Electrocatalytic Nitrate Reduction to Ammonia on Metals and Alloys

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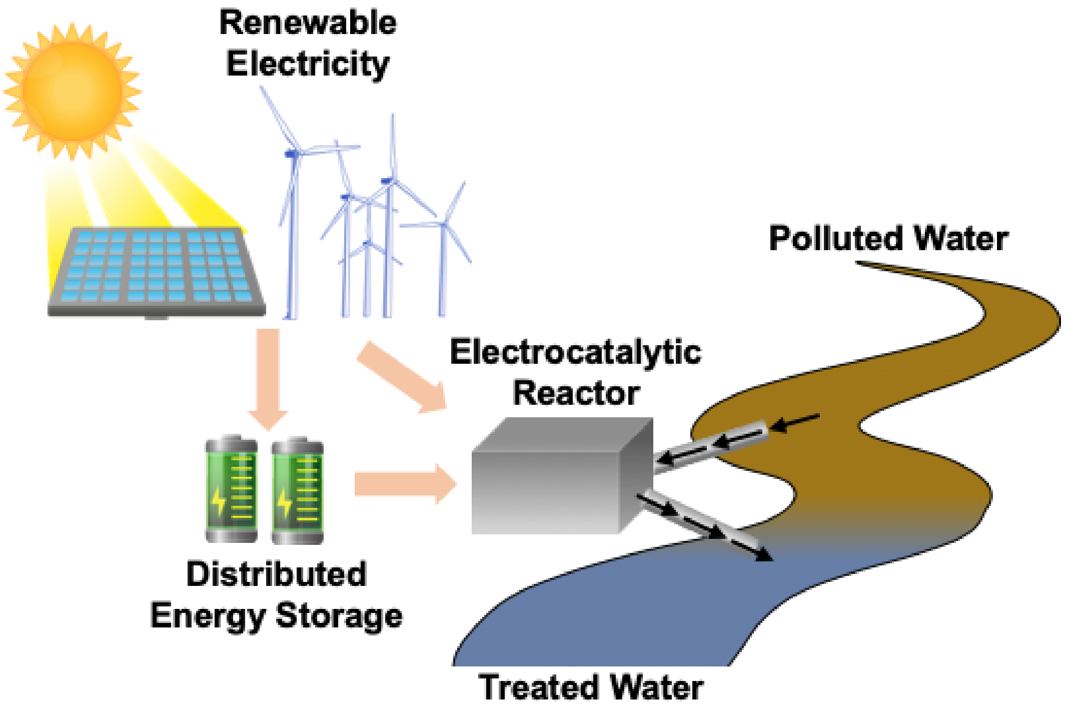

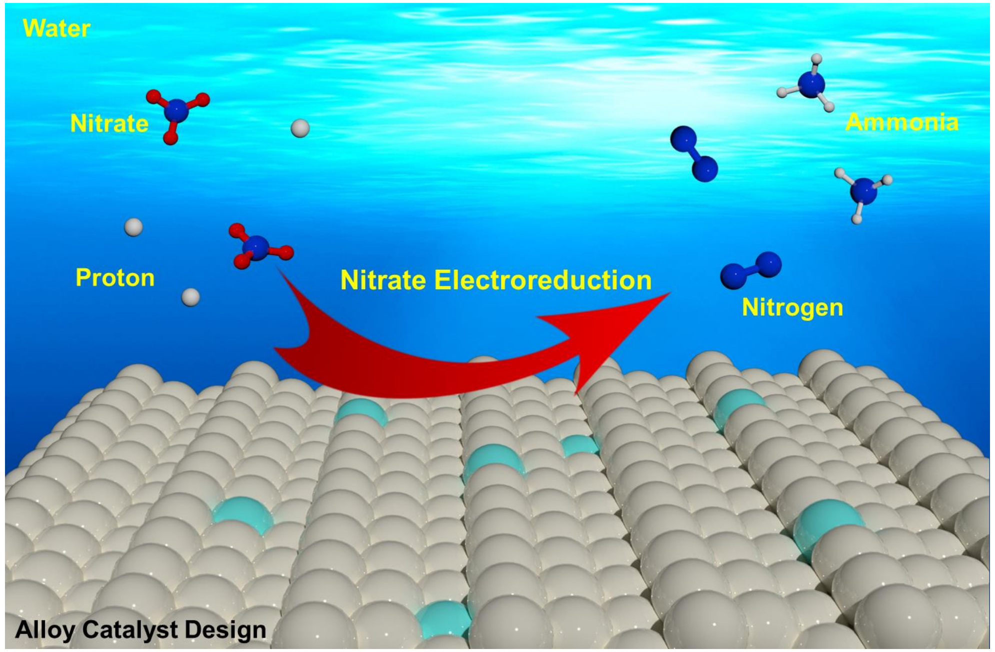

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CHEMICAL ENGINEERING
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Materials
Modeling
Data Science
Descriptors
Catalysis
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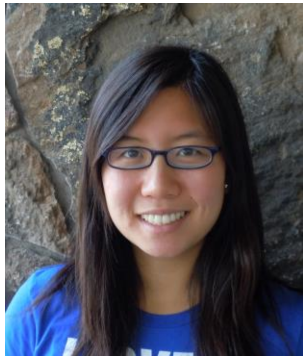
Collaborators on the work presented herein

Prof. Nirala Singh
(UofM)

Dr. Jin-Xun Liu
(now a Prof at USTC)

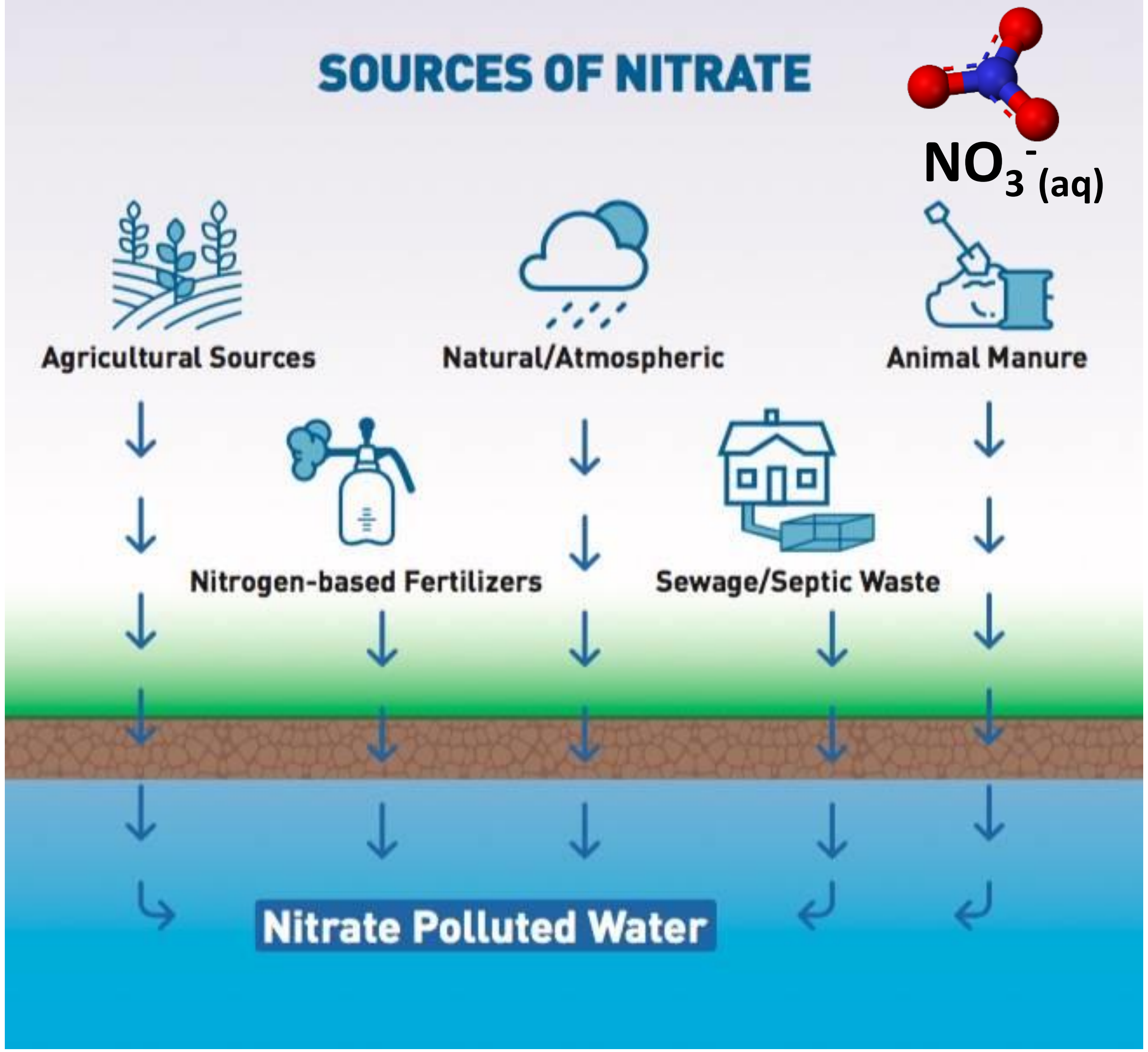
Dr. Zixuan Wang
(now a policy fellow)



