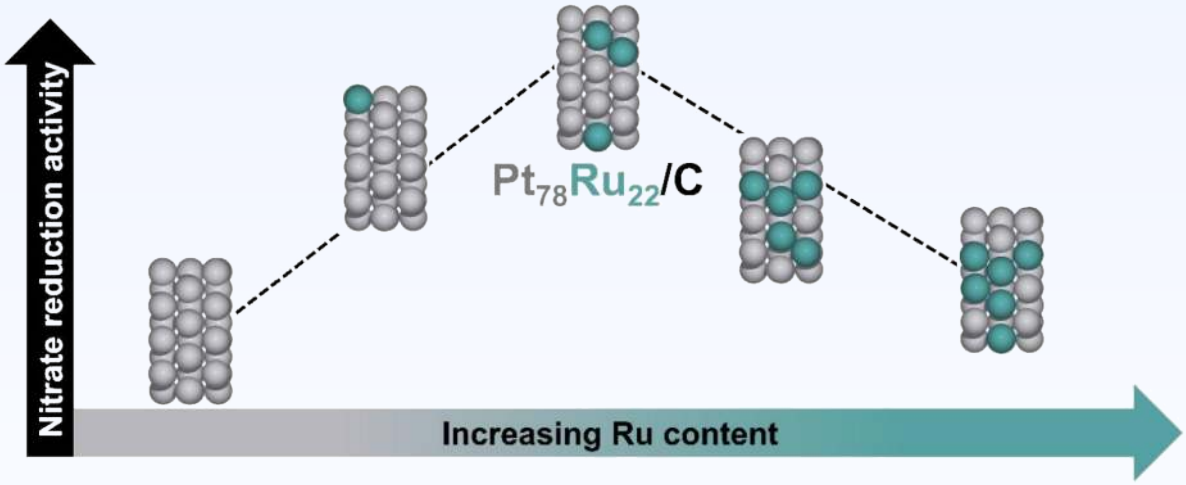

Platinum-Ruthenium Alloys for Efficient Aqueous Nitrate Reduction

Samuel D. Young

16 Nov 2021

Wang, Z., Young, S. D., Goldsmith, B. R. & Singh, N. Increasing electrocatalytic nitrate reduction activity by controlling adsorption through PtRu alloying. *Journal of Catalysis* **395**, 143–154 (2021).

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Nitrate is a Major Water Pollutant

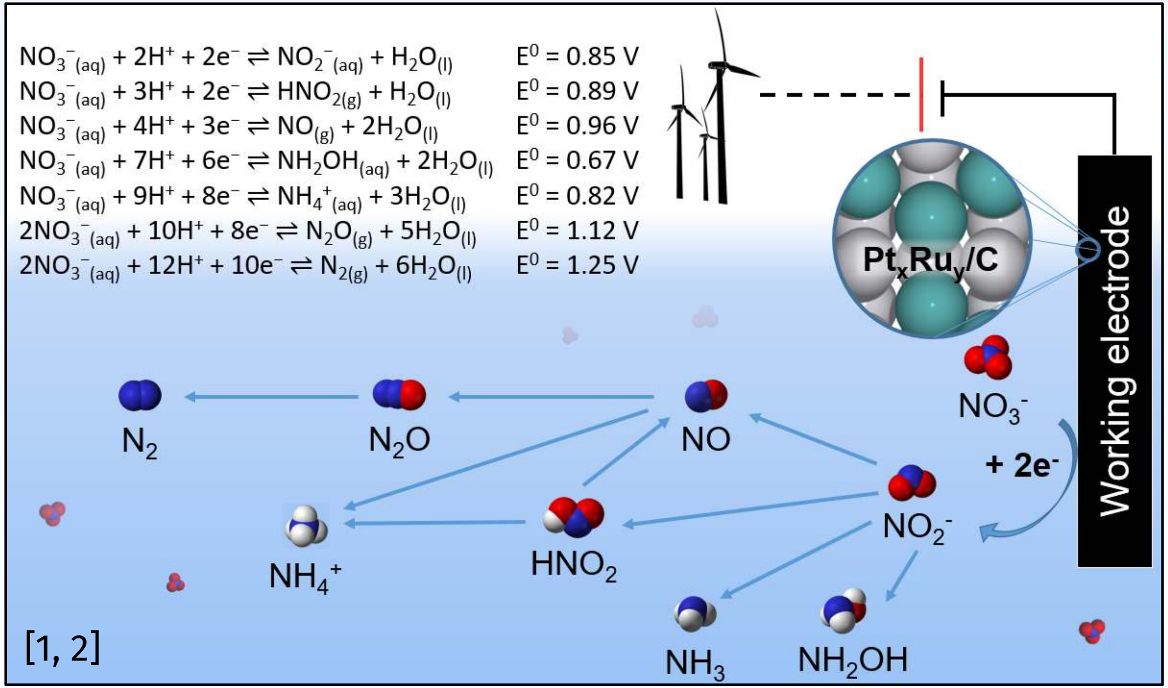
- Human N contribution to environment: 10^8 tonnes/yr[1, 2]
  - Largest source: ammonia fertilizer (> 100 Tg N)
  - Makes NO_3^- is one of the most widespread water pollutants.
- Adverse health effects:[3–5]
  - Methemoglobinemia
  - Ovarian and thyroid cancers


