.99	–229.30	–224.55	–201.76	–214.06	–236.67	–193.18	–208.45
N–NH•	–202.91	–233.72	–229.06	–205.36	–217.79	–240.27	–196.72	–211.20
HN–NH	–206.46	–237.02	–232.05	–208.61	–221.01	–243.86	–200.07	–215.25
$N–NH_2$	–205.64	–236.42	–231.81	–208.83	–220.99	–243.91	–200.46	–215.81
N•	–190.11	–220.79	–216.16	–192.58	–204.95	–227.50	–184.61	–199.65
$HN–NH_2$•	–208.45	–239.14	–234.74	–211.57	–223.76	–246.54	–203.06	–217.99
NH	–194.10	–224.89	–220.45	–196.52	–209.11	–231.72	–188.33	–203.40
$H_2N–NH_2$	–210.22	–240.50	–235.99	–213.72	–225.67	–248.11	–205.28	–220.06
NH_2•	–197.50	–228.02	–223.63	–199.83	–212.17	–234.71	–191.73	–206.49
NH_3	–199.67	–229.98	–225.56	–202.95	–215.23	–237.16	–194.72	–209.59

Table S4. Gibbs free energies at 298.15 K (ZPE and D3 corrections applied), in eV, corresponding to the different states **for the hydrogenation of the MXene surface** along the N_2 conversion mechanism catalysed by M_3C_2 MXenes (M = Ti, Zr, Hf, V, Nb, Ta, Cr, and Mo).

$M_{12}C_8$ super-cell	d^2			d^3			d^4	
Species	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo
N_2 + H•	–203.25	–231.98	–226.25	–205.95	–218.07	–241.54	–197.71	–211.84
N–NH• + H•	–206.97	–234.60	–228.86	–209.81	–221.53	–244.25	–200.30	–215.66
N_2H_2[a] + H•	–210.63	–239.59	–234.12	–212.70	–225.39	–248.60	–204.41	–219.36
N_2H_3•/N•[b] + H•	–213.25	–242.15	–237.07	–196.71	–208.61	–231.14	–188.48	–204.09
NH + H•	–198.70	–229.60	–223.13	–200.33	–213.08	–235.30	–192.22	–207.00
NH_2• + H•	–202.33	–233.11	–226.07	–204.91	–216.90	–239.34	–195.51	–210.25

[a]For d^2 MXenes (M = Ti, Zr, and Hf), the second reduced-species for its minimum energy path corresponds to the HN–NH state, while for the rest, to N–NH_2.

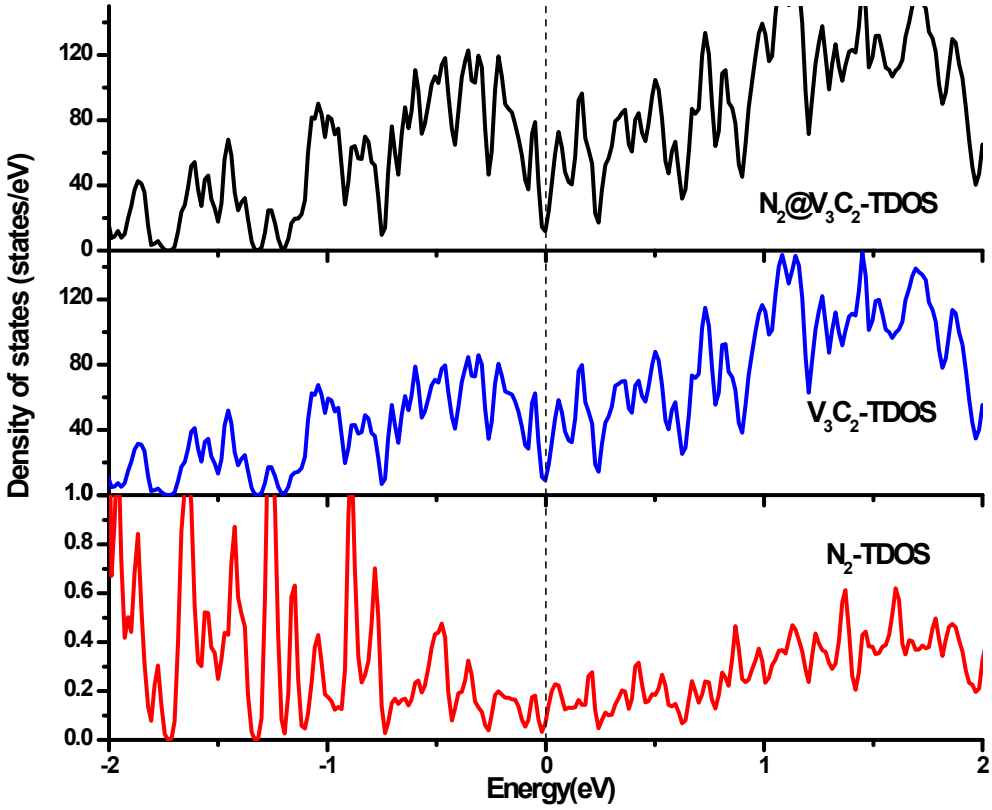
[b]For d^2 MXenes (M = Ti, Zr, and Hf), the third reduced-species for its minimum energy path corresponds to the HN–NH_2• state, while for the rest, to N•.

