A Theoretical Study of Fe Adsorbed on Pure and Nonmetal (N, F, P, S, Cl)-Doped Ti$_3$C$_2$O$_2$ for Electrocatalytic Nitrogen Reduction

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Abstract: The possibility of using transition metal (TM)/MXene as a catalyst for the nitrogen reduction reaction (NRR) was studied by density functional theory, in which TM is an Fe atom, and MXene is pure Ti$_3$C$_2$O$_2$ or Ti$_3$C$_2$O$_{2-x}$ doped with N/F/P/S/Cl. The adsorption energy and Gibbs free energy were calculated to describe the limiting potentials of N$_2$ activation and reduction, respectively. N$_2$ activation was spontaneous, and the reduction potential-limiting step may be the hydrogenation of N$_2$ to *NNH and the desorption of *NH$_2$ to NH$_3$. The charge transfer of the adsorbed Fe atoms to N$_2$ molecules weakened the interaction of N≡N, which indicates that Fe/MXene is a potential catalytic material for the NRR. In particular, doping with nonmetals F and S reduced the limiting potential of the two potential-limiting steps in the reduction reaction, compared with the undoped pure structure. Thus, Fe/MXenes doped with these nonmetals are the best candidates among these structures.

Keywords: DFT; MXene; nitrogen reduction; electrocatalysis; Gibbs free energy

1. Introduction

Ammonia is a raw material for the production of various fertilizers and is a potential energy source that is easy to store and transport, environmentally friendly, and relatively safe. Ammonia synthesis is important in agricultural production and energy development. However, most ammonia synthesis still relies on the Haber–Bosch method proposed in the 20th century, which requires harsh reaction conditions (400–600 °C and 20–40 MPa) [1–3]. This method consumes a large amount of energy and causes significant greenhouse gas emissions [4]. In addition, other negative effects, such as adverse effects on the equipment under high-temperature and high-pressure conditions, need to be considered. Therefore, the development of environmentally friendly and less energy-demanding methodologies for NH$_3$ synthesis is urgently needed. Electrocatalytic ammonia synthesis has attracted increasing attention owing to its high efficiency and environmental friendliness. The introduction of electrical energy has a remarkable influence on N$_2$ activation and changes the reaction pathways [5], which is beneficial for the development of new stable and efficient catalysts.

New catalysts can be developed from unique structures, such as core–shell Ni–Au nanoparticles for CO$_2$ hydrogenation [6], or from new materials. The excellent physical, electronic, and chemical properties of two-dimensional (2D) materials have attracted extensive scientific research [7–15]. In addition, 2D materials, such as molybdenum disulfide, graphene, and metal–organic frameworks (MOFs) [14–16], have emerged as potential candidates for electrochemical nitrogen reduction reactions (NRRs). Notably, MXene, a new member of the 2D material family that joined in 2011 [17], has developed rapidly in the past nine years [17–19]. The general formula of MXene is $M_{n+1}X_nT_x$, where M represents early transition metals (TMs), X represents carbon or nitrogen, T$_s$ represents the surface...
functional groups O, OH, or F, and n = 1, 2, 3. MXenes are synthesized by the chemical etching of A layers in the MAX \((M_{n+1}AX_n)\) phase. Although a variety of 2D MXenes have been theoretically predicted [20], only a few have been synthesized. MXenes are applied in a wide range of fields, including electrocatalysis [21], hydrogen storage [22,23], lithium-ion batteries [24,25], and supercapacitors [26]. MXene is a potential candidate for electrochemical NRRs (e-NRRs) because of its large specific surface area, adjustable structure, and excellent stability [27–29].