Ammonia fertilizer in agriculture [1].


Methemoglobinemia patient (left) versus healthy patient (right) [5].

1. Fields, S. *Environmental Health Perspectives* **112**, A556–A563 (2004).
2. Duca, M. & Koper, M. T. M. *Energy Environ. Sci.* **5**, 9726–9742 (2012).
3. Farkas, J. Methemoglobinemia in *Internet Book of Critical Care* (2019).
4. Xie, L. *et al. Oncotarget* **7**, 56915–56932 (2016).
5. Soliman, D. S. & Yassin, M. Congenital methemoglobinemia misdiagnosed as polycythemia vera: Case report and review of literature. *Hematol Rep* **10**, (2018).

Electrocatalytic Nitrate Reduction (NO_3RR) is a Sustainable Route for Nitrate Remediation



- Can be powered with renewable electricity
- Don't need continuous 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] Wang, Z., Young, S. D., Goldsmith, B. R. & Singh, N. Increasing electrocatalytic nitrate reduction activity by controlling adsorption through PtRu alloying. *Journal of Catalysis* **395**, 143–154 (2021).

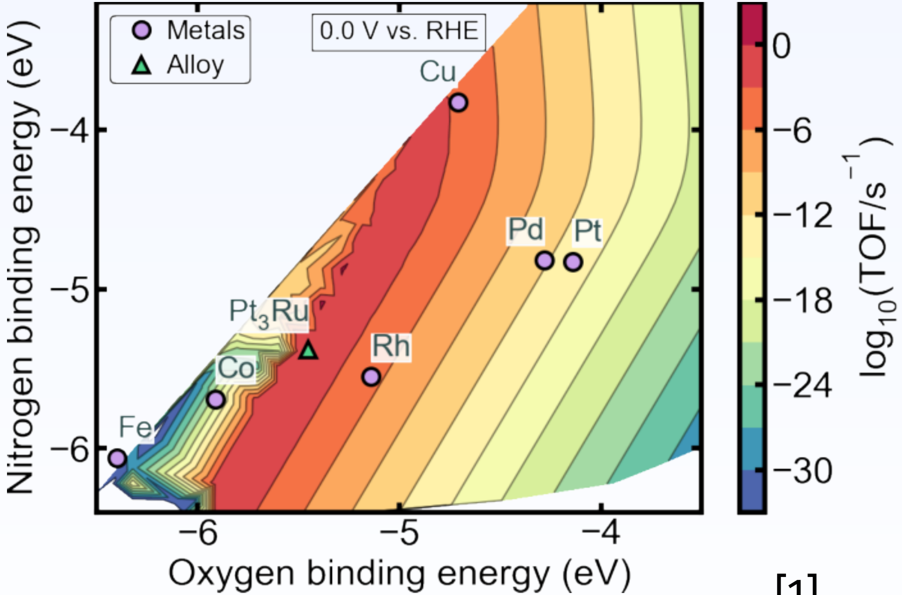
[2] Singh, N. & Goldsmith, B. R. Role of Electrocatalysis in the Remediation of Water Pollutants. *ACS Catal.* **10**, 3365–3371 (2020).