Samuel Young
(UofM)

Danielle Richards
(UofM)

Large amounts of nitrate are accumulating in aquatic ecosystems, especially because of fertilizer usage



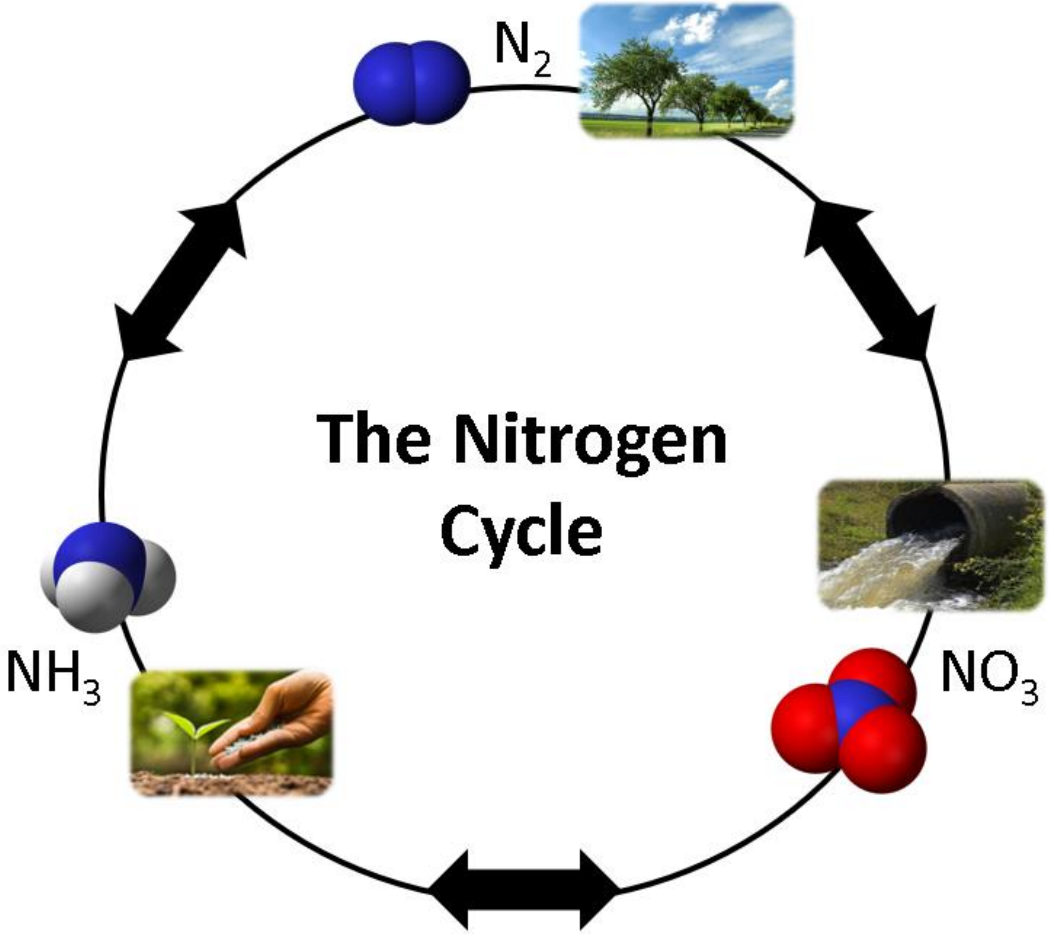


Image credit: https://www.betalabservices.com/nitrate-test/

Nitrate accumulation has detrimental environmental and health effects

Algal Blooms and Dead Zones

Lake Erie, Michigan (2017)

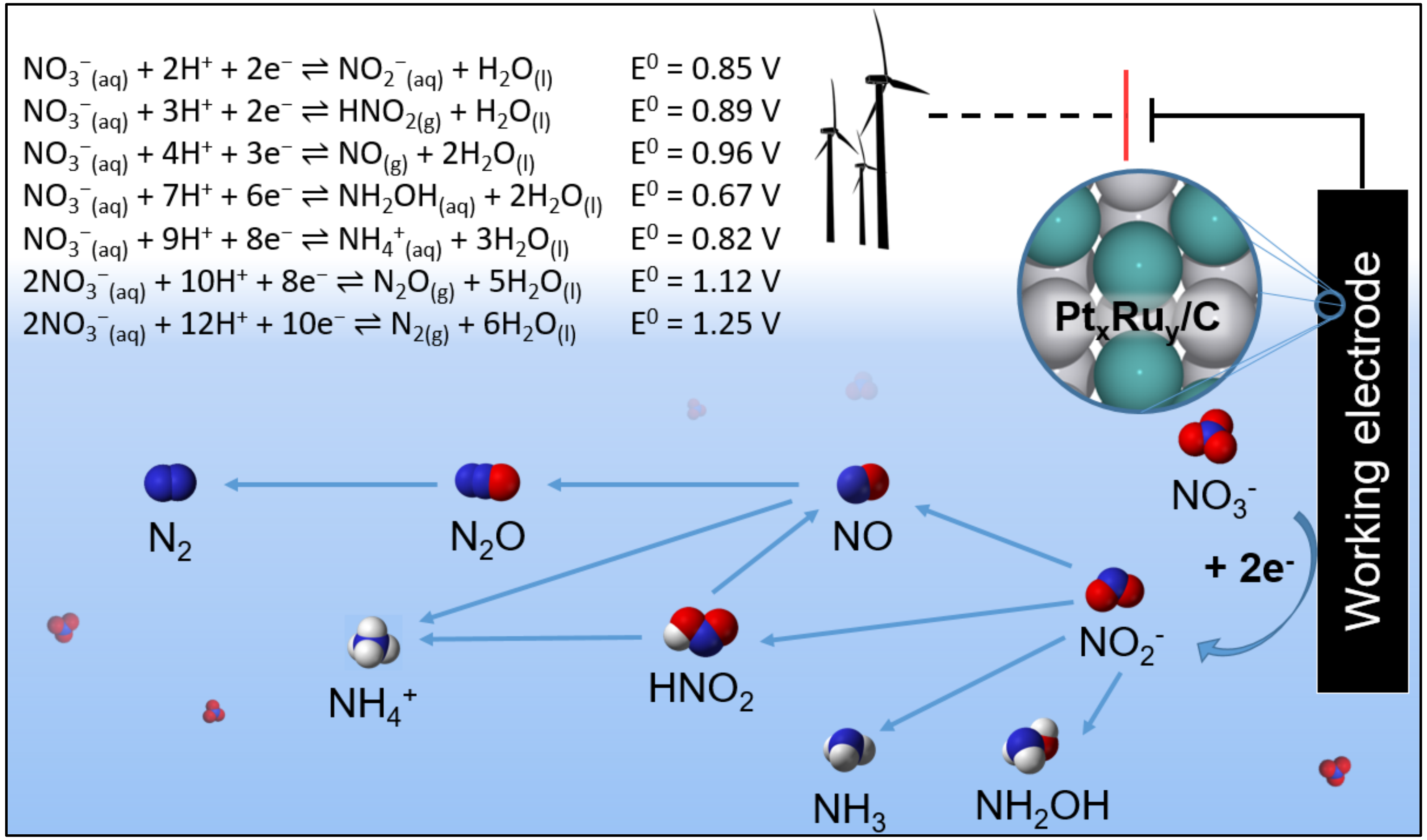
Northern Indian River Lagoon, Florida (2016)

Human toxicity

- "Blue baby syndrome"

[1] Image from Aerial Associates Photography, Inc. by Z. Haslick

The electrocatalytic nitrate reduction reaction (NO_3RR) may be a sustainable route for nitrate remediation while producing ammonia



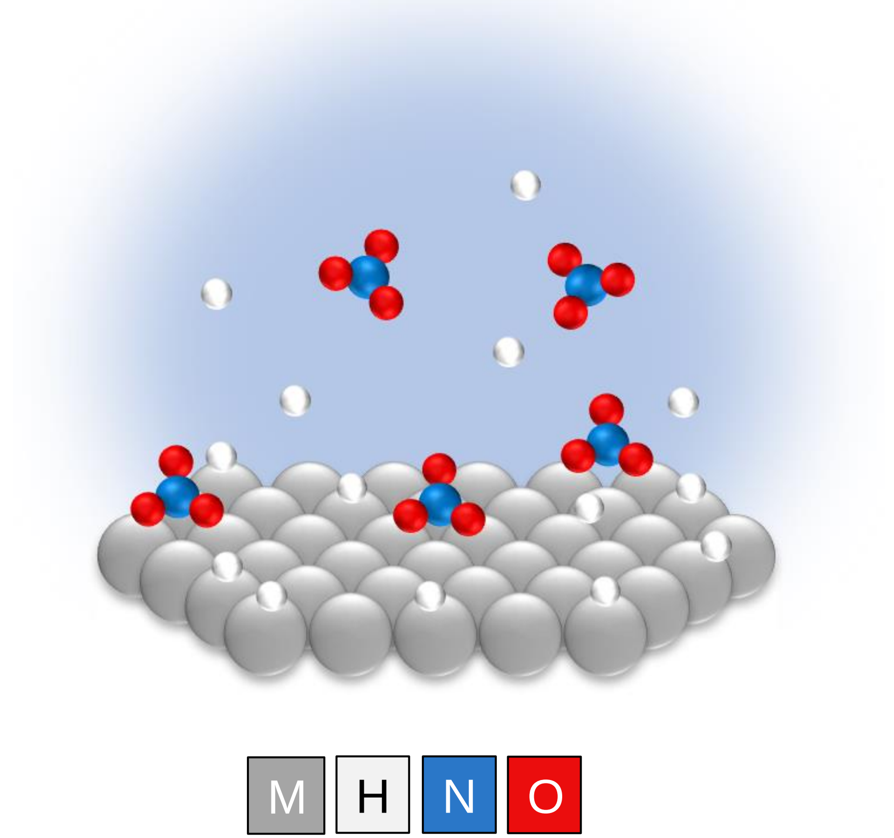
- Can be powered with renewable electricity.
- Don't need reductant (H_2) stream.
- Many benign or value-added products possible, especially NH_3/NH_4NO_3.
- *Challenge:* need more active, selective, and stable electrocatalysts.

