Termination-Accelerated Electrochemical Nitrogen Fixation on Single-Atom Catalysts Supported by MXenes

Kaifeng Niu, Lifeng Chi,* Johanna Rosen, and Jonas Björk*  

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**ABSTRACT:** The synthesis of ammonia (NH₃) from nitrogen (N₂) under ambient conditions is of great significance but hindered by the lack of highly efficient catalysts. By performing first-principles calculations, we have investigated the feasibility for employing a transition metal (TM) atom, supported on Ti₃C₂T₂ MXene with O/OH terminations, as a single-atom catalyst (SAC) for electrochemical nitrogen reduction. The potential catalytic performance of TM single atoms is evaluated by their adsorption behavior on the MXene, together with their ability to bind N₂ and to desorb NH₃ molecules. Of importance, the OH terminations on Ti₃C₂T₂ MXene can effectively enhance the N₂ adsorption and decrease the NH₃ adsorption for single atoms. Based on proposed criteria for promising SACs, our calculations further demonstrate that the Ni/Ti₃C₂O₁.19(OH)₁.81 exhibits reasonable thermodynamics and kinetics toward electrochemical nitrogen reduction.

Ammonia synthesis, based on the Haber–Bosch process (N₂ + H₂ → NH₃), has been considered as one of the most important industrial catalytic reactions and has had a critical role in the growth of human population for over 100 years. Nevertheless, harsh conditions including high pressure (200–400 atm) and moderately high temperature (400–600 °C) are required, which contributes not only to the large consumption of global energy but also to the emission of greenhouse gases. Alternatively, the electrochemical nitrogen reduction reaction (NRR) has emerged as a sustainable strategy in which NH₃ can be synthesized by using H₂O and N₂ as raw materials on the cathode under ambient conditions. Tremendous efforts have been devoted into the rational design of effective catalysts toward NRR, including noble metals, non-transition metals, carbon nanotubes, and conducting polymers. However, the practical challenge remains at the slow reaction kinetics resulting from the nonpolar N≡N bonds, leading to limited ammonia selectivity and unsatisfactory yield.

Single-atom catalysts (SACs), which contain isolated and exclusively dispersed transitional metal atoms, have been put forward as a promising class for different catalytic systems including NRR with high atomic utilization. For instance, single Fe atoms anchored in N-doped porous carbon are superior to commercial Pt/C catalysts for electrochemical oxygen reduction. In particular, the undercoordinated atomic environment of single atoms due to the active d-electrons would effectively enhance the adsorption and activation of N₂ in NRR. As a result, the SACs can achieve outstanding catalytic performance for the production of ammonia compared to their bulk counterparts in terms of both activity and selectivity. For example, Li and co-workers have successfully synthesized Ru single atoms supported on Cu oxides (Ru/CuₓOₙ), which exhibit outstanding catalytic performance with an NH₃ yield rate of 42.4 μg/(mgcat. h) and a Faradaic efficiency up to 14.1%. Nevertheless, the experimental discovery of SACs toward highly efficient NRR is mostly based on a trial-and-error approach, consuming much time, expense, and manpower.

