Facile Heterogeneously Catalyzed Nitrogen Fixation by MXenes

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Abstract: The rate-limiting step for ammonia (NH₃) production via the Haber-Bosch process is known to be the dissociation of molecular nitrogen (N₂), which requires quite harsh working conditions, even when using appropriate heterogeneous catalysts. Here, motivated by the demonstrated enhanced chemical activity of MXenes—a new class of two-dimensional inorganic materials—towards the adsorption of quite stable molecules such as CO₂ and H₂O, we use density functional theory including dispersion to investigate the suitability of such MXene materials to catalyze the N₂ dissociation. Results show that MXenes exothermically adsorb N₂, with rather large adsorption energies ranging from -1.11 to -3.45 eV and elongation of the N₂ bond length by ~20%, greatly facilitating its dissociation with energy barriers below 1 eV, reaching 0.28 eV in the most favorable studied case of W₂N. Microkinetic simulations indicate that the first hydrogenation of adsorbed atomic nitrogen is feasible at low pressures and moderate temperatures, and that the production of NH₃ may occur above 800 K on most studied MXenes, in particular in W₂N. These results reinforce the promising capabilities of MXenes to dissociate nitrogen and suggest combining them co-catalytically with Ru nanoparticles to further improve the efficiency of ammonia synthesis.

Keywords: 2D Materials; Adsorption; Ammonia Synthesis; Clean MXenes; Density Functional Theory; Metal Carbides and Nitrides; Microkinetic Modeling.
Introduction

Ammonia (NH₃) is the essential precursor in the synthesis of many N-containing compounds,¹² several of them having a high impact in our daily life, from sterilizing and cleaning products, to fertilizers and medicines.³ Moreover, NH₃ emerges as an alternative energy carrier to reduce the fossil fuel consumption due to its large hydrogen capacity (17.6 wt%) and its energy density of 22.5 MJ/kg, comparable to that of fossil fuels such as low-ranked coals (around 20 MJ/kg).⁴ The growing NH₃ demand has motivated a great interest in the artificial N₂ fixation.⁵ However, the high N₂ stability, with a triple covalent bond dissociation energy of almost 10 eV, makes its chemical capture and activation a real challenge. In fact, industrial NH₃ synthesis via the Haber-Bosch (HB) process requires appropriate catalysts working at high temperatures (400-500 ºC) along with high pressures (100-300 bar) due to thermodynamic constraints.⁶

In particular, fused iron catalysts are well consolidated catalysts for HB synthesis.⁷ The origin of the catalytic activity of Fe surfaces towards N₂ has been disclosed in several landmark surface science studies.⁸⁻¹¹ For instance, an experimentally-measured kinetic energy barrier of ~0.80 eV for N₂ dissociation on Fe(111) has been reported at near-operational HB conditions.¹² More recently, small iron Fe₃ supported on the 0-Al₂O₃(010) surface have been also proposed as feasible heterogeneous catalyst for ammonia synthesis.¹³ Other suitable catalysts such as Ru nanoparticles (NPs),¹⁴ graphene-based substrates (GraN₄-Cr),¹⁵ and dicoordinate borylenes¹⁶ have been recently explored, all displaying good catalytic activity for N₂ dissociation. For instance, energy barriers for N₂ dissociation in the 0.4–1.9 eV interval have been predicted for the reaction on Ru nanoparticles, depending on whether terrace or step sites are considered as catalytic active sites. Similar dissociation barriers are found on well-defined V(110) surfaces.¹⁷ Despite the fact that active sites at operating conditions could not necessarily coincide with those exhibiting the lowest energy barriers,¹⁴,¹⁷ a small energy barrier for N₂ dissociation is still considered as a requisite for an efficient conversion. Consequently, research endeavors are aimed at finding improved catalysts that can potentially operate HB synthesis at milder conditions.¹⁸