MXene-based electrocatalysts for the e-NRR can be divided into two categories: pure MXene and MXene-based hybrid electrocatalysts [30]. Pure MXene is a potential candidate for the e-NRR. For example, Azofra et al. [31] found that \(M_2C_2\) exhibited good \(N_2\) capture and activation behavior. However, bare-metal atoms on the surface of \(M_2C_2\) are considered active sites [31,32], which tend to bind to functional groups such as oxygen groups; thus, the electrical conductivity is decreased, and the active sites are inactivated. Pure MXene still faces challenges as a catalyst for the e-NRR; therefore, MXene hybrids have been designed. Li et al. [33] loaded nanosized Au particles onto \(Ti_3C_2\) nanosheets (Au/Ti3C2) for the e-NRR. Their research indicated that the hybrid is conducive to \(N_2\) chemisorption and decreases the activation energy barrier. Au/Ti3C2 shows excellent catalytic performance. MnO2-decorated \(Ti_3C_2Tx\) (MnO2-Ti3C2Tx) has also been studied as an efficient electrocatalyst for ammonia synthesis under environmental conditions [34]. MnO2 and Ti3C2Tx synergistically promote electrocatalytic activity to achieve superior catalytic activity. In addition, single-atom catalysts (SACs) have been widely studied because of their low cost, superior performance, and full use of metal atoms. Gao et al. [5] studied the reaction pathways and overpotentials of Ti3C2O2-supported TM (Fe, Co, Ru, Rh) SACs. These MXene hybrids, including noble metal–MXene, TM oxide–MXene, and MXene-based SACs, have effectively changed the catalytic performance, providing more possibilities for the screening of new efficient and stable catalysts.

In this study, a 2D MXene, \(Ti_3C_2O_2\), was modified with nonmetals (N, F, P, S, and Cl) and adsorbed TM (Fe atom, Fe/Ti3C2O2) to study the catalytic performance of the e-NRR. Gibbs free energy \((\Delta G)\) was used to analyze the reaction pathway and limit the potential of each catalyst, and the main potential-limiting steps of the reaction were determined as \(*N_2 + H \rightarrow *NHH\) and \(*NH_3 \rightarrow NH_3\).

### 2. Computational Methods

Density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package v. 5.4.4. (University of Vienna, Vienna, Austria) [35,36]. The generalized gradient approximation with Perdew–Burke–Ernzerhof was used as an exchange-correlation function [37]. The projector-augmented wave method was adopted to describe the effect of the core electrons on the valence electron density [38]. The cut-off energy was set to 600 eV. The convergence criteria for the energy and force were \(10^{-5}\) eV and \(10^{-2}\) eV/Å, respectively. The thickness of the vacuum layer was more than 20 Å to avoid interactions in the \(z\)-direction, and the \(x\)-and \(y\)-directions were set as periodic boundary conditions. A \(3 \times 3 \times 1\) supercell was used for all the structures. For geometric optimization, the Brillouin zones were sampled with \(4 \times 4 \times 1\) Monkhorst–Pack meshes [39], and DFT-D3 was used to accurately describe Van der Waals interactions [40]. Charge transfer was computed by Bader charge population analysis [41,42] and the electron localization function (ELF) was analyzed using the VESTA code [43].

The substitution energies \((\Delta E_{sub})\) of doping different nonmetallic elements (N/F/P/S/Cl) on the surface of \(Ti_3C_2O_2\) can be expressed as

\[
\Delta E_{sub} = E_{NM-Ti_3C_2O_2-x} - E_{Ti_3C_2O_2} + E_O - E_{NM}
\]

where \(E_O\) and \(E_{NM}\) represent the energies of a single O atom and nonmetallic elements (N, F, P, S, Cl), respectively, and were calculated using \(H_2\) [44], \(H_2O\) [45], \(NH_3\) [46], \(HF\) [47], \(H_3PO_4\) [48], \(H_2S\) [49], and \(HCl\) [50] from the Open Quantum Materials Database (OQMD) [51,52].
The adsorption energy (\(\Delta E_{\text{ads}}\)) of Fe anchored on NM-Ti3C2O2−x (NM represents the surface nonmetals, O, N, F, P, S, and Cl) was calculated using the following formula:

\[
\Delta E_{\text{ads}} = E_{\text{Fe/NM-Ti3C2O2−x}} - E_{\text{NM-Ti3C2O2−x}} - E_{\text{Fe}}
\]  