Objective: Verify Whether Pt_3Ru Alloy Predicted Using Pure Metal Microkinetics is Active Towards NO_3RR

Dr. Jin-Xun Liu

Danielle Richards

- Previous study of pure metals found N, O binding energies as thermodynamic descriptors.
- Pt_3Ru alloys predicted to be promising.[1, 2]
- **Questions:**
  - **Is Pt_3Ru more active than Pt?**
  - **Can we systematically tune NO_3RR kinetics through alloying?**
  - **Can we use *pure metal* microkinetics to predict *alloy* activity?**

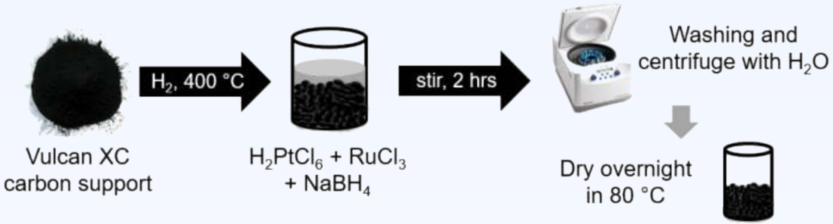


[1]

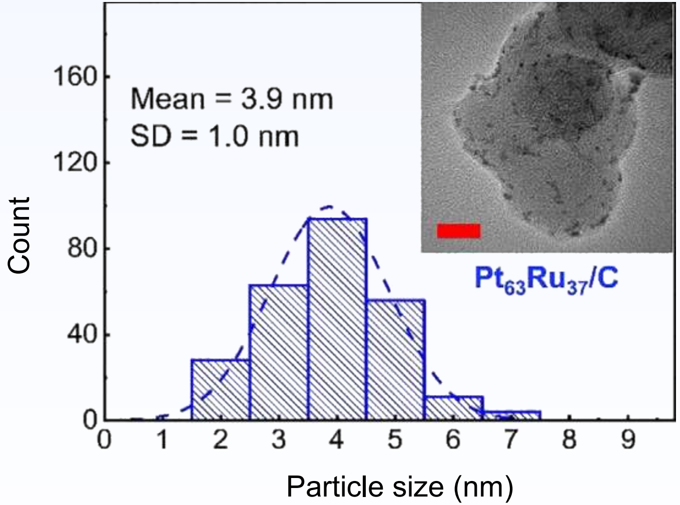
[1] Liu, J.-X., Richards, D., Singh, N. & Goldsmith, B. R. Activity and Selectivity Trends in Electrocatalytic Nitrate Reduction on Transition Metals. *ACS Catal.* **9**, 7052–7064 (2019).
[2] All potentials are relative to the reversible hydrogen electrode (RHE).

Synthesis of Experimental 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 catalyst crystallites of ~3–6 nm in diameter.
- No significant phase or surface segregation observed.
- Stable repeated cyclic voltammagrams of prepared electrodes suggests stability under electrochemical conditions.