Recently, a fast-growing family of two-dimensional (2D) inorganic materials, usually referred to as MXenes, has been isolated by HF selective etching from precursor MAX phases.¹⁹ The resulting 2D flake materials have been fully characterized as made up of close-packed layers of transition metals (M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, or W) intercalated by layers of carbon or nitrogen (X = C or N), with the general formula Mₓ₊₁XₙTx (n = 1–3), where Tₓ represents the surface terminations bonded to the outer M layers.²⁰ MXenes may display different Tₓ terminations depending on the synthesis conditions, with O, OH, F, and H being the most common.²¹ More recently, HF-free syntheses have been reported where MXenes are terminated by H and OH only.²²,²³ In addition, post-synthesis heating treatments have been shown to successfully defunctionalize MXene surfaces.²⁴,²⁵ When devoid of Tₓ, MXenes are naturally quite reactive and are known to strongly adsorb molecules, facilitating their posterior conversion. The use of MXenes in catalysis has been reviewed very recently.²⁶ Other, recent examples include CO₂ and H₂O adsorption and
In addition, the possibility to use conducting MXenes as electrodes in electrocatalysis has also been considered. In particular, Seh et al. explored the performance of Mo$_2$CT$_x$ and Ti$_2$CT$_x$ as electrocatalysts in the hydrogen evolution reaction (HER), whereas Yi et al. theoretically studied the performance of a Ti$_2$C monolayer as a cathode substrate to improve the performance of the Li–N$_2$ battery. The latter authors found a very strong interaction between N$_2$ and the bare Ti$_2$C and, interestingly, the presence of Li atoms seemed to facilitate the N$_2$ dissociation. In another computational keynote work, Azofra et al. investigated the mechanism of NH$_3$ electrocatalytic synthesis from N$_2$ using a family of M$_3$C$_2$ MXenes as catalysts. These two previous studies on the N$_2$ electrochemical reduction considered a mechanism involving a series of proton-electron transfers, resulting in the successive hydrogenation of one or both N atoms of N$_2$, thus, concomitantly weakening the N≡N bond and eventually leading to the NH$_3$ formation.

However, it is worth pointing out that the literature of N$_2$ reduction via heterogeneous catalysis on MXenes is scarce, despite the demonstrated stability of these surfaces in inert, oxidizing, and reducing environments (e.g. V$_2$CT$_x$), and thermal stability (800 °C at least), which open the possibility of using MXenes at operando conditions of the HB process. In the case of the Ti$_3$C$_2$Tx MXene, thermal and mechanical stabilities were reported up to a temperature of 900 °C and a pressure of 26.7 GPa. Recent computational studies also provide compelling evidence that bare MXene materials are mechanically and dynamically stable. All these findings strongly suggest that MXenes could display an efficient activity towards heterogeneous catalytic N$_2$ dissociation and, eventually, towards NH$_3$ synthesis in the HB process.

Motivated and inspired by this, the present work explores the chemical activity of 18 MXenes from groups IV-VI —nine carbide and nine nitride MXenes— towards N$_2$ adsorption and subsequent direct dissociation by means of density functional theory (DFT) methods and microkinetic modeling. The obtained results confirm the hypothesis that these new materials can dissociate N$_2$ at rather mild conditions, which may have implications in the N$_2$ utilization in general, and on the ammonia synthesis in particular.

**MXene Models and Computational Details**

To understand the nitrogen fixation by MXenes, the N$_2$ dissociation mechanism was firstly investigated, using first-principles calculations as implemented in the Vienna ab initio simulation package (VASP). Then, the potential energy diagram for NH$_3$ synthesis from N$_2$ and H$_2$ on selected surfaces was thoroughly investigated. The MXenes basal (0001) surfaces are modeled by a periodic hexagonal p(3×3) supercell containing 27 atoms (Figure 1), with lattice parameters as displayed in Table S1 of the Supporting Information (SI). The valence electron densities have been expanded in a plane wave basis set with a cutoff for the kinetic energy of 415 eV, whereas the effects of the core electrons on the valence electron densities were taken into account by means of the projector-augmented wave (PAW) method. The Brillouin zone was sampled using a Monkhorst-Pack 5×5×1 grid of k-points. The calculations were carried out within the generalized gradient approximation (GGA), using the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional, including dispersion interactions through the Grimme D3 method. The convergence criteria for the self-consistent energies and forces for relaxed structures were set to 10$^{-6}$ eV and...
0.01 eV·Å⁻¹, respectively. Spin polarization was found to be necessary to properly describe the Ti₂C, Zr₂C, and Cr₂C MXenes. Further details regarding the definition of adsorption energy and related quantities as well as Gibbs free energies calculation are reported in the SI.