(2)

\(\Delta G\) was calculated as described by Nørskov et al. [53]. Under standard reaction conditions, the chemical potential of a proton and electron pair (\(\mu[H^+ + e^-]\)) is equal to half that of gaseous hydrogen (\(\mu[H_2]\)). \(\Delta G\) was calculated using the following formula:

\[
\Delta G = \Delta E_{\text{DFT}} + \Delta ZPE - T\Delta S - neU + \Delta G_{\text{pH}}
\]  

(3)

where \(\Delta E\) is the potential energy change calculated by DFT, \(\Delta ZPE\) is the zero-point energy correction, and it is calculated by calculating the frequency of the adsorbed species. \(T\Delta S\) is the entropy correction, which is usually available from some database, where \(T = 298\) K; \(\Delta G_{\text{pH}}\) and \(neU\) are the contributions from the pH and electrode potential (U), respectively; \(n\) is the number of electrons transferred; \(U\) is the applied bias. \(\Delta G_{\text{pH}}\) is defined as

\[
\Delta G_{\text{pH}} = -k_B T \ln [H^+] = pH \times k_B T \ln 10
\]  

(4)

where \(k_B\) is Boltzmann's constant. For all the calculations, the pH was set to zero. The \(\Delta E_{\text{ads}}\) values of different adsorbates were calculated as follows:

\[
\Delta E_{\text{ads}} = E_{\text{cat–mol}} - E_{\text{cat}} - E_{\text{mol}}
\]  

(5)

where \(\Delta E_{\text{cat–mol}}\) is the energy of the entire adsorption structure, \(E_{\text{cat}}\) is the energy of the catalyst, and \(E_{\text{mol}}\) is the energy of the adsorbate molecules such as \(N_2\) and \(N_2H_4\).

3. Results and Discussion

3.1. Geometric Structure

Bare Ti3C2 is a hexagonal lattice with \(P3m1\) group symmetry, five atomic layers of Ti–C–Ti–C–Ti, two exposed Ti layers, and an experimental lattice constant of 3.057 Å [54]. After structural optimization, \(a = b = 3.020\) Å, which was in good agreement with the experimental values. Bare MXenes are unstable under relevant NRR operating conditions [55], and they are always functionalized by electronegative functional groups [56], as they are chemically exfoliated from the bulk MAX phase by HF [17,57]. O-terminated Ti3C2 was used for further experiments. There are different possibilities for the adsorption of O on Ti3C2. According to previous studies [5], the most stable structure is O adsorbed at the hollow sites of the contralateral surface Ti atoms, as shown in Figure 1a,b. Nonmetallic elements (N/F/P/S/Cl) were used to modify the Ti3C2O2 surface. \(\Delta E_{\text{sub}}\) indicates the stability of a surface before and after doping with nonmetallic elements. The \(\Delta E_{\text{sub}}\) values for N, F, P, S, and Cl were 1.79, −1.04, 0.81, −0.27, and −1.01 eV, respectively. The structure became more stable after doping with F, S, and Cl when \(\Delta E_{\text{sub}} < 0\) and became more unstable after doping with N and P when \(\Delta E_{\text{sub}} > 0\). Among these doping situations, doping with F had the best stability, compared with doping with other nonmetallic elements.