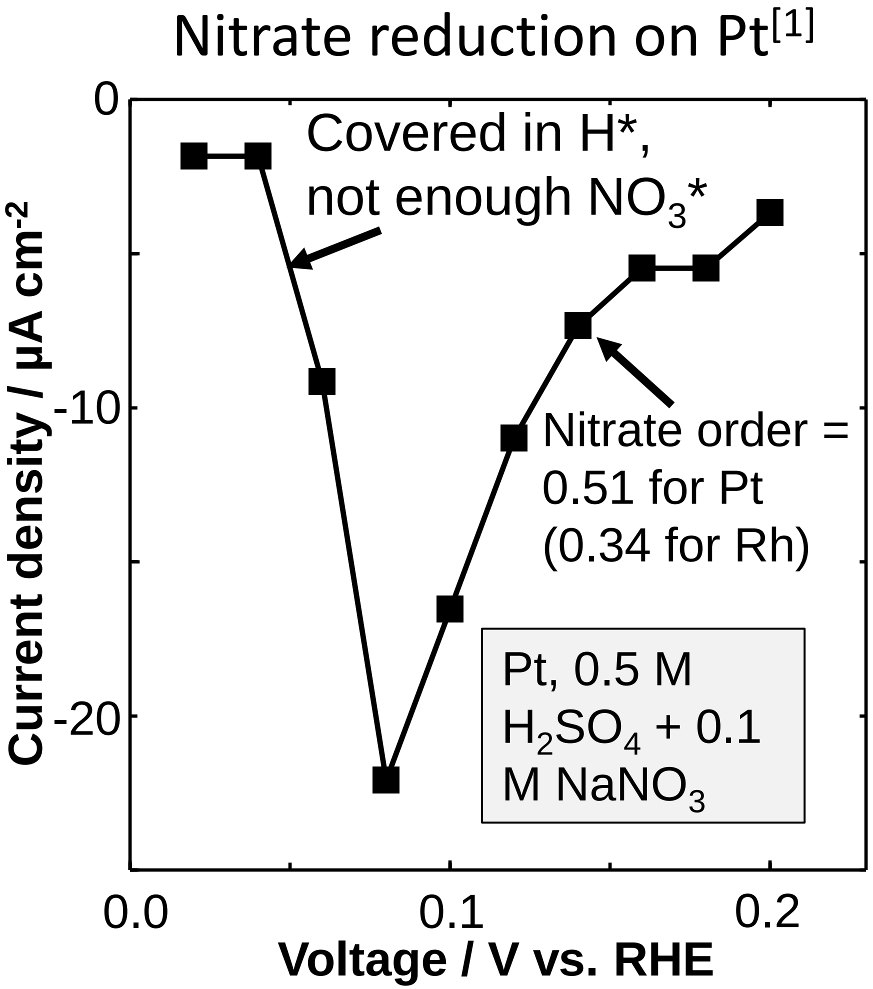
[1] P. van Langevelde, I. Katsounaros, and M. TM Koper. "Electrocatalytic nitrate reduction for sustainable ammonia production." *Joule* 5.2 (2021): 290-294.

Nitrate reduction is dependent on hydrogen and nitrate surface coverages

$$NO_3^- + * \rightleftharpoons NO_3* + e^-$$

$$H^+ + e^- + * \rightleftharpoons H*$$





[1] G. Dima, A. De Vooys and M. Koper, J. *Electroanal. Chem.*, 2003, **554**, 15

Multiple areas remain underexplored for NO_3RR, which hinders catalyst design and practical implementation

(i) Nitrate reduction catalyst activity and selectivity trends across metals and bimetallics.

(ii) Competitive adsorption between surface intermediates vs. applied potential and impact on catalyst performance.

(iii) Theoretical volcano plots not yet well-developed for this system.

(iv) Study of catalysts that can tolerate realistic nitrate-laden waste streams.

"Future work should also aim at theoretical studies trying to rationalise reactivity trends for NO_3 reduction…." [1]

[1] M. Duca and M. Koper. *Energy Environ. Sci* 2012, **5**, 9726 (*Perspective*)

In this talk, I will discuss:

Part 1: Elucidate nitrate reduction electrocatalyst activity and selectivity trends across metals and bimetallic alloys.[1-2]

Part 2: Synthesize and test Pt_xRu_y alloy catalysts for nitrate reduction based on theoretical volcano plot.[3]

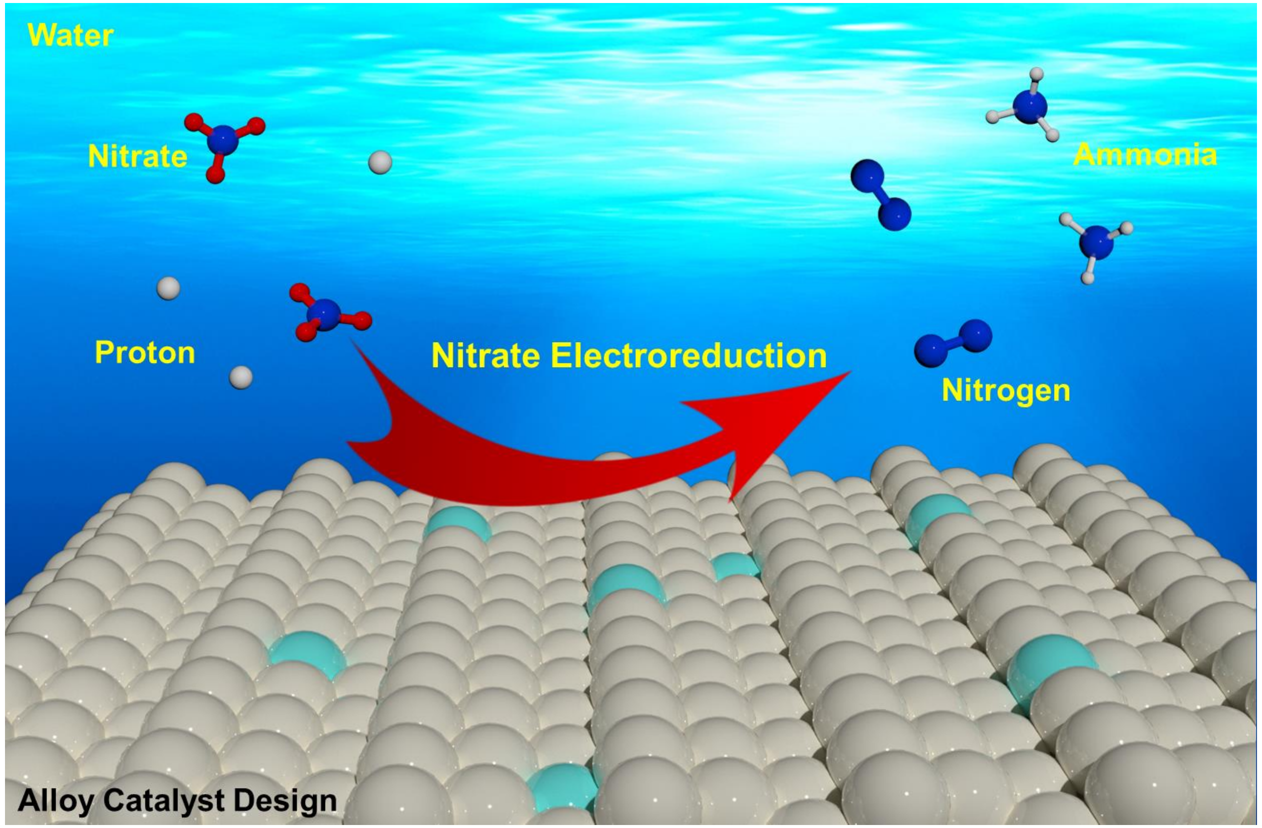
[1] Activity and selectivity trends in electrocatalytic nitrate reduction on transition metals, J.-X. Liu, D. Richards, N. Singh, B. R. Goldsmith, *ACS Catal.* 9, 7052 (2019).

[2] Role of electrocatalysis in the remediation of water pollutants, N. Singh, B. R. Goldsmith, *ACS Catal.* 10, 3365 (2020).

