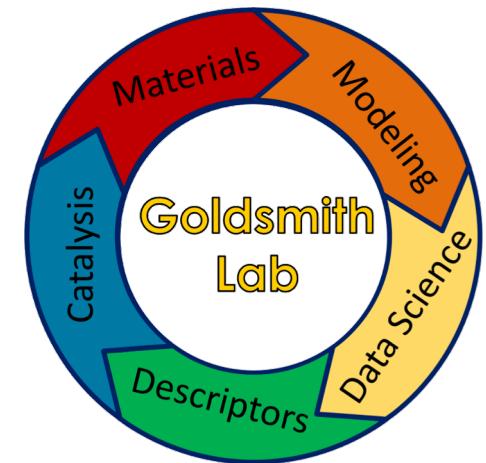
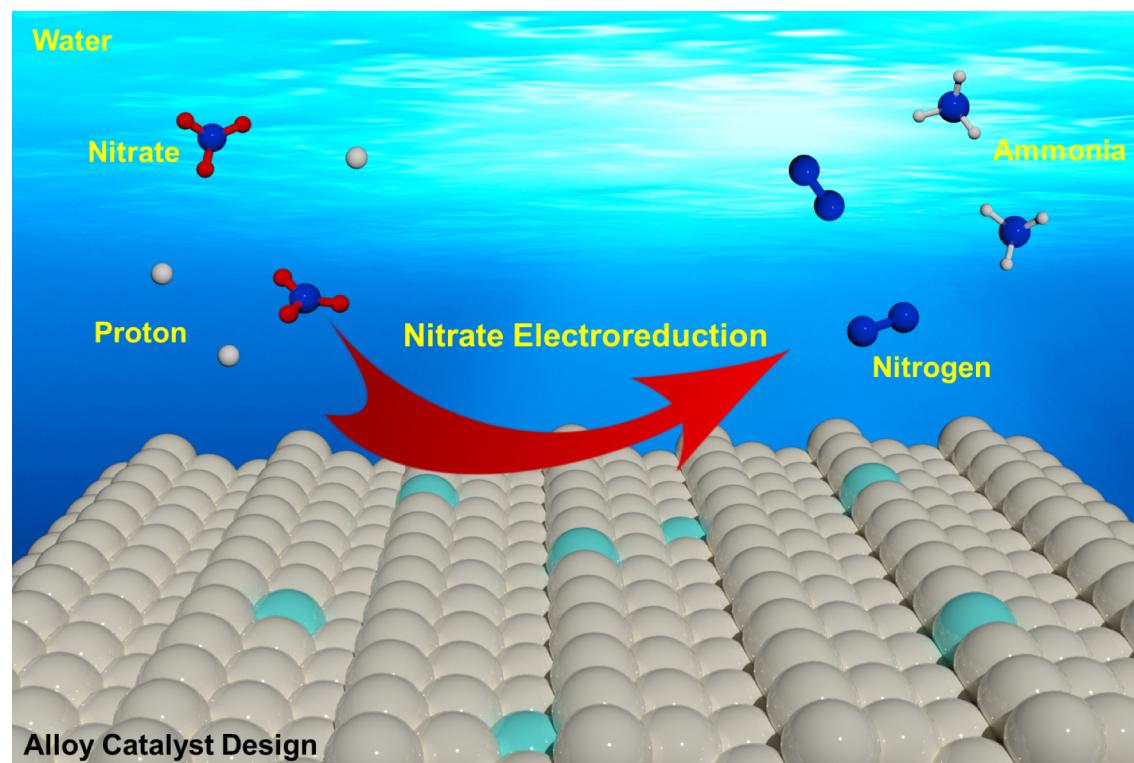


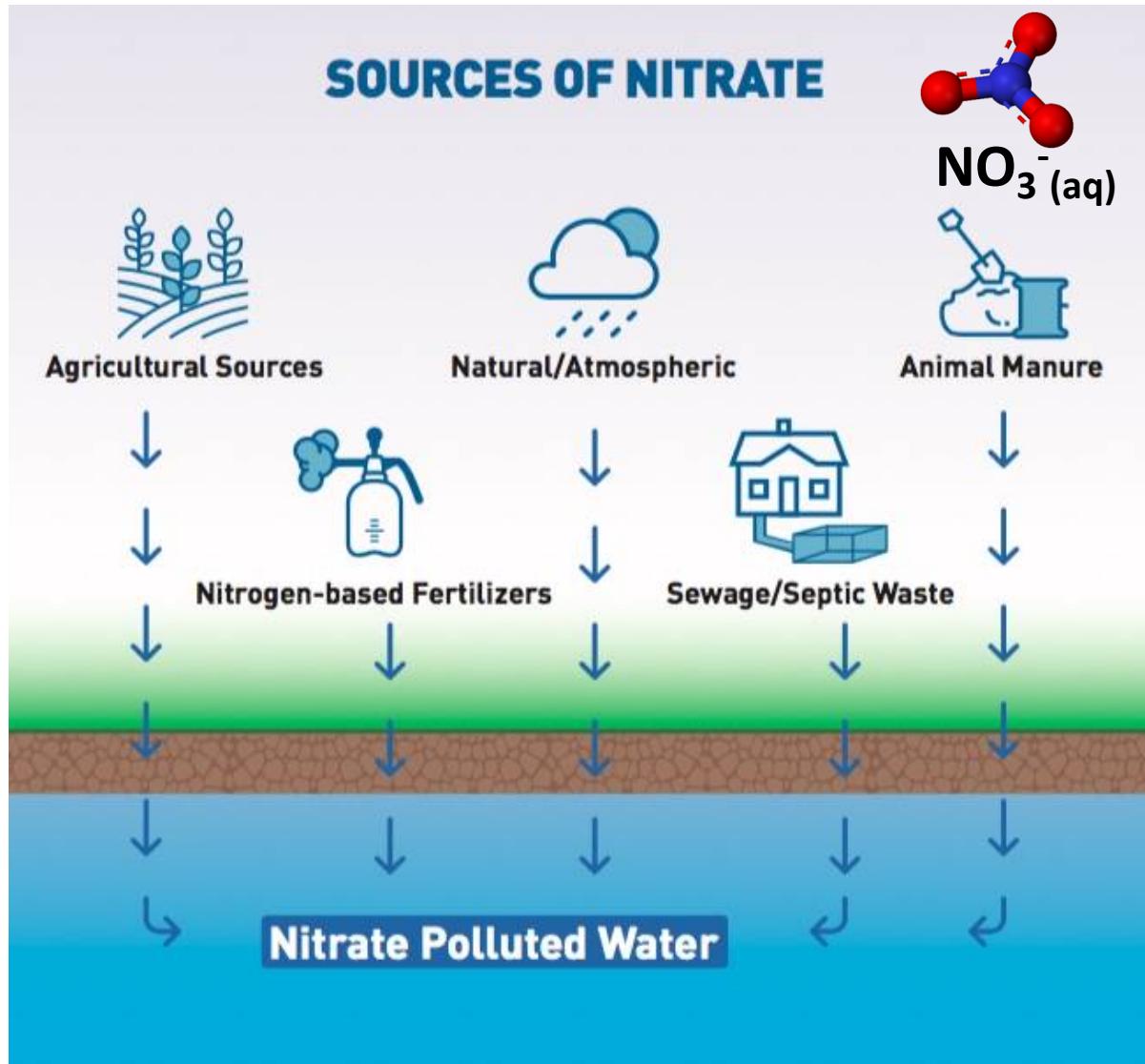
# Activity and Selectivity Trends in Electrocatalytic Nitrate Reduction on Transition Metals

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Department of Chemical Engineering*



# Nitrate accumulation in aquatic ecosystems results largely from fertilizer production



## Industrial $\text{N}_2$ fixation

roughly  $10^8$  metric tonnes per year

## Low level nuclear waste (non-radioactive portion)



Nitrate accumulation has detrimental environmental and health effects

### Algal blooms and dead zones



[1]

*Lake Erie, Michigan (2017)*



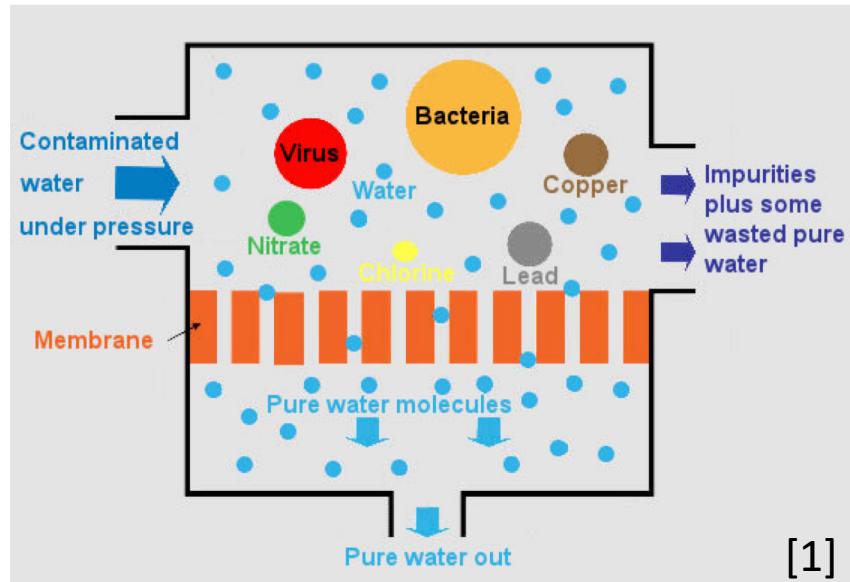
*Northern Indian River Lagoon, Florida (2016)*

### Human toxicity

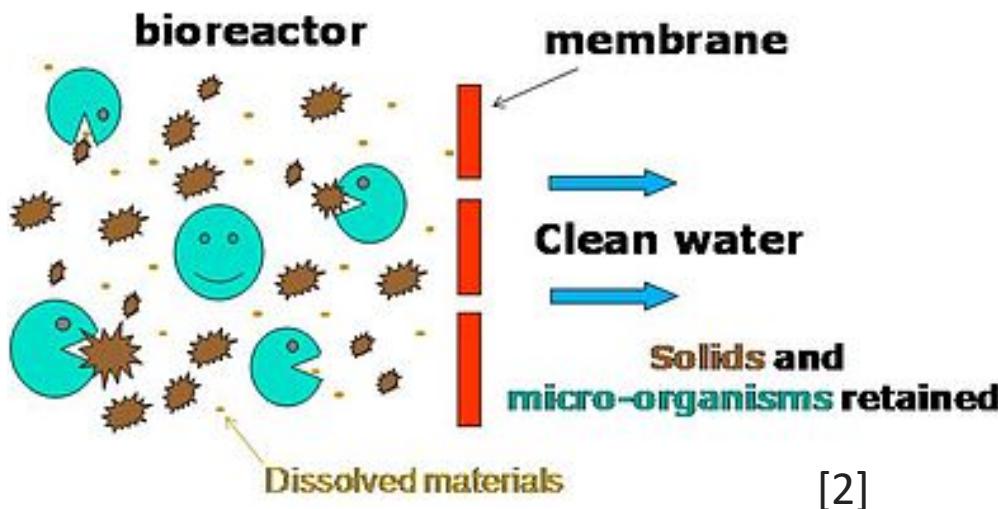
- “Blue baby syndrome”

