

Nitrate Reduction - an Investigation into Catalyst Structure for Selective Nitrogen Formation

S. M. McIntyre¹, C. A. Casey-Stevens¹, J. T. A. Gilmour¹, C. Ruffman¹ and A. L. Garden¹

¹Department of Chemistry, University of Otago, Dunedin, New Zealand and the MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand.



Introduction

Reactive nitrogen species have become prevalent pollutants in the biosphere, meaning we need an effective denitrification procedure.

Electrocatalytic reduction of NO₃⁻ to N₂ shows promise as a solution to increasing NO₃⁻ pollution, however, this requires an effective catalyst.¹

A range of pure metal catalysts (Ag, Au, Cu, Ir, Pd, Pt, Rh and Ru) have been tested experimentally. Selective N₂ formation is only seen on Pd.²

→ What conditions are required to form N₂?

How is N₂ Formed?

DFT calculated mechanisms of formation:

→ N₂O is a key intermediate.

Barriers too high

Feasible pathways via N₂O

ΔG_{ads} = 2.97 eV

ΔG_{ads} = 2.90 eV

The reduction of NO is the selectivity-determining step of the overall NO₃⁻ reaction.³ Both Pd(111) and Pt(111) preferentially bind N₂O on the top site with similar strength.

→ No appreciable difference in N₂O binding of Pd vs. Pt.

Onset Potentials for N₂O and N₂ Formation

Experimental onset potentials²

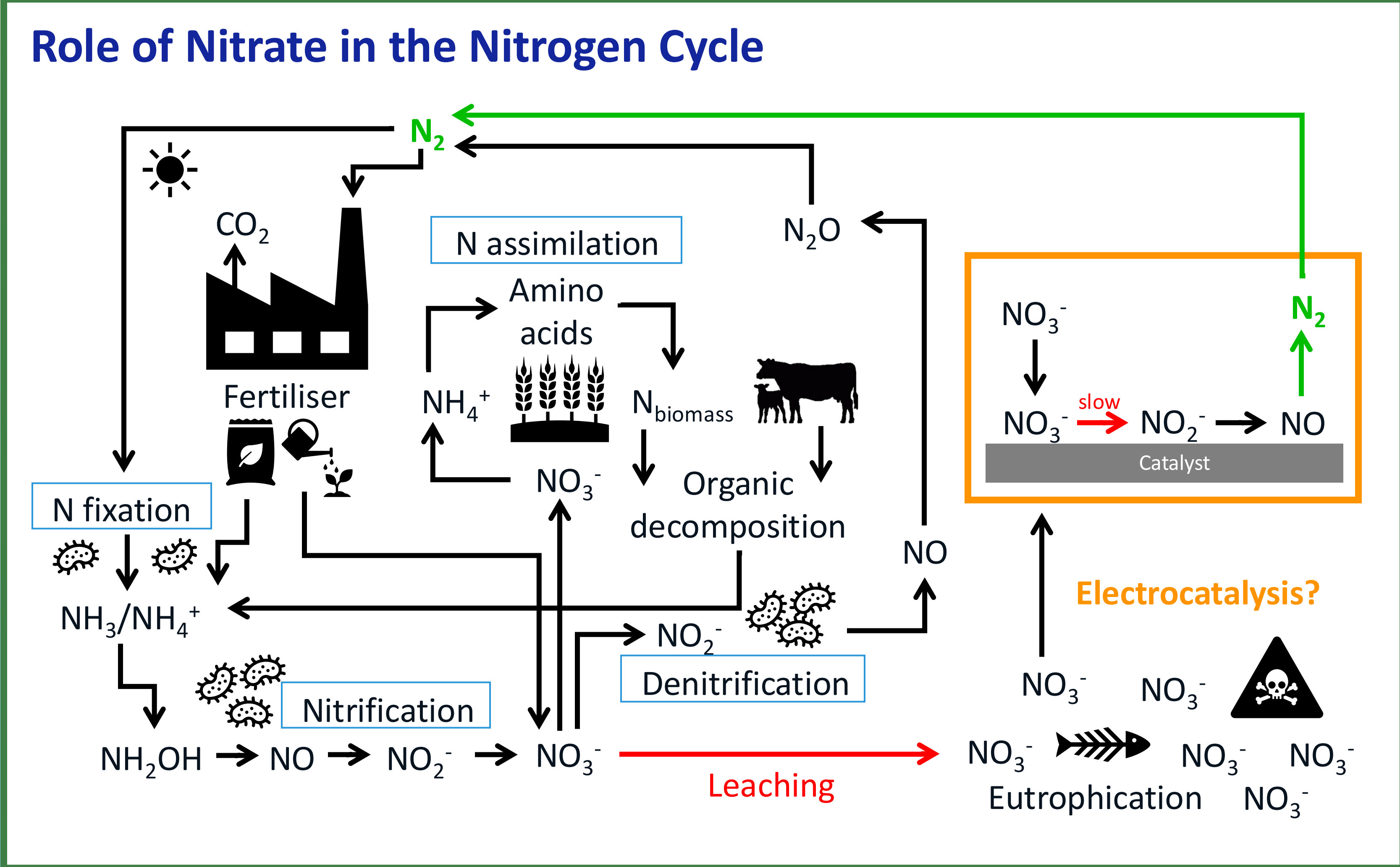
N₂O formed at positive potentials on both Pt and Pd. At mid potentials on Pd N₂O tails off to favour N₂ formation.