Considering that SACs contain isolated metal atoms on the support materials, a central factor for fabricating stable SACs is to create a strong interaction between the single atom and the substrate. In this regard, density functional theory (DFT) calculations can be used as an effective approach for the fast screening of potential SACs and providing guidelines to design effective catalytic systems. For example, Reuter et al. have generated a database for 27 transition metal atoms on the vanadium disulphide (VS₂) substrate and predicted that Ta would exhibit high activity toward electrochemical NRR. Similarly, Yang and co-workers have examined the feasibility for anchoring single transition metal atoms on the MoS₂ monolayer. By calculating the binding energy of metal atoms on the MoS₂ and the adsorption energy of N₂ on the metal active sites, the Mo single atom is expected to have the best catalytic performance. Nevertheless, the agglomeration of...
isolated single metal atoms to nanoparticles is usually inevitable, leading to a decrease in the catalytic activity. Accordingly, employing appropriate materials for anchoring single atoms plays a vital role in promoting the catalytic performance. Previous studies have shown that two-dimensional (2D) materials such as C\textsubscript{2}N monolayers and nitrogen-doped porous carbon can be utilized as substrates for embedding transition metal atoms and improving the catalytic performance.\textsuperscript{26,27} Of importance, MXenes, as a large family of embedding transition metal atoms and improving the catalytic doped porous carbon can be utilized as substrates for stability.\textsuperscript{37,38} In addition, studies focusing on the catalytic leads to uncertainty of the catalytic performance and unavoidably form other terminations, such as OH groups, a account that MXenes with other terminations in solution inevitably form other terminations, such as OH groups, and their catalytic performance.\textsuperscript{25} Previous theoretical investigations have predicted that MXenes containing Ti and/or Mo atoms may possess high catalytic activity toward electrochemical NRR.\textsuperscript{30-32} Moreover, tuning surface chemical states of basal planes of MXenes has been proved as an effective approach to increase the catalytic activity. As an example, Zhi and co-workers have shown Fe-modified Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{2} MXene nanosheets present excellent Faradaic efficiency, outperforming other MXene-based NRR catalysts.\textsuperscript{33} In addition, the MXene structure provides adequate adsorption sites for anchoring single atoms because of their high degree of freedom including termination species and their distribution. Very recently, Ge et al. have theoretically proposed that single Ir atom decorated \(\nu\)-Mo\textsubscript{3}CT\textsubscript{2} MXene \((\nu\) represents the termination vacancy) possesses the optimal catalytic performance toward electrochemical NRR. The high catalytic activity is ascribed to synergetic effects of Ir atom and O terminations.\textsuperscript{34} Despite that great success has been achieved in SACs/MXenes toward electrochemical NRR, most studies have focused on bare MXenes and/or O terminated MXenes.\textsuperscript{35,36} Taking into account that MXenes with O terminations in solution unavoidably form other terminations, such as OH groups, leads to uncertainty of the catalytic performance and stability.\textsuperscript{37,38} In addition, studies focusing on the catalytic performance of single atoms supported on MXenes with a mixture of termination groups are limited in number. Therefore, it is necessary to take the OH terminations into consideration for both the stabilization of single metal atoms and the influence on the catalytic performance.

In the present work, we have investigated the feasibility for anchoring single transition metal atoms on the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{2} MXene with different terminations and their catalytic performance toward NRR by first-principles calculations. In all, atoms of 19 different transition metals (TMs), including Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, and Cd, are examined on fully O-terminated and O/OH-terminated Ti\textsubscript{3}C\textsubscript{2} MXene. The promising SACs are screened based on three criteria: (i) the stability for anchoring transition metal atoms to achieve single-atom dispersion, (ii) the adsorption of \(\text{N}_2\) being sufficiently strong to proceed hydrogenations, and (iii) the adsorption of \(\text{NH}_3\) being relatively weak so that active sites are available in further reduction cycles. Despite that the O terminations provide stable adsorption for single transition metal atoms, agglomeration is shown to be an issue for the fabrication of stable SACs in practical applications.\textsuperscript{39,40} By comparison of the adsorption of single atoms and their corresponding dimer structure, a selection of transition metals such as Sc, Nb, Cu, Cr and Ni are expected to form SACs with high stability. Although the \(\text{N}_2\) can be stabilized on most of the single transition metal atoms, further calculations suggest that SACs on Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2} would suffer from the strong \(\text{NH}_3\) adsorption, resulting in a limited life cycle. Nevertheless, introducing OH terminations can both effectively reduce the adsorption of single \(\text{NH}_3\) and suppress the coadsorption of two \(\text{NH}_3\) molecules. As a result, the Ni/Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{1.19}(OH)\textsubscript{1.81} (labeled as Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{2} MXenes for convenience) is predicted to possess the best catalytic performance. DFT calculations show that OH terminations will not strongly influence the hydrogenation steps while the desorption of \(\text{NH}_3\) molecules is promoted. In addition, thermodynamics and kinetic analysis suggest that Ni/Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{2} can be used as an effective catalyst toward electrochemical NRR.