**Results and discussion**

The interactions of atomic and molecular nitrogen with the above-mentioned MXene surfaces have been investigated by sampling four relevant high-symmetry sites, see Figure 1. On most MXenes the N atom adsorbs preferably on the H_M site, yet in the case of W₂C and d⁴ nitrides the H_X site is energetically favorable. The calculated N adsorption energies relative to 1/2·E_{N₂} for carbide and nitride MXenes are all negative indicating exothermic adsorptions —see Table S2 of the SI for further details. In general, the atomic N adsorption becomes weaker as one moves from d² to d⁴ MXenes. The N₂ molecule adsorbs in a similar way on all MXenes, with one of the N atoms lying above an H_M site and the other above a nearby H_X site —B site for Mo₂C, W₂C, Nb₂N, and Ta₂N— with results summarized in Table 1 and Figure 2. For the H_M-H_X adsorption configurations, the molecule adsors approximately parallel to the plane of the surface, with a tilting angle of ~15°. In both configurations, the N atom closest to the surface is placed ~1 Å above the metal atoms layer and the N-N distance is ~1.35 Å, *i.e.* about 20% longer than the corresponding gas phase value of 1.11 Å. Analogously to N adsorption, N₂ adsorption is stronger on d² MXenes and becomes weaker as we move to d³ and d⁴ metals.

The large N₂ adsorption energy and the noticeable bond length elongation are already indicative of N₂ activation, and so, forecast an easy N₂ dissociation. However, a firm statement requires locating the N₂ dissociation transition state (TS) along different breaking pathways on the studied MXene surfaces. The TSs have been determined and characterized as indicated in the SI. All of them can be described as early states, since the corresponding structure closely resembles the initial configuration just with the N atoms slightly farther from each other, ~1.8 Å. Taking Zr₂C as an example, the most favorable adsorption site of N₂ is H_M-H_C, whereas the N atoms adsorb on H_M sites, see Figure 2. The associated TS structure keeps one N at H_M while moving the other farther away, so that, after the molecular dissociation, both N adatoms sit at H_M sites. However, in the case of Nb₂C, Ta₂N, and W₂N, the configuration after dissociation is such that one of the N adatoms remains on its most stable adsorption site, while the second one sits on the nearest hollow site at a distance of around 2.5 times the calculated N₂ bond length. In this situation, there is a strong lingering lateral interaction between the two N adatoms that is released by moving the second N adatom to its most favored adsorption site. Table 1 compiles the related energies and shows that the calculated energy barriers, E_b, range from 0.28 to 1.1 eV, tending to decrease along the group or period of the metal. This implies that E_b is often smaller than the N₂ adsorption energy, a feature not easily fulfilled by standard catalysts and the reason why high pressures are needed in the HB process. All dissociation steps are found to be exothermic, with reaction energies, E_{reac}, as large as -3.19 eV on W₂N, and exothermicity increasing as the group or period of the MXene increases. Hence, the most exothermic dissociation occurs on the MXene with the
lowest $E_b$, suggesting that the overall process may follow a Brønsted-Evans-Polanyi (BEP) relationship.\textsuperscript{48-50} Indeed, the plot in Figure 3 of $E_b$ vs. $E_{\text{reac}}$ shows that BEP holds and leads to a faster way to predict results for other possible MXenes.