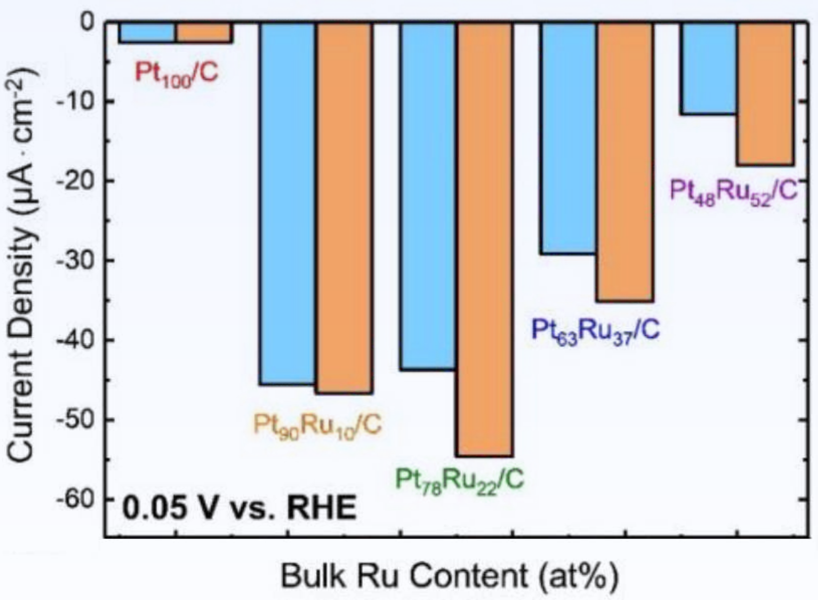


Dr. Zixuan Wang



Steady-state Current Density Results

- NO_3RR reduction current was normalized to ECSA, calculated using both H_{UPD} and Cu_{UPD} methods.
- By both metrics, $Pt_{78}Ru_{22}/C$ is the most active towards NO_3RR at 0.1 V.
- **Results suggest that Pt_3Ru/C is indeed active (~6 times as much as Pt/C) at 0.1 V as well as at 0 V.**
- $Pt_{78}Ru_{22}/C$ estimated to be *half as expensive* as Rh/C and *a third as expensive* as Pt/C to remediate NO_3^-.



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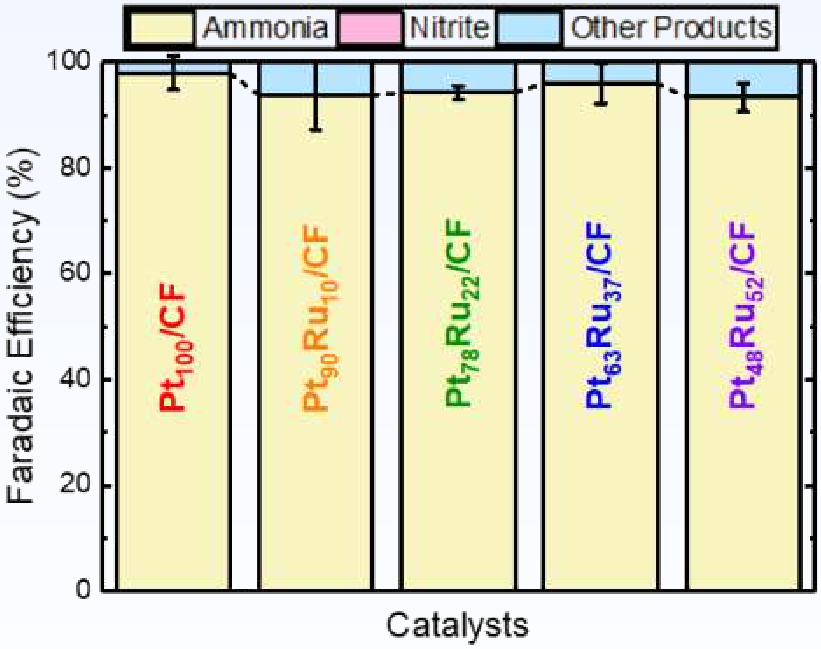
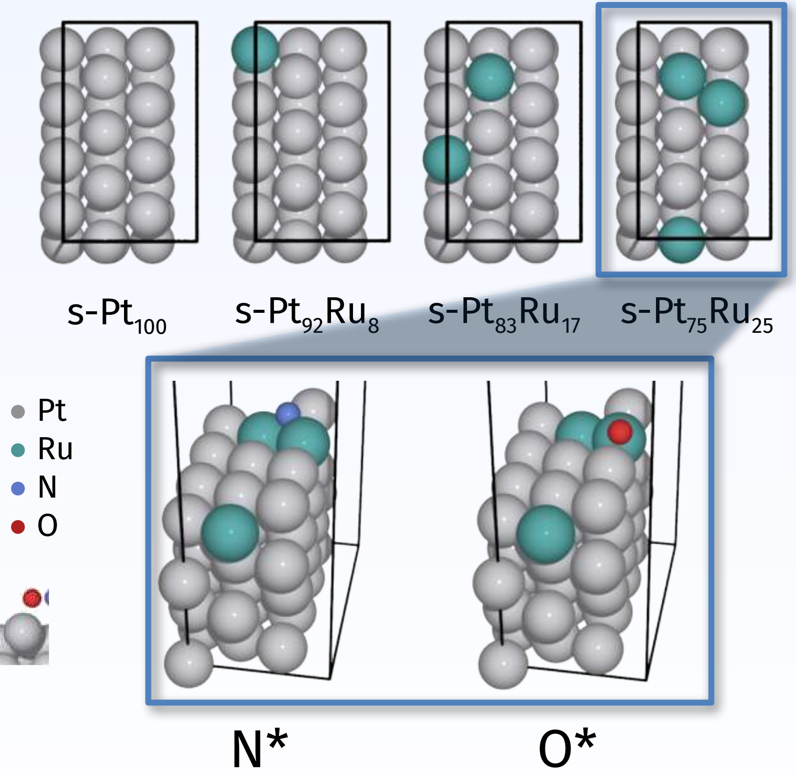
Selectivity Results