Our first criterion for employing SACs into electrochemical NRR is achieving stable single-atom dispersion on the substrate. As the prototype of the MXene family, Ti\textsubscript{3}C\textsubscript{2} with O terminations have been employed in various catalysis systems serving as either catalyst or substrate.\textsuperscript{11,14,42} Moreover, Ti\textsubscript{3}C\textsubscript{2}-based SACs have been successfully fabricated for electrochemical reactions such as hydrogen evolution and water splitting.\textsuperscript{43} In this regard, we screen a series of transition metals, including 3d and 4d elements, supported on the Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2} MXene, to investigate the feasibility of achieving single-atom dispersion. Because O terminations occupy FCC hollow sites in the Ti\textsubscript{3}C\textsubscript{2} lattice, two possible sites for anchoring single transition metal atoms are generated (see

**Figure 1.** Adsorption energies of single transition metals and metal dimers on the Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2} MXene in (a) a vacuum and (b) implicit solvation, calculated with eq 1.
Figure S1), namely, C site (the HCP hollow site on top of C) and M site (the FCC hollow site on top of the Ti in the first Ti atomic layer). Our calculations show that most transition metals prefer the C site, resulting in metal−oxygen bonds that stabilize single transition metal atoms (Figure S1). However, the single-atom dispersion requires not only the stable adsorption but also preventing the agglomeration. To this end, we propose to use the average adsorption energy of metal atoms in dimers to characterize the possibility of agglomeration, calculated as

\[
E_{\text{ad}} = \frac{1}{n} (E_{\text{TM+MXenes}} - E_{\text{MXenes}} - nE_{\text{TM}})
\]

Figure 2. (a) Optimized structures for the TM/Ti3C2O2 and TM/Ti3C2O0.19(OH)1.81 (Ti3C2T2 for simplification). (b) Adsorption energies of the NH3 on the TM/Ti3C2O2 and TM/Ti3C2T2. Adsorption energies of N2 on the TM/Ti3C2O2 and TM/Ti3C2T2 in the (c) end-on configuration and (d) side-on configuration. The implicit solvation model is employed for all adsorption energies. The Ti, C, O, H, and TM atoms in (a) are represented by the blue, brown, red, white, and green spheres, respectively.

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\]

where \(E_{\text{TM+MXenes}}\), \(E_{\text{MXenes}}\), and \(E_{\text{TM}}\) represent the energy of metal atoms adsorbed on the \(\text{Ti}_3\text{C}_2\text{O}_2\), the pristine \(\text{Ti}_3\text{C}_2\text{O}_2\), and the reference energy of transition metals (see eq S1), respectively, while \(n\) is the number of metal atoms. Herein, the adsorption behavior of transition metal atoms is investigated under both vacuum and implicit solvent conditions. Figure 1a shows the correlation between average adsorption energy for metal dimers and adsorption energy for single metals in a vacuum. As seen, many transition metals exhibit similar adsorption energies for single atoms and dimers. For instance, the V dimer is only 0.06 eV more stable than the single V atom, indicating it is possible to obtain the coexistence of V clusters and single V atoms on the \(\text{Ti}_3\text{C}_2\text{O}_2\). Nevertheless, the possibility of agglomeration increases if there are more unpaired electrons in transition metals (gray region in Figure 1). Particularly, Ru(4d6) and Rh(4d7) are more likely to form metal clusters since the dimer adsorption is 0.54 and 0.68 eV stronger than the single-atom dispersion, respectively. On the other hand, stable single-atom adsorption can be achieved on transition metals with either more empty or fully occupied d orbitals. For example, the single-atom adsorption on the \(\text{Ti}_3\text{C}_2\text{O}_2\) for Sc(3d1), Zr(4d2), Ni(3d8), and Ag(4d9) is energetically favored. Moreover, single transition metals tend to bind stronger in the solvent. As seen in Figure 1b, most transition metals (except Ru, Rh, and Pd) exhibit stronger single-atom adsorption energies with the implicit solvent model. Consequently, the possibility to achieve single-atom dispersion is enhanced with implicit solvation. Such adsorption behavior effectively guarantees stability of the single-atom catalysts and provides unsaturated active sites for the further application in catalysis. In addition, the stability for the single-atom adsorption is assessed by the corrosion potential of TM/Ti3C2O2 with the implicit solvation model. The corrosion
reaction of transition metals are the dissolution of transition metals to form the most stable cations/anions (eqs S9−S11) and corrosion potentials (calculated by eqs S12−S14) at pH = 0 are the highest potentials to stabilize the single-atom adsorption (Table S1). It is found that corrosion potentials for the majority of single transition metal atoms on the Ti3C2O2 are in the range from −1.0 to 0.2 V (vs SHE). Taking into account that the electrochemical NRR requires negative potentials, the corrosion can be effectively prevented during the NRR process.