# Overview of competing methods for nitrate remediation

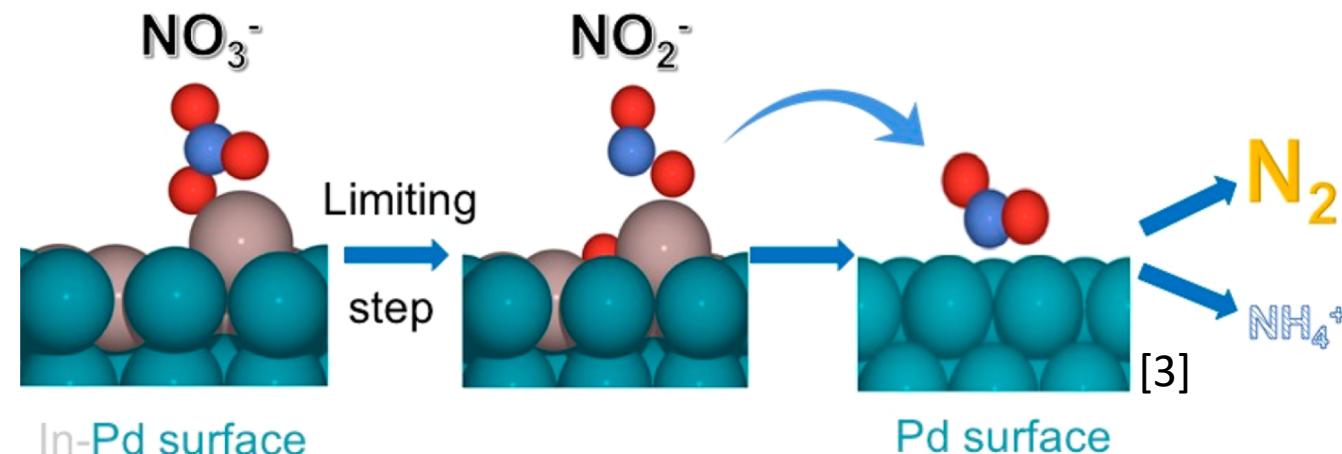
## Physical



## Biological



## Thermocatalytic or electrocatalytic

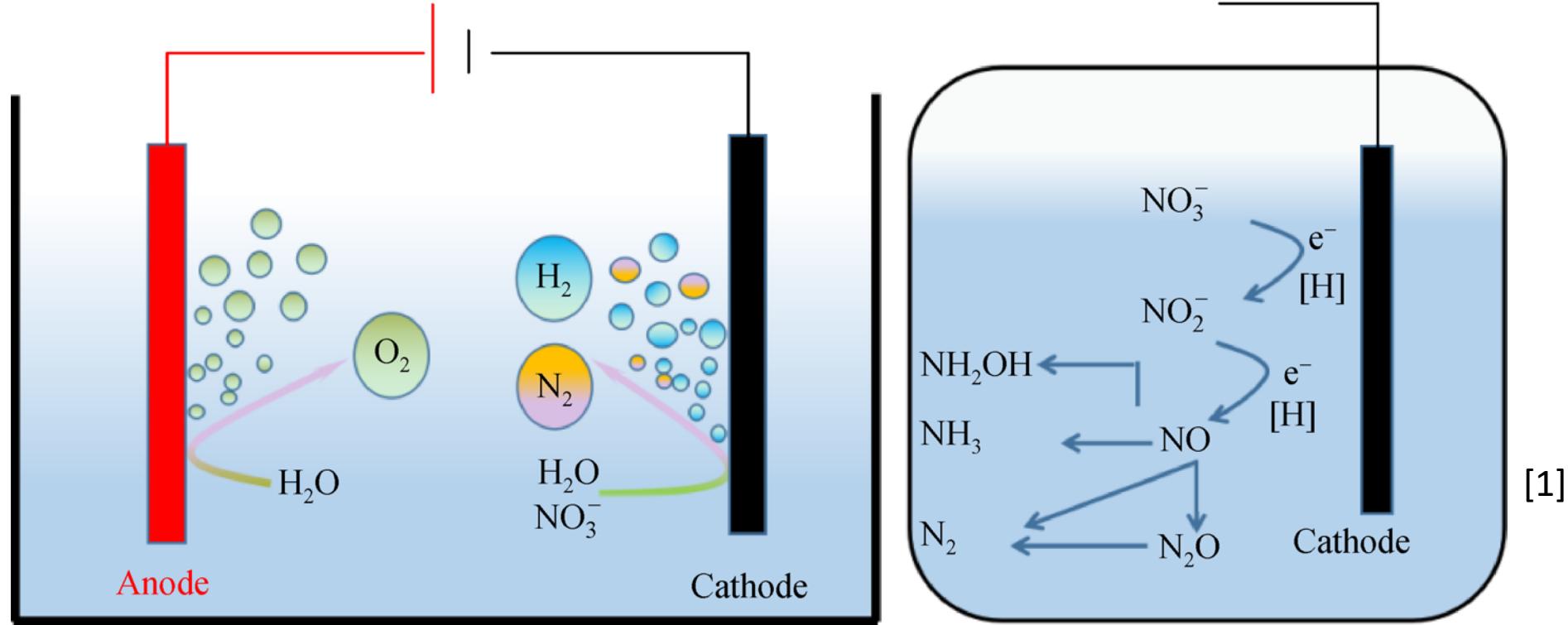


[1] <https://www.ampac1.com/reverse-osmosis>

[2] Smith, R. L., Ceazan, M. L., & Brooks, M. H. (1994). *Appl. Environ. Microbiol.*, 60(6), 1949-1955.

[3] Guo, Sujin, et al. *ACS Catalysis* 2017, 8, 503

Electrocatalytic nitrate reduction (NO<sub>3</sub>RR) is a promising way to remove nitrate using renewable electricity without producing a secondary waste stream<sup>[1-3]</sup>



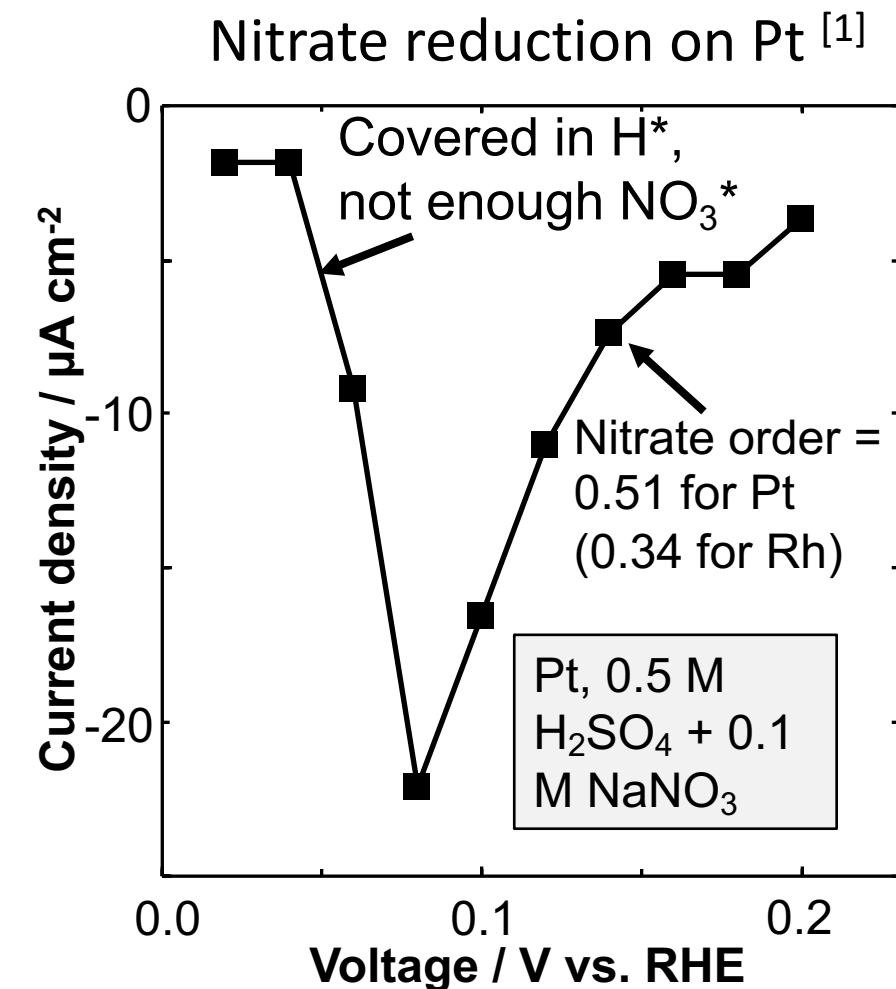
- [1] Xu, Dong, et al. *Frontiers of Environmental Science & Engineering* 2018, 12, 9  
[2] M. Duca and M. Koper. *Energy Environ. Sci.* 2012, 5, 9726  
[3] S. Garcia-Segura et al. *Appl. Catal., B*, 2018, 236, 546

The widespread use of  $\text{NO}_3\text{RR}$  is hindered because no sufficiently active, selective, and stable electrocatalyst is known.

$\text{NO}_3\text{RR}$  on Pt and Rh has a measured TOF  $\approx 0.1 - 1 \text{ s}^{-1}$

### Measured $\text{NO}_3\text{RR}$ activity trends<sup>[1]</sup>

- Platinum group metals: Rh > Ru > Ir > Pd  $\approx$  Pt.
- Coinage metals less active than PGMs for  $\text{NO}_3\text{RR}$ , with the exception of Cu, and have relative activities of Cu > Ag > Au.
- Alloys can have superior activity and selectivity



# Multiple areas remain underexplored for $\text{NO}_3\text{RR}$ , which hinders catalyst design

- (i) Nitrate reduction electrocatalyst activity and selectivity trends across metals and bimetallics.
- (ii) Competitive adsorption between surface intermediates vs. applied potential and impact on catalyst performance
- (iii) Volcano plots not yet shown for this system

*“Future work should also aim at theoretical studies trying to rationalise reactivity trends for  $\text{NO}_3$  reduction....” and “We stress that *in situ* measurements should routinely become part of any fundamental study [of nitrate reduction]”<sup>[1]</sup>*

In this talk, we use DFT modeling and microkinetics simulations combined with experimental *in situ* XANES and EXAFS, cyclic voltammetry, and steady-state activity measurements to study the nature of  $\text{NO}_3\text{RR}$  on transition metal electrocatalysts.<sup>[2]</sup>

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

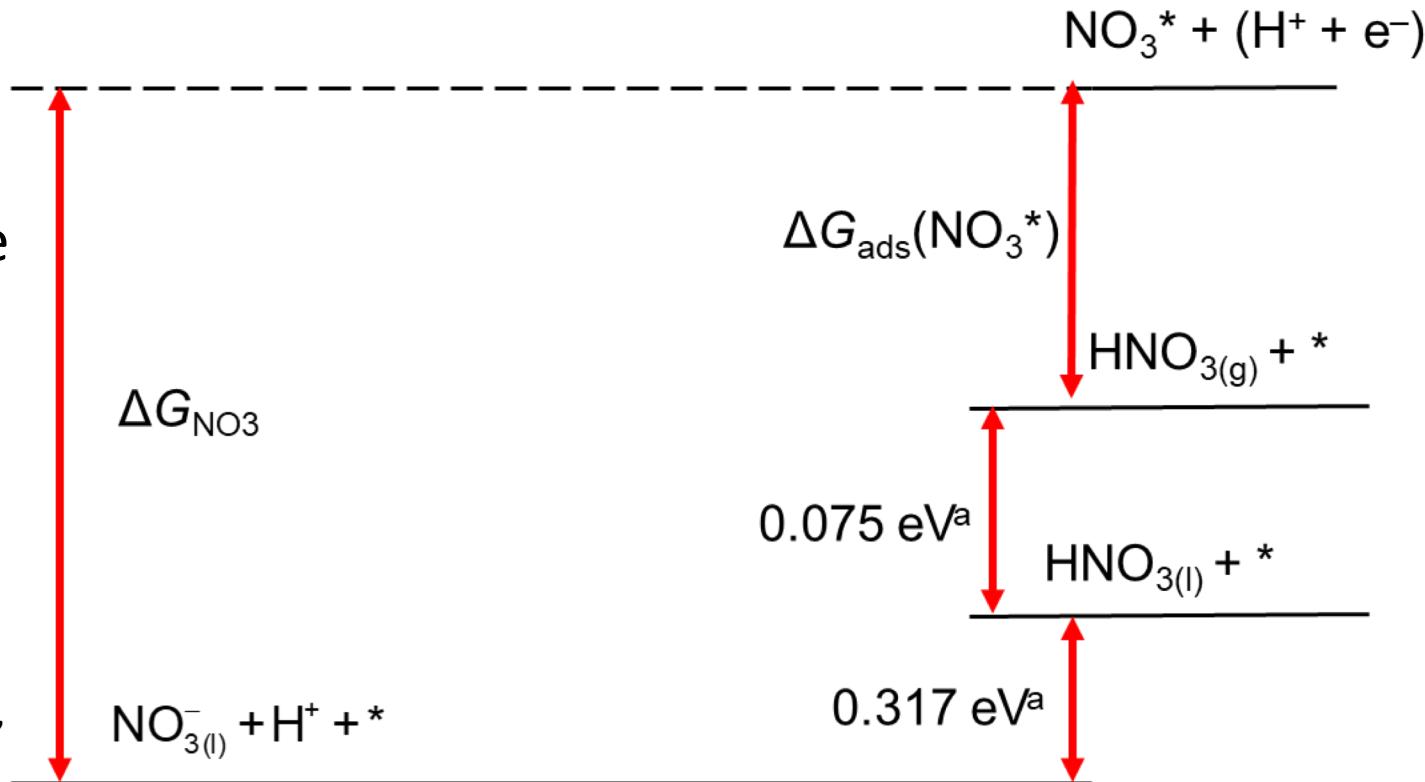
[2] J.-X. Liu, D. Richards, N. Singh\*, B. R. Goldsmith\*, *Under Review*

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.