- Faradaic efficiency measured using ion chromatography and indophenol blue methods.
- All alloy materials show ≥ 93% Faradaic efficiency towards NH_3.
- **Pt_xRu_y/C shows reliably high selectivity towards a single desirable NO_3RR product.**

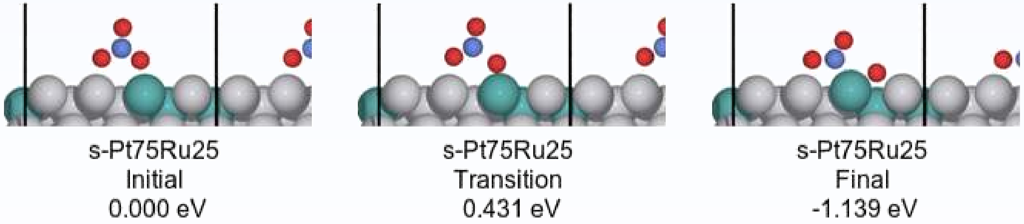


Computational Modeling of Pt_xRu_y catalysts

- How to control surface compositions? Alloy the surface.
- Computed N, O binding energies using density functional theory.
- Computed pure metal volcano plot for 0.1 V vs. RHE.
- Computed $NO_3^* \rightarrow NO_2^* + O^*$ barrier.



$NO_3^* \rightarrow NO_2^* + O^*$ on s-$Pt_{75}Ru_{25}$



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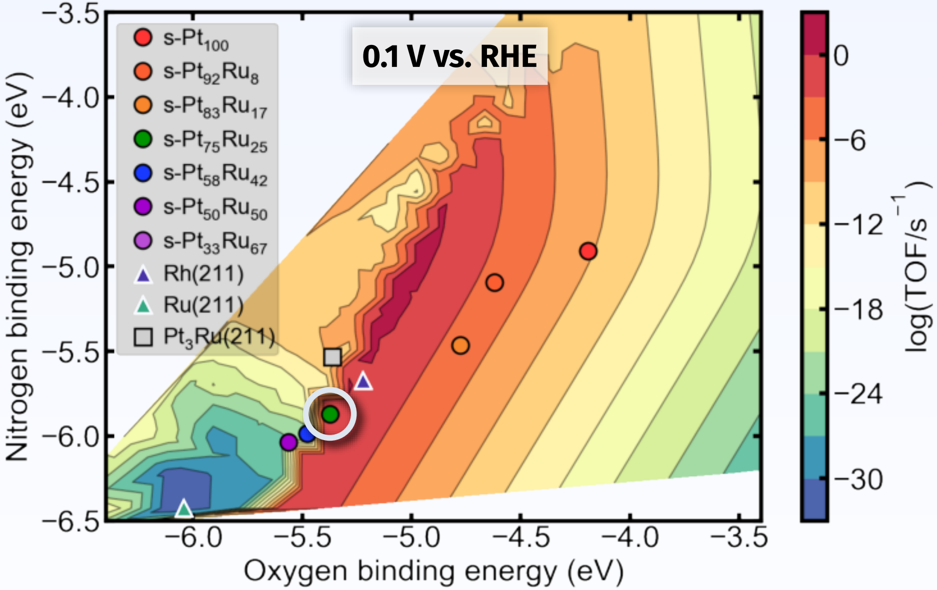
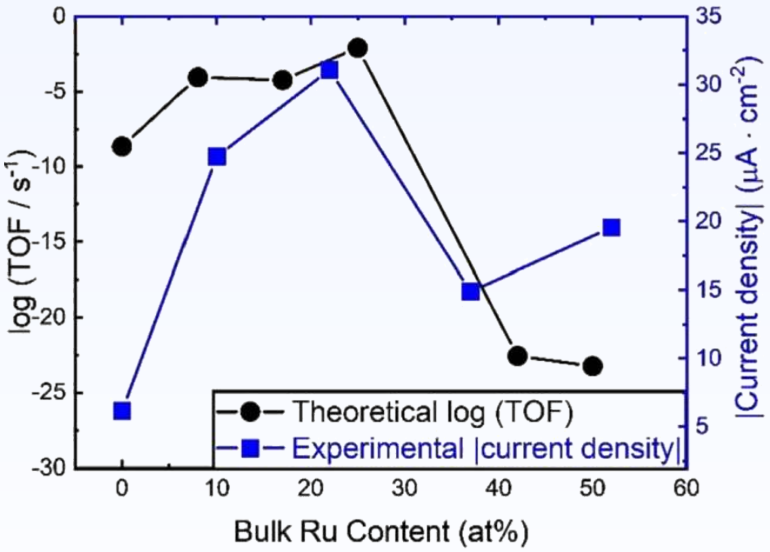
Alloy Trends Mirror Metal Trends