The catalytic performance of SACs supported on the Ti3C2O2 can be predicted by considering the second and the third criteria given above: the adsorption behavior of both N2 and NH3. However, the capabilities for SACs to capture N2 molecules is enhanced by OH terminations, as shown in Figure 2c,d. The interactions between the NH3 and 3d metals such Ni, Co, and Fe have decreased dramatically to adsorption energies around −0.4 eV on the O/OH-terminated MXene. Notably, the NH3 possesses positive adsorption energies on Ag, Nb, and Mo single atoms, indicating a spontaneous desorption of NH3. Such weakened NH3 adsorption would presumably accelerate the reaction after the NH3 is generated. Second, the ability for single atoms to capture N2 molecules is enhanced by OH terminations, as shown in Figure 2c,d. The data points in the white regions are referring to transition metals that exhibit stronger N2 adsorption on the Ti3C2T2 than that of Ti3C2O2, indicating that the N2 reduction can take place easier on the TM/Ti3C2T2. As seen in Figure 2a, the adsorption energies of NH3 on SACs are smaller than −0.2 eV). However, further calculations indicate that the NH3 exhibits stronger adsorption than the most stable N2 adsorption configuration on all considered TM/Ti3C2O2 (Figure S3). Specifically, adsorption energies for NH3 on SACs are smaller than −1.0 eV while adsorption energies for N2 are in the range from −0.2 to −0.8 eV (negative values refer to exothermic adsorption). Consequently, the desorption of NH3 would be prohibited due to the strong interactions, leading to limited activity for the transition metal atoms. Nevertheless, such an obstacle can be overcome by modifying MXene surfaces, as the catalytic performance of MXene-based catalysts is highly related to the MXene surface chemistry.34 Specifically, surface terminations play a vital role. In addition, it has been shown that the surface hydroxyl modification of Ti3C2 can boost electrolysis of ammonia, in which OH terminations can enhance the N2 adsorption on the Ti3C2T2.46

To this end, we have proposed a new strategy for enhancing the catalytic performance for SACs by modifying the surface chemistry of the MXene support. Instead of the fully O terminated Ti3C2 MXene, the OH terminations are introduced, except for the three most adjacent termination sites, generating the composition Ti3C2O0.19(OH)1.81 labeled as Ti3C2T2 (Figure 2a). The advantages for employing Ti3C2 MXene with mixed terminations are twofold. First, introducing OH termination into the Ti3C2 MXene can effectively reduce the adsorption strength of NH3 on the single TM atom. As shown in Figure 2b, the adsorption energies of NH3 have become less favorable by more than 0.5 eV with respect to that on the Ti3C2O2 MXene, except for Pd, Sc, and Zn (data points in the white region). Interactions between the NH3 and 3d metals such Ni, Co, and Fe have decreased dramatically to adsorption energies around −0.4 eV on the O/OH-terminated MXene. Notably, the NH3 possesses positive adsorption energies on Ag, Nb, and Mo single atoms, indicating a spontaneous desorption of NH3. Such weakened NH3 adsorption would presumably accelerate the reaction after the NH3 is generated.

Figure 3. Comparison of the adsorption energy of the first NH3 and the second NH3 molecule on the TM/Ti3C2T2 MXene with the implicit solvation model.
molecules on the active site is considered as an important intermediate state in electrochemical NRR. \(^27\) Therefore, we further investigate the capability of transition metals for loading ammonia molecules by calculating the adsorption energy of the second NH\(_3\) on single atoms with one NH\(_3\) already attached according to

\[
E_{\text{ad}}^{\text{NH}_3(2)} = E_{\text{SAC}+2\text{NH}_3} - E_{\text{SAC}+\text{NH}_3} - E_{\text{NH}_3}
\]  