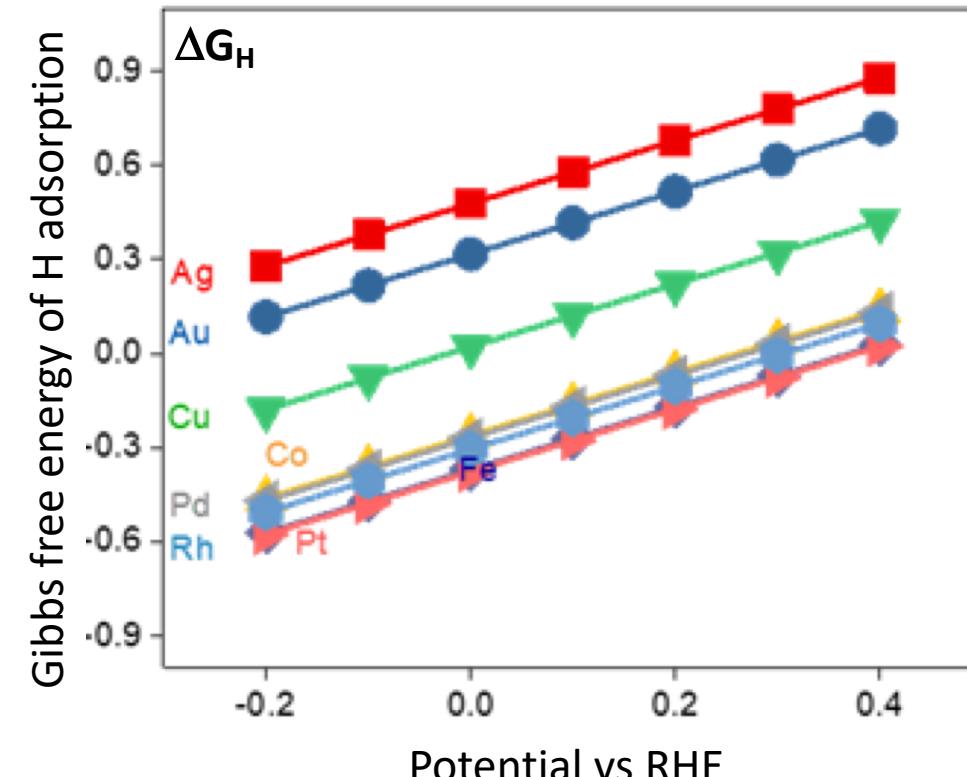
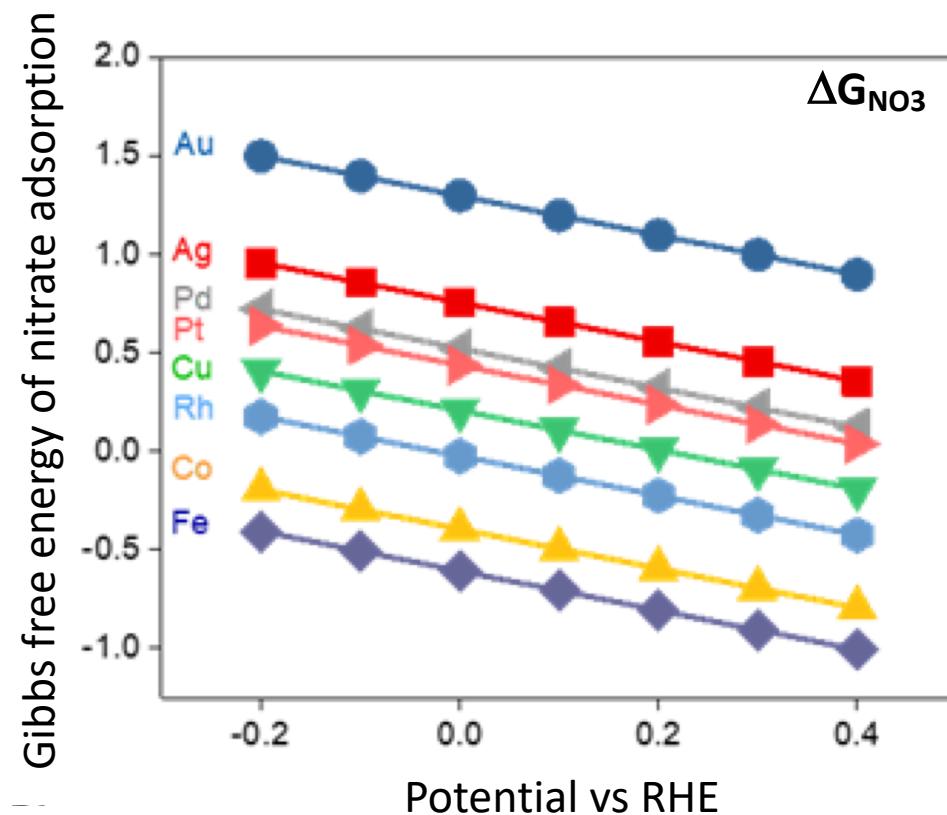
Thermodynamic cycle used to calculate the adsorption Gibbs free energy of  $\text{NO}_3^-$  in the aqueous phase.<sup>[1]</sup>



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

# Modeling the potential dependent thermodynamics and kinetics

- Applied potential on thermodynamics treated using the computational hydrogen electrode.<sup>[1]</sup>

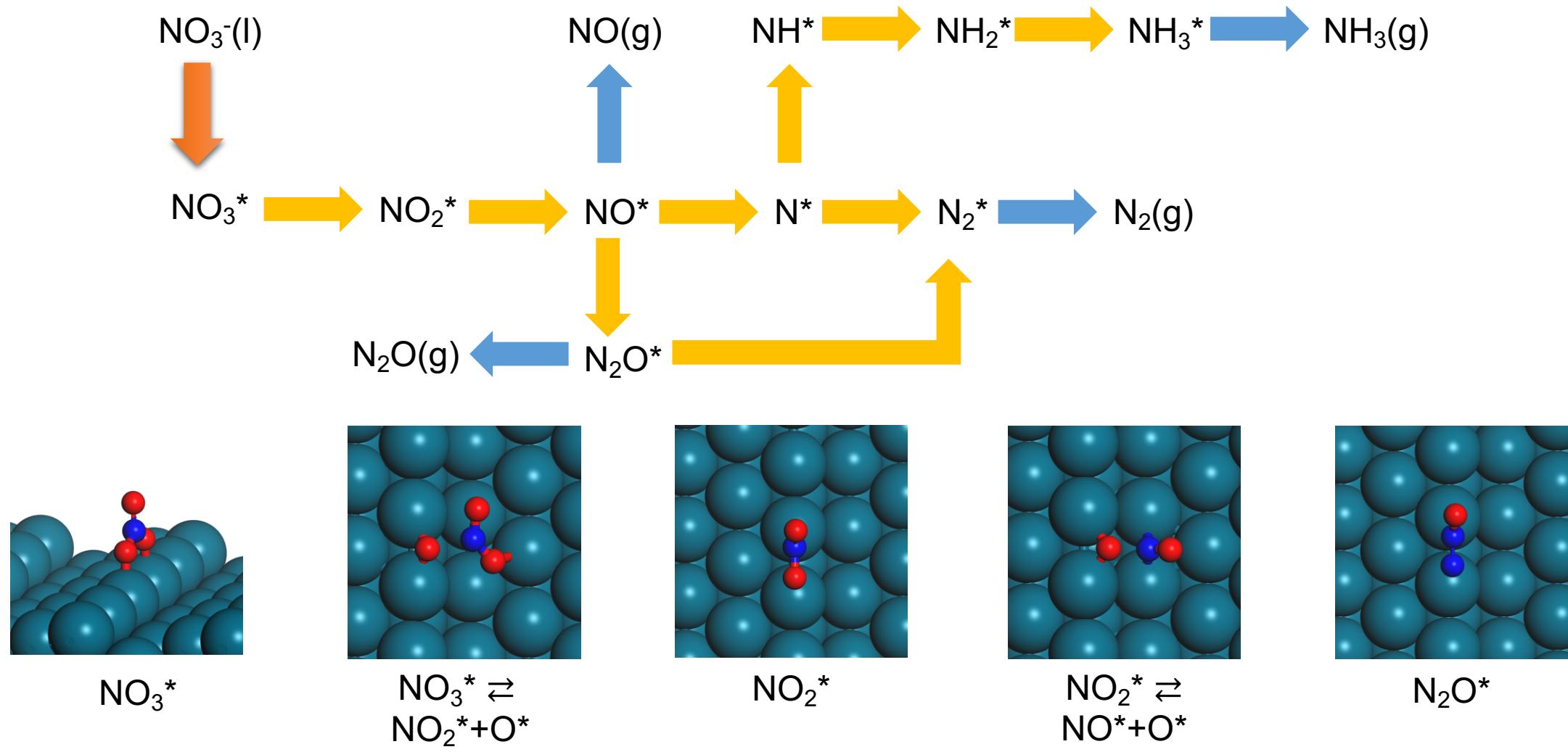


- Potential-dependent kinetics treated using two-step procedure inspired by Marcus theory, which was developed by M. Janik, S. Akhade, and colleagues.<sup>[2]</sup>

[1] G. Karlberg, T. Jaramillo, E. Skulason, J. Rossmeisl, T. Bligaard and J. K. Nørskov, *Phys. Rev. Lett.*, 2007, **99**, 126101.

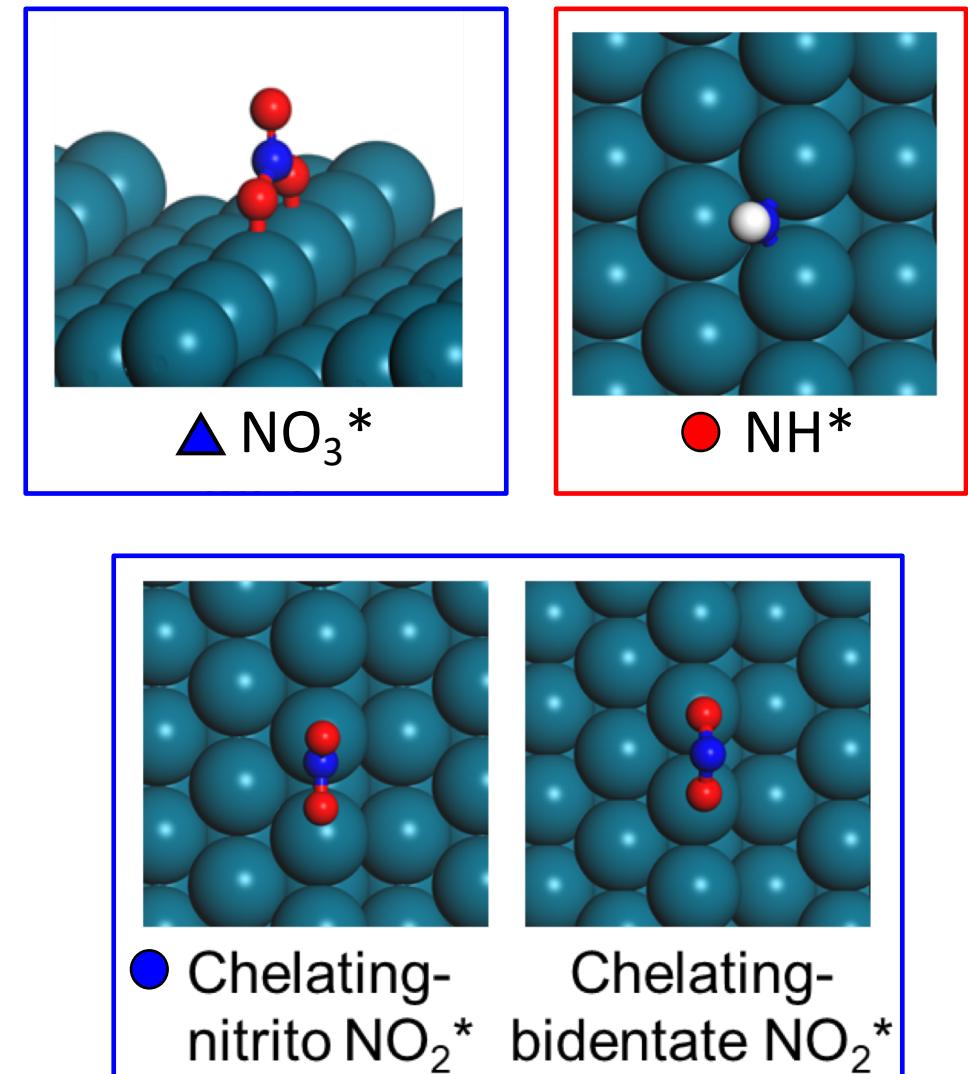
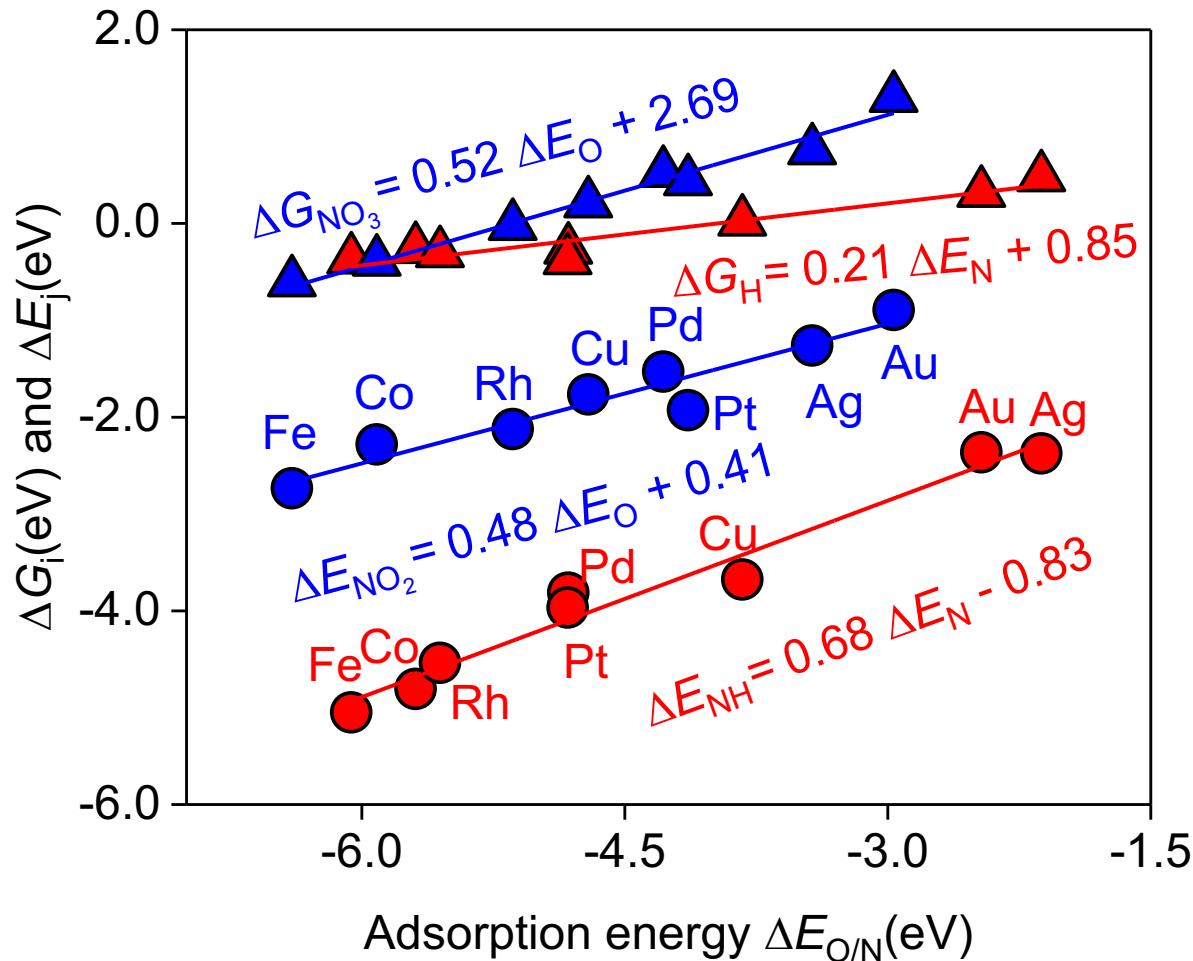
[2] S. A. Akhade, N. J. Bernstein, M. R. Esopi, M. J. Regula and M. J. Janik, *Catal. Today*, 2017, **288**, 63

