First-principles Modeling of Heterogeneous Catalysts for Sustainable Chemical Conversion

Bryan R. Goldsmith
Dow Corning Assistant Professor
Department of Chemical Engineering
University of Michigan, Ann Arbor
9/30/20

Catalysis is a multibillion-dollar industry and has a profound impact on everyday life

Early Nobel Prizes for work related to catalysis

Wilhelm Ostwald
”Investigations into the fundamental principles governing chemical equilibria and rates of reaction”, 1909

“For discoveries that confer the greatest benefit on mankind”

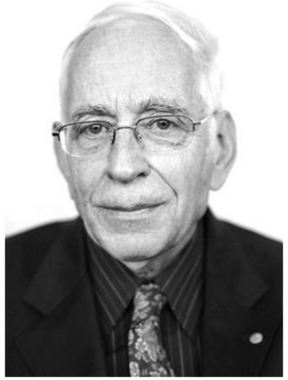
Paul Sabatier
“For his method of hydrogenating organic compounds in the presence of finely disintegrated metals", 1912

Fritz Haber
“For the synthesis of ammonia from its elements”, 1918

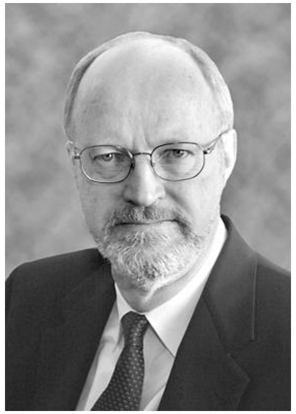
Irving Langmuir
“For his discoveries and investigations in surface chemistry”, 1932

Cyril Hinshelwood
”For researches into the mechanism of chemical reactions”, 1956

21st-century Nobel Prizes for catalysis related work



Yves Chauvin, Lyon, France, 2005



Robert Grubbs,
Pasadena, CA, 2005