\(E_{\text{SAC}+2\text{NH}_3}, E_{\text{SAC}+\text{NH}_3}\), and \(E_{\text{NH}_3}\) refer to the potential energy of SACs with two NH\(_3\) adsorbed, SACs with only one NH\(_3\) attached, and a NH\(_3\) molecule, respectively. To achieve fast cycle for the electrochemical NRR, spontaneous desorption of the second NH\(_3\) is desired; that is, the adsorption energy for the second NH\(_3\) should be positive. However, for majority of the transition metals such as Ti, Co, Cr, Zn, and V, the second NH\(_3\) tends to bind even stronger than the first NH\(_3\) to the active site. In Figure 3, the data points in the gray region represent transition metal atoms with a stronger second NH\(_3\) adsorption. Such enhanced adsorption can be ascribed by the formation of hydrogen bonds that stabilize the entire system. Consequently, hydrogenation steps of N\(_2\) would be hindered due to occupied active sites. Despite this, the adsorption behavior of NH\(_3\) molecules on Fe, Pd, and Ni is desired due to weak interactions between the second NH\(_3\) and SACs. Of great importance, the second NH\(_3\) exhibits positive adsorption energy on the single Ni atom, indicating that a spontaneous desorption can take place. Taking into account that the single

**Scheme 1.** Possible Reaction Pathways for the Electrocatalytic Reduction of N\(_2\) to NH\(_3\) on Single Metal Atoms Supported on Ti\(_3\)C\(_2\)T\(_2\) MXene

**Figure 4.** Reaction pathways and Gibbs free energy profiles for the nitrogen fixation on the (a) Ni/Ti\(_3\)C\(_2\)T\(_2\) and (b) Ni/Ti\(_3\)C\(_2\)O\(_2\) catalysts. (c) Enzymatic pathway and corresponding Gibbs free energy profiles for NRR on Ni/Ti\(_3\)C\(_2\)T\(_2\). The Ti, O, C, H, N, and Ni atoms are represented by the blue, red, brown, white, light green, and dark green circles, respectively.
Ni atom exhibits stable adsorption on the Ti3C2 MXene and the desired interactions with both N2 and NH3, we therefore propose that Ni/Ti3C2T2 can serve as an efficient catalyst toward electrochemical NRR.

As illustrated in Scheme 1, three alternative reaction pathways for electrochemical NRR have been considered on the Ni/Ti3C2T2 catalyst, namely, distal, alternating, and enzymatic pathway. As seen, the distal and alternating pathways (red and blue lines) initiate from the end-on adsorption of N2, but possess different hydrogenation sequences afterward, while the enzymatic pathway (purple lines) starts from side-on adsorption of N2. In the distal pathway, hydrogenations consecutively take place at the upper N until the first NH dissociates from the catalysts. In the alternating and enzymatic pathway, however, hydrogenations proceed on both N atoms to form two NH2 in succession. In this work, the catalytic performance of Ni SAC is evaluated based on all three possible NRR pathways. In addition, two scenarios for hydrogenations are considered: (1) hydrogens come from the electrolyte in the form of (H+ + e−) pairs to attack N atoms, and (2) OH terminations contribute H atoms for the reduction of the nitrogen.

We first focus on the scenario 1, in which the electrolyte serves as the source of hydrogen. Figure 4a displays the energy profiles of electrochemical NRR on the Ni/Ti3C2T2 catalyst. As seen, the Ni single atom supported on Ti3C2T2 MXene exhibits strong interactions with the N2 molecule. The adsorption free energies of N2 are −0.62 and −0.73 eV for end-on and side-on configurations with respect to SHE, which are significantly larger than other SACs. As seen, the first hydrogenation is the energy-limiting step for electrochemical NRR in the alternating and enzymatic pathways, exhibiting free energy barriers of 1.47 and 1.56 eV, respectively. Subsequent hydrogenation can proceed along the enzymatic pathway due to the low Gibbs free energy profile (overall 0.86 eV). As discussed above, the weak interaction with single NH2 and/or double NH2 on the Ni/Ti3C2T2, for which the relative Gibbs free energies are −0.60 and −0.28 eV, can accelerate the Ni SAC to retain the initial state for the next reduction cycle. The effect of OH terminations on the catalytic performance is elucidated by calculating the activity of the Ni/Ti3C2O2 catalyst. As seen in Figure 4b, the termination groups on the Ti3C2 support do not significantly influence the catalytic activity of the Ni active sites. The limiting step for the Ni/Ti3C2O2 catalyst remains at the first hydrogenation (N2 → N2H) with a barrier of 1.29 eV (enzymatic pathway) and 1.28 eV (distal/alternating pathway). Moreover, the second hydrogenation step along the enzymatic pathway exhibits an exothermic characteristic on the Ni/Ti3C2O2 (Figure 4b). Such a discrepancy in Gibbs free energy profiles indicates that the single Ni atom exhibits different selectivity on the Ti3C2T2 and Ti3C2O2. As a result, the enzymatic pathway is no longer energetically favored while the alternating pathway exhibits the lowest overall Gibbs free energy of 1.05 eV on the Ni/Ti3C2O2. However, the catalytic performance of the Ni/Ti3C2O2 catalyst is profoundly limited by the strong interactions between the single Ni atom and NH2 molecules (G(NH2) = −1.60 eV and G(NH2H) = −1.51 eV). Such a strong adsorption of synthesized NH2 would hinder further reactions. Furthermore, our calculations show that the Ni/Ti3C2T2 exhibits better catalytic activity under implicit solvation condition. As seen in Figure S4, the limiting step for the Ni/Ti3C2T2 along the enzymatic pathway is decreased from 1.56 to 1.36 eV. In addition, the relative Gibbs free energy of NH2H is reduced to −0.11 eV in solution, indicating a more stable intermediate. Of importance, the accelerated reaction kinetics can be expected in the solution because the relative Gibbs free energy of NH2H has been increased from −0.28 eV (in vacuum) to −0.04 eV (in implicit solvation).

