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MXene Materials for the Electrochemical Nitrogen **Reduction—Functionalized or Not?**

Luke R. Johnson,[†] Sudiksha Sridhar,[†] Liang Zhang,^{†©} Kurt D. Fredrickson,[†] Abhinav S. Raman,[†] Joonbaek Jang,[†] Connor Leach,[†] Ashwin Padmanabhan,[†] Christopher C. Price,^{‡©} Nathan C. Frey,^{‡©} Abhishek Raizada,[†] Vishwanathan Rajaraman,[†] Sai Aparna Saiprasad,[†] Xiaoxin Tang,[†] and Aleksandra Vojvodic^{*,†}

[†]Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

[‡]Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

Supporting Information

ABSTRACT: We use density functional theory calculations to study a group of 2D materials known as MXenes toward the electrochemical nitrogen reduction reaction (NRR) to ammonia. So far, all computational studies have only considered the NRR chemistry on unfunctionalized (bare) MXenes. In this study, we investigate a total of 65 bare and functionalized MXenes. We establish free energy diagrams for the NRR on the basal planes of 55 different M_2XT_x MXenes (M = Ti, V, Zr, Nb, Mo, Ta, W; X = C, N) to span a large variety of possible chemistries. Energy trends with respect to the metal as well as nonmetal constituent of the MXenes are established for both bare and functionalized MXenes. We determine the limiting potentials and find that either the formation of NH₃ from *NH₂ or the formation of *N₂H is the potential limiting reaction step for bare and functionalized MXenes, respectively. We find several Mo-, W-, and V-based MXenes (Mo₂C, Mo₂N,



W2N, W2NH2, and V2N) to have suitable theoretical overpotentials for the NRR. Importantly, calculated Pourbaix stability diagrams combined with selectivity analysis, however, reveal that all bare MXenes are not stable under relevant NRR operating conditions. The only functionalized MXene with the three minimum required properties (i) having a low theoretical overpotential, (ii) being stable under NRR conditions, and (iii) having selectivity toward NRR rather than the parasitic HER is W2CH2, which is a H-terminated MXene. Finally, on the basis of our findings, we explore other routes for improving the NRR chemistry by studying 10 additional MXenes with the chemical formula $M_3X_2T_x$ and MXenes with other functional groups (T_x = S, F, Cl). This opens up a larger variety and tunability of MXenes to be considered for the NRR.

KEYWORDS: MXenes, electrocatalysis, nitrogen reduction, ammonia, functionalization, DFT, electrochemistry

INTRODUCTION

Ammonia (NH_3) has helped shape both the history and ecology of our planet, being used as a chemical feedstock and biochemical agent. The industrial process of making NH₃ from hydrogen and nitrogen known as the Haber-Bosch process is considered to be one of the most important inventions of the 20th century, used mainly for producing fertilizer, which has positively affected population growth.¹⁻⁴ The thermal nitrogen reduction reaction is exothermic with the dissociation of nitrogen being identified as the rate-determining step.^{5–9} The industrial Haber-Bosch process is catalyzed by an Fe metal catalyst at high temperatures and pressures, using $\sim 2\%$ of the world's energy consumption, and produces 500 million tons of NH₃ annually.^{2,10,11}

Computationally, it has been confirmed that Ru and Fe are the most catalytically active elemental metals for NH₃ synthesis even when error estimates in the computational approximation are taken into account.^{5,12} The electrochemical nitrogen reaction provides a clean way to produce ammonia if the catalyst can activate an N2 molecule efficiently without producing H₂ or other byproducts in the process. Several studies have computationally examined the challenges of nitrogen reduction for the thermal and electrochemical reactions not only on metals but also on more complex materials, including metal compounds.^{8,13,14} For example, heterogeneous metal carbide and nitride materials have been explored for the electrochemical ammonia synthesis, and some of them show promising properties.¹⁵⁻¹⁸ Nitrides have also been suggested as nitrogen reduction systems for the production of ammonia through a looping scheme.¹⁹ Overall, the drive to design sustainable and novel catalysts for ammonia production under less energy intensive and sustainable

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Figure 1. (a) Atomic structure of the xy plane (top view) and yz plane (side view) of the Mo_2C bare MXene, and the Mo_2C MXene functionalized with 1 ML of H, O, and N, respectively. The high-symmetry points considered as adsorption sites for the NRR intermediates are indicated on the bare MXene. The supercell is indicated with black solid lines. The atoms included are Mo (green), C (gray), N (blue), O (red), and H (white) (b) Reaction pathway for the adsorbates considered on a prototypical MXene.

methods is of utmost interest. Considering that in nature there exist biological systems such as nitrogen-fixing bacteria, using the nitrogenase enzymes, that perform this chemistry under milder conditions, although it requires a significant amount of energy, indicates that this electrochemistry could be achievable by an artificial material.^{20–26} For such a material to be considered as a candidate for the electrochemical NRR, it must at a bare minimum have the following essential characteristics: being able to activate the N₂ molecule, being stable, and having the appropriate selectivity toward the NRR: i.e., outperforming other competing electrochemical reactions such as the hydrogen evolution reaction (HER).^{13,14}