[3] Increasing electrocatalytic nitrate reduction activity by controlling adsorption through PtRu alloying, Z. Wang, S. D. Young, B. R. Goldsmith, N. Singh, *J. Catal.* 395, 143 (2021).

[4] Comparing electrocatalytic and thermocatalytic conversion of nitrate on platinum-ruthenium alloys, Z. Wang, E. Ortiz, B. R. Goldsmith, N. Singh, *Catal. Sci. Tech.* (2021). [just accepted]

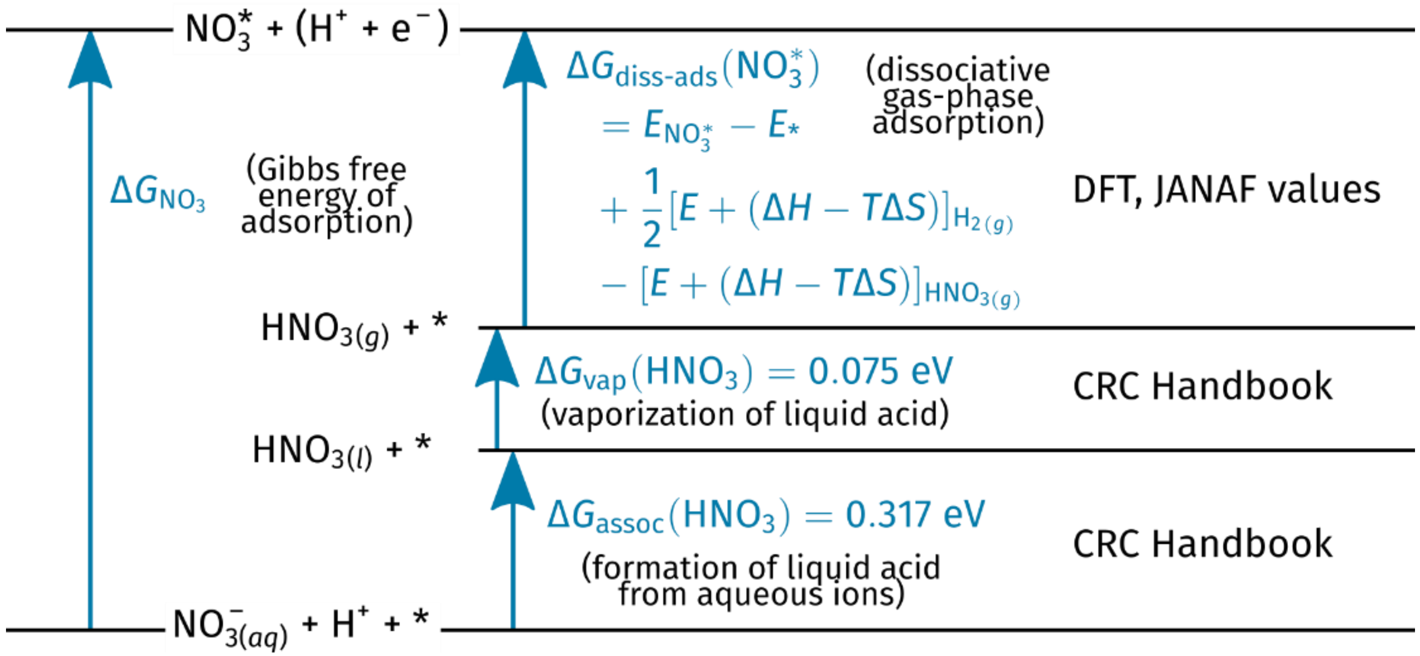
Part 1: Nitrate reduction electrocatalyst activity and selectivity trends across metals and bimetallic alloys



Studied eight transition metal stepped [(211) or (310)] surfaces under acidic conditions, namely, Co, Cu, Rh, Pd, Pt, Ag, Au, and Fe

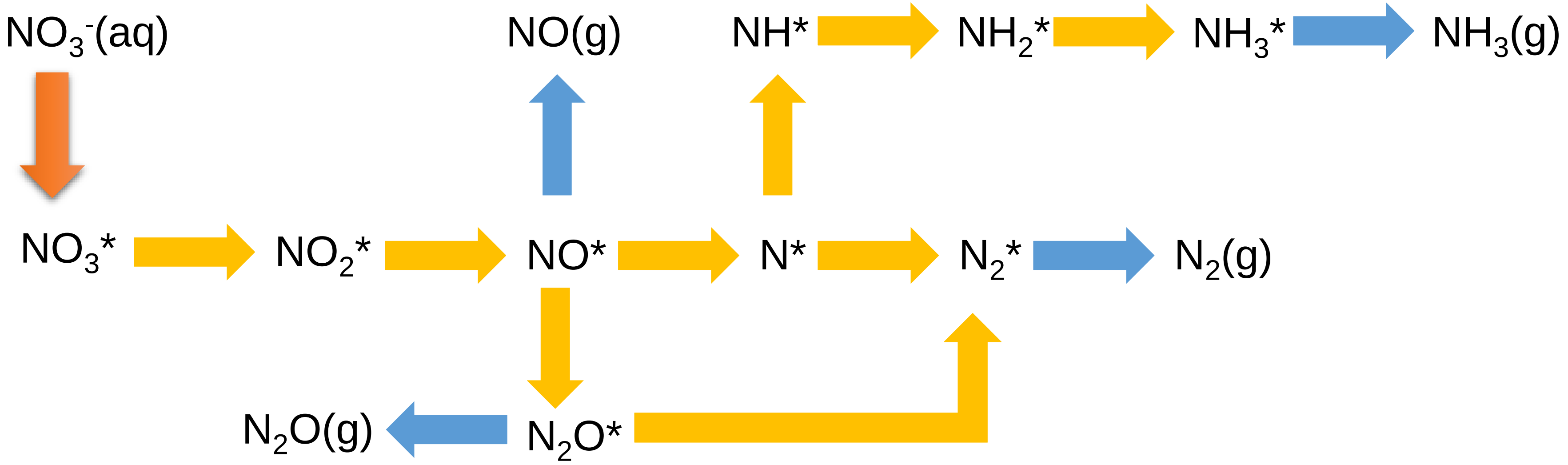
All DFT calculations were performed using PAW potentials and the PBE functional as implemented in the VASP package.

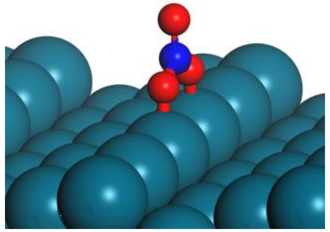
Thermodynamic cycle used to calculate the adsorption Gibbs free energy of NO_3^- in the aqueous phase.[1]



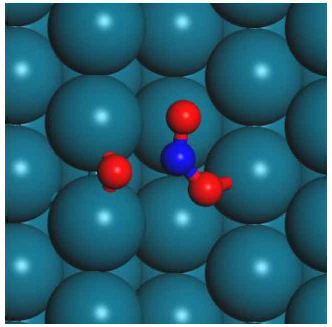
[1] F. Calle-Vallejo, M. Huang, J. B. Henry, M. T. Koper, A. S. Bandarenka, *PCCP*, 2013, **15**, 3196

We studied 19 elementary steps for electrocatalytic nitrate reduction on the eight transition metals

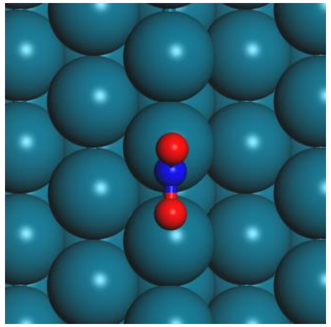




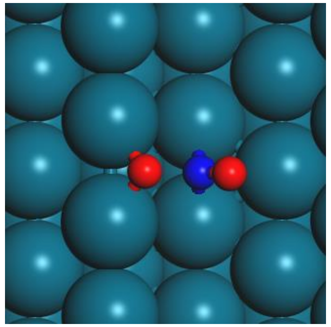
NO_3*



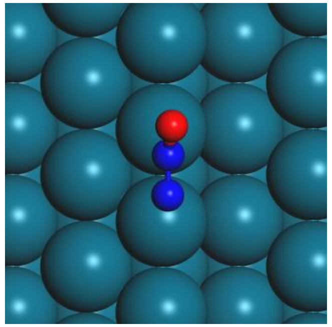
$NO_3^* \rightleftarrows NO_2^* + O^*$



NO_2*



$NO_2^* \rightleftarrows NO^* + O^*$



N_2O*

- Hydroxylamine formation not considered

Analyzing the origin of activity dependence on applied potential for NO_3RR over transition metal catalysts

Perform microkinetic modeling for NO_3RR on the 8 metal surfaces between –0.2 and 0.4 V vs RHE at 300 K.

$$r_i = \sum_{j=1}^{N} \left(k_j \nu_i^j \prod_{k=1}^{M} c_k^{\nu_k^j} \right)$$

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

$$\frac{\partial \theta_i}{\partial t} = \sum_{j}^{2R} \left(\nu_{j,i} k_j \prod_{q}^{N_i} \theta_{q,j}^{\nu_{q,j}} \right)$$

Input file for mkmcxx code:

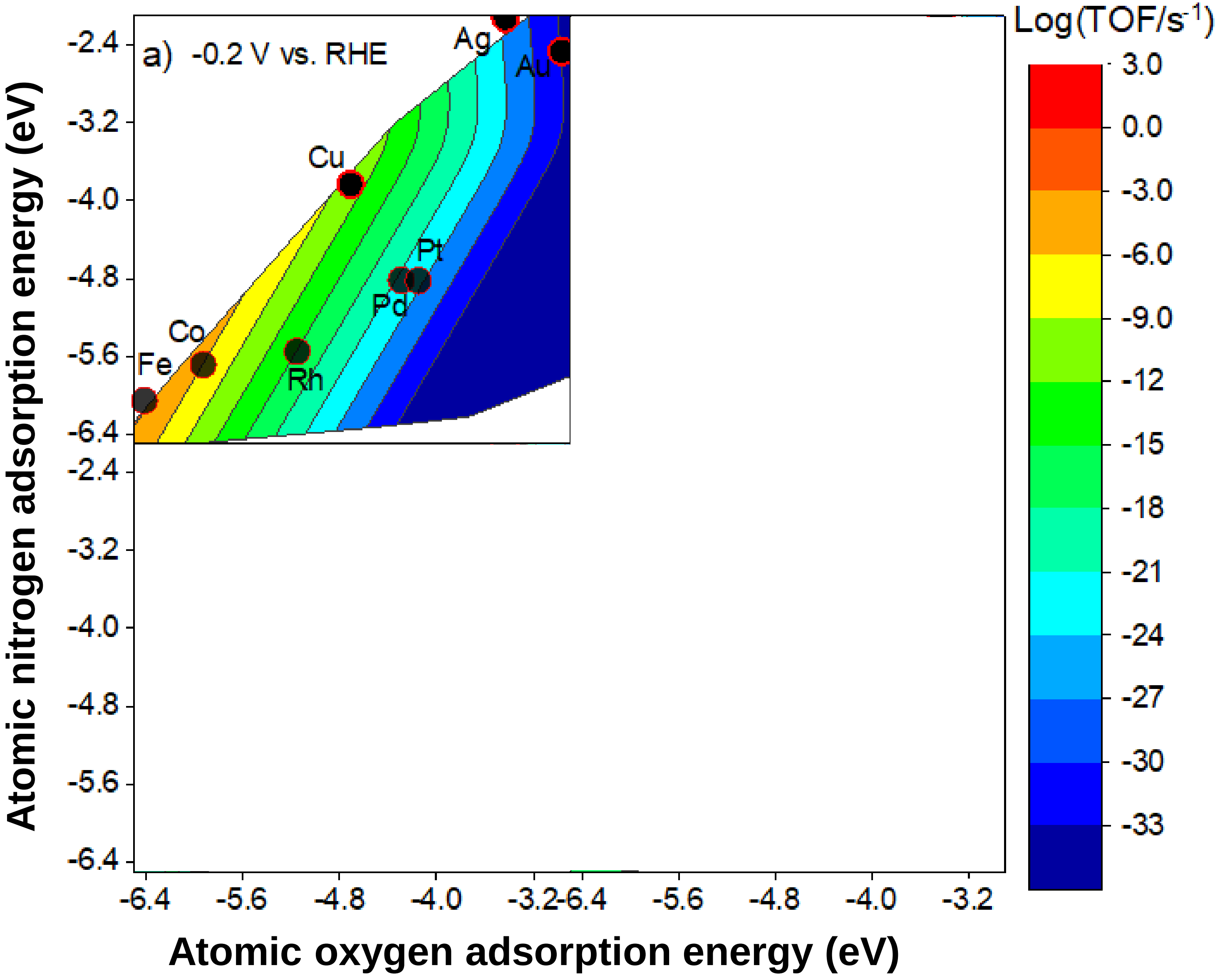
- ✓ Adsorption energies of reactant and product
- ✓ Forward and backward activation barriers and reaction energetics
- ✓ Temperature, pressure

Output:

- ✓ Reaction rate, coverages, degree of rate control, selectivity

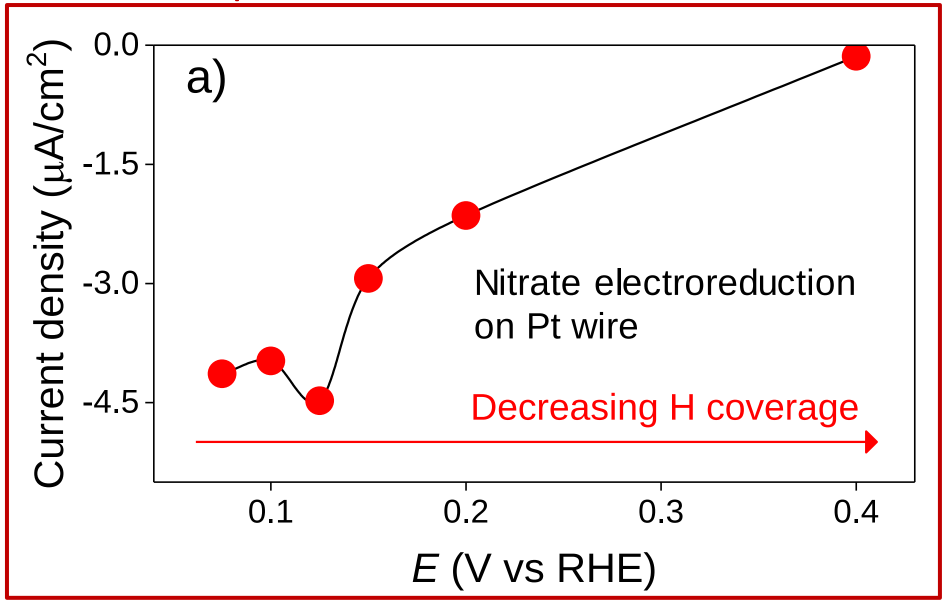
https://www.mkmcxx.nl/

Theoretical volcano plots as a function of potential



Reaction conditions are T = 300 K with a H^+/NO_3^- molar ratio of 1:1.

The maximum rates with applied potential on Pt qualitatively agree between DFT calculations and our experimental measurements