To go beyond the previous thermodynamic and kinetic analyses and to account for real operando conditions, we consider the variation of the Gibbs free energy of adsorption of the reacting systems at 1 bar and 300 K—see details in the SI. For all the studied MXenes, trends in Gibbs free energy of adsorption of N and N$_2$ are similar to those reported for $E_{\text{ads}}$, although weaker by 0.25 and 0.50 eV, respectively. The reaction energy values are practically unaffected by temperature and pressure, with differences lower than 0.01 eV with respect to the values listed in Table 1, while $E_b$ values are reduced by circa 0.06 eV. From this set of results, one can conclude that increasing the temperature is, if any, beneficial for the dissociation of N$_2$ on MXenes, as it both lowers the $E_b$ values and contributes towards replacing the MXene surface termination by N$_2$. Furthermore, the obtained values do not seem to be assignable solely to the explored M:X 2:1 stoichiometry, as test simulations for N$_2$ dissociation on the experimentally isolated Ti$_4$N$_3$, Nb$_4$C$_3$, and Ta$_4$C$_3$, all 4:3 stoichiometric MXenes,$^{51,52}$ yield nearly identical results to those obtained for the M$_2$X stoichiometry, with $E_{\text{ads}}$ and $E_b$ values differing by up to 0.05 eV at most. These findings strongly support that conclusions taken from the present calculations are likely to apply to thicker MXenes as well, in line with the already reported very small variation of the CO$_2$ capture capabilities of MXenes of different thickness.$^{53}$

To further assess the catalytic capability of MXene for nitrogen fixation, we compare the present results with available data in the literature. To this end we rely on $E_b$ values for N$_2$ dissociation although a comparison of present and previously reported N$_2$ adsorption energies on MXenes is provided in the SI. In the case of Ti$_2$C, the present value for $E_b$ of 0.98 eV compares well with the 1.17 eV value reported by Yi et al.$^{31}$ Note, however, that the latter has been acquired in the different context of the electrocatalytic HER. In any case, to find that these two values are only slightly larger than the experimentally measured barrier of 0.80 eV for N$_2$ dissociation on Fe (111) at conditions close to the ones required for the HB process$^{12}$ is really remarkable. Encouragingly, lower $E_b$ values are predicted for other MXenes, see Table 1, where W$_2$N MXene (0001) surface features the lowest value of 0.28 eV. It is worth to point that this activation barrier is similar to that reported for the step regions of Ru surfaces$^{54}$ and on a cesium-promoted ruthenium particle supported on MgO$^{55}$ that show 0.40 and 0.34 eV, respectively (Tables S3 and S5). Nevertheless, other MXenes exhibit quite low $E_b$ values close to 1.0 eV. In general, carbide and nitride MXenes emerge as potentially suitable materials for N$_2$ dissociative adsorption with a reactivity comparable or even superior to other reported transition metal surfaces or NPs.$^{12,14,17}$ Therefore, MXenes appear as potential catalysts candidates for N$_2$ fixation; \textit{i.e.} in the NH$_3$ synthesis. However, the latter requires considering the successive N adatom hydrogenation steps as well. These have been studied in detail for Nb$_2$C, Mo$_2$N, and W$_2$N, chosen because of their low N$_2$ dissociation energy barriers. The total and Gibbs free energy profiles at standard conditions, plotted in Figure 4, reveal that, for such a catalyzed process, the rate-limiting step would be these
hydrogenation steps instead of the N\textsubscript{2} dissociation one. Actually, for the three systems with smallest N\textsubscript{2} dissociation barriers, the energy barriers for these hydrogenation steps are somewhat higher than those reported, for instance, on a model Ru (001) surface\textsuperscript{54}, yet surmountable at working conditions, especially for W\textsubscript{2}N. At this point, it is worth considering whether PBE results provide an accurate enough comparison to experiment.\textsuperscript{56} From Figure 4, it is clear that, as expected, PBE poorly describes the gas phase thermochemistry of this reaction (see gray lines in Figure 4). Nevertheless, there is compelling evidence that this DFT approach performs satisfactorily for surface reactions,\textsuperscript{14} where the electron density is less localized. This is further supported by the good agreement between experimental turnover frequencies and predictions from kinetic Monte Carlo and microkinetic simulations using DFT derived rates.\textsuperscript{57,58}