Recently, there has been an interest in using MXenes, a group of 2D transition-metal carbide and nitride materials, for electrochemical reactions including catalysis and electrochemical storage. These 2D MXene materials are synthesized from their parent bulk MAX materials via an etching procedure of the A constituent.^{27,28} Similarly, quaternary *i*-MAX phases are parent materials for synthesizing MXenes with in-plane chemical ordering.^{29,30} MXenes have thus far been studied for the hydrogen evolution reaction (HER), $^{14,31-36}$ CO₂ reduction to hydrocarbons, CO₂ abatement, 37,38 CO oxidation, 39 and oxygen evolution and reduction reactions.^{40,41} In ref 31, Oterminated Mo₂C was computationally predicted and experimentally validated to be an efficient HER electrocatalyst. Computational screening studies on MXene materials have also been attempted for energy storage applications.⁴²⁻⁴⁴ It has also been shown computationally that the basal plane termination of the MXenes depends on the applied potential.^{31,45} The importance of the termination on the HER performance was portrayed in ref 46, where it was shown that the presence of F as the functional group hinders HER activity. In other words, modeling MXenes with appropriate termination is crucial to correctly capture and predict their chemistry and activity.

A couple of studies have also investigated MXenes for nitrogen reduction.⁴⁷⁻⁵² However, many of these studies have focused on the chemistry of the bare basal planes of the MXenes, while it has been shown that MXenes are functionalized when they are synthesized under most operating

conditions.^{45,46,53,54} For example, bare Nb_3C_2 and V_3C_2 have been presented as promising catalyst materials from a group of bare MXenes with the chemical formula M₃X₂.⁵⁵ Bare Mo2TiC2, a bimetallic MXene, was also examined for its basal plane activity in catalyzing the NRR.⁵⁶ In ref 57, the reactivity descriptors and activity of MXenes with the chemical formula M_2X (M = Mo, Ta, Ti, W; X = C, N) were studied and bare Mo₂C and W₂C were identified as candidate catalyst materials. Another 2D material, a MoN₂ nanosheet, was modeled for the NRR and found to be too reactive as a bare metallic sheet, which was adjusted by doping the sheet with Fe.⁵⁸ Emerging 2D materials including MXenes deserve more attention as potentially promising electrocatalysts, as they can offer a large number of active sites assuming these are located on the basal planes, which was shown for the HER,^{31,46} in contrast to layered materials as dichalcogenides which have active edges; if they are functionalized properly, they can be metallic and have high electrical conductivity.^{28,31,45}

In this paper, we computationally screen 65 MXenes and investigate their feasibility to perform the electrochemical nitrogen reduction reaction. We demonstrate variations and trends in the reactivity and stability of these MXenes by tuning their functional groups present at the basal planes. We identify MXenes with suitable theoretical overpotentials on the basis of the calculated free energy diagrams and limiting potentials. One of our main findings is that the basal planes of MXenes are always functionalized under electrochemical NRR operating conditions. Hence, bare MXenes which have been extensively studied as NRR catalysts in earlier studies are unsuitable and unstable NRR catalyst materials. In addition, we perform a selectivity analysis of the competing parasitic hydrogen evolution reaction in comparison to NRR. On the basis of thermodynamics, the only functionalized MXene with the three minimum required properties (i) having low theoretical overpotential, (ii) being stable under NRR conditions, and (iii) having selectivity toward the NRR rather than the parasitic HER is W₂CH₂, which is a H-terminated MXene. Overall, we demonstrate that the composition of the functional group on the basal plane, i.e. termination, is of utmost importance in modeling the catalytic activity and

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chemistry of MXene materials. Finally, we suggest new directions to be explored and expand our computational search to MXenes with other functional groups and crystal structures.

CALCULATION DETAILS

Density Functional Theory Calculations. In this paper, the investigated MXenes include M_2XT_{u} with M = Ti, V, Zr, Nb, Mo, Ta, W and X = C, N, and T_x being a functional group of none (bare), H, O, or N, in addition to Ti₃C₂T_x and F-, Cl-, and S-functionalized Mo₂C and Mo₂N. We first constructed a total of 66 MXenes and optimized their structure, allowing for relaxation of both the supercell and atomic positions inside. Each MXene is modeled as a single layered 2D sheet in a supercell consisting of a 1×1 unit cell geometry (two metal atoms, one carbon or nitrogen atom, and if functionalized one T_x atom on each of the basal planes of the sheet corresponding to a 1 monolayer (ML) coverage of the functional group) separated by 16 Å of vacuum. The initial placement of the functional group is taken to be one of the high-symmetry points of the basal planes. The optimized lattice parameters are presented in Table S1 in the Supporting Information. We find that the functional groups are strongly bound to the basal planes of the bare MXenes and prefer the fcc or hcp site. The structure for W₂CN₂ did not converge to these conditions and was removed from further analysis.

The NRR activity of the MXenes is evaluated on the basis of their basal plane chemistry toward each of the NRR reaction intermediates. We performed the adsorption calculations using a 2 \times 2 unit cell of M₂XT_r in a supercell with the lattice parameters determined above. The intermediates were adsorbed on one side of the basal plane with a θ = 0.25 ML coverage relative to the metal constituent of one of the exposed basal planes (note that this corresponds to an overall θ = 0.125 ML coverage relative to both exposed basal planes that is the total number of metal atoms in the supercell). The initially considered adsorption sites are the four high-symmetry points on the basal plane of the bare MXene, fcc, hcp, bridge, and top sites (see Figure 1), which are also the sites that are used for the functionalized MXenes with the same nomenclature. All adsorption trajectories for the studied MXenes of varying functionalizations are included in Figure S5 in the Supporting Information.