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



- Hydroxylamine formation not considered

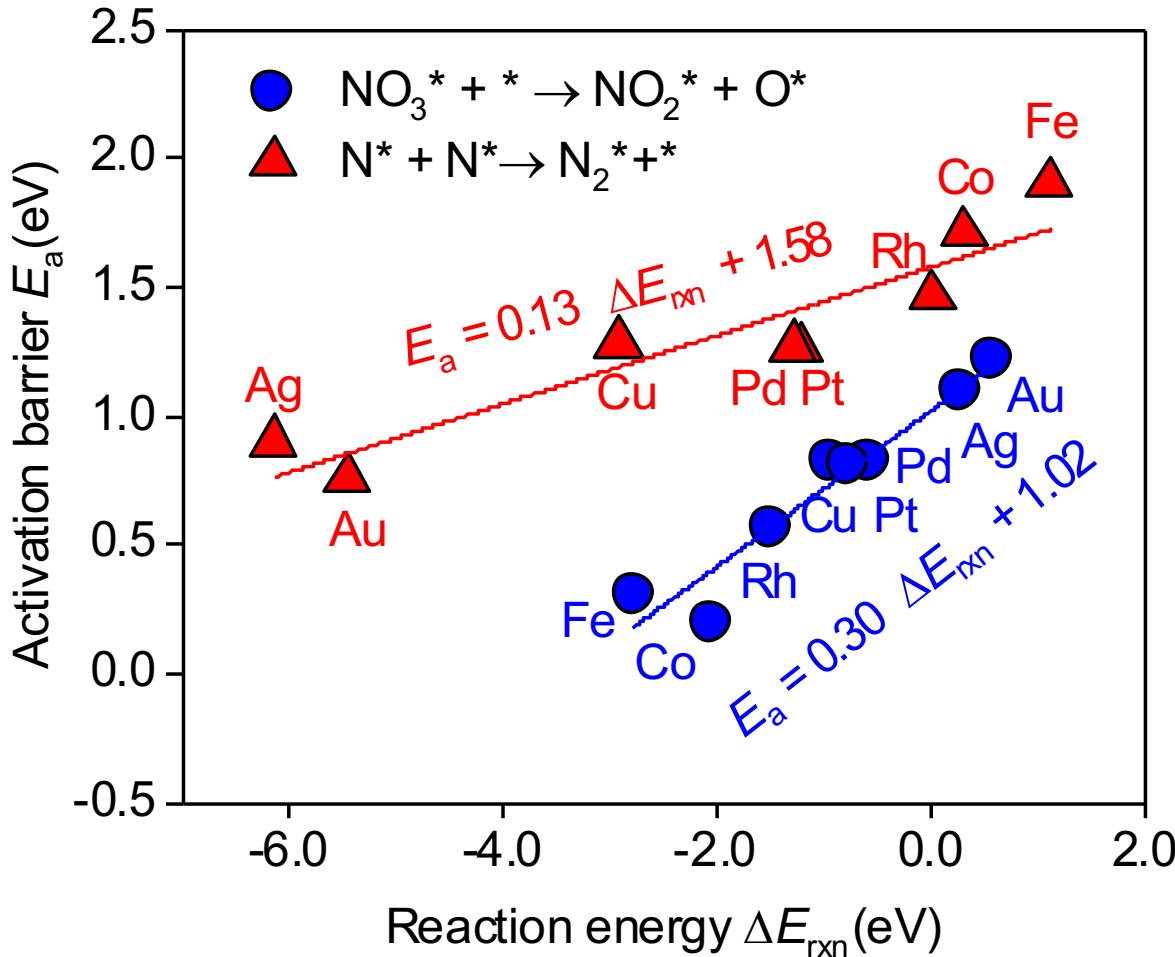
# All adsorption energies of intermediates scale with N and O adsorption energies



Only select adsorbate scaling relations are shown for clarity

Brønsted-Evans-Polanyi relations exist for each elementary step in  $\text{NO}_3\text{RR}$  on the eight metal surfaces

➤ N and O atom adsorption energies can be used as descriptors



Only select BEP relations are shown for clarity

Combining the adsorbate scaling relations with the BEP relations allows the activation barriers to be rapidly calculated as a function of  $\Delta E_N$  or  $\Delta E_O$

**Perform microkinetic modeling for  $\text{NO}_3\text{RR}$  on the eight transition metal stepped surfaces between  $-0.2$  and  $0.4$  V vs RHE at  $300$  K.**

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

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

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

$$X_{\text{RC},i} = \frac{k_i}{r} \left( \frac{\partial r}{\partial k_i} \right)_{k_{j \neq i}, K_i} = \left( \frac{\partial \ln r}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i}$$

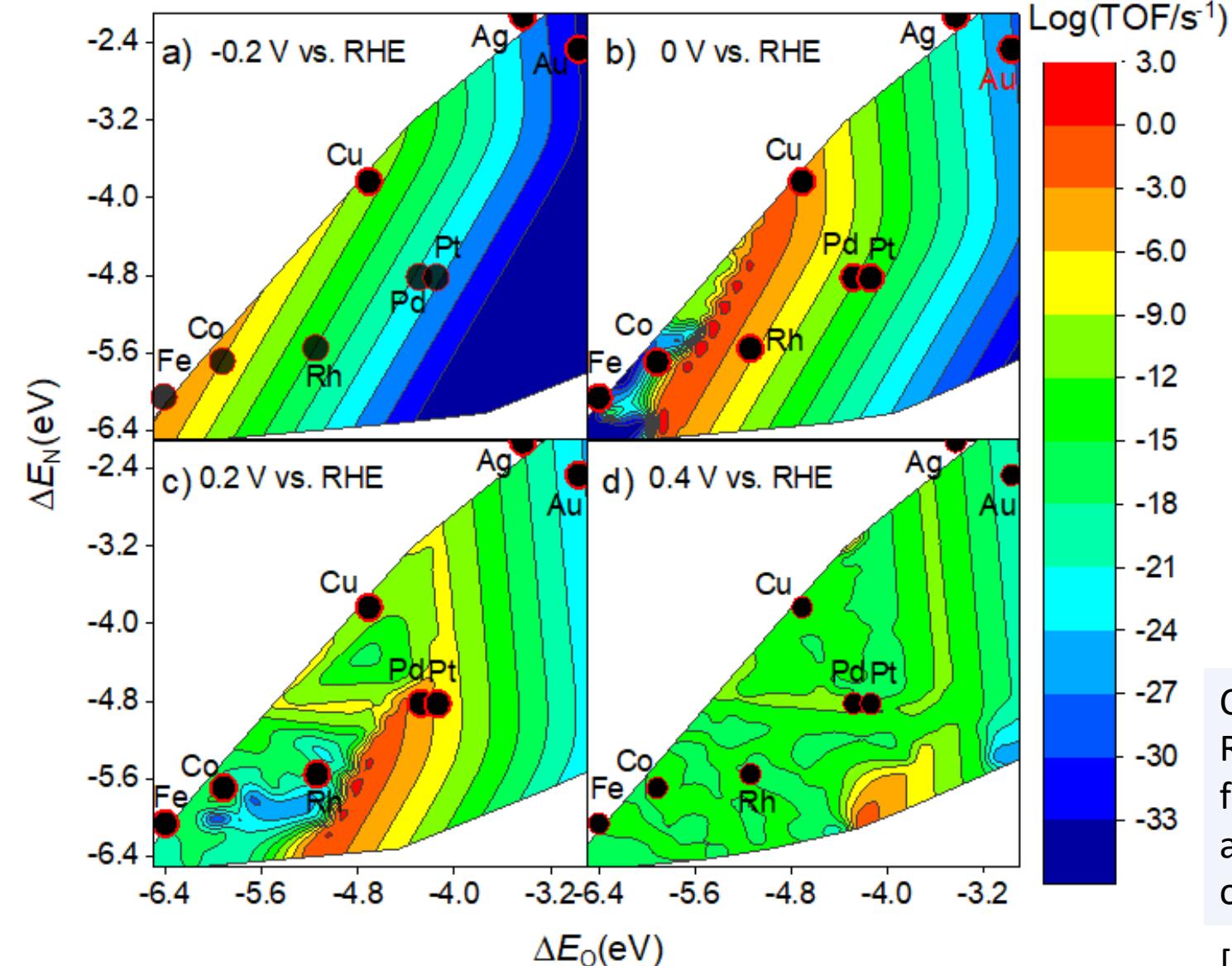
Input file for mkmcxx code:

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

Output:

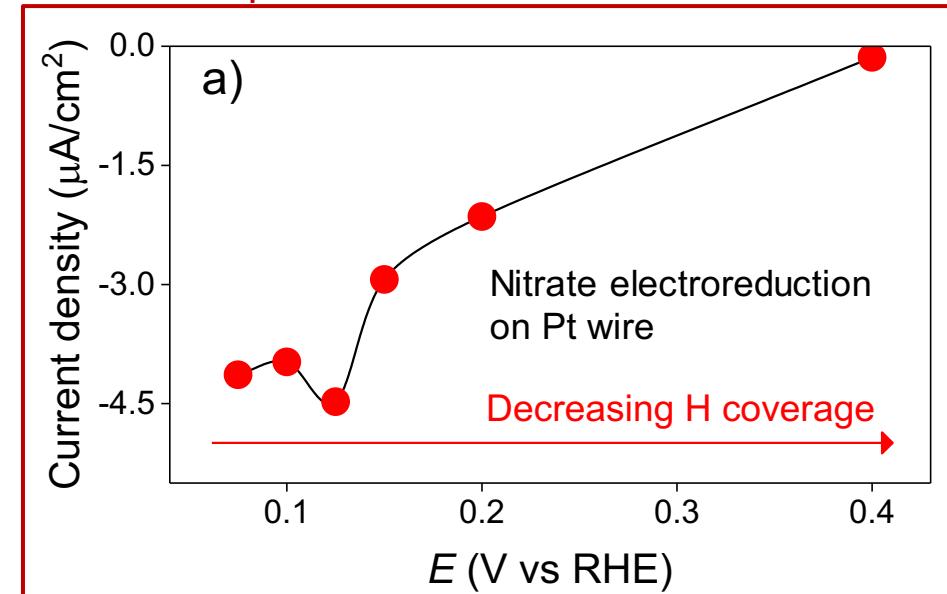
- ✓ Reaction rate, coverages, degree of rate control, selectivity