Pure Ti3C2O2 and Ti3C2O2 modified with nonmetallic elements (Figure S1) were used to support single Fe atoms. Two different hollow sites (H1 and H2) and an O-top site on the surface were considered, as shown in Figure 1a. The O-top was unstable, and the \(E_{\text{ads}}\) values of Fe adsorbed on H1 and H2 are listed in Table 1. Except for the F-doped structures, the Fe atoms preferred to adsorb on the H1 site, as the \(E_{\text{ads}}\) was smaller. Notably, in the F-doped structure, the Fe atom was adsorbed on the next-nearest H1 site (Figure 1e). As shown in Table 1, the doping of N, F, P, and S facilitates the adsorption of Fe, while it is more difficult for Fe to adsorb on the Cl-doped structure. Figure 1c–h show the most stable adsorption positions for the different catalysts.
Figure 1. (a) Top view and different adsorption sites on Ti$_3$C$_2$O$_2$ and (b) side view of Ti$_3$C$_2$O$_2$. The most stable structure of Fe adsorbed on (c) Ti$_3$C$_2$O$_2$, (d) N-doped Ti$_3$C$_2$O$_2$, (e) F-doped Ti$_3$C$_2$O$_2$, (f) P-doped Ti$_3$C$_2$O$_2$, (g) S-doped Ti$_3$C$_2$O$_2$, and (h) Cl-doped Ti$_3$C$_2$O$_2$.

Table 1. Adsorption energies of Fe adsorbed on different sites and N$_2$ adsorbed on different catalysts, the charge on N$_2$, and the charge transferred after N$_2$ adsorption.

| Species             | $E_{ads}$ of Fe (eV) | $E_{ads}$ of N$_2$ (eV) | Charge Transferred on N$_2$ (e) |
|---------------------|----------------------|-------------------------|-------------------------------|
| Fe/Ti$_3$C$_2$O$_2$ | $-3.57$ $-3.30$      | $-0.92$                 | 0.19                          |
| Fe/N-Ti$_3$C$_2$O$_2$ | $-4.32$ $-3.90$    | $-0.77$                 | 0.15                          |
| Fe/F-Ti$_3$C$_2$O$_2$ | $-3.61$ $-3.60$    | $-0.78$                 | 0.18                          |
| Fe/P-Ti$_3$C$_2$O$_2$ | $-5.12$ $-4.68$    | $-0.55$                 | 0.13                          |
| Fe/S-Ti$_3$C$_2$O$_2$ | $-4.33$ $-4.02$    | $-0.59$                 | 0.16                          |
| Fe/Cl-Ti$_3$C$_2$O$_2$ | $-3.39$ $-3.11$   | $-0.85$                 | 0.21                          |

3.2. N$_2$ Adsorption

Based on the Fe/NM-Ti$_3$C$_2$O$_2$−x structure, N$_2$ adsorption was calculated using $E_{ads}$. There are two different positions for N$_2$ adsorption, and advanced research has shown that N$_2$ adsorption is closer end to end than side to side [5]. Figure 2a–f show the most stable structure of N$_2$ adsorbed on different catalysts from end to end, and Figure 2g–l show the ELF of these structures. $E_{ads}$ ranged from $-0.55$ eV to $-0.92$ eV, which indicates that the N$_2$ adsorption has strong spontaneity, and the absolute value of $E_{ads}$ from small to large was in the order: Fe/P-Ti$_3$C$_2$O$_2$−x $<$ Fe/S-Ti$_3$C$_2$O$_2$−x $<$ Fe/N-Ti$_3$C$_2$O$_2$−x $<$ Fe/F-Ti$_3$C$_2$O$_2$−x $<$ Fe/Cl-Ti$_3$C$_2$O$_2$−x $<$ Fe/Ti$_3$C$_2$O$_2$ (Table 1). After N$_2$ adsorption, the N≡N bond lengths in Fe/Ti$_3$C$_2$O$_2$, Fe/N-Ti$_3$C$_2$O$_2$−x, Fe/F-Ti$_3$C$_2$O$_2$−x, Fe/P-Ti$_3$C$_2$O$_2$−x, Fe/S-Ti$_3$C$_2$O$_2$−x, and Fe/Cl-Ti$_3$C$_2$O$_2$−x, are 1.128, 1.125, 1.129, 1.123, 1.126, and 1.130 Å, respectively. Compared with the N≡N bond length in the gas phase (1.11 Å), all of them became longer. The
calculation of charge transfer is shown in Table 1. The results show that N\textsubscript{2} gains electrons in all these catalysts and the translated charges increase with an increase in the number of valence electrons from N to O or from P to S and Cl in the same period. However, doping with F did not obey this rule, which may be due to the special adsorption site of Fe. Fe was adsorbed on the first nearest H\textsubscript{1} site and followed the trend from N to O and F. These findings were consistent with those of Wang et al. [58]. A strong positive correlation exists between the electron gains of N\textsubscript{2} and the change in bond length: N\textsubscript{2} on Fe/Cl-Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2−x} gained the most electrons and had the largest increase in bond length relative to the gas phase, whereas N\textsubscript{2} on Fe/P-Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2−x} gained the least electrons and had the smallest increment in bond length relative to the gas phase.