All density functional theory (DFT) calculations were performed using the Quantum Espresso software package as implemented in the Atomic Simulation Environment.^{59,60} Ultrasoft Vanderbilt pseudopotentials were employed with a plane-wave energy cutoff of 700 eV. The Brillouin zone was sampled using a $4 \times 4 \times 1$ Monkhorst–Pack *k*-point grid.⁶¹ Periodic boundary conditions and a dipole correction were used in all calculations.⁶² The convergence criterion for structure optimization was set to 0.05 eV/Å. We used the BEEF-vdW exchange and correlation functional,⁶³ which previously has been successfully utilized to model both the structure and electrochemical properties of MXenes.^{31,45,46}

Electrochemical Reactions and Modeling. The overall electrochemical NRR reaction taking place on the cathode is

$$N_2(g) + 6(H^+ + e^-) \rightarrow 2NH_3(g)$$
 (1)

and the corresponding considered anode reaction is the hydrogen oxidation, serving as the source of protons and electrons. For the associative NRR mechanism,⁶⁴ the reaction

occurs via subsequent hydrogenation of N_{2} , where the addition of hydrogen to the surface represents a combined proton supplied from the solvent and an electron from the electrode surface. This mechanism has been implemented in similar studies modeling the electrochemical nitrogen reduction.^{13,18,37,55,65} The subreactions of the associative NRR mechanism are

$$N_2(g) + H^+ + e^- \to *N_2H$$
 (2)

$$*N_2H + H^+ + e^- \rightarrow *N_2H_2$$
 (3)

$$*N_2H_2 + H^+ + e^- \rightarrow N^* + NH_3(g)$$
 (4)

$$N^* + H^+ + e^- \to *NH \tag{5}$$

$$*\mathrm{NH} + \mathrm{H}^{+} + \mathrm{e}^{-} \to *\mathrm{NH}_{2} \tag{6}$$

$$*\mathrm{NH}_2 + \mathrm{H}^+ + \mathrm{e}^- \to \mathrm{NH}_3(\mathrm{g}) \tag{7}$$

where * denotes an adsorption site on the basal plane of the MXene. To obtain the energetics for the reaction, we perform DFT calculations as outlined above to find the minimum adsorption energy configuration for each of the intermediates on the basal planes of the MXenes: N_2H , N_2H_2 , N^* , NH, and $*NH_2$. In this study, as has been done in previous studies, we assumed in the initial round of our computational high-throughput screening study that activation barriers for protonation steps can be neglected during the electrochemical reactions for fast identifications of a subset of potential candidate catalyst materials. The free energy of each elemental step is calculated using

$$\Delta G_i = \Delta E_i + \Delta E_{i,\text{ZPE}} - T\Delta S - neU + 2.303k_BT \text{pH}$$
(8)

where ΔE_i is the potential energy change as obtained from DFT calculations. $\Delta E_{i,ZPE}$ and $T\Delta S$ are zero-point energy and entropy corrections, respectively, referenced to the free gasphase species. They are calculated using standard vibrational corrections in the harmonic approximation and are provided in Table S2 in the Supporting Information. The coupled protonelectron transfer energetics is taken into account by employing the computational standard hydrogen electrode (CHE) method.⁶⁶ Under standard conditions (pH 0, p = 1 atm, and T = 25 °C) and no applied bias (U = 0), the CHE method relates the chemical potential of $(H^+ + e^-)$ with $1/2H_2(g)$ and the free energy difference of $*A + (H^+ + e^-) \rightarrow *AH$ with the free energy change of $*A + 1/2H_2(g) \rightarrow *AH$. An applied bias *U* is taken to contribute to each of the electrochemical steps by -neU, where *n* is the number of electrons involved in the particular reaction. The reaction is assumed to occur under STP conditions, and the chemical potentials are referenced to the gas-phase species; hence, our chemical potential is varied only through the applied voltage and the pH of the system. In addition, pH is included in the calculation through a linear temperature term shifting the free energy by $2.302k_{\rm B}TpH$. We note that potential changes in the adsorption energetics can exist due to the explicit presence of water. However, these calculations require significant computational resources and there are indications from other studies that these effects might be significantly smaller than the energy differences between different materials; therefore, such corrections are excluded at this point.^{17,67–70}



Figure 2. Calculated free energy diagrams for nitrogen reduction via the associative mechanism on all investigated M_2XT_x MXenes (top) and MXenes with different functional groups T_x = bare (a), H (b), O (c), N (d), respectively. Calculations were performed for U = 0 V, T = 300 K, p = 1 atm, and pH 0.

RESULTS AND DISCUSSION

Figure 2a shows a combined calculated free energy diagram for electrochemical nitrogen reduction to ammonia on 55 of the 65 investigated MXenes. These are based on the adsorption energies from the most stable adsorbate configuration for each intermediate in each system. All adsorption energies are reported in Table S3 in the Supporting Information. We find that functional groups T_x adsorb more strongly on the fcc and hcp sites in comparison to the top and bridge sites. Previous computational MXene studies have found preferred terminations over the fcc or hcp geometry on the basal plane.^{31,32,34,35,45,46,71} As a result, the presence of functional groups and their occupancy of certain sites on the basal planes of the MXenes affect the adsorption geometries of the NRR intermediates and the corresponding adsorption energy.

