

Activity and Selectivity Trends in Electrocatalytic Nitrate Reduction on Transition Metals

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Introduction

Nitrate (NO_3^-) pollution of aquatic ecosystems and drinking water has become a global problem and poses a threat to human health and the environment due to fertilizer overuse, wastewater discharge, and contaminant leaching from landfills.¹⁻² Consequently, the National Academy of Engineering recognizes the treatment of nitrate in wastewater as a grand challenge. The electrocatalytic nitrate reduction reaction (NO_3RR) is a promising approach to remediate nitrate in wastewater; however, the widespread use of NO_3RR is hindered because no sufficiently active, selective, and stable electrocatalyst is known. Because of the complexity of NO_3RR , multiple questions remain unanswered regarding: (i) nitrate reduction electrocatalyst activity and selectivity trends across metals and alloys, (ii) the nature and abundance of the surface intermediates, and (iii) if the rate-determining step changes as a function of applied potential. Mechanistic insight into the activity and selectivity trends of NO_3RR is needed to engender a framework for electrocatalyst design with superior selectivity toward benign N_2 or useful NH_3 .

Materials and Methods

Density functional theory (DFT) calculations have been performed to study the NO_3RR mechanism. The Vienna Ab initio Simulation Package (VASP) with the PBE functional is used. The impact of applied potential on thermodynamics is treated using the well-known computational hydrogen electrode approach.³ The potential dependence on activation energies is incorporated using the Butler-Volmer formalism, where we assume the activation energy of a redox reaction is linearly dependent on the potential with symmetry factor of 0.5. First-principles microkinetic modeling is achieved using the MKMCXX software⁴ to predict the reaction rate, the surface coverage of intermediates, degree of rate control, and product selectivity as a function of temperature and potential.

Results and Discussion

We clarified the activity and selectivity trends of transition metals for NO_3RR to benign or value-added products such as N_2 and NH_3 . Adsorbate linear scaling relations between the adsorption strengths of oxygen and nitrogen atoms with nitrate and its reduction intermediates were found on eight transition metal (i.e., Co, Cu, Rh, Pd, Pt, Ag, Au, Fe) surfaces using DFT modeling. Brønsted-Evans-Polanyi (BEP) relations were also identified for each elementary step of the nitrate reduction reaction for the considered transition metals. Nitrate reduction rates, surface species coverages, and the degree of rate control were predicted for these metals as a function of applied potential using first-principles microkinetic modeling. We compare our microkinetics simulations to our experimental NO_3RR studies and reports in the literature⁵ to give mechanistic insight into nitrate reduction on metal surfaces. We predict the NO_3RR

activity of 28 metals and single-atom alloy electrocatalysts using adsorbate and Brønsted-Evans-Polanyi linear scaling relations with microkinetics modeling. Theoretical volcano plots and selectivity predictions, while considering metal stability, show that high activity and selectivity toward N_2 or NH_3 is unfeasible using pure transition metals regardless of the potential under acidic conditions. Single-atom alloys containing Fe, however, are computed to have superior selectivity to N_2 or NH_3 than their pure metal counterparts while maintaining activity.

Significance

This work gives insight into nitrate reduction on transition metal surfaces and serves to guide the design of improved electrocatalysts.

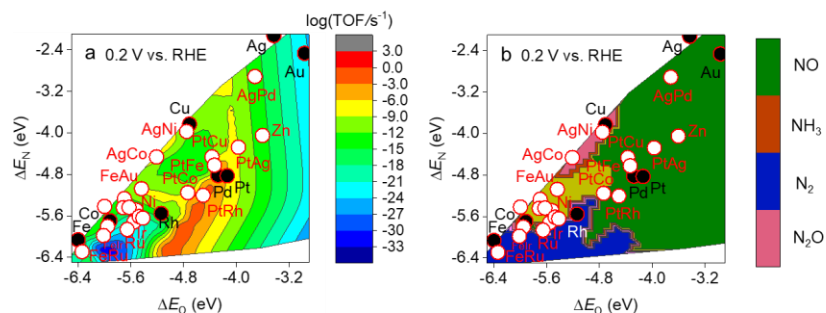


Figure 1. Theoretical turnover frequencies (TOF) (a) and selectivity (b) of metal and single-atom alloy catalysts for NO_3RR at 300 K with a H^+/NO_3^- molar ratio of 1:1 at 0.2 V vs. RHE. The solid black circles denote the pure transition metals predicted via DFT-computed catalytic cycles, whereas the solid white circles show the activity and selectivity of single-atom alloy (PtM, FeM, and AgM (M = single-atom dopant) catalysts and Ru, Ir, Ni, and Zn metals predicted using adsorbate and Brønsted-Evans-Polanyi linear scaling relations.

References

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