Theoretical Study of Nitrogen Reduction over MXenes

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ABSTRACT

Ammonia (NH_3) is an important commodity for chemical industry. So far, the demand of 150 million tons per year is covered by the Haber-Bosch process, which, however, is environmentally unfriendly, consuming about 1% of global energy and emitting significant amounts of greenhouse gases including CO_2. To address these issues, sustainable alternatives are imperative to minimize energy use and carbon emissions, aligning with environmental conservation and green energy principles.

Electrochemical synthesis of ammonia from dinitrogen by electrocatalytic nitrogen reduction (NRR) offers an environmentally benign route for ammonia production. However, the low intrinsic activity due to the transfer of six proton-electron pairs and modest selectivity due to the competing hydrogen evolution reaction (HER) in the same potential window limits its widespread utility so far.

In the present study, we present fundamental insights into the NRR over MXenes, a promising class of two-dimensional metal carbides and nitrides for energy conversion and storage. Applying density functional theory calculations, we construct surface Pourbaix diagrams to determine thermodynamically stable surface configurations under cathodic reaction conditions. Based on the energetically stable surfaces, we model more than 20 pathways for the competing NRR and HER by the combination of free-energy diagrams and descriptor-based analysis. Although it is considered a general consensus that either the adsorption of dinitrogen or the desorption of ammonia is limiting the electrocatalytic activity when applying volcano analyses [1]. our work sheds light on the importance of the entire breadth of mechanistic pathways in the analysis of the complex six proton-coupled electron transfer steps of the NRR. This finding is further substantiated by the fact that for highly active surface configurations, different hydrogenation steps govern the rate [2]. Our modeling study provides guidelines for the rational design of NRR catalysts on the atomic scale.

References

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