We find that the energetics of the studied associative nitrogen reduction reaction mechanism spans a large energy space from very negative to very positive, depending on the fine details of the considered MXene. To allow for an in-depth analysis of how the metal constituent, the nonmetal constituent, and the functional group of the MXene affect the basal plane chemistry, we present the free energy landscapes corresponding to the different groups of MXenes M_2XT_2 with varying terminations T_x in Figure 2 and discuss them in detail below.

Free Energy Diagrams. *Bare MXenes.* The basal planes of bare MXenes expose metal atoms, allowing for direct bond formation between the metal atoms of the MXene and the NRR intermediates. The preferred adsorption site for each of the studied systems is indicated in Tables S4–S10 in the Supporting Information together with an illustration of all

investigated adsorption sites. As mentioned above, the relaxed geometry for each considered adsorption site on the basal plane and the selected most preferred adsorption sites are shown in Figure S5 in the Supporting Information. For the investigated bare MXenes, we find that the NRR intermediates preferentially adsorb in a 3-fold site, which is either an fcc or hcp site, with the exception of *NH₂ on W_2N (see further details in Tables S4–S9 in the Supporting Information). Using these adsorption geometries and energetics, we next analyze the free energy landscape of bare MXenes.

The calculated free energy diagrams for the studied bare MXenes are shown in Figure 2a. In general, we find that the reaction pathways are significantly downhill in the first part of the reaction and become significantly uphill in the later part of the reaction, suggesting the possibility of a poisoning effect due to strong interactions between the MXene and the early NRR intermediates. Attention should be given to reaction steps eqs 2 and 4, as their respective energies define the initial downhill nature of the pathway on bare MXenes. We find that the *N₂H intermediate is very stable on the basal plane of bare MXenes, exhibiting a lying adsorption configuration due to the formation of a secondary bond between the top N atom and an empty adjacent site on the basal plane. *N₂H₂ is relatively stable in comparison to *N₂H, showing a slanted adsorption configuration, which indicates a change in bond order upon interaction with H. These observed adsorption phenomena are illustrated in Figure S5 in the Supporting Information. We find that both carbide and nitride MXenes with the metal constituent in the same group demonstrate similar reaction pathways. In addition, both bare carbide and nitride MXenes in the same period show smoother, that is more thermoneutral,

reaction profiles with increasing group number of the metal constituent. With respect to the nonmetal constituent of the MXene, we find that Ti-, Zr-, Mo-, and W-based bare MXenes show very similar reaction pathways for the carbide vs the nitride. On the other hand, we find that the Ta- and Nb-based carbides have flatter energy diagrams in comparison to their corresponding nitrides. In contrast, we observe that V_2N has a preferred energy diagram over V_2C . The observed trends with respect to the different constituents of the bare MXenes are indicative of direct strong interactions between the basal plane and adsorbate.

For a material to be a promising candidate for electrochemical NRR catalysis, it should at least have a suitable theoretical overpotential: that is, it should have as small of an $|\Delta G_i|$ value as possible for each of the individual elementary reaction steps *i* given by eqs 2-7. All investigated bare MXenes spontaneously form *N₂H, i.e. $\Delta G_i < 0$, with the exception of Mo-based MXenes, with $\Delta G_i < 0.1$ eV, and all bare MXenes release energy ($\Delta G_i < 0$) in the reaction step eq 4. For all bare MXenes, reaction steps in eqs 3, 6, and 7 require an energy input. We identify Mo₂C, Mo₂N, W₂C, and W₂N, all bare MXenes in group 6, as materials with suitable theoretical overpotentials for the NRR on the basis of small free energy changes in the reaction pathway. This is in agreement with recent studies of bare Mo₂C and W₂C MXenes.⁵⁵⁻⁵⁷ However, it is important to note that we disagree with the statement of these MXenes being promising for N2 fixation to make NH3, since they do not fulfill stability or selectivity arguments, as discussed in sections below. We next proceed with a discussion of results for functionalized MXenes and will then target the question of stability of these materials.

H-Functionalized MXenes. Figure 2b shows the free energy diagrams for MXenes where the basal planes have been functionalized with H corresponding to a 1 ML coverage relative to the metal constituent on each of the basal planes of the MXene 2D sheet. One of the first observations is that the preferred adsorption sites for the reaction intermediates vary significantly when the MXenes are functionalized in comparison to adsorption on the bare MXenes. For all H-terminated MXenes, *NH preferentially adsorbs in the hcp site above the MXene where there is no H (see definition of adsorption sites on H-terminated MXenes in Figure 1), with the exception of W_2CH_2 . We find that N* adsorbs in the hcp or top site, except for Ti₂CH₂, where N* adsorbs directly over H** in the fcc site. More details are provided in Tables S4-S10 in the Supporting Information. We also find that fewer NRR intermediates are stable in the as-initialized high-symmetry adsorption sites on the H-terminated MXenes, in comparison to the bare MXenes, undergoing significant relaxation or even reconstruction in some cases (see Tables S4-S10 in the Supporting Information for $*N_2H$, $*NH_2$, and $*N_2H$) due to the formation of NH_{x+1} from NH_{*x*} where $0 \le x < 3$. When constructing the free energy diagrams, we only consider the relaxed structures where intermediates have not caused severe reconstruction (see Figure S5 in the Supporting Information, where the minimum energy structures are highlighted in green). We find that Hfunctionalized MXenes have a lower tendency to initialize the NRR than bare MXenes due to the reaction step in eq 2 having $\Delta G_{*N,H} > 0.$