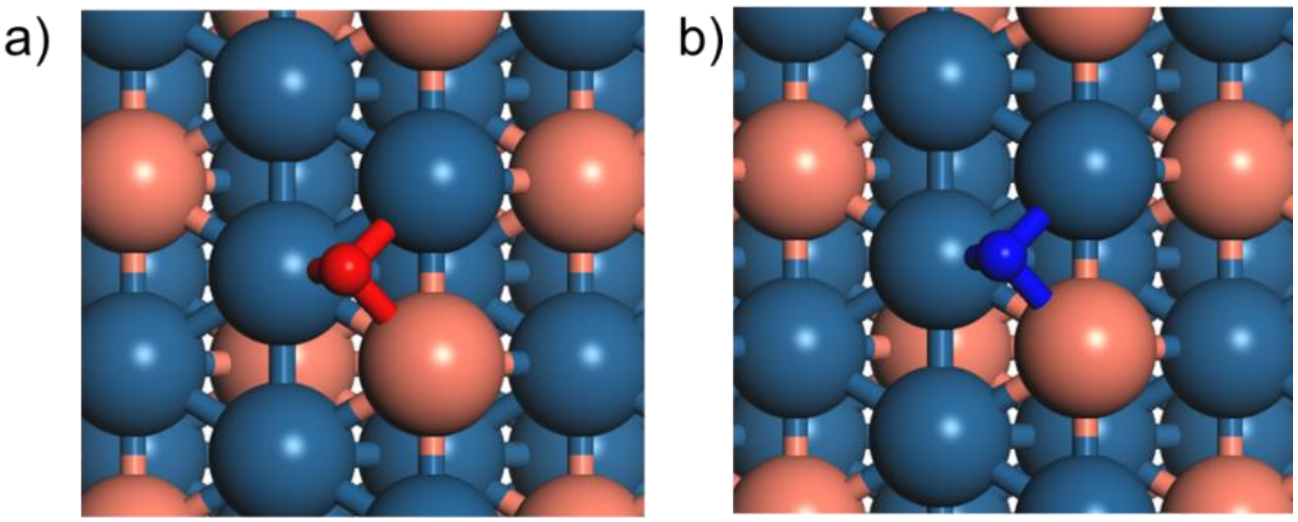
General trends in activity with metal

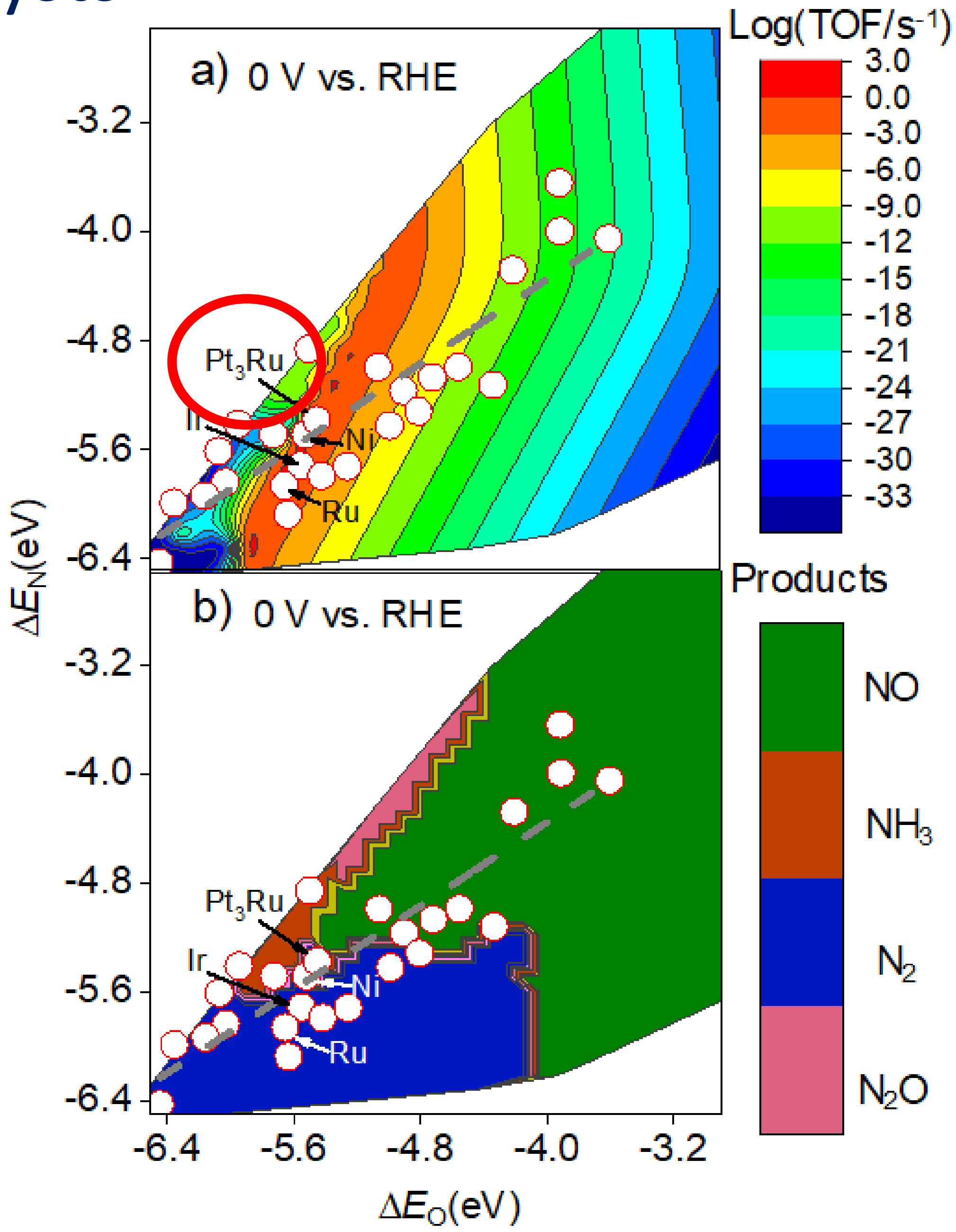
Max activity trends of Rh > Cu > Pd/Pt > Ag > Au agree with experimental observations in acids. [1]

[1] G. Dima, A. De Vooys and M. Koper, J. *Electroanal. Chem.*, 2003, **554**, 15

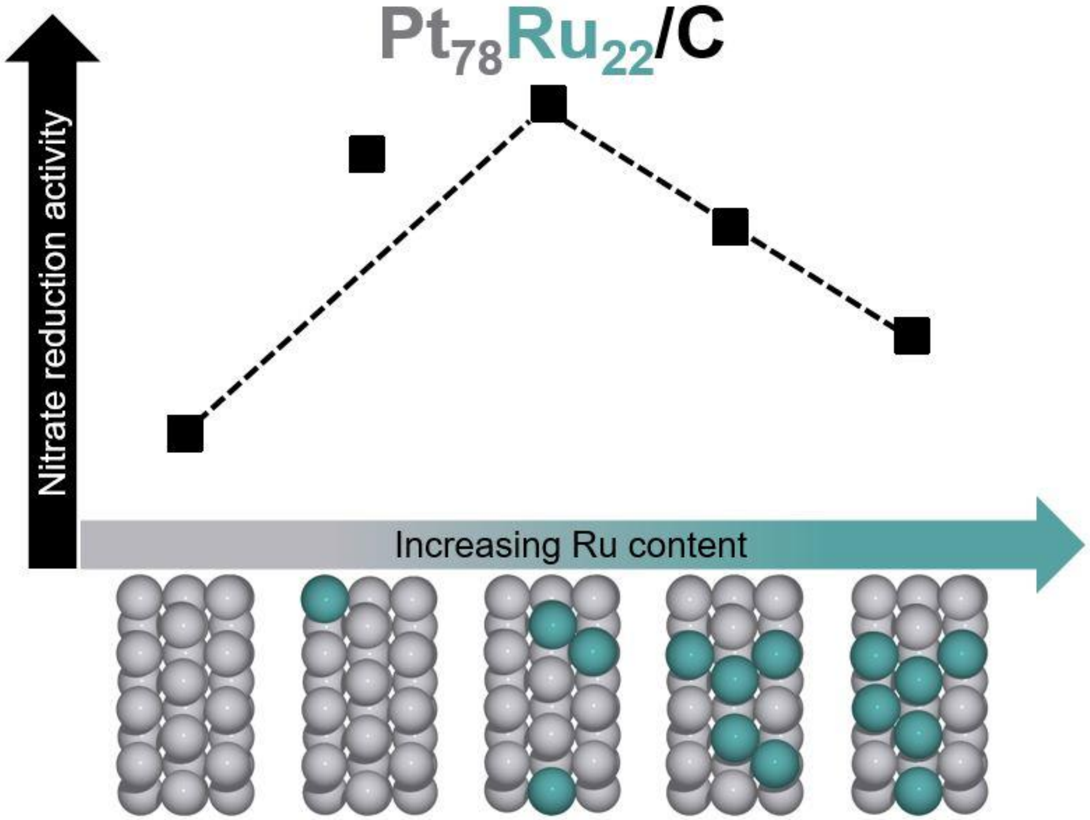
Predicting metal and bimetallic alloy catalysts for NO_3RR using linear scaling relations

Studied the NO_3RR activity and selectivity of four additional transition metals (Ru, Ir, Ni and Zn) and 22 Fe_3M, Pt_3M, and Rh_3M alloys.





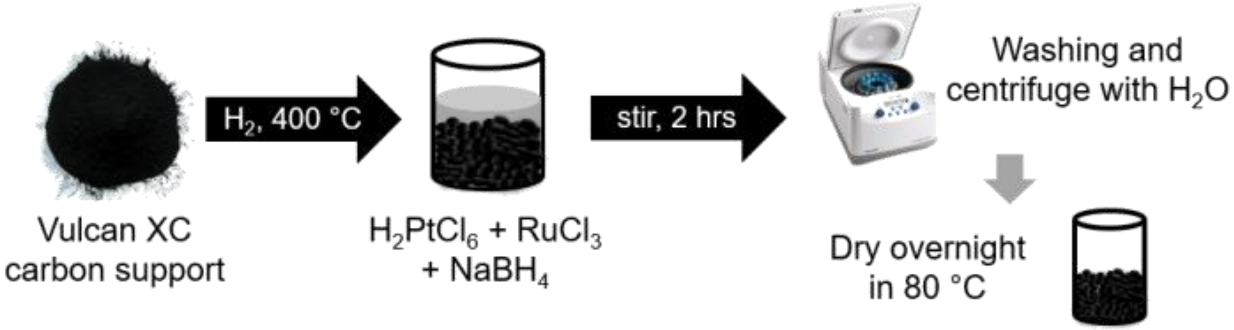
Part 2: Synthesize and test Pt_xRu_y alloy catalysts for nitrate reduction based on theoretical volcano plot

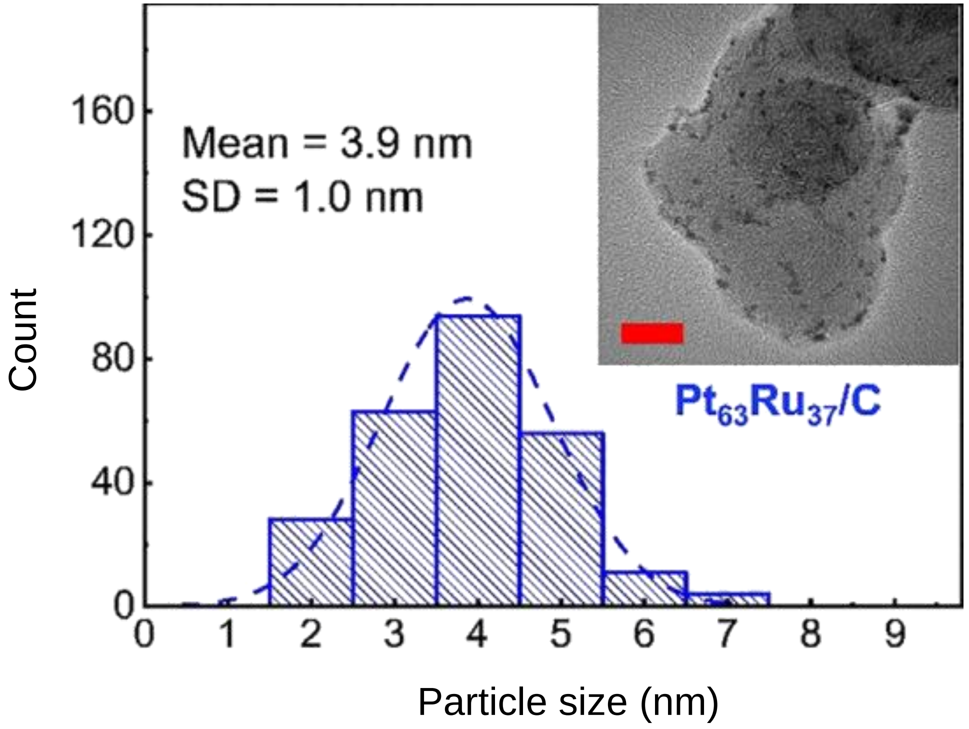


[1] Z. Wang, S. D. Young, B. R. Goldsmith, N. Singh, *J. Catal.* 395, 143 (2021).

