Optimizing the Lattice Nitrogen Coordination to Break the Performance Limitation of Metal Nitrides for Electrocatalytic Nitrogen Reduction

Haiyang Yuan, Chen Zhu, Yu Hou, Hua Gui Yang, and Haifeng Wang*
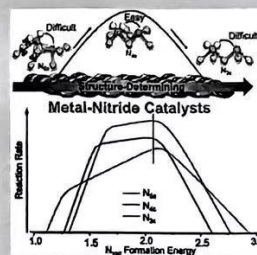
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ABSTRACT: Metal nitrides (MNs) are attracting enormous attention in the electrocatalytic nitrogen reduction reaction (NRR) because of their rich lattice nitrogen (N_{lat}) and the unique ability of N_{lat} vacancies to activate N_2. However, continuing controversy exists on whether MNs are catalytically active for NRR or produce NH_3 via the reductive decomposition of N_{lat} without N_2 activation in the in situ electrochemical conditions, let alone the rational design of high-performance MN catalysts. Herein, we focus on the common rocksalt-type MN(100) catalysts and establish a quantitative theoretical framework based on the first-principles microkinetic simulations to resolve these puzzles. The results show that the Mars-van Krevelen mechanism is kinetically more favorable to drive the NRR on a majority of MNs, in which N_{lat} plays a pivotal role in achieving the Volmer process and N_2 activation. In terms of stability, activity, and selectivity, we find that MN(100) with moderate formation energy of N_{lat} vacancy (E_{vac}) can achieve maximum activity and maintain electrochemical stability, while low- or high-E_{vac} ones are either unstable or catalytically less active. Unfortunately, owing to the five-coordinate structural feature of N_{lat} on rocksalt-type MN(100), this maximum activity is limited to a yield of NH_3 of only $\sim 10^{-15}$ mol s^{-1} cm^{-2}. Intriguingly, we identify a volcano-type activity-regulating role of the local structural features of N_{lat} and show that the four-coordinate N_{lat} can exhibit optimal activity and overcome the performance limitation, while less coordinated N_{lat} fails. This work provides, arguably for the first time, an in-depth theoretical insight into the activity and stability paradox of MNs for NRR and underlines the importance of reaction kinetic assessment in comparison with the prevailing simple thermodynamic analysis.

KEYWORDS: electrocatalytic nitrogen reduction, metal nitrides, activity limitation, surface topology, density functional theory calculation, microkinetic

INTRODUCTION

The ammonia synthesis is one of the most critical reactions in modern industry.[1-5] The Haber-Bosch process as the primary route to produce NH_3 is energy-intensive.[6,7] The electrosynthesis offers a promising strategy to produce NH_3 at mild conditions, such as lithium-mediated ammonia synthesis, nitrate/NO_x reduction and direct N_2 reduction reaction [nitrogen reduction reaction (NRR)],[8-12] in which the direct NRR is the most attractive technology.[13] Unfortunately, although much effort has been made to develop superior catalysts for NRR,[13-30] many of them are demonstrated to produce only tiny amounts of NH_3 or even do not produce NH_3 under the protocols with rigorous isotope labeling experiments.[9,31-33] Therefore, there is a strong desire to design and prepare advanced catalysts for NRR or at least provide a relatively explicit direction for optimizing catalysts.

Metal nitrides (MNs), which can provide rich lattice nitrogens (N_{lat}) to form NH_3 and abundant N_{lat} vacancies to activate N_2, have been widely tested in experiments for nitrogen reduction.[17-26,34,35] In electrocatalytic NRR, one of the most significant ambiguities for MNs is where NH_3 comes from, i.e., the decomposition of N_{lat} or the catalytic reduction

of N_2.[36-39] Whether MNs are suitable for electrocatalytic NRR has been confused. For example, VN, which possesses good conductivity and has been used for oxygen electroreduction,[40,41] was synthesized by some research groups and demonstrated to be efficient in the electrosynthesis of NH_3 with high selectivity (vs H_2 evolution reaction, HER).[22,23] However, under the rigorous testing protocols, some studies found that the inability of VN to catalyze the electrosynthesis of NH_3 from N_2 and VN could release N_{lat} in a noncatalytic process, leading to the formation of NH_3.[36-38] A similar controversy exists for Mo_2N catalyst.[26,39] These different observations could be due to different fine structures exposed under different preparation conditions;[36] for example, all facets of VN except (100) were predicted to show a faster migration