With respect to the nonmetal constituent of the MXene, we find that the free energy landscape improves with increasing group number for period 4 and 5 carbides, while it decreases for their corresponding nitrides. On the other hand, period 6

MXenes show improvement in the free energy diagrams for both carbides and nitrides with increasing group number. Group 4 MXenes exhibit a more uphill free energy landscape, as opposed to group 5 and 6 MXenes, where it is improving with increasing period number. The thermodynamic activity is greater for nitrides than for carbides with the exception of W-, V-, and Ta-based MXenes. The V- and Ta-based MXenes have little variation in their reaction pathways; however, V₂N has a slightly higher ΔG_{*N_2H} value than V₂C. On the other hand, Ta₂C and Ta₂N express similar reaction pathways. In comparison to bare MXenes, the trends with respect to the different constituents are not as apparent for H-terminated MXenes.

For all investigated H-terminated MX enes, we find that the $\Delta G_{*\mathrm{N_2H}}$ value is uphill in energy, with $\mathrm{Ti_2CH_2}$ having the largest $\Delta G_{*\mathrm{N_2H}}$ value of 2.752 eV in comparison to the smallest value of 0.77 eV for W_2NH_2. On the basis of the free energy diagrams, we identify W_2CH_2 and W_2NH_2 as materials with suitable theoretical overpotentials for catalyzing the NRR. Taken together, our analysis indicates how drastically surface functionalization affects activity and the importance of modeling MX enes with correct termination on the basal planes. Observing that the surface functionalization can greatly affect the surface chemistry, we proceed to examine other type of surface functionalizations that can exist on the basal planes of MX enes.

O-Functionalized MXenes. Figure 2c shows the calculated free energy diagrams for MXenes with the basal planes functionalized with 1 ML of oxygen. Note that experimentally it has been observed that some of the investigated MXenes can have high or partial coverage of O, OH, and F as functional groups when they are synthesized.⁵³ Hence, modeling the Oterminated MXenes is unquestionably a necessity. The adsorption geometry for a given NRR intermediate varies significantly ammong the different O-terminated MXenes (see Tables S4–S10 in the Supporting Information for details). The first observation is how difficult it is to adsorb *N₂H on the basal planes of such MXenes. In general, we find that Ofunctionalized MXenes are less reactive than both the bare and the H-functionalized MXenes toward NRR intermediates, most probably due to the weak interactions resulting from the strongly electronegative nature of O atoms.

When it comes to trends with resepct to the metal constituent, we find that group 4 MXenes improve with increasing period number, group 5 MXenes do not show any apparent trend, and Nb₂C and Ta₂C have similar energy pathways. At the same time, the energy pathways are improved with increasing group number for period 4, 5, and 6 MXenes, with the exception of period 5 nitrides and period 6 carbides, where it decreased. This ties into the previous notion that MXenes can be improved by using group 6 MXenes in periods 5 and 6. Nitrides perform better than carbides, with the exception of Nb- and Ta-based MXenes. The Nb-based MXenes have similar $\Delta G_{*N,H}$ values, but Ta_2C has a considerably lower $\Delta G_{*N,H}$ value than Ta₂N. We again emphasize that H- and O-functionalized MXenes do not present trends across the periodic table as crisp as those for bare MXenes.

Adsorption of *N₂H is energetically extremely uphill and initially has difficulty in forming on O-functionalized MXenes. As an example, Ti₂CO₂ greatly resists adsorbing *N₂H, in comparison to V₂NO₂ with a $\Delta G_{*N,H}$ value of 1.16 eV. Among

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Figure 3. Limiting potentials, $U_L = -\Delta G_{\nu}$ for the associative NRR mechanism on the basal planes of $M_2 X T_x$ MXenes with different functional groups $T_x =$ bare, H, O, N. Note that the plot is not scaling dependent (based on the free energy diagram), as the lines represent linear fits for each mechanistic step.

the O-functionalized MXenes, V_2NO_2 shows the flattest energy diagram; however, its ΔG_{*N_2H} value still makes it inactive for NRR catalysis. We next investigate the fourth and remaining termination of this study, the N termination, which is reflective of the main reactant, N_2 , and a functional group that potentially might be present under NRR operating conditions.

N-Functionalized MXenes. Figure 2d shows the calculated free energy diagrams for N-functionalized MXenes. The preferred N* adsorption site on N-terminated MXenes is either the metal bridge site near the terminating N or the top site above the terminating N, which forms a N–N bond and an intermediate that in some case desorbs from the basal plane. First, we note that the *N₂H adsorbate is more easily adsorbed on the N-terminated basal plane in comparison to O-functionalized MXenes. We find that Zr-, Nb-, and Ti-based carbides have lower energy diagrams in comparison to their respective nitrides while Mo- and V-based MXenes have C/N pairs with similar free energy diagrams.