Table S5. Gibbs free energies at 298.15 K (ZPE and D3 corrections applied), in eV, and U_0 potentials, in V, corresponding to the TSs along the N_2 conversion mechanism catalysed by V_3C_2 and Nb_3C_2 MXenes.

$M_{12}C_8$ super-cell	V_3C_2		Nb_3C_2	
Species	*G*	U_0	*G*	U_0
TS1	–204.93	0.74	–216.93	0.57
TS2	–208.98	1.00	–220.48	0.29
TS3	–196.67	0.49	–209.09	0.71
TS4	–199.90	0.37	–212.03	0.53

DOS PROFILE N_2:V_3C_2

In black, blue, and red colours, the projected DOS profiles for the N_2:V_3C_2 system, and their respective V_3C_2 and N_2 contributions, being N_2 in a chemisorbed form.



CARTESIAN COORDINATES

Structures (2×2×1 super-cell) corresponding to the minimum energy path for the N_2 conversion into NH_3 catalysed by V_3C_2 MXene at the DFT+D3 computational level

In all cases:

a	5.90572815	0.00000000	0.00000000
b	2.95286407	5.11451061	0.00000000
c	0.00000000	0.00000000	20.00000000

Clean surface

V	5.83136883	0.01375244	7.56694182
V	2.87876649	1.71807806	5.36838288
V	2.87832707	0.01372153	7.56699766
V	5.83162690	1.71806541	5.36829255
V	7.30769071	2.57088281	7.56706265
V	4.35519795	4.27533623	5.36843700
V	4.35485964	2.57101083	7.56682538
V	7.30805519	4.27537061	5.36823127
V	1.40314999	0.86688736	9.76639836
V	4.35601370	0.86687314	9.76673226
V	2.87959551	3.42410489	9.76676071
V	5.83243758	3.42411676	9.76658984
C	2.87852123	1.71899779	8.81834073
C	1.40184407	0.86553981	6.31650213
C	5.83171031	1.71911675	8.81841193
C	4.35457335	0.86562081	6.31655000
C	4.35522517	4.27652180	8.81838474
C	2.87830166	3.42283770	6.31650942
C	7.30786305	4.27635842	8.81829139
C	5.83099467	3.42292037	6.31655818