Alternatively, the OH terminations can provide the H atoms for NRR (scenario 2). Full Gibbs free energies and geometry structure of all species including transition states for NRR via the enzymatic pathway are presented in Figure 4c. In this work, hydroxyl groups are assumed to be re-formed after each hydrogenation step. However, the first hydrogenation step requires high-energy input (2.03 eV for passing through TS1 and TS2). Such a high-energy requirement can be ascribed to the stability of OH terminations on the Ti3C2MXene. Nevertheless, such alternative reaction mechanism provides potential pathways for achieving NH3 fixation via heterogeneous catalysis.

As a final remark, F terminations are also commonly observed in experiments. However, additional calculations show that F terminations exhibit limited promotion on the catalytic performance of single Ni atoms (Figure S5 and Table S2). Similar results can be observed for other terminations including Cl, Br, I, and S. Interestingly, the Ni/Ti3C2O0.19Te1.81 exhibits positive adsorption energies for the second NH2, suggesting promising reaction kinetics for electrochemical NRR. However, the synthesis of multilayers of the Te-terminated Ti3C2 requires high temperatures (300–600 °C), and the fabrication of the Ti3C2Te2 monolayer has not been reported yet. Such obstacles would therefore hinder the further application of Te-terminated Ti3C2 in single-atom catalysis. Consequently, it is important to maintain a considerable concentration of OH terminations to obtain high efficiency.

In conclusion, on the basis of first-principles calculations, we investigated the potential of a single transition metal atom anchored on the Ti3C2T2 (T = O and/or OH) MXene as electrocatalyst for NRR and the effect OH terminations on the catalytic performance. Our computational screening of anchoring single TM atoms on the Ti3C2T2 MXene has shown that a single atom supported on Ti3C2O2 MXene can bind N2 with considerable adsorption energy but suffer from the strong interaction with NH3 leading to limited life cycle. Importantly, we reveal that introducing OH terminations to Ti3C2 MXene can effectively enhance the N2 adsorption and suppress the NH3 adsorption. Furthermore, an in-depth understanding for the NH3 adsorption was obtained by considering the coadsorption of two NH3 molecules. Our DFT calculations predict that the single Ni atom supported on Ni/Ti3C2O0.19(OH)1.81 is a promising SAC toward electrochemical NRR among all considered systems. Subsequent calculations indicate the existence of OH terminations will not significantly influence the catalytic performance of the single Ni atom but accelerate reduction reactions by weakening the binding energy of NH3. We anticipate that our study can provide fast screening criteria for evaluation the catalytic performance of MXene-based SACs and a comprehensive understanding on effects of surface chemistry on their performance in the electrochemical processes of NRR.
Computational parameters and methods; adsorption of single transition metal atoms on the Ti3C2O2; corrosion potentials for transition metal atoms on the Ti3C2O2; adsorption behavior of the N2 molecule on the TM/Ti3C2O2 with the implicit solvation model; adsorption of the NH3 on the TM/Ti3C2O2 with the implicit solvation model; implicit solvation effect on the electrochemical NRR on the Ni/Ti3C2T2 along the enzymatic pathway; influence of other terminations including F, Cl, Br, I, S, and Te on the catalytic performance of the Ni SAC (PDF)

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