To further assess the capability of MXenes for ammonia synthesis, microkinetic simulations were carried out to obtain insights into the production of NH\textsubscript{3} on W\textsubscript{2}N by using the MKMCXX program\textsuperscript{59,60} — further details of the microkinetic simulations are given in the SI. Note that the choice of the W\textsubscript{2}N MXene is justified as this material exhibits the lowest energy barriers for N\textsubscript{2} dissociation and subsequent hydrogenation steps leading to the formation of ammonia, see Table S3. The simulations were carried out taking a gas phase mixture with a N\textsubscript{2}:H\textsubscript{2} molar ratio of 1:3 at 1 bar. Two limiting cases were studied separately; assuming that after N\textsubscript{2} dissociation the two N* species are located at the nearby surface sites, or that instead they immediately migrate to outlying regions, see Figure 5. In the first scenario, displayed in Figures 5a and 5b, the formation of NH* is predicted to take place at 1 bar and below 600 K. However, the backward reactions towards the N* and H* species are favored by higher temperatures. This simulation confirms that the formation of NH\textsubscript{3} could be affordable (Figure 5b) reaching the maximum of production at 1075 K, where the apparent activation energy is zero (Figure S2). The reaction orders of N\textsubscript{2} and H\textsubscript{2} as a function of temperature are depicted in Figure S3. From this figure, it can be seen that the reaction orders of the reactants increase with temperature, they are related with the decreasing of the coverage, in consistency with Figure 5a. The degree of rate control (DRC) shown in Figure S4, concludes that the NH\textsubscript{2}+H recombination on the W\textsubscript{2}N MXene (0001) surface is the rate-limiting step. Finally, the rates of the reaction following eight elementary reaction steps are depicted in Figure S5. In the second situation, the W\textsubscript{2}N catalyst is poisoned by the N* species (Figure 5c) and, consequently, the formation of NH\textsubscript{3} does not take place. Interestingly, the differences between these two situations may be found in the backward reaction, which corresponds to the recombination of the N* species into N\textsubscript{2}, see Table S5. These activation barriers are 1.12 and 3.46 eV for the nearby and outlying situation, respectively. In conclusion, a large backward energy barrier indicates that the W\textsubscript{2}N MXene dissociates the nitrogen molecule poisoning the surface and cutting the reaction off. For the most interesting scenario, \textit{i.e.} N* species adsorbed at nearby surface sites, results from microkinetic simulations in Figures S6-S8 obtained for a gas phase mixture with N\textsubscript{2}:H\textsubscript{2} molar ratio of 1:3 but at a higher pressure, viz. 200 bar, show that it is not only possible to form significant amounts of NH* but that it is possible to reach NH\textsubscript{2}* at temperatures below 600 K.
The present computational study strongly suggests that MXenes may constitute appropriate materials for dissociating the $N_2$ molecule even at standard pressure, reporting better forward activation barriers for the dissociation of $N_2$ molecule than Ru nanoparticles, see Table S5. Finally, although the hydrogenation of easily formed N adatoms on MXenes may be more difficult, other strategies can be envisaged to overcome this possible hurdle, e.g. using MXenes as a support material for Ru NPs in a tandem, bifunctional catalyst, with the MXene substrate adsorbing and dissociating $N_2$, whereas the Ru active centers would be better suited in hydrogenating the formed N adatoms towards $NH_3$, thus ideally permitting the Haber-Bosch $NH_3$ synthesis at milder conditions.

Conclusions

To summarize, MXenes are introduced here as potential catalysts to adsorb and exothermically dissociate $N_2$ at mild conditions, with energy barriers ranging from 0.28 to 1.10 eV, which are comparable to, or even lower than, those corresponding to models of transition metal-based industrial catalysts. Even though the present conclusions hold for MXenes with M:X 2:1 ratio, additional simulations on MXenes with 4:3 ratio revealed negligible material thickness effect. Moreover, the fact that the N adatom hydrogenation steps are somewhat more costly than the same steps on commercial transition metal-based catalysts suggests synergistically using MXenes as supports of metal nanoparticles used in the Haber-Bosch process leading to bifunctional catalysts with better activities at a lower cost. The remarkable chemistry of MXenes towards $N_2$ suggest that they could be used in the Haber-Bosch ammonia synthesis. Nevertheless, additional work from both modelling and experimental points of view are needed to further confirm this hypothetical and, at the same time, appealing catalytic activity.
Table 1 N₂ adsorption sites, adsorption energies, $E_{ads}$, dissociation energy barriers, $E_b$, and dissociation reaction energies, $E_{reac}$, on the studied MXene (0001) surfaces. The N₂ adsorption site is specified by the surface sites occupied by the two nitrogen atoms, see Figure 1. All values are given in eV and include the zero point energy (ZPE) contribution.