N_2

V	0.02918526	0.00933567	7.46171793
V	2.99834435	1.71970516	5.16924793
V	2.93598504	0.00223164	7.45859147
V	5.79652764	1.76109092	5.16465725
V	1.47649168	2.51627846	7.46201117
V	4.43330315	4.20508181	5.16918308
V	4.44272513	2.54173669	7.48780621
V	7.42780006	4.22877509	5.25391973
V	1.48530880	0.83935842	9.73191006
V	4.43362227	0.83586893	9.73010965
V	2.95816571	3.39878609	9.72956704
V	5.91537704	3.40237402	9.73002851
C	2.95649822	1.69032199	8.74351571
C	1.45968385	0.85512242	6.15339478
C	5.91331334	1.69278507	8.75111595
C	4.43258956	0.83498062	6.24247634
C	4.43705806	4.25469425	8.74340212
C	2.96878736	3.39336901	6.27535885
C	7.38729881	4.25152586	8.74940863
C	5.91628948	3.40488500	6.24261049
N	4.53772106	2.48812391	3.87990100
N	3.45795333	3.11144912	3.57767245

TS1

V	6.01134179	0.38218700	7.35266864
V	3.19209646	2.14013535	4.98673650
V	3.00763138	0.37765296	7.33249835
V	5.91521785	2.03363546	5.08426152

V	7.45092815	2.88964433	7.29851364
V	4.46936869	4.58137655	5.13222222
V	4.51672415	2.92939319	7.36728480
V	7.48231033	4.66071597	5.12416898
V	1.55681679	1.23361036	9.55881560
V	4.49763850	1.21291183	9.56668208
V	3.01025830	3.77575158	9.55874816
V	6.00426048	3.78556520	9.55780902
C	3.02839928	2.07138449	8.58196779
C	1.59039127	1.23131951	5.99731723
C	5.98270850	2.07520252	8.61635421
C	4.51063115	1.23872865	6.20444250
C	4.50636855	4.63477247	8.63109303
C	3.04871912	3.78082160	6.17849956
C	7.46209379	4.63334623	8.57315649
C	5.96327456	3.76234657	6.07257016
N	4.73353074	1.96108003	3.32279222
N	4.57574774	0.80368609	3.72312453
H	3.49235999	3.63636286	3.87630695

N–NH•

V	5.67132952	0.02154869	7.54853961
V	2.80176152	1.73065616	5.29861405
V	2.66013122	0.02097307	7.54774494
V	5.52935176	1.73092318	5.29852670
V	7.11735459	2.57259002	7.48672593
V	4.16519266	4.22595651	5.32430779
V	4.16622571	2.61645071	7.57668053
V	7.11942227	4.40677453	5.29957526
V	1.21293522	0.90252586	9.75260366
V	4.16414543	0.87586218	9.76623303
V	2.66774321	3.43830703	9.76334116
V	5.66233693	3.43984344	9.76354165
C	2.68848178	1.73776207	8.79832469
C	1.21280309	0.87191305	6.18215473
C	5.64216690	1.73784673	8.80007514
C	4.16589208	0.90196636	6.47110680
C	4.16531597	4.29636697	8.83855962
C	2.69497659	3.44928004	6.30395269
C	7.11836972	4.29037969	8.77412169
C	5.63665994	3.44985178	6.30293702
N	4.16609994	1.95934366	3.70957662
N	4.16708289	0.62035891	3.96331164
H	4.16741278	2.18321497	2.71049729

TS2

V	8.37972050	5.07011386	7.24834551
V	2.51300980	1.73248292	5.01151359
V	5.39265071	5.07794164	7.24293657
V	5.41297952	1.70782993	4.99529658
V	6.89631558	2.46651813	7.27180511
V	3.93860551	4.07333254	5.02429003

V	3.93455373	2.46897170	7.28975123
V	6.88026540	4.18740406	5.10696308
V	0.98030809	0.78420012	9.48406601
V	3.93464987	0.78410810	9.48991993
V	2.45967296	3.34619263	9.48635826
V	5.40920578	3.34370893	9.48102658
C	2.45680515	1.63734525	8.53427469
C	0.98750853	0.76679524	5.99614605
C	5.41288936	1.63613297	8.53091974
C	3.95178104	0.79168054	6.06777501
C	3.93289042	4.19656718	8.53318852
C	2.46769062	3.35651125	6.08444997
C	6.88617896	4.19549990	8.55098900
C	5.41418586	3.35235997	6.09544305
N	3.88815802	2.51225459	3.75799598
N	4.87307977	1.94940791	3.02252901
H	4.57923854	1.05852781	2.58456851
H	6.94100375	2.54896377	4.13754045