# 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



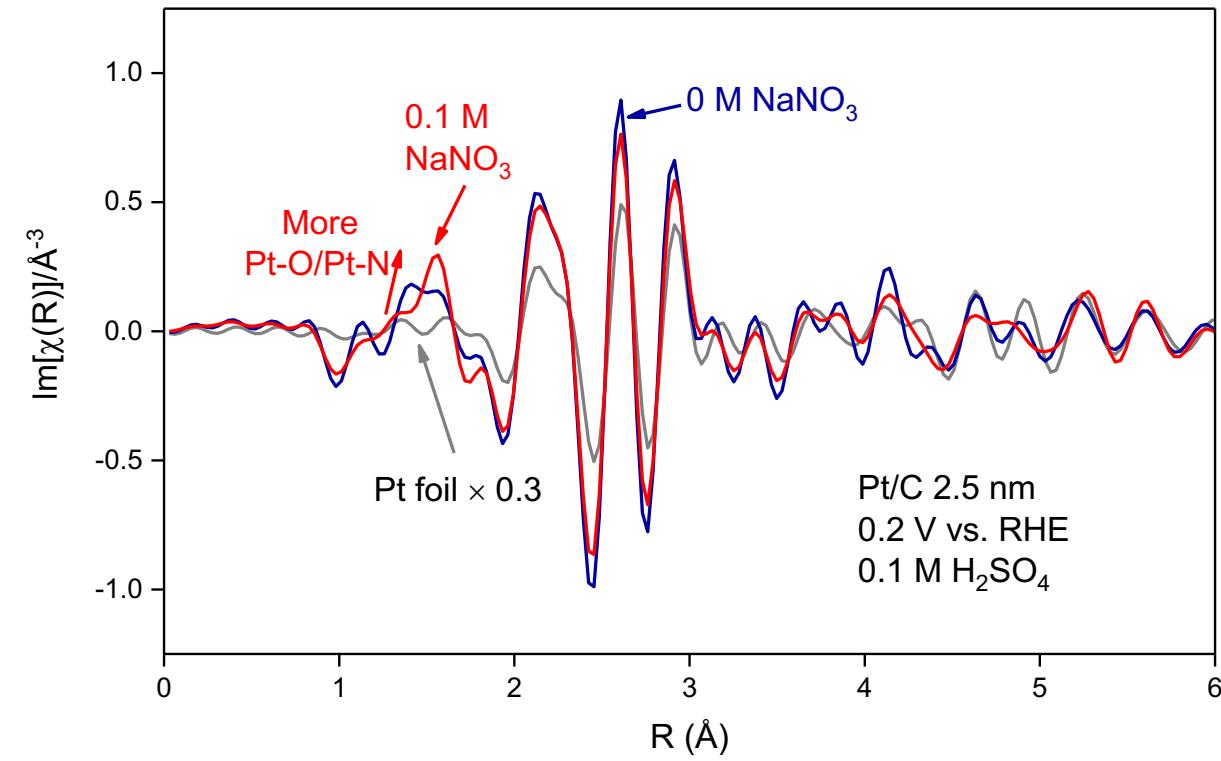
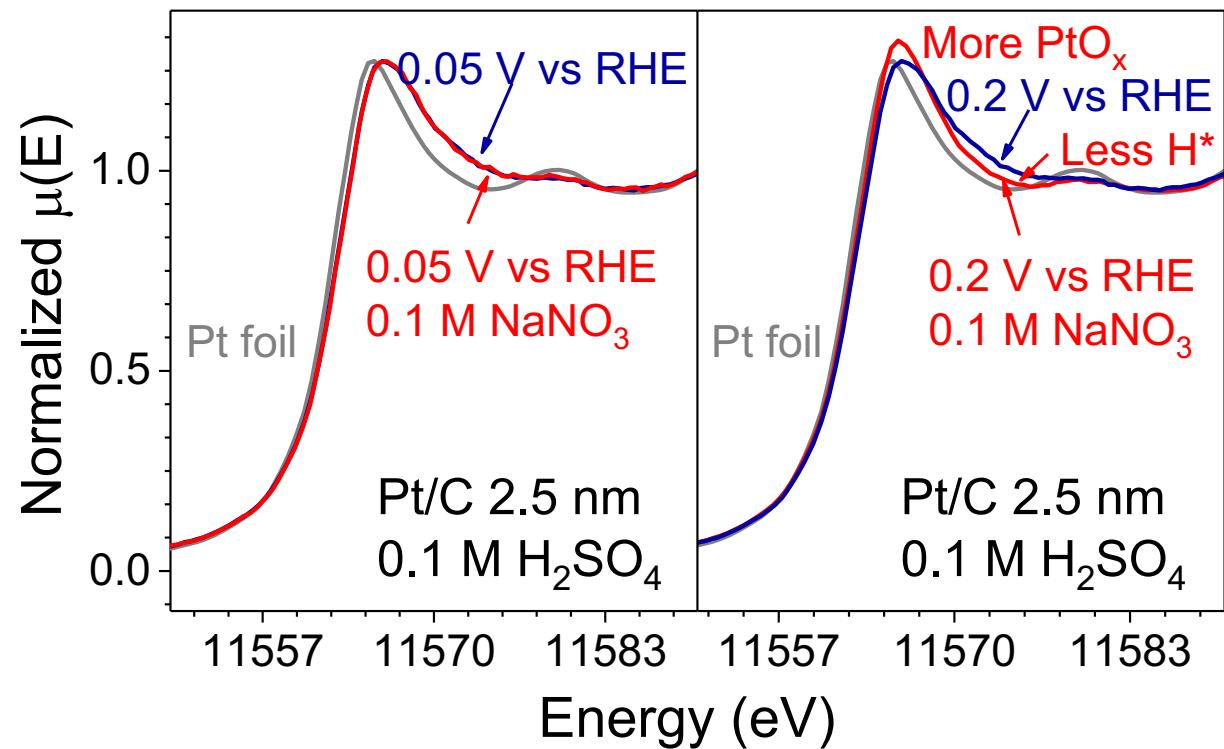
## General trends in activity with metal

Comparing the maximum activities for each metal, Rh has the highest activity for  $NO_3$ RR (at 0.1 V), followed by Cu (at 0 V), Pd/Pt, Ag and Au. This activity ordering is in agreement with experimental observations in acidic solution. [1]

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

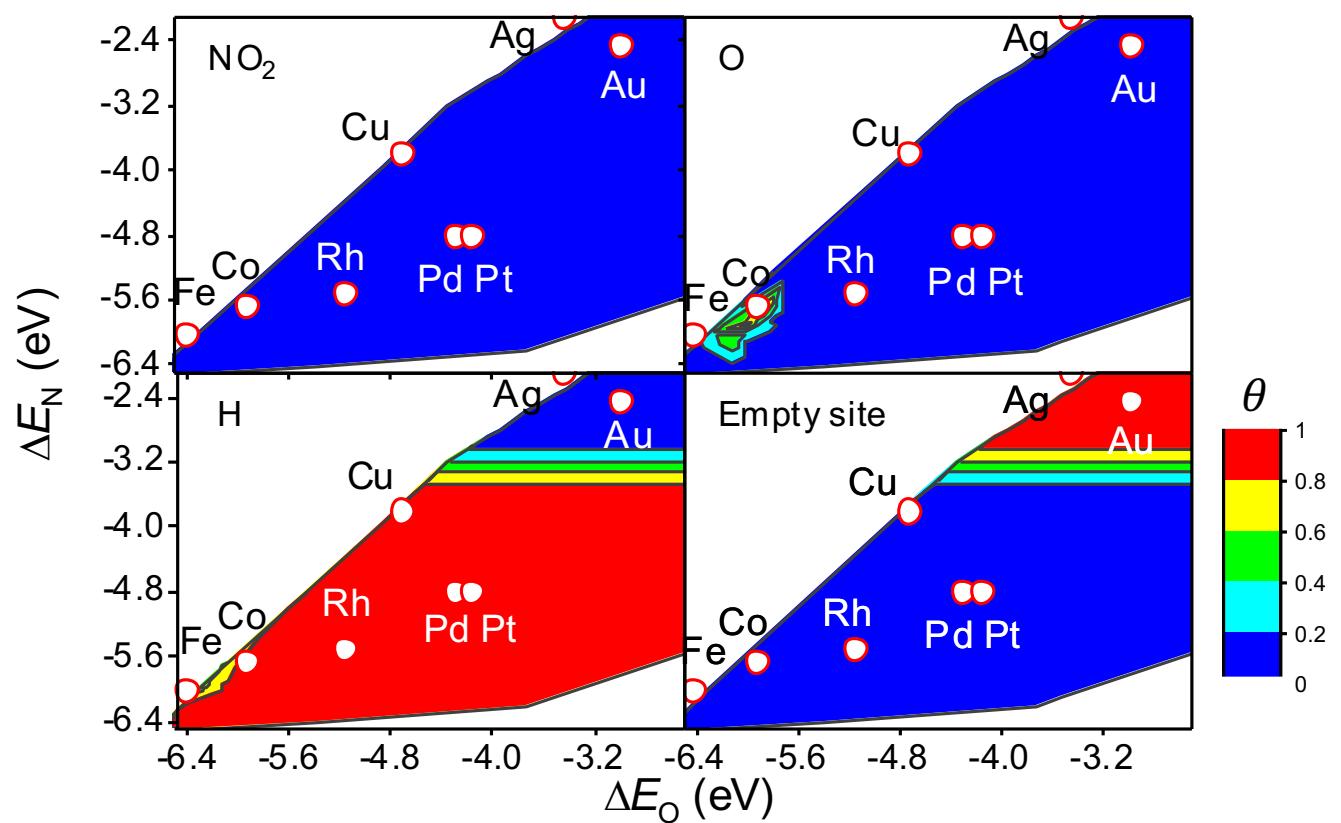
At 0.05 V vs RHE, the presence of nitrate in solution does not inhibit or block adsorbed hydrogen on the Pt surface, whereas at 0.2 V vs RHE, nitrate blocks hydrogen adsorption.

### In situ XANES and EXAFS of Pt/C in presence of nitrate

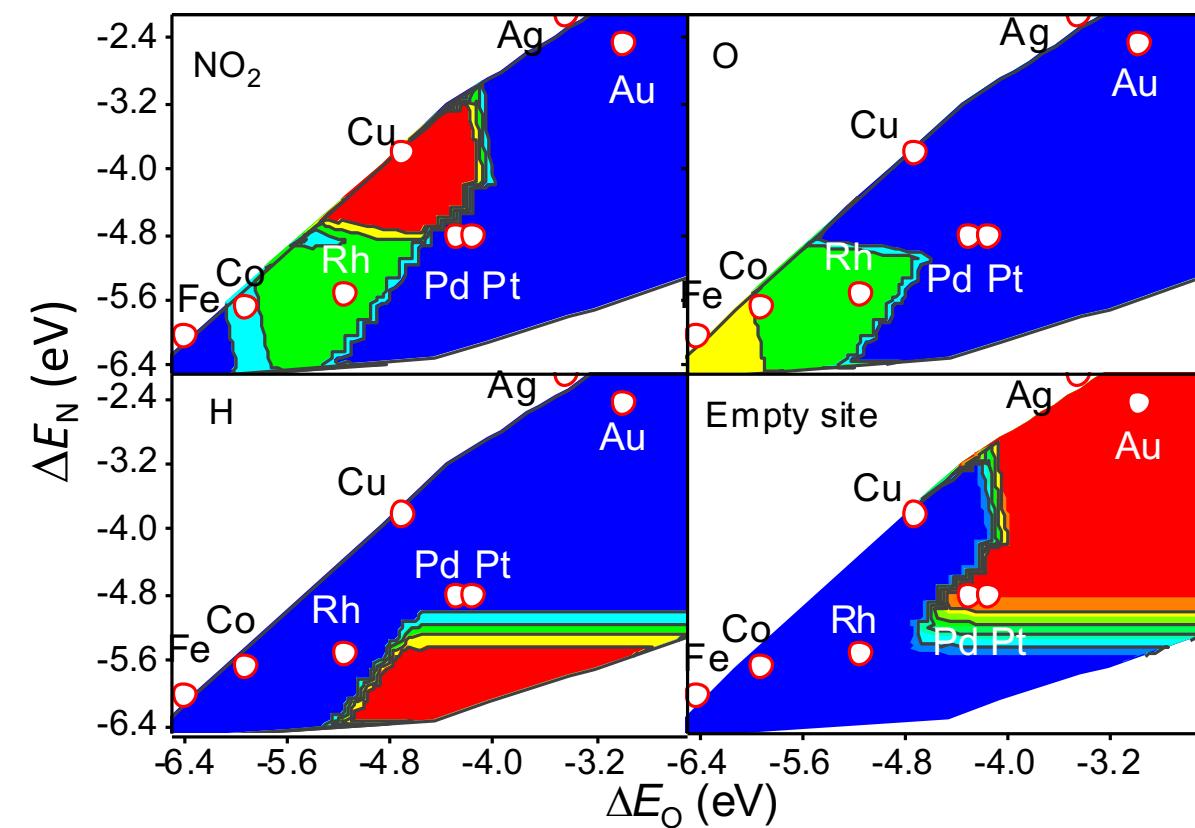


The metal surfaces are either almost completely covered in hydrogen or empty at -0.2 V, but hydrogen coverage greatly decreases at +0.2 V