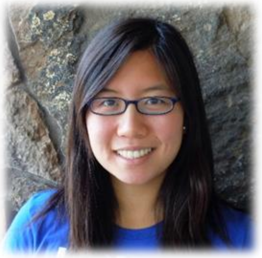
Synthesis of Pt_xRu_y/C Catalysts

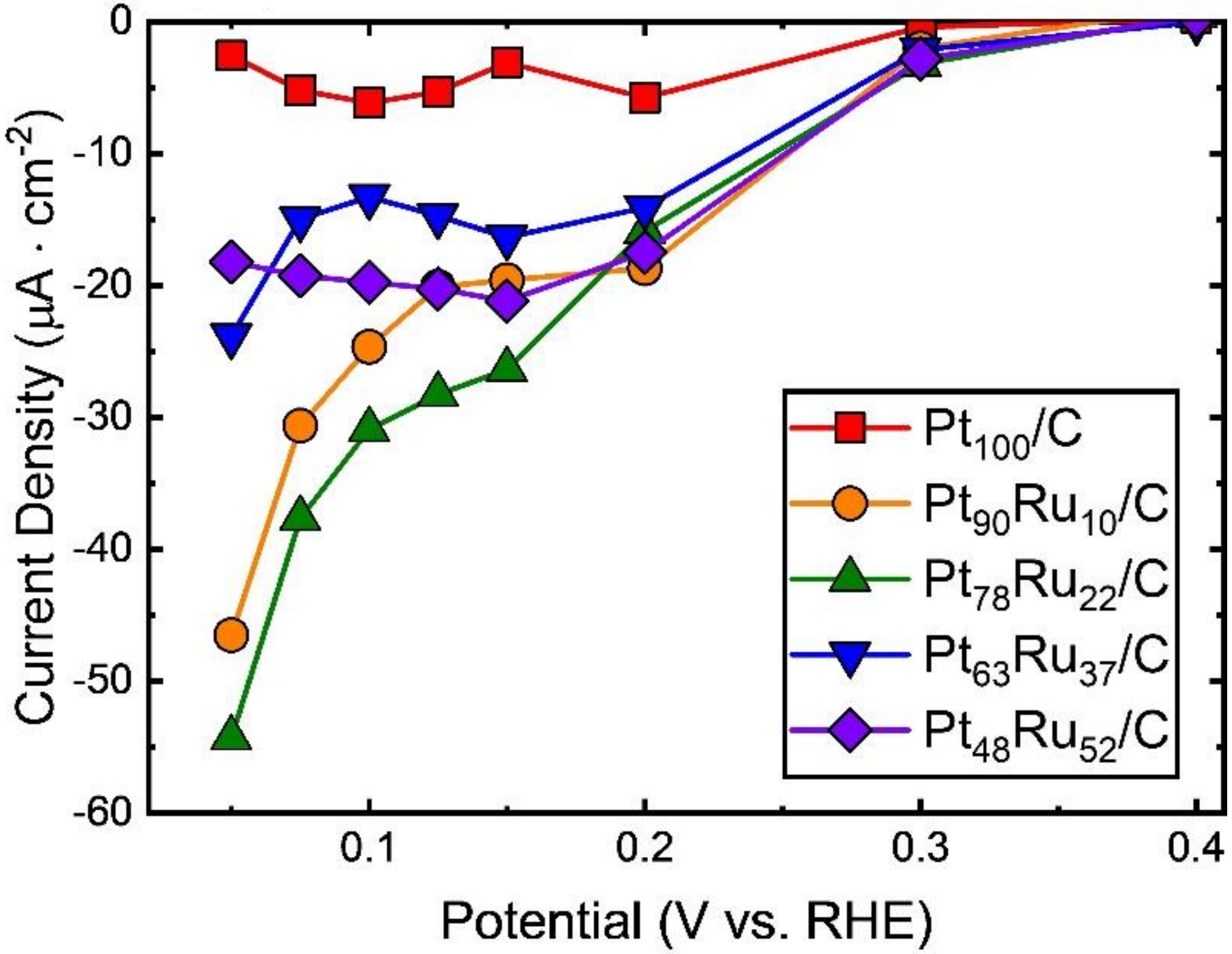
- Five Pt_xRu_y/C catalysts synthesized using a $NaBH_4$ reduction technique:
  - Pt_{100}/C, $Pt_{90}Ru_{10}$/C, $Pt_{78}Ru_{22}$/C, $Pt_{62}Ru_{37}$/C, and $Pt_{48}Ru_{52}$/C.
- Synthesis created nanoparticles of 3–6 nm in diameter.
- No significant phase or surface segregation observed.
- Stable repeated cyclic voltammograms of prepared electrodes suggests stability under electrochemical conditions.

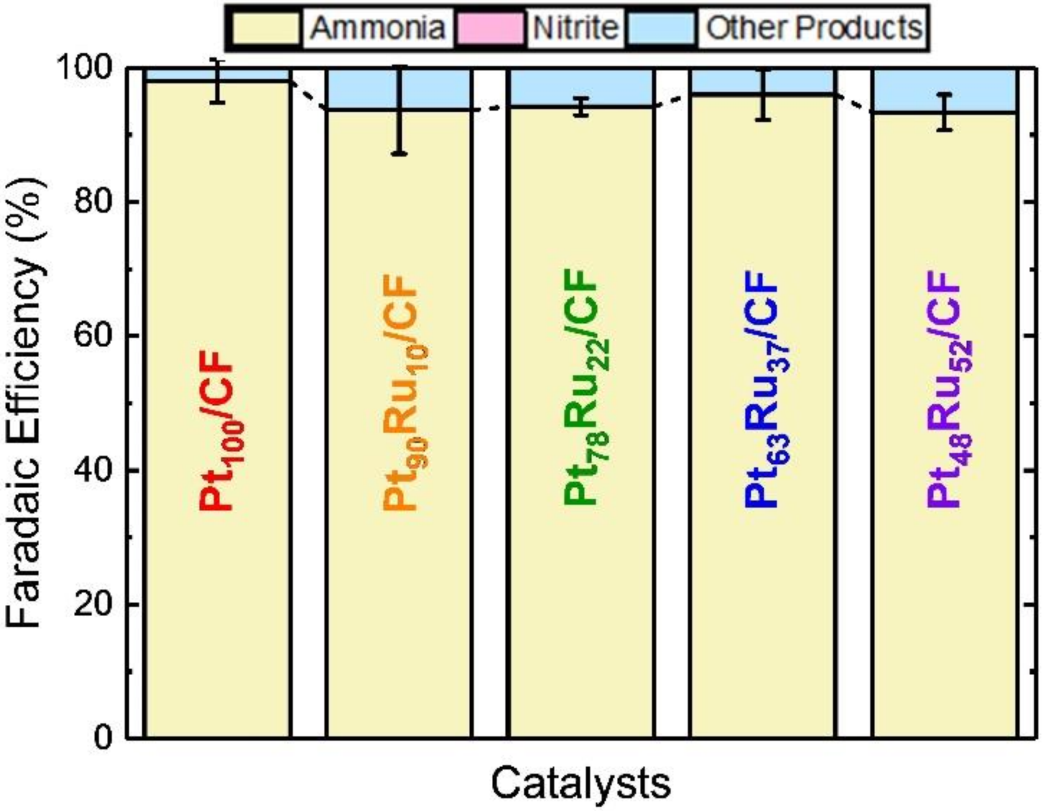




Synthesized and tested Pt_xRu_y alloys.
→ found to be more active than pure Pt and have high FE to ammonia