There are few trends with respect to the different constituents of the MXenes. The energy pathway improves across groups in period 4 from V to Ti N-terminated MXenes. For period 6, the W₂N pathway appears more promising than the Ta₂N pathway. Group 4 MXenes in this study perform similarly to each other. We find that free energy diagrams of group 5 carbides improve on moving from Ta₂C to V₂C, whereas diagrams for group 6 nitrides improve across the period from Mo₂N to W₂N. Interestingly, we observe that N-terminated MXenes have the greatest variation in the activity, as they show both positive and negative ΔG_{*N_2H} values. On the basis of the free energy analysis, we conclude that Zr₂CN₂

and $({\rm Ti}_2N)N_2$ may be favorable MXenes for the NRR; however, a more detailed analysis is needed to make such a conclusion, as described below.

Comparative Analysis of Reactivity. We find that functionalization leads to reaction pathways that are more uphill in free energy in comparison to those for bare MXenes. In particular, all studied functionalized MXenes share a similar characteristic of endergonic free energy changes to form the initial *N2H intermediate, which should be contrasted with bare MXenes that spontaneously form *N2H. The higher reactivity of bare MXenes toward NRR intermediates was expressed through distinct adsorbate geometries: for example, *N₂H adsorbed in a highly tilted geometry involving two adjacent adsorption sites on the bare basal plane and direct interaction with unsaturated metal atoms of the bare MXene. In contrast, the existence of functional groups on the basal plane prevents direct interaction between NRR intermediates and unsaturated metal atoms of the MXene, which result in more upright adsorbate geometries. Overall, we find that bare Mo- and W-based (group 6) MXenes demonstrate the most ideal adsorption energetics of the NRR intermediates in comparison to both bare group 4 and 5 MXenes and all of the functionalized MXenes. Figure S1 in the Supporting Information shows the changes in the free energy diagrams as a function of applied potential, V, and pH. We next determine and discuss what reaction steps limit the NRR on the studied MXenes.

Limiting Potentials and Onset Potentials. In this section, we analyze the potential limiting steps for NRR on MXenes with different functional groups. The limiting potentials for each elementary step as a function of ΔG_{*N} for

the different functional groups are shown in Figure 3. This allows us to identify the mechanistic step that overall limits the reaction and determines the onset potential. In addition, as part of this analysis, we have established adsorbate scaling relations between each of the NRR intermediates and the $\Delta G_{\rm *N}$ value , provided in Figure S2 in the Supporting Information.

We find that the associative NRR on bare MXenes is limited either by the *NH to *NH₂ step or by the *NH₂ to NH₃(g) step, eqs 6 and 7, respectively. On the other hand, the reaction on functionalized MXenes is limited by ΔG_{*N_2H} formation, as given by eq 2. These functionalized systems exhibit a greater variety of onset potentials in comparison to that of the bare MXenes and allow for structure-sensitive reactivity tuning and modification of the potential determining step. A similar change in the limiting potential step is also observed for rutile oxides, 3D nitrides, and metals.^{13,15,17,72}

Figure 4 shows the calculated onset potentials for all studied MXenes, and the explicit values are reported in Table S11 in



Figure 4. Explicitly calculated onset potentials, $\max{\{\Delta G_i\}}$, for the investigated $M_2 X T_x$ MXenes with different functional groups T_x = bare, H, O, N. The MXenes are ordered by the atomic number of their M constituent.

the Supporting Information. We find that bare Mo_2C has the overall lowest overpotential for the NRR with a value of 0.56 V, while Ti_2CO_2 has the largest overpotential. For each M_2XT_x MXene, we find that the bare MXenes have the smallest overpotentials except for Ti_2N , Zr_2C , Zr_2N , Ta_2C , and Ta_2N . We identify that, as the period number of the M constituent of the MXene increases, the overpotential of the bare MXene, the overpotential for both bare carbide and nitride for each

period increases across the group number (IV to VI). A more detailed analysis of how the constituents affect the reactivity is given above in Free Energy Diagrams.

The MXenes with the lowest overpotentials are $Mo_2C < Mo_2N < W_2N < W_2NH_2 < V_2N < W_2C < W_2CH_2 < Nb_2C$, chosen on the basis of their performance relative to the best single-metal electrocatalyst, Ru(111).¹³ The overpotentials for the investigated MXenes are comparable to or smaller than those reported on metals,¹³ most rutile oxide and mononitride electrocatalysts,^{16,72} offering promising overpotentials similar to that of nitrogenase, 0.63 V.⁷³ We want to emphasize the importance of the functional group on the performance of the MXenes. For example, we find that O-terminated MXenes have the largest overpotentials among the functionalized systems for all MXenes, with the exception of V₂NO₂ and Ta₂CO₂. This clearly illustrates that O-functionalized MXenes are not suitable for catalyzing the NRR.

NRR vs HER as Competing Reactions. One of the challenges of electrochemical NRR is overcoming the selectivity issue set by competing reactions; one in particular is the hydrogen evolution reaction (HER).^{13,14} Therefore, we perform an analysis of the energetics for the above identified potential limiting steps for NRR on MXenes, namely the formation of *N₂H and *NH₂, and compare them to the calculated ΔG_{H*} values on MXenes, which have been shown to be a descriptor for the HER overpotential on transition-metal surfaces.⁷⁴

Figure 5 shows the calculated HER and NRR limiting potentials. We find that Mo₂C, Mo₂N, W₂C, and W₂N are the only bare MXenes that favor H* adsorption over N₂H formation at low H coverages (1/4 ML). Although several H- and O-terminated MXenes have ΔG_{*NH_2} values that compete against ΔG_{H^*} , as shown in the right graph of Figure 5, such MXenes are not limited by the specified reaction steps. However, when the left graph in Figure 5 is examined, with the exception of Ta₂NH₂ and W₂NH₂, H- and O-terminated MXenes do not compete against the HER.