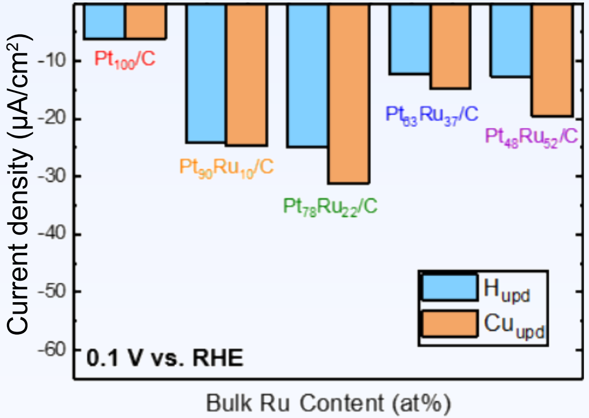


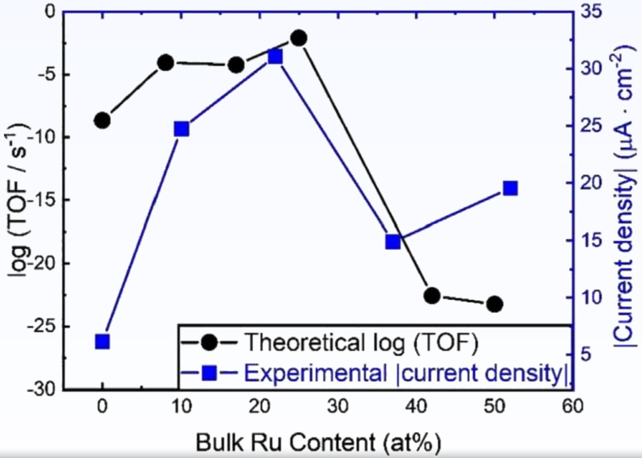


We hypothesize that the maximum in activity arises from a shift in the rate-determining step from nitrate dissociation to another step.

Conclusions and Implications

- Pt_3Ru ($Pt_{78}Ru_{22}/C$) is active for NO_3RR at 0.1 V vs. RHE (6 times more than Pt/C), and most active of all alloy compositions.
- Electrochemically stable, > 93% Faradaic efficiency towards NH_3, and three times cheaper than using Pt/C.
- Pure metal microkinetics rationalize activity trends of alloys (Pt_xRu_y/C).
- *Can potentially accelerate screening for other performant alloy electrocatalysts.*





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Dr. Zixuan Wang

Prof. Bryan R. Goldsmith

Dr. Jin-Xun Liu

Danielle Richards

Read our paper in *Journal of Catalysis:*

DOI: 10.1016/j.jcat.2020.12.031

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Also read our paper on Rh sulfides:

DOI: 10.1039/D1CY01369F

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Questions?