![Figure 2. Most stable structures of N\textsubscript{2} adsorbed on (a) Fe/Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2}, (b) Fe/N-Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2−x}, (c) Fe/F-Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2−x}, (d) Fe/P-Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2−x}, (e) Fe/S-Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2−x}, and (f) Fe/Cl-Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2−x} and ELFs of N\textsubscript{2} adsorbed on (g) Fe/Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2}, (h) Fe/N-Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2−x}, (i) Fe/F-Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2−x}, (j) Fe/P-Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2−x}, (k) Fe/S-Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2−x}, and (l) Fe/Cl-Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2−x}.]

The partial density of states of N\textsubscript{2} adsorbed on Fe/Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2} or Fe/NM-Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2−x} (Figure 3) shows spin-up and spin-down of the d orbital of the Fe atom and the p orbital of the N atom. At the Fermi level, almost no spin-up was observed, whereas the spin-down was more obvious, and the d orbital of Fe effectively overlapped with the P orbital of N near the Fermi level. The electrons in the occupied d orbital of Fe/NM-Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2−x} transferred to the antibonding orbitals of N\textsubscript{2}, as shown in Table 1, and the adsorbed N\textsubscript{2} on different catalysts gained electrons from 0.13 e to 0.21 e, thus lowering the bond energy of N\textsubscript{2}.
3.3. N₂ Reduction Mechanism

The overall e-NRR reaction on the cathode is

\[ \text{N}_2(g) + 6(H^++e^-) \rightarrow 2\text{NH}_3(g) \]  

(6)

and the anode reactions provide protons and electrons. Liu et al. [59] summarized the mechanism of the e-NRR. The e-NRR is divided into dissociation and association mechanisms by different hydrogenation (protonation and reduction) sequences and the breaking of the \( \text{N}≡\text{N} \) triple bond. In the dissociation mechanism, the \( \text{N}≡\text{N} \) bond is broken during the adsorption process (* denotes the adsorption site).

\[ 2^* + \text{N}_2 \rightarrow 2^* \text{N} \]  

(7)

Then, two separated N atoms on the surface of the catalysts receive protons and electrons, and ammonia is formed in the last hydrogenation step:

\[ ^*\text{N} + \text{H}^+ + e^- \rightarrow ^*\text{NH} \]  

(8)

\[ ^*\text{NH} + \text{H}^+ + e^- \rightarrow ^*\text{NH}_2 \]  

(9)

\[ ^*\text{NH}_2 + \text{H}^+ + e^- \rightarrow ^*\text{NH}_3 \]  

(10)

\[ ^*\text{NH}_3 \rightarrow \text{NH}_3 \]  

(11)

In the association mechanism, the \( \text{N}≡\text{N} \) bond breaks at a certain hydrogenation step. According to the hydrogenation sequence, it can be further classified into distal, alternating, and enzymatic pathways. The hydrogenation step in the enzymatic pathway is similar to that in the alternating pathway; the difference is that \( \text{N}_2 \) adsorbs side to side in the
enzymatic pathway, but ends in the distal and alternating pathways. For the distal and alternating pathways, the first two steps are

\[ \star + \text{N}_2 \rightarrow \star \text{N}_2 \quad (12) \]

\[ \star \text{N}_2 + \text{H}^+ + \text{e}^- \rightarrow \star \text{N}_2\text{H} \quad (13) \]