-0.2 V vs. RHE



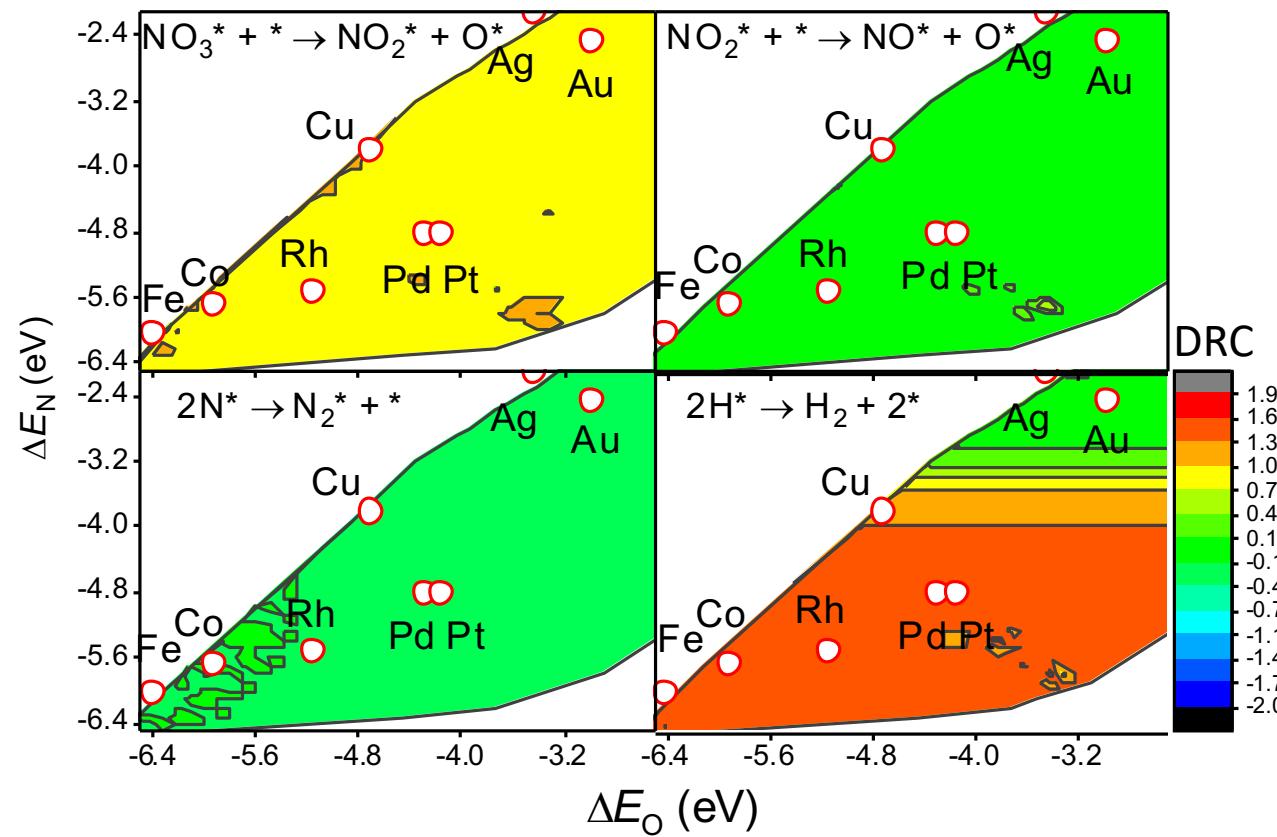
+0.2 V vs. RHE



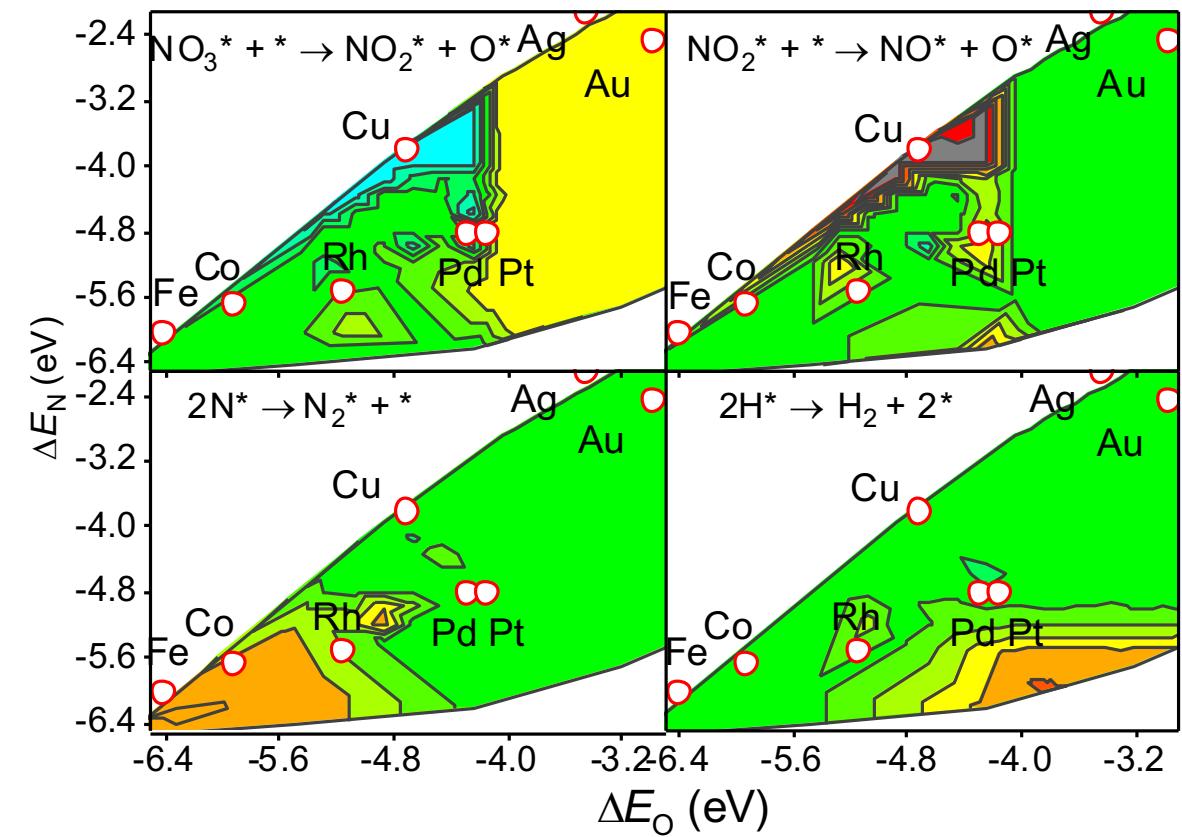
# Degree of rate control comparison at -0.2 V and +0.2 V

➤ The change in RDS with potential on these metals mirrors the change in maximum in activity with potential.

**-0.2 V vs. RHE**



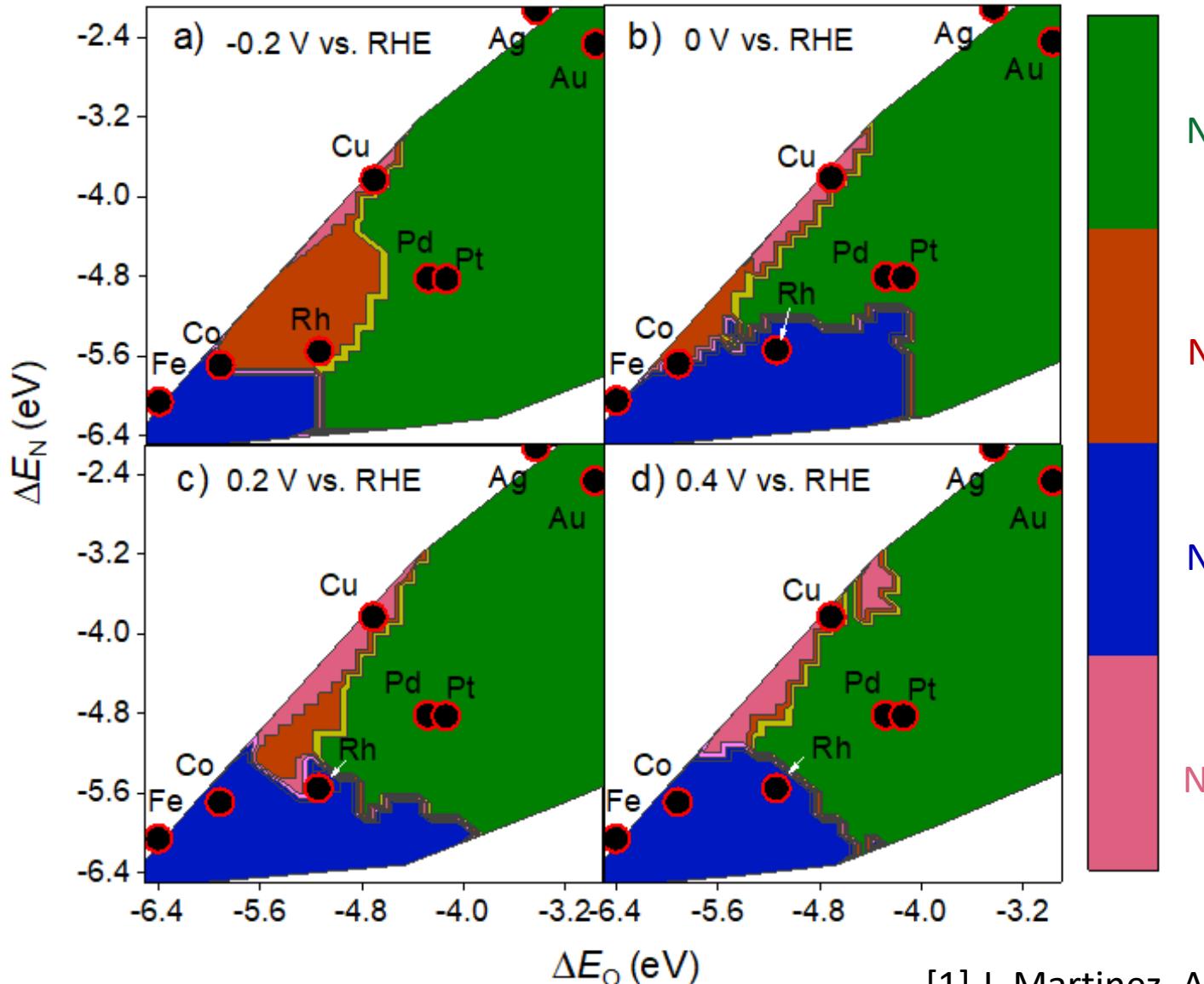
**+0.2 V vs. RHE**



[1] Degree of rate control: CT Campbell *ACS Catal.* (2017): 2770-2779.

[2] M. Duca and M. Koper. *Energy Environ. Sci.* 5.12 (2012): 9726-9742.

# Theoretical selectivity trends as a function of potential



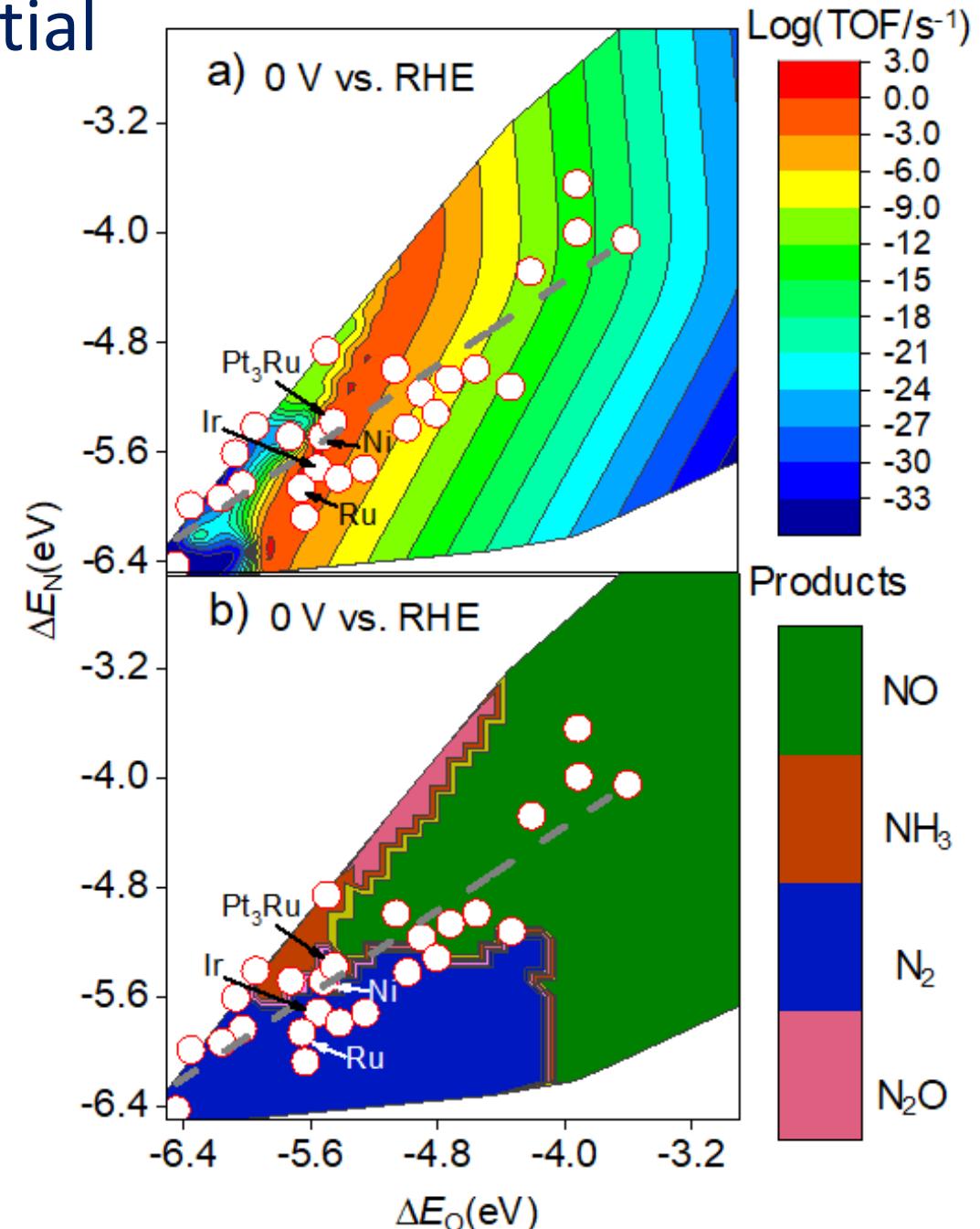
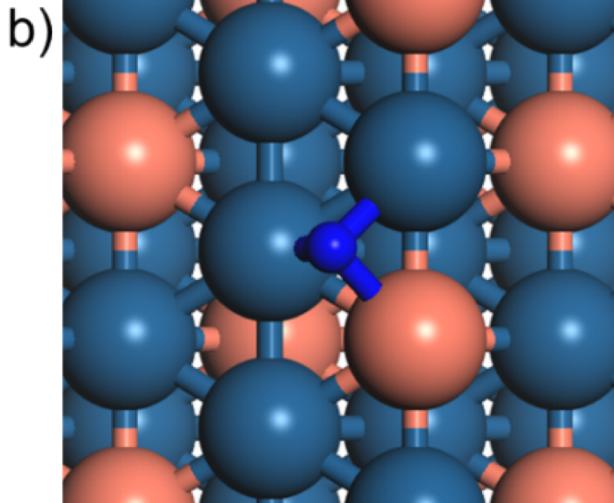
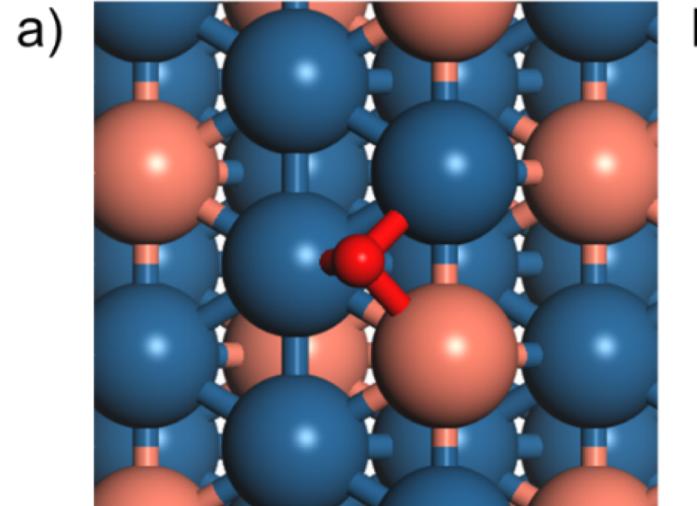
$\text{N}_2$  formation requires strong adsorption of O and N at all potentials.

Selectivity toward  $\text{NH}_3$  is obtained by catalysts with moderate adsorption of O and N.

$\text{Fe}$  exhibits high selectivity toward  $\text{N}_2$  because it strongly adsorbs  $\text{NO}^*$  and promotes its dissociation to form  $\text{N}^*$  and  $\text{O}^*$ , but lacks stability [1]

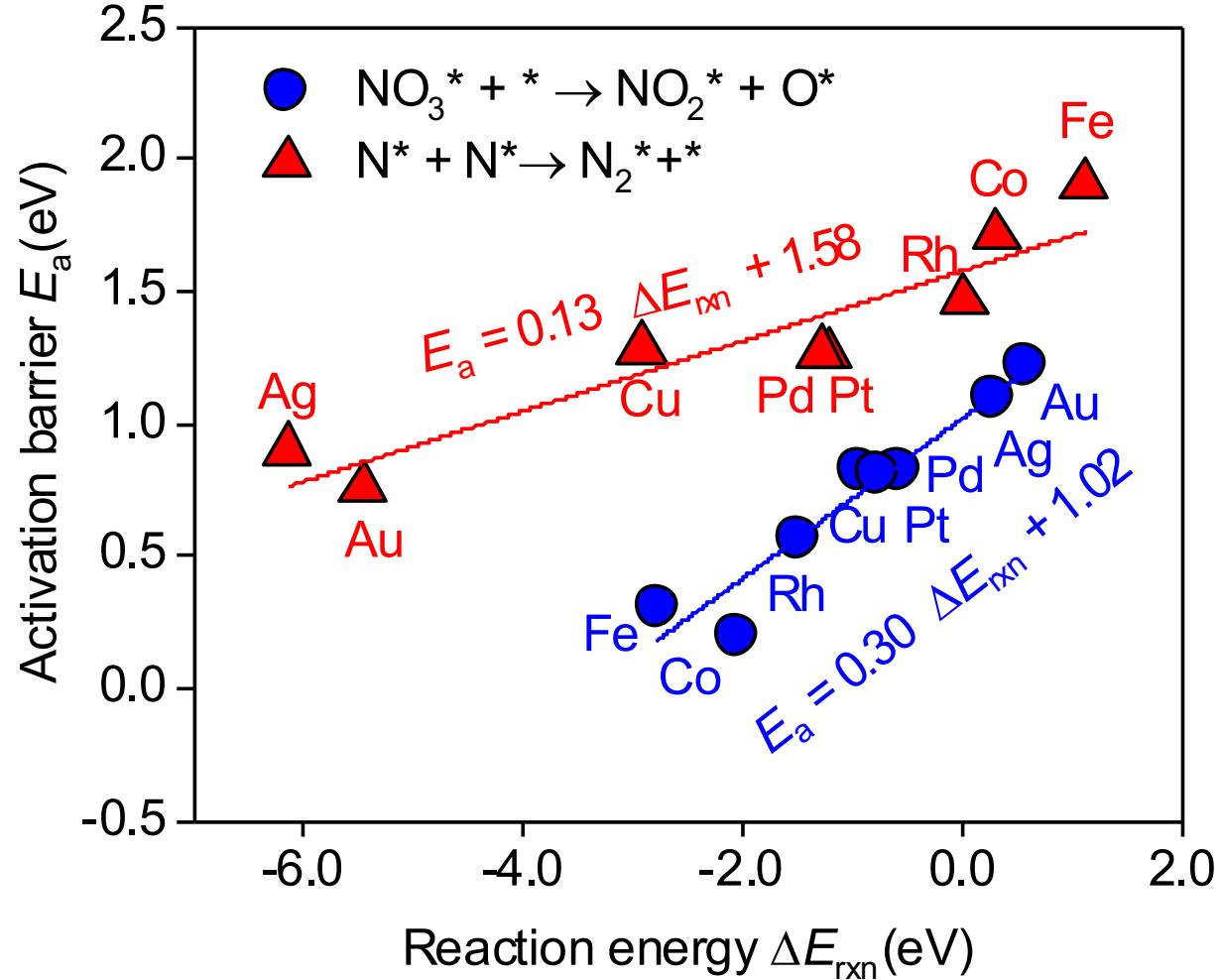
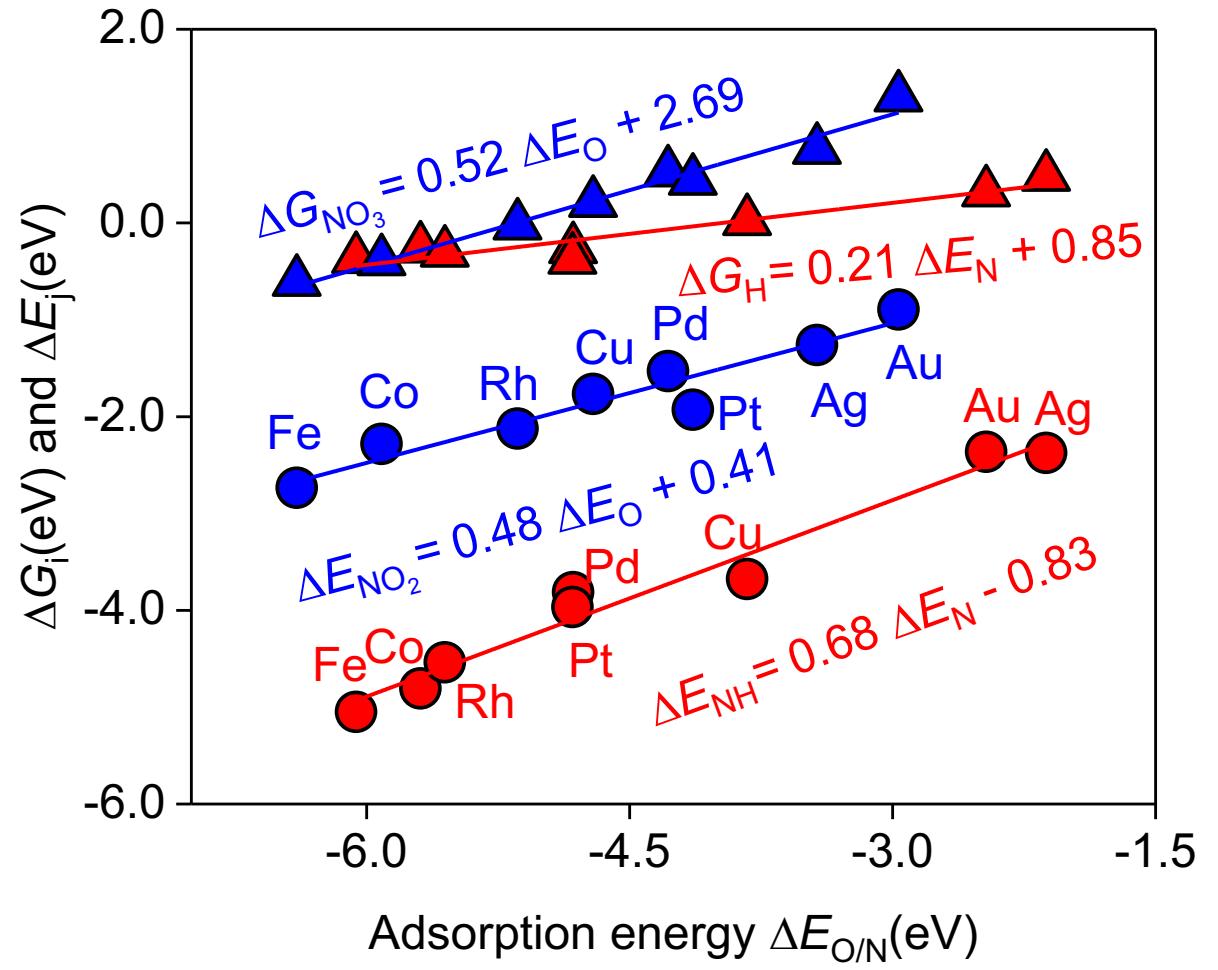
# $\text{Fe}_3\text{Ru}$ , $\text{Fe}_3\text{Ni}$ , $\text{Fe}_3\text{Cu}$ and $\text{Pt}_3\text{Ru}$ are potential catalysts for $\text{N}_2$ formation at $\leq 0 \text{ V}$

Studied the  $\text{NO}_3\text{RR}$  activity and selectivity of four additional transition metals (Ru, Ir, Ni and Zn) and 22  $\text{Fe}_3\text{M}$ ,  $\text{Pt}_3\text{M}$ , and  $\text{Rh}_3\text{M}$  alloys.



# Recap of most significant results

## 1. Adsorbate and BEP scaling relations hold for each step in $\text{NO}_3\text{RR}$ on transition metals.



# Recap of most significant results and future work

1. Adsorbate and BEP scaling relations hold for each step in  $\text{NO}_3\text{RR}$  on transition metals.

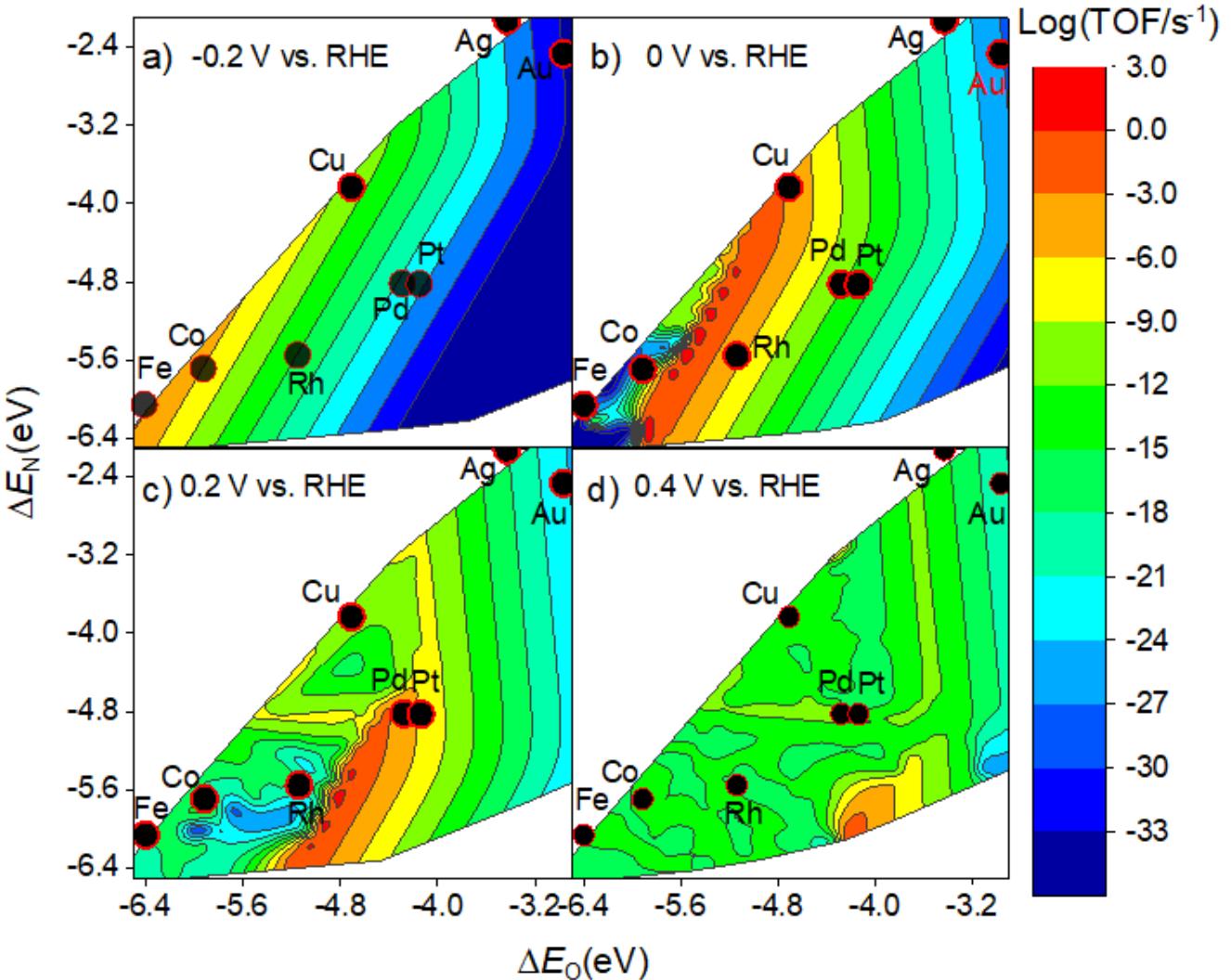
**2. The adsorption strength of N and O atoms are catalyst descriptors for  $\text{NO}_3\text{RR}$  activity and selectivity.**

Elementary step	Activation energy, $E_a(0 \text{ V})$	$R^2$
$\text{NO}_3^* + * \rightleftharpoons \text{NO}_2^* + \text{O}^*$	$E_a = 0.234E_O + 0.054E_N + 2.047$	0.93
$\text{NO}_2^* + * \rightleftharpoons \text{NO}^* + \text{O}^*$	$E_a = 0.451E_O + 0.080E_N + 3.522$	0.69
$\text{NO}^* + * \rightleftharpoons \text{N}^* + \text{O}^*$	$E_a = 0.652E_O + 0.238E_N + 5.453$	0.96
$\text{N}^* + \text{N}^* \rightleftharpoons \text{N}_2^* + *$	$E_a = -0.250E_O - 0.063E_N - 0.117$	0.99
$\text{NO}^* + \text{NO}^* \rightleftharpoons \text{N}_2\text{O}^* + \text{O}^*$	$E_a = 1.725E_O - 1.887E_N + 1.640$	0.94
$\text{N}_2\text{O}^* + * \rightleftharpoons \text{N}_2^* + \text{O}^*$	$E_a = 1.049E_O - 0.742E_N + 2.188$	0.82
$\text{H}^* + \text{O}^* \rightleftharpoons \text{OH}^* + *$	$E_a = -0.273E_O - 0.131E_N - 1.104$	0.91
$\text{OH}^* + \text{H}^* \rightleftharpoons \text{H}_2\text{O}^* + *$	$E_a = 0.054E_O - 0.369E_N - 0.400$	0.91
$\text{N}^* + \text{H}^* \rightleftharpoons \text{NH}^* + *$	$E_a = 0.189E_O - 0.415E_N + 0.097$	0.89
$\text{NH}^* + \text{H}^* \rightleftharpoons \text{NH}_2^* + *$	$E_a = 0.211E_O - 0.397E_N + 0.356$	0.88
$\text{NH}_2^* + \text{H}^* \rightleftharpoons \text{NH}_3^* + *$	$E_a = -0.018E_O - 0.175E_N + 0.437$	0.63

# Recap of most significant results and future work

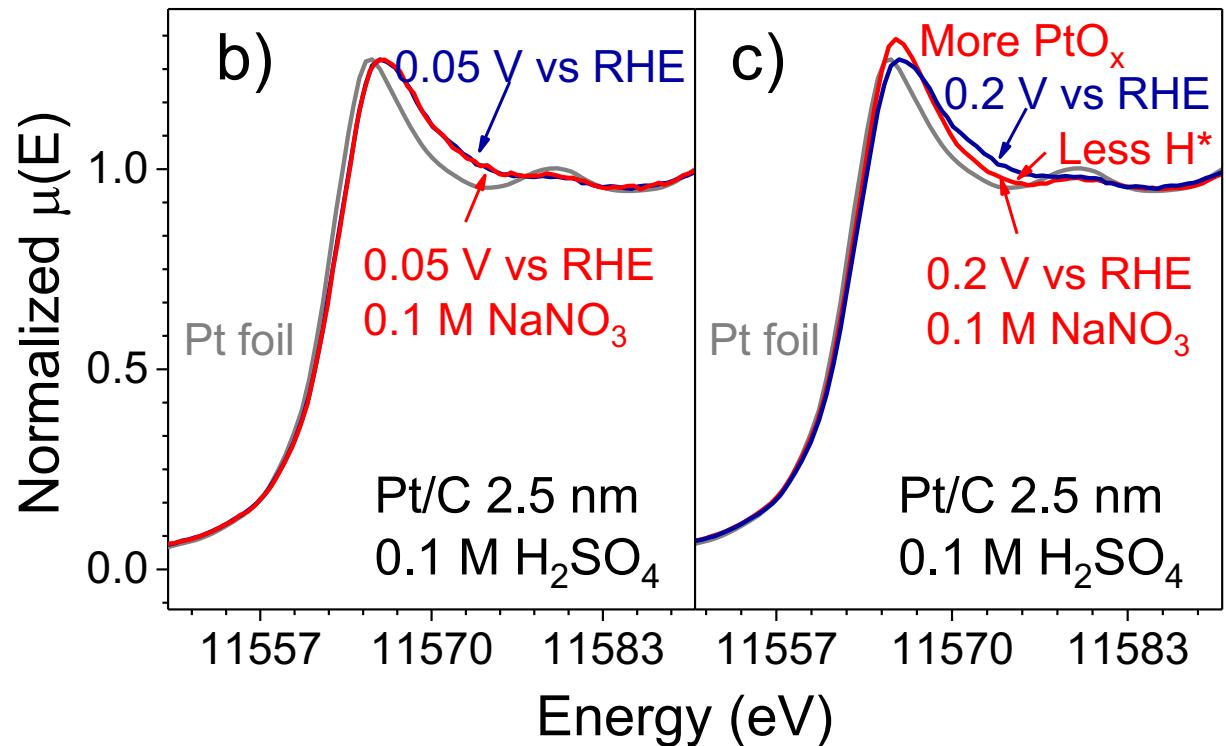
1. Adsorbate and BEP scaling relations hold for each step in  $\text{NO}_3\text{RR}$  on transition metals.
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3. **First-principles based microkinetics model predicts activity trends that qualitatively match what has been reported experimentally in the literature.**

*Rh has the highest activity for  $\text{NO}_3\text{RR}$  (at 0.1 V), followed by Cu (at 0 V), Pd/Pt, Ag and Au.*



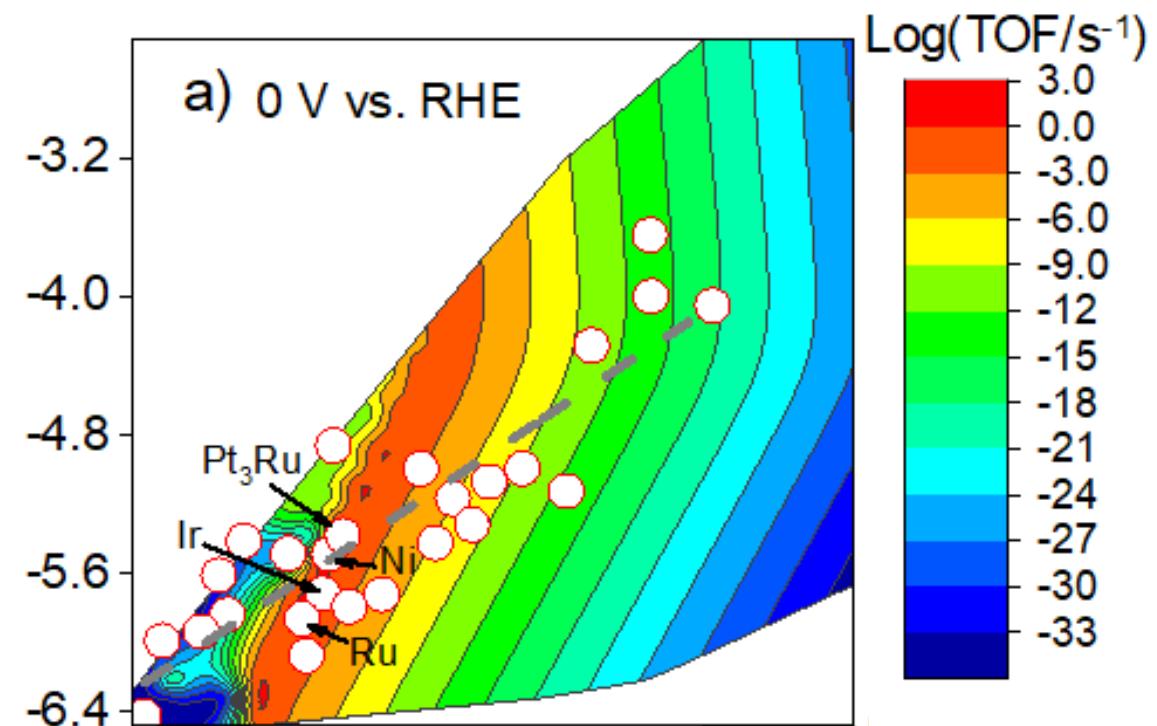
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# Recap of most significant results and future work

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5. Bimetallics such as  $\text{Fe}_3\text{Ru}$ ,  $\text{Fe}_3\text{Ni}$ ,  $\text{Fe}_3\text{Cu}$  and  $\text{Pt}_3\text{Ru}$  are promising electrocatalysts to further study for nitrate conversion to  $\text{N}_2$ .



# Acknowledgements

Jin-Xun Liu



Nirala Singh



Danielle Richards