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Figure 1. Top view of the $p(3\times3)$ supercell employed to model the MXene (0001) surfaces. The transition metal atoms are shown as grey spheres, while X atoms are shown as green spheres. The dashed rhombus represents the boundaries of the employed supercell. The labels refer to the four relevant high-symmetry sites on the surface: bridge (B), top (T), hollow metal (H_M), and hollow carbon/nitrogen (H_X) —in practice, H_C or H_N.
Figure 2. Initial state (IS - left), transition state (TS - middle), and final state (FS – right) configurations of N\textsubscript{2} dissociation on the Zr\textsubscript{2}C MXene (0001) surface, as seen from the side (top) and top (bottom) views. Color code as in Figure 1, N atoms are shown as dark blue spheres. Note that this particular case is representative for most carbide and nitride MXene (0001) surfaces investigated, while on Nb\textsubscript{2}C, Mo\textsubscript{2}N, Ta\textsubscript{2}N, and W\textsubscript{2}N the two N adatoms remain on their original H\textsubscript{M} and H\textsubscript{X} sites after dissociation, but about twice as far from each other as in the TS.
Figure 3. Plot of the BEP relationship for N$_2$ dissociation reaction energy barrier, $E_b$, and the dissociation energy, $E_{\text{reac}}$, on the MXene surfaces investigated; the black line defines the linear regression, with equation $E_b = 0.387 \cdot E_{\text{reac}} + 1.611$, and correlation coefficient $R = 0.79$. Blue and red dots correspond to carbide and nitride MXenes, respectively.
Figure 4. Total (top) and Gibbs (down) free energy reaction profiles of ammonia synthesis on Nb$_2$C (blue), Mo$_2$N (red), and W$_2$N (black) MXene (0001) surfaces. Gibbs energy profiles are obtained assuming a temperature of 300 K and N$_2$ and H$_2$ partial pressures of 1 bar. The energy barriers are collected in Table S3. Gray lines correspond to accurate thermochemistry description of this reaction in the gas phase, considering the golden standard coupled cluster with single, doubles, and perturbative triples—CCSD(T)—method (top), and the experimental reaction Gibbs energy at a working temperature of 300 K and a pressure of 1 bar for H$_2$ and N$_2$ gases (down). The CCSD(T)/cc-pVTZ calculations were taken from the Computational Chemistry Comparison and Benchmark Database (https://cccbdb.nist.gov/).
**Figure 5.** Results from microkinetic simulations performed on the W$_2$N MXene (0001). The gas phase contains a mixture of N$_2$ and H$_2$ in a 1:3 molar ratio at a total pressure of 1 bar. Two different scenarios are analyzed: (a) and (b) correspond to a situation where the N* species are close to each other (high-coverage), whereas in (c) and (d) the N* species are far from each other (low-coverage). The coverage of the most abundant species for the N$_2$ fixation on MXene surface along with the ammonia production as a function of the temperature are figures a-c and b-d, respectively for each of the investigated scenarios. The gray bar indicates the temperature conditions at which the industrial HB process takes place.
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Notes
The authors declare no competing financial interest.

ASSOCIATED CONTENT

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Additional computational details and comparison to previous work. Tables S1 and S2 report the calculated lattice parameters and adsorption related properties. Tables S3 and S4 report the energy barriers of the total and Gibbs free energy reaction profiles of ammonia synthesis. Table S5 compiles a comparison of the forward and backward energy barriers corresponding to Ru NPs and W2N MXene (0001) surface. Figure S1 shows the configurations of transition states and ground state adsorption involved in the process of the triple hydrogenation of a nitrogen adatom. Figure S2 shows the apparent activation energy of the N2 fixation over W2N MXene (0001) surface resulted from the microkinetic simulations for the situation where the N* species are located in nearby regions. Additional references are also included.

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$N_2$ dissociation: A question of tug-of-war