In the distal pathway, the N atom moves away from the catalytically gained protons and electrons, releasing the first NH\textsubscript{3} molecule, as follows:

\[ \star \text{N}_2\text{H} + \text{H}^+ + \text{e}^- \rightarrow \star \text{NH}_2 \quad (14) \]

\[ \star \text{NH}_2 + \text{H}^+ + \text{e}^- \rightarrow \star \text{N} + \text{NH}_3 \quad (15) \]

Hydrogenation then occurs on the remaining N atom and releases the second NH\textsubscript{3} molecule according to Reactions (8)–(11). In the alternating pathway, hydrogenation occurs on two newton atoms alternatively, and NH\textsubscript{3} is formed until the N≡N bond is completely broken.

\[ \star \text{N}_2\text{H} + \text{H}^+ + \text{e}^- \rightarrow \star \text{NHNH} \quad (16) \]

\[ \star \text{NHNH} + \text{H}^+ + \text{e}^- \rightarrow \star \text{NHNH}_2 \quad (17) \]

\[ \star \text{NHNH}_2 + \text{H}^+ + \text{e}^- \rightarrow \star \text{NH}_2\text{NH}_2 \quad (18) \]

\[ \star \text{NH}_2\text{NH}_2 + \text{H}^+ + \text{e}^- \rightarrow \star \text{NH}_2 + \text{NH}_3 \quad (19) \]

After the first NH\textsubscript{3} is released, the remaining \( \star \text{NH}_2 \) obtains protons and electrons and releases the second ammonia according to Reactions (10) and (11). Figure 4 shows the other mixed pathways that follow neither the distal nor alternating pathways but a combination of two paths. Optimized structures of all the possible elementary steps in NRR is showed in Figure S2.

**Figure 4.** Possible pathway and reaction intermediates for NRR with the associated mechanism. Dark brown, blue, red, brown, light blue, and light pink represent C, Ti, O, Fe, N, and H, respectively.

The \( \Delta G \) values calculated by DFT calculations considered all correction terms, including the zero-point energy, temperature, and entropy corrections. Table 2 illustrates the \( E_{\text{ZPE}} \) and entropy corrections (TS) of different reaction intermediates on Fe/Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2} using the TS values obtained from the National Institute of Standards and Technology \([60]\) at \( T = 298 \) K. The catalyst as a substrate is immobilized, although the surface is different, we compared the zero-point energy with the study of Ling \([61]\); the difference is marginal, as N\textsubscript{2} reduction also occurred on the transition metal atoms in Ling’s research, and only the \( E_{\text{ZPE}} \) of NH\textsubscript{3} was significantly different. NH\textsubscript{3} is a gas phase, not an adsorbent, so other research was also compared \([5]\). The calculated \( E_{\text{ZPE}} \) and TS of H\textsubscript{2} are 0.27 and 0.4 eV \([60]\), respectively.
As shown in Figure 5a–f, for all structures, the first protonation was likely to generate *NNH species; the ∆G values for Fe/Ti3C2O2, Fe/N-Ti3C2O2-x, Fe/F-Ti3C2O2-x, Fe/P-Ti3C2O2-x, Fe/S-Ti3C2O2-x, and Fe/Cl-Ti3C2O2-x increased to 0.90, 1.04, 0.85, 0.99, 0.88, and 1.01 eV, respectively. The second step is more likely to form *NNH2 instead of the *NNH4 species in the alternate path, as the energy requirements are higher, and the increments in ∆G for Fe/Ti3C2O2, Fe/N-Ti3C2O2-x, Fe/F-Ti3C2O2-x, Fe/P-Ti3C2O2-x, Fe/S-Ti3C2O2-x, and Fe/Cl-Ti3C2O2-x were 0.1, 0.06, 0.12, −0.05, 0.12, and 0.07 eV to form *NNH2, respectively. In the subsequent hydrogenation steps, the intermediate configuration in the alternating pathway was easier to form than the first NH3 molecule desorption in the distal pathway. The first NH3 is not desorbed until the fifth proton is added, and adsorptive *NH3 is formed when the sixth proton is added. The reaction *NNH2 → *NNH2H2 → *NH2 → NH3 is exothermic, and larger energy input is required until the adsorptive *NH3 is desorbed to form the second NH3 molecule. The ∆G values of Fe/Ti3C2O2, Fe/N-Ti3C2O2-x, Fe/F-Ti3C2O2-x, Fe/P-Ti3C2O2-x, Fe/S-Ti3C2O2-x, and Fe/Cl-Ti3C2O2-x were 1.95, 1.11, 0.97, 1.07, 1.09, 0.99 eV, respectively. However, it was reported that the use of an acidic electrolyte can promote NH3 desorption, as the protonation of adsorbed NH3 to form NH4+ can easily proceed [62,63], so the actual energy barrier is even smaller. For all these structures, the two potential limiting steps were the first hydrogenation of N2 to form the *NNH species and the last process of NH3 desorption to form the second NH3 molecule. Compared with the original structure, nonmetallic doping was beneficial for the desorption of the last NH3 molecule, but only the doping of F and S was beneficial for the formation of *NNH and NH3.