N–NH_2

V	8.51920276	5.10301367	7.40766145
V	2.66752432	1.74379053	5.16693508
V	5.51066517	5.11386987	7.40634978
V	5.50727521	1.70758518	5.16511392
V	7.02417839	2.51436245	7.40719637
V	4.05566470	4.14942105	5.16819722
V	4.06345505	2.53969317	7.43951371
V	6.99466169	4.25802856	5.26136810
V	1.10768844	0.83539537	9.62914977
V	4.06800927	0.83435107	9.62942459
V	2.58735266	3.39052591	9.63758360
V	5.54149028	3.38664933	9.62981968
C	2.58785308	1.68817065	8.67923045
C	1.11442558	0.83431945	6.14411292
C	5.54320017	1.68498566	8.66964450
C	4.06900505	0.83407048	6.22111422
C	4.06279000	4.24252376	8.67940932
C	2.58310240	3.39522858	6.21636492
C	7.01888968	4.24242259	8.69608923
C	5.54425479	3.38920128	6.22133810
N	3.96435618	2.60091494	3.91035090
N	4.97734722	2.02302639	3.12207316
H	4.65071464	1.22562048	2.56479615
H	5.50530619	2.71284407	2.57545158

N•

V	8.65372393	5.06284774	7.51991125
V	2.81022431	1.68816885	5.26449906
V	5.63449339	5.06211855	7.52011089
V	5.57329844	1.68840923	5.26381180
V	7.14347101	2.44773465	7.52002016
V	4.19201436	4.08131877	5.26415402

V	4.19111061	2.48607240	7.55736933
V	7.14395501	4.19088357	5.39816970
V	1.23782883	0.78132983	9.74765738
V	4.19063523	0.78330357	9.74662303
V	2.71583588	3.33765138	9.74648249
V	5.66526943	3.33755346	9.74674694
C	2.71317563	1.63296520	8.79550081
C	1.23851053	0.78119680	6.26728393
C	5.66852086	1.63300800	8.79566279
C	4.19156380	0.77491331	6.34387825
C	4.19088659	4.19239789	8.79555929
C	2.70939591	3.34174814	6.34367336
C	7.14366341	4.19096094	8.83293910
C	5.67315080	3.34139359	6.34396558
N	4.19106692	2.48607544	4.20295029

TS3

V	8.56845479	5.05483421	7.49079147
V	2.71974533	1.70042261	5.22140691
V	5.55203255	5.05444655	7.49025416
V	5.49462105	1.69675902	5.22343719
V	7.06053097	2.41740619	7.50921853
V	4.11143853	4.06543057	5.24071461
V	4.10765245	2.46677995	7.53132435
V	7.06319390	4.11929567	5.38045287
V	1.15352621	0.76184994	9.71950914
V	4.10635651	0.76065151	9.72231072
V	2.62848536	3.32858363	9.72250644
V	5.58477219	3.32966251	9.72206371
C	2.63079798	1.61472930	8.77265885
C	1.15507940	0.76574370	6.21702738
C	5.58263973	1.61571835	8.77312580
C	4.10910708	0.76804937	6.28047432
C	4.10594827	4.17513720	8.76508729
C	2.63743985	3.32204787	6.33418139
C	7.06067060	4.17697838	8.78257732
C	5.58397144	3.32020776	6.33315193
N	4.10817100	2.48523065	4.17795838
H	7.09374306	3.41394304	3.82998299

NH

V	8.65006557	5.05793780	7.51571184
V	2.78349258	1.67071675	5.27896678
V	5.63604983	5.05703201	7.51573790
V	5.59651572	1.67090803	5.27840916
V	7.14227686	2.44760164	7.51563124
V	4.19016440	4.10654640	5.27835688
V	4.19002338	2.48305093	7.54495797
V	7.14271169	4.18772805	5.37300883
V	1.23693294	0.77824438	9.74519381
V	4.18964262	0.78032431	9.73768813
V	2.71502268	3.33429316	9.73764944