For comparison, we also include the high-coverage H* adsorption limit (1 ML) on the bare MXenes and compare those to $\Delta G_{*\mathrm{N,H}}$ and $\Delta G_{*\mathrm{NH}_2}$ values on corresponding bare MXenes. Note that due to poor HER activity for Hfunctionalized MXenes, with ΔG_{H^*} > 0, at HER relevant potentials, the coverage of H is probably between $\theta_{\rm H} = 1/4$ and 1 ML. Hence, the simplified analysis here gives an idea if saturating the basal planes with H would make the HER compete with the formation of relevant limiting NRR intermediates. For 1 ML H-covered MXenes, the HER outcompetes both of the NRR limiting steps, except for W_2CH_2 with $\Delta G_{*N,H}$. This shift in competition is due to an increase in the ΔG_{H^*} value, as it approaches the equilibrium HER potential for these materials. In the next section, we evaluate the stability of the investigated MXenes under relevant NRR conditions.

Stability of MXenes as a Function of Applied Potential. It has become a common procedure to examine the termination and coverage dependence of a heterogeneous catalyst surface being considered for a reaction under certain operating conditions. However, high-throughput screening studies do not always allow for that due to prohibited computational cost and, in the best case scenario, they perform this analysis as a step after identifying "the most promising candidate" materials, which corresponds to materials with



Figure 5. Comparison of the energetics for the two NRR intermediates (a) N_2H and (b) NH_2 relevant in the limiting reactions of the NRR vs H* adsorption on the basal planes of the studied M_2X MXenes. Dashed lines indicate where ΔG_H and the corresponding adsorption free energy of the NRR intermediates are equal. Points below the dashed line have limiting potential steps that compete against H* adsorption. The right triangle uses a ΔG_{H*} value corresponding to $\theta = 1$ ML coverage of H adsorbed on a bare MXene, where the adsorbate on the bare surface is compared to absorbed H of the H-terminated MXene.



Figure 6. Calculated Pourbaix diagrams for (a) Mo₂C and (b) Ti₂C with different functional groups T_x = bare, H, O, N. The free energy is computed as $\Delta G(U) = \Delta G(0) - neU$. The relative stability at an applied voltage is referenced to the free energy of the bare MXene.

suitable theoretical overpotentials. Previous studies on MXenes have not always examined in a thorough way surface terminations on the basal planes under relevant electrochemical conditions. We next perform this analysis for our NRR screening study.

Figure 6 shows the calculated Pourbaix diagrams of two representative MXenes, Mo_2CT_x and Ti_2CT_{xy} in order to determine how 1 ML coverages of H, O, and N affect their stability relative to each other and to bare MXenes at different applied potentials. The stability diagrams for all other MXenes can be found in Figure S3 of the Supporting Information. The preferred coverage changes from O to H termination at more negative applied potentials. The HER is activated at negative

potentials, and it seems plausible that H functionalization would subsequently occur at a more negative potential. This agrees with thermodynamic stability plots produced on O- and H-terminated Mo_2C and Ti_2C .⁴⁵ Another observed trend for all MXenes is the phase change from O- to N-terminated MXenes at highly positive potentials, greater than 1.4–1.5 V. Bare and N-terminated MXenes are not favored at NRR- or HER-relevant potential windows. The intricate relationship between the applied potential and the functionalization of the basal planes can be viewed positively, since it directly influences the catalytic activity and in principle can guide us in designing better-performing systems by using more appropriate functional groups.



Figure 7. Calculated free energy diagrams for the proposed associative NRR mechanism on (a) $Ti_3C_2T_x$ and Ti_2CT_x MXenes with T_x = bare, H, O, and N and (b) Mo_2CT_x MXenes with T_x = bare, H, O, N, Cl, F, S.

New Routes for Improved MXene Chemistry. Finally, we focus our study on possible future directions for design of MXenes for the electrochemical NRR. So far in this paper, we have focused on a group of MXenes with the chemical formula M_2XT_x . Our approach of changing the chemistry of the MXenes has been through a limited set of functional groups on the basal plane. However, there are numerous unexplored routes to identify potential MXenes for the NRR and other chemistries, including studies of other functional groups, MXenes with other chemical formulas (i.e. structures such as M_3X_2 and M_4X_3), alloying or doping the MXenes with other undercoordinated sites and defects present in the MXene core and among the functional groups.

A search for new MXene materials for a given chemical transformation needs to go beyond the search for a material with optimal thermodynamic free energy reaction pathways and should at least include stability measures under relevant conditions and an analysis of selectivity that is a discussion of the parasitic and competing reactions such as the HER for the NRR. We end this paper by investigating the possibility of tuning the performance of the MXenes by extending our initial screening study to new, already synthesized MXenes that exist with known initial stability prior to any electrochemical testing. We focus on 10 new MXene systems, bringing the total number of studied MXenes in this paper to 65, and three design aspects, structure tuning, functional group modification, and selectivity tuning, by exploring if MXenes with low HER performance⁴⁶ could be suitable for the NRR.