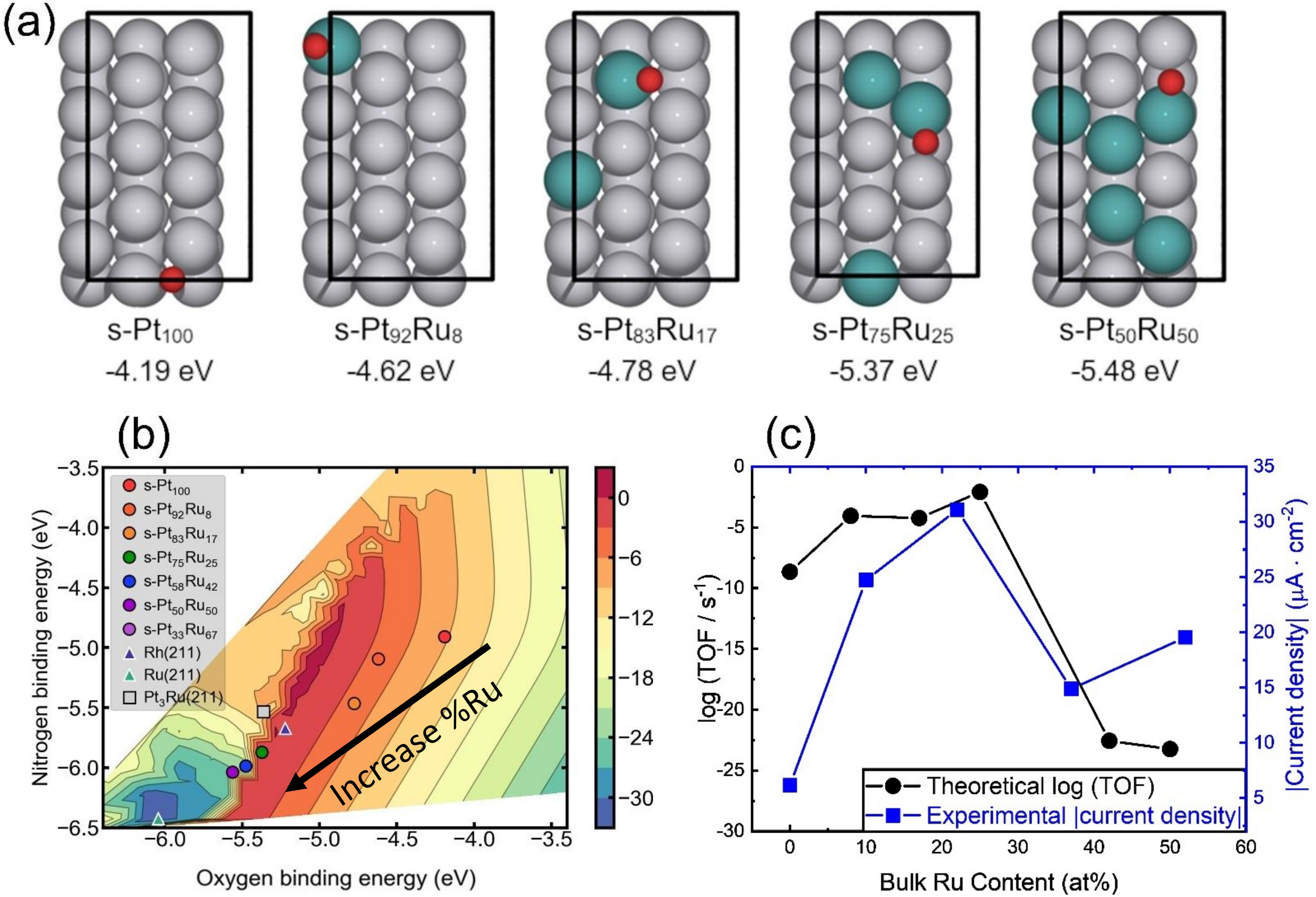






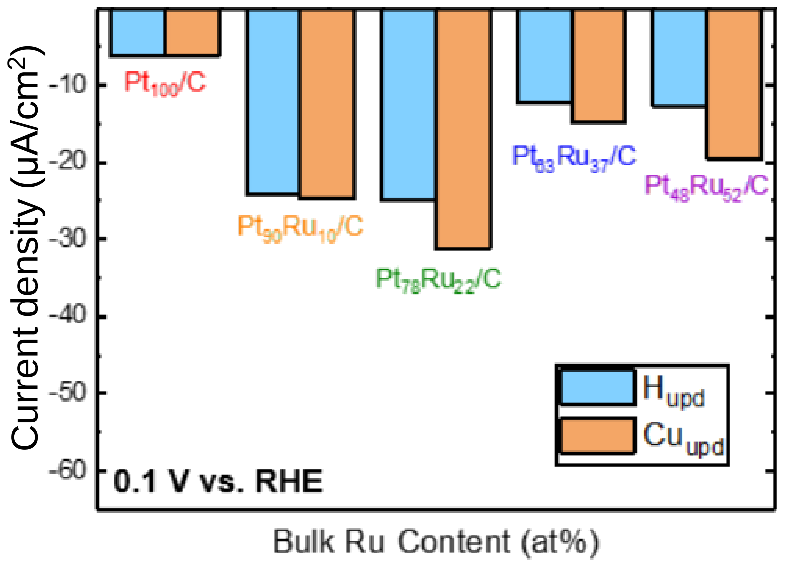
*ECSA measured by Cu underpotential deposition

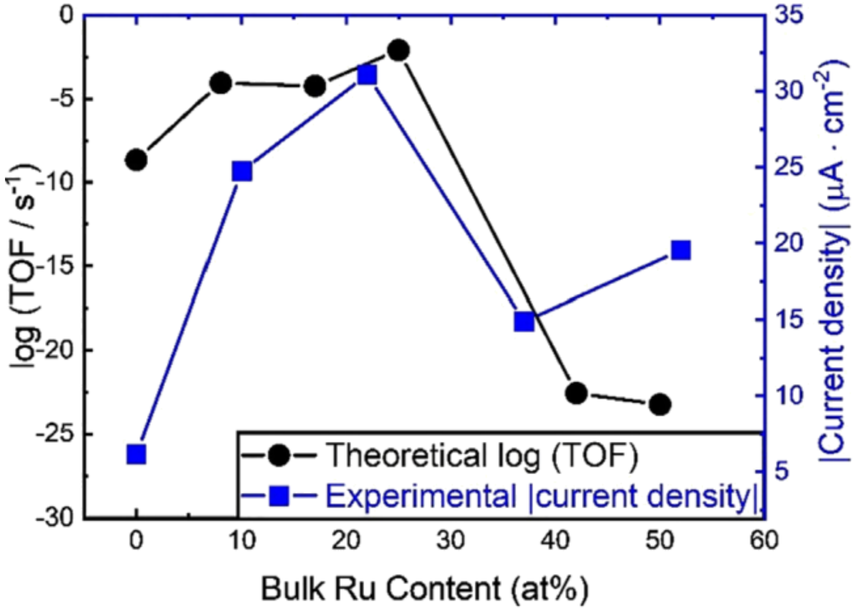
Increasing electrocatalytic nitrate reduction activity by controlling adsorption strength through PtRu alloying



Summary of Part 2 on Pt_xRu_y

- $Pt_{78}Ru_{22}/C$ is 6 times more active than Pt/C at 0.1 V vs. RHE.
- Electrochemically stable, > 93% Faradaic efficiency towards NH_3, and three times cheaper than using Pt/C.
- Theoretical volcano plot based on pure metal microkinetics rationalized the activity trends of Pt_xRu_y/C.





[1] Z. Wang, S. D. Young, B. R. Goldsmith, N. Singh, *J. Catal.* 395, 143 (2021).

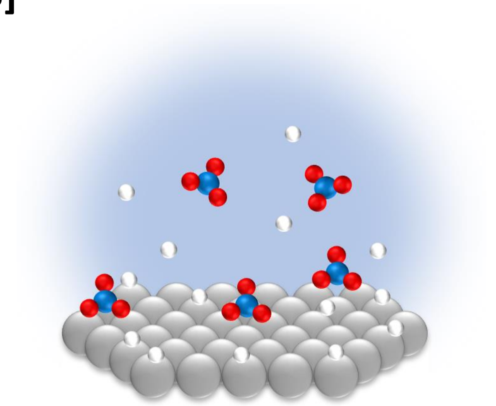
[2] Z. Wang, E. Ortiz, B. R. Goldsmith, N. Singh, *Catal. Sci. Tech.* (2021). [just accepted]

To Summarize:

- Predicted NO_3RR electrocatalyst activity and selectivity trends across metals and bimetallic alloys. Developed theoretical volcano plots.[1-2]

- Synthesized and tested Pt_xRu_y alloys for nitrate reduction based on theoretical volcano plot. Six times more active than pure Pt and high FE to ammonia.[3]

<u>Future work should entail:</u>



(1) Testing NO_3RR catalysts in flow reactors.

(2) Performing detailed techno-economic analysis.

(3) Studying catalysts in the presence of poisons.

(4) Atomistic modeling studies that explicitly include solvent and pH effects are also needed.

(5) More direct comparisons of electrocatalytic vs. thermocatalytic nitrate reduction.[4]

[1] J.-X. Liu, D. Richards, N. Singh, B. R. Goldsmith, *ACS Catal.* 9, 7052 (2019).
[2] N. Singh, B. R. Goldsmith, *ACS Catal.* 10, 3365 (2020).
[3] Z. Wang, S. D. Young, B. R. Goldsmith, N. Singh, *J. Catal.* 395, 143 (2021).
[4] Z. Wang, E. Ortiz, B. R. Goldsmith, N. Singh, *Catal. Sci. Tech.* (2021). [just accepted]