V	5.66428232	3.33431012	9.73804156
C	2.71154511	1.62930365	8.78526741
C	1.23720008	0.77757769	6.26051528
C	5.66816212	1.62942772	8.78548615
C	4.19019281	0.77166533	6.32165341
C	4.18995606	4.18990225	8.78556197
C	2.70833856	3.33838606	6.32132471
C	7.14271356	4.18774467	8.81514112
C	5.67169176	3.33818555	6.32140893
N	4.18977553	2.48033953	4.04040363
H	4.18998808	2.47879570	3.01726234

TS4

V	8.43754112	4.97529882	7.47958014
V	2.65760700	1.59737520	5.20970050
V	5.43963870	4.98040063	7.47953984
V	5.42892313	1.57249598	5.27315727
V	6.96187668	2.37322637	7.47752364
V	3.97605560	4.04542993	5.26518221
V	3.99697385	2.39505180	7.51189747
V	6.94585760	4.10007429	5.32109830
V	1.03587003	0.69617088	9.70397388
V	3.99334039	0.69369958	9.70398746
V	2.51815987	3.25634600	9.69967233
V	5.47311663	3.25420758	9.69966453
C	2.51514540	1.54760738	8.75270652
C	1.07030438	0.71701983	6.19115026
C	5.47306487	1.54710333	8.74604525
C	3.98482772	0.68677743	6.29775940
C	3.99482997	4.11227344	8.74588725
C	2.51692335	3.24619831	6.27694680
C	6.94465404	4.10576006	8.75934798
C	5.47830260	3.26063161	6.28827386
N	4.17581444	2.54485423	3.89737515
H	5.54190269	2.45381594	3.77089699
H	4.06223623	2.60113452	2.88293525

NH_2•

V	8.71911421	5.00813392	7.56047847
V	2.84521202	1.62372621	5.31574639
V	5.74218144	4.99543973	7.54799300
V	5.76315618	1.57362633	5.35744269
V	7.21959312	2.41064498	7.56052249
V	4.26153266	4.07612350	5.31674815
V	4.28981803	2.42395398	7.57191849
V	7.22157540	4.14119167	5.39562391
V	1.33406610	0.72069385	9.76895161
V	4.27563139	0.72057303	9.77019493
V	2.80612341	3.28055116	9.76431268
V	5.75780776	3.28786682	9.77019233
C	2.80110926	1.57464533	8.80784143
C	1.32001195	0.72946783	6.27823528

C	5.75479282	1.57812493	8.82940319
C	4.27909840	0.74026779	6.32279182
C	4.28097073	4.13786176	8.80775208
C	2.79065674	3.28981658	6.35873177
C	7.23211003	4.13489266	8.81620650
C	5.74302005	3.27528960	6.32317479
N	3.58316396	2.83521783	3.72876051
H	4.29141100	2.42702697	3.10823789
H	2.88936717	3.24084928	3.09242146

NH_3

V	2.87960219	1.72005413	5.33194476
V	2.87960538	0.01644204	7.56805022
V	5.83258174	1.71757999	5.38206665
V	7.31039835	2.57147035	7.56790112
V	4.35482479	4.27872060	5.38222969
V	4.35468221	2.57136933	7.56793386
V	7.30964820	4.27816719	5.38250271
V	1.40776583	0.87015355	9.77311908
V	4.35365303	0.87006893	9.77314827
V	2.88087570	3.42034563	9.77311972
V	5.83380052	3.42510331	9.77349175
C	2.88009689	1.71969404	8.81675634
C	1.41051091	0.87179457	6.31877609
C	5.83297097	1.71887073	8.82200452
C	4.34809162	0.87170035	6.31855935
C	4.35561752	4.27767279	8.82242981
C	2.87935969	3.41582379	6.31789498
C	7.31052532	4.27768453	8.82226098
C	5.83185190	3.42408382	6.34020802
N	2.88795072	1.73722201	3.15144355
H	2.03996196	1.28596133	2.79373558
H	2.92076614	2.70603107	2.81822800
H	3.71079899	1.23369751	2.80538522

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