Figure 7a shows the calculated free energy diagrams for bare and H-, O-, and N-terminated Ti_3C_2 and the corresponding energy pathways for Ti_2C , allowing us to investigate the change in chemistry as the structure of the MXene is changed. It should be noted that both Ti_2C and Ti_3C_2 terminated with a mixture of O, OH, and F functional groups have been successfully synthesized.^{27,53,71} Also, in ref 31 it was found that Ti_2C is an unsuitable MXene for the HER, hence giving us the opportunity to test the HER vs NRR selectivity hypothesis using two groups of Ti-based MXenes. We find that increasing the thickness of the MXene yields a less negative and more smooth reaction pathway for bare Ti_3C_2 in comparison to the bare Ti_2C ; however, this results only in a slight change in the overpotential. For the H- and O-functionalized Ti-based MXenes, we find that the overpotential decreases with increased thickness, from 1.72 to 0.92 V and from 3.02 to 2.25 V, respectively. However, for the N-terminated Ti_3C_2 , the onset potential increased in comparison to the N-terminated Ti_2C . In other words, our results show that the performance of the Ti-based carbide MXenes can be improved as the structure changes from Ti_2CT_x to $Ti_3C_2T_x$; however, the exact change will be strongly dependent on the functional group.

Figure 7b shows the free energy diagrams for NRR on functionalized Mo₂C with functional groups beyond those already discussed above and include Cl, F, and S. A corresponding extended study of Mo₂N is provided in Figure S4 in the Supporting Information. Note that there is experimental evidence that these functional groups are present on the MXenes due to the synthesis or testing procedures.⁴⁶ Current synthesis routes of MXenes require use of HCl, HF, or LiF agents to successfully etch away the A components of the MAX phase. 46,53 In addition, H_2SO_4 has been used as an electrolyte during operating conditions for electrochemical reactions under acidic conditions, being one potential source of S in these systems.^{31,46} A Pourbaix stability diagram of bare and H-, O-, N-, Cl-, F-, and S-terminated Mo₂C (see Figure S6 in SI), here used as a prototype MXenes, shows O- and Htermination to be favorable in the for NRR relevant operating conditions. In addition, stability with respect to pH of functionalized Mo₂C (see Figure S6 in the Supporting Information) further supports this. This suggests that the presence of functional groups other than O and H on the basal planes of the MXenes under NRR operating conditions has to be engineered during synthesis. We find that Cl-terminated Mo₂C has an overpotential of 3.45 V, which is very close to the overpotential of O- and S-terminated Mo₂C. Cl-terminated Mo₂C has the ability to greatly stabilize N* on the functionalized basal plane. Using F as a functional group, a more electronegative halogen than Cl, significantly decreases the $\Delta G_{*N,H}$ value for initializing the reaction in comparison to the O-terminated Mo₂C. We have identified that the Hterminated Mo₂C has the lowest overpotential among the investigated functionalized MXene systems. However, it is still significantly higher than that found for the bare Mo₂C, which as was pointed out, does not exist under relevant operating conditions. Although the newly explored functional groups described in this section did not result in the identification of improved overpotentials of Mo_2CT_{xv} this part of our study illustrates two major points: (i) there is a large tunability space with respect to the functional group, providing insights into the performance of already synthesized MXenes and what functional groups to avoid, and (ii) importantly, we find that F functional groups enhance the NRR performance in comparison to O functional groups, which is exactly the opposite trend to what was found for the HER, where F functionalization resulted in worse performance.⁴⁶ Therefore, we conclude that extended studies of the suggested design routes would enlighten the search for new 2D MXene catalyst materials for electrochemical NRR and other chemical transformations.

CONCLUSIONS

Our DFT high-throughput computational study of bare and functionalized MXenes show a plethora of tuning possibilities in the basal plane chemistry of these materials toward the electrochemical nitrogen reaction reaction (NRR). Initially we support findings from previous studies that the theoretically calculated overpotentials of bare Mo₂C, Mo₂N, W₂C, and W₂N are suitable for the associative NRR mechanism on the basis of thermal neutrality and their relative performance to explored metal electrocatalysts. However, importantly a combination of stability analysis and selectivity analysis with respect to the competing HER revealed that all the bare MXenes are not stable under NRR operating conditions. On the basis of thermodynamics, the only functionalized MXene with the three minimum required properties (i) having low theoretical overpotential, (ii) being stable under NRR conditions, and (iii) having selectivity toward the NRR rather than the parasitic HER is W₂CH₂, which is a H-terminated MXene. Finally, we ended our study with an investigation of a few different pathways to further modify MXenes for the electrochemical NRR by increasing model complexity through surface functionalization and crystal structure, to name a few, and suggested other routes for activity tuning to be considered in future studies.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.9b01925.

DFT energies, references, Pourbaix diagrams of all MXenes, adsorption scaling relations, all figures of MXenes, and stable adsorption sites of intermediates (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail for A.V.: alevoj@seas.upenn.edu.

ORCID 💿

Liang Zhang: 0000-0002-9718-0436 Christopher C. Price: 0000-0002-4702-5817 Nathan C. Frey: 0000-0001-5291-6131 Aleksandra Vojvodic: 0000-0002-5584-6711

Notes

The authors declare no competing financial interest.

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