

Theoretical Study of Nitrogen Reduction over MXenes

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Ammonia (NH₃) is an important basic chemical in various industrial sectors, with fertilizer production being one of its key applications. So far, the Haber-Bosch process corresponds to the predominant method for the global production of ammonia, with approximately 150 million tons annually to meet industrial demands. Despite its widespread use, the Haber-Bosch process poses significant environmental challenges. Its reliance on non-renewable energy sources results in the consumption of approximately 1% of the world's total energy output. Moreover, substantial amounts of CO₂ are emitted, contributing to an enrichment of greenhouse gas in the atmosphere and environmental degradation. In the light of these concerns, there is an urgent need to develop and implement sustainable alternatives that align with the principles of environmental conservation and green energy to minimize energy consumption and to reduce carbon dioxide emissions.

The electrochemical synthesis of ammonia from dinitrogen represents a promising alternative to the conventional Haber-Bosch process, offering potential advantages in terms of environmental sustainability and energy efficiency. However, the nitrogen reduction reaction (NRR) faces significant challenges that, hitherto, hinder its widespread adoption. One of these challenges refers to the low intrinsic activity observed during the NRR process as the conversion of one molecule of dinitrogen to ammonia requires the transfer of six proton-electron pairs accompanied with the stabilization of at least five different reaction intermediates on the electrode surface. Given that the adsorption energies of the reaction intermediates are intrinsically coupled by scaling relations, the NRR is thermodynamically restrained, and this limits the overall efficiency of the electrochemical process. Additionally, the NRR encounters a selectivity problem due to the competing hydrogen evolution reaction (HER) in the same potential window, thus reducing the Faradaic efficiency of ammonia production.

Overcoming the above-outlined challenges requires innovative approaches to enhance the intrinsic activity of NRR catalysts as well as to mitigate the competing HER.^{2,3} In the present contribution, we present our results on the NRR over MXenes, a promising material class consisting of two-dimensional metal carbides and nitrides.¹ Applying density functional theory calculations, we compile Pourbaix diagram and discuss the elementary steps of the NRR and HER by the concept of free-energy diagrams and volcano analyses. Although it is considered a general consensus that either the adsorption of dinitrogen or the desorption of ammonia is limiting the electrocatalytic activity,^{2,3} our work sheds light on the importance of considering various pathways in the mechanistic analysis of the complex six proton-coupled electron transfer steps of the NRR.⁴ We discuss our results in the context of volcano plots and span a bridge to the optimization of NRR catalysts by means of breaking scaling relation and catalytic resonance theory.⁵ Our modeling study provides guidelines for the rational design of NRR catalysts on the atomic scale.

References:

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