Calculated onset potentials

Product	Onset potential / V vs. RHE	
	Pt(111)	Pd(111)
N ₂ O(g)	1.09	0.70
N ₂ (g)	0.40-0.54	0.42-0.45

→ Pt should be able to form N₂ at similar potentials to Pd.

Why is it not seen?



Co-adsorbates – What is the Influence of H?

Fig 1. Coverage of H as a function of potential.

At the calculated onset potentials for N₂ formation, there is likely to be H on the surface. However, both Pt and Pd start to adsorb H at similar potentials and have similar hydrogen coverage profiles.

→ H atoms were found to adsorb differently to Pt and Pd.

The top site (required for N₂O binding) is free on Pd.

References

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Cluster Expansion for Statistical Modelling

→ How do we define a computationally efficient Hamiltonian?

Cluster Expansion techniques (based on the generalised Ising model) were used to generate the required energies for statistical modelling.⁴ Monte Carlo simulations of H coverage at given potentials provide a more realistic snapshot of the H atom coverage.

Energy of a given configuration per lattice site $E^{CE}(\sigma) = \sum_f J_f \Pi_f(\sigma)$

Spin-products averaged over the entire lattice

Figures (clusters) $\rightarrow \Pi_f$

Effective interaction strength

$\Pi(\sigma) = [\Pi_1, \Pi_2, \Pi_3, \Pi_4, \Pi_5, \dots, \Pi_f]$

As we are interested in low H-coverages, our model consists of DFT calculated energies for 3x 1-body terms, 20x 2-body terms and 19x 3-body terms.

→ Preliminary Monte Carlo simulations support the hypothesis that the sites for N₂ formation are blocked on the Pt surface.

Further Monte Carlo simulations to more explicitly account for H coverage and surface interactions between H atoms at different potentials.

Future Directions

Once the mechanism to form N₂O (and subsequently N₂) is known we will endeavour to design the optimal NO₃⁻ reduction catalyst. This will involve investigation into different 38-atom Cu_xPd_y nanoparticle morphologies. Next, the impact that different supports (graphene, MgO and CeO₂) have on the nanoparticle structures and segregation patterns will be investigated. Finally, the NO₃⁻ reduction reaction will be modelled on these different structures to understand what impacts the overall efficiency of this reduction process.

→ Rational design of nitrate reduction catalysts selective N₂ formation.