As shown in Figure 5a–f, for all structures, the first protonation was likely to generate *NNH4 species; the ∆G values for Fe/Ti3C2O2, Fe/N-Ti3C2O2-x, Fe/F-Ti3C2O2-x, Fe/P-Ti3C2O2-x, Fe/S-Ti3C2O2-x, and Fe/Cl-Ti3C2O2-x increased to 0.90, 1.04, 0.85, 0.99, 0.88, and 1.01 eV, respectively. The second step is more likely to form *NNH2 instead of the *NNH4 species in the alternate path, as the energy requirements are higher, and the increments in ∆G for Fe/Ti3C2O2, Fe/N-Ti3C2O2-x, Fe/F-Ti3C2O2-x, Fe/P-Ti3C2O2-x, Fe/S-Ti3C2O2-x, and Fe/Cl-Ti3C2O2-x were 0.1, 0.06, 0.12, −0.05, 0.12, and 0.07 eV to form *NNH2, respectively. In the subsequent hydrogenation steps, the intermediate configuration in the alternating pathway was easier to form than the first NH3 molecule desorption in the distal pathway. The first NH3 is not desorbed until the fifth proton is added, and adsorptive *NH3 is formed when the sixth proton is added. The reaction *NNH2 → *NNH2H2 → *NH2 → NH3 is exothermic, and larger energy input is required until the adsorptive *NH3 is desorbed to form the second NH3 molecule. The ∆G values of Fe/Ti3C2O2, Fe/N-Ti3C2O2-x, Fe/F-Ti3C2O2-x, Fe/P-Ti3C2O2-x, Fe/S-Ti3C2O2-x, and Fe/Cl-Ti3C2O2-x were 1.95, 1.11, 0.97, 1.07, 1.09, 0.99 eV, respectively. However, it was reported that the use of an acidic electrolyte can promote NH3 desorption, as the protonation of adsorbed NH3 to form NH4+ can easily proceed [62,63], so the actual energy barrier is even smaller. For all these structures, the two potential limiting steps were the first hydrogenation of N2 to form the *NNH species and the last process of NH3 desorption to form the second NH3 molecule. Compared with the original structure, nonmetallic doping was beneficial for the desorption of the last NH3 molecule, but only the doping of F and S was beneficial for the formation of *NNH and NH3.

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Table 2. E_ZPE and TS of different reaction intermediates on Fe/Ti3C2O2, T = 298 K.

| Adsorption Species | E_ZPE (eV) | E_ZPE′ (eV) | E_ZPE Difference (eV) | TS [60] (eV) |
|--------------------|------------|-------------|----------------------|-------------|
| N2                 | 0.15       | 0.15 [61]   | 0                    | 0.59        |
| *N≡N               | 0.19       | 0.20 [61]   | 0.01                 | 0.23        |
| *N≡NH              | 0.47       | 0.49 [61]   | 0.02                 | 0.20        |
| *N−NH2             | 0.78       | 0.82 [61]   | 0.04                 | 0.25        |
| *N                 | 0.09       | 0.08 [61]   | 0.01                 | 0.06        |
| *NH                | 0.31       | 0.35 [61]   | 0.04                 | 0.14        |
| *NH2               | 0.63       | 0.65 [61]   | 0.02                 | 0.18        |
| *NH3               | 1.00       | 1.02 [61]   | 0.02                 | 0.23        |
| *NH=NH            | 0.81       | 0.80 [61]   | 0.01                 | 0.25        |
| *NH−NH2           | 1.11       | 1.13 [61]   | 0.02                 | 0.31        |
| *NH2−NH2          | 1.50       | 1.49 [61]   | 0.01                 | 0.27        |
| NH3                | 0.92       | 0.96 [3]    | 0.04                 | 0.60        |
Figure 5. Gibbs free energy diagrams of (a) Fe/Ti$_3$C$_2$O$_2$, (b) Fe/N-Ti$_3$C$_2$O$_2$–x, (c) Fe/F-Ti$_3$C$_2$O$_2$–x, (d) Fe/P-Ti$_3$C$_2$O$_2$–x, (e) Fe/S-Ti$_3$C$_2$O$_2$–x, and (f) Fe/Cl-Ti$_3$C$_2$O$_2$–x.

Figure 6 shows the most possible reaction pathway for different catalysts. All these structures are likely to follow the mixed pathway: N$_2$ $\rightarrow$ *N$_2$ $\rightarrow$ *NNH $\rightarrow$ *NNH$_2$ $\rightarrow$ *NHNH$_2$ $\rightarrow$ *NH$_2$NH$_2$ $\rightarrow$ *NH$_2$ $\rightarrow$ *NH$_3$ $\rightarrow$ NH$_3$. In addition, the doping of nonmetals has
Figure 6. Nitrogen reduction reaction pathways for all structures.

4. Conclusions

The reaction pathway of the TM atom, Fe, adsorbed on pure Ti$_3$C$_2$O$_2$ and surface nonmetal (N/F/P/S/Cl)-doped Ti$_3$C$_2$O$_2$ as the N$_2$ reduction reaction catalyst was calculated using DFT. The main limiting steps of the reaction are *N$_2$ + H → *NNH and *NH$_3$ → NH$_3$, and the limiting potentials of the two steps can reach 0.85–1.01 and 0.97–1.95 eV, respectively. Compared with pure Ti$_3$C$_2$O$_2$, nonmetal doping has an impact on catalytic performance. The doped nonmetal (N/F/P/S/Cl) reduces the energy barrier to form NH$_3$ in the last step, and only the doping of F and S is beneficial to the formation of *NNH in the first step and the desorption of *NH$_3$ in the last step. Therefore, the materials doped with F and S are considered better candidate materials for NRR among the tested catalysts. Our research demonstrates a feasible way to search for new NRR catalysts by modifying the surface of MXenes and loading TM atoms as new catalysts.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/nano12071081/s1, Figure S1: Top and side views of Ti$_3$C$_2$O$_2$ and its nonmetal doped structure, Figure S2: Optimized structures of all the possible elementary steps in NRR, taking Ti$_3$C$_2$O$_2$ as an example. Other nonmetal-doped Ti$_3$C$_2$O$_2$ show similar geometric structure.

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