Single-Atom Catalysts for the Electrochemical Conversion of Nitrate with DFT and Machine Learning

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Abstract

Anthropogenic activities, particularly within the agricultural sector, contribute significantly to the climate crisis and aquatic ecosystem strain. Fertilizers produced through the Haber-Bosch process emit undesirable greenhouse gases and disrupt the nitrogen cycle, resulting in eutrophication. To address this, this research focuses on studying the behavior of single-atom catalysts for nitrate reduction using Density Functional Theory (DFT), machine learning techniques, and kinetic Monte Carlo simulations. The goal of this study is to expand the archive of potential catalysts for nitrate reduction to include SACs, thereby improving the economic viability of the electrochemical conversion of nitrate to valuable NH_3 or benign N_2.

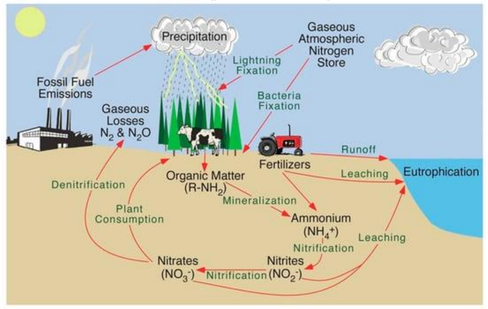

Figure 1. *Natural/anthropogenic activities resulting in eutrophication.*(1)

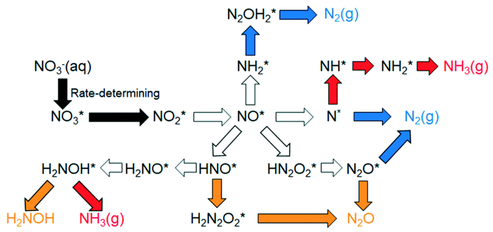

Figure 2. *Electrocatalytic nitrate reduction reaction pathway*(2)

Obstacles

- **Time:** Data collection for DFT can be particularly time intensive, where the speed is dependent on relaxing the geometries of the molecules on the surface, which can take multiple iterations to achieve convergence.
- **PCA and Machine Learning Model Tuning:** Machine learning models often have several parameters that may be tuned to further optimize their performance. Identifying which parameters that would improve the performance can typically only be completed through manual analysis, which will be a part of the future work for this research.

Methods

1) Density of State Calculations from DFT:
Calculate the DOS to determine the number of electronic states at a given energy level using DFT/VASP for a subset of SACs/metal combinations that span transition metals group.

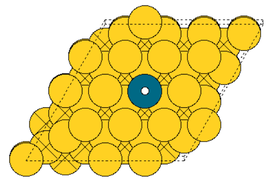

Figure 3. *Visualization of the converged geometry of a catalyst (Au on Pd) on "HTOP"*

2) Machine Learning – Predicting Energies
The DFT information collected for the subset of SACs can be utilized to predict binding and activation energies for each using machine learning.

- **Binding energy:** measures adsorption of nitrate ions to NH_3
- **Activation energy:** measures speed of adsorption reaction & conversion of nitrate to NH_3

3) Kinetic Monte Carlo

- Elucidate the catalytic reaction mechanism of nitrate on a given SAC using KMC, which provides a more detailed description of a catalyst's behavior than traditional kinetics models.

Future Work

1) **Decrease machine learning model(s) error:** Fine tune parameters of higher performing machine learning models to improve error/variance in the machine learning model performance.
2) **Conduct Kinetic Monte Carlo simulations for the SACs of interest:** Following the DFT calculations and machine learning analysis, kMC simulations can be conducted to identify the ideal single atom catalysts for nitrate reduction.

Data

Dimensionality Reduction (PCA) for ExtraTrees Regressor in ScikitLearn (3)

- 6 reaction steps tested: (NH_3+* → NH_3*), (H_2+2* → 2H*), (H_2O+* → H_2O*), (N*+H* → NH*+*), (O*+H* → OH*+*) & (OH*+H* → H_2O*+*).
- Best number of estimators = 10 for all PC's
  - Exception of 5 PC's = 8 estimators
- Best number of components = 3

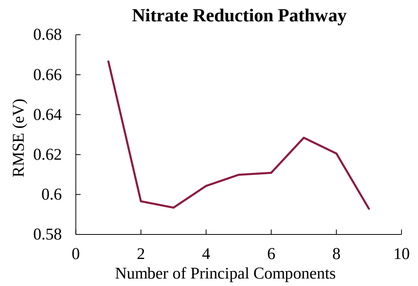

Figure 4. *Root mean squared error (eV) for the ExtraTrees Regressor as a function of the number principal components and the best number of estimators for 6 of the reaction steps in the nitrate reduction reaction pathway.*

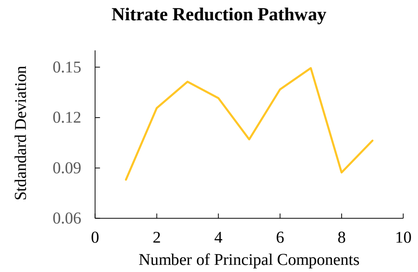

Figure 5. *Standard deviation of error (eV) for the ExtraTrees Regressor as a function of the number principal components and the best number of estimators for 6 of the reaction steps in the nitrate reduction reaction pathway.*

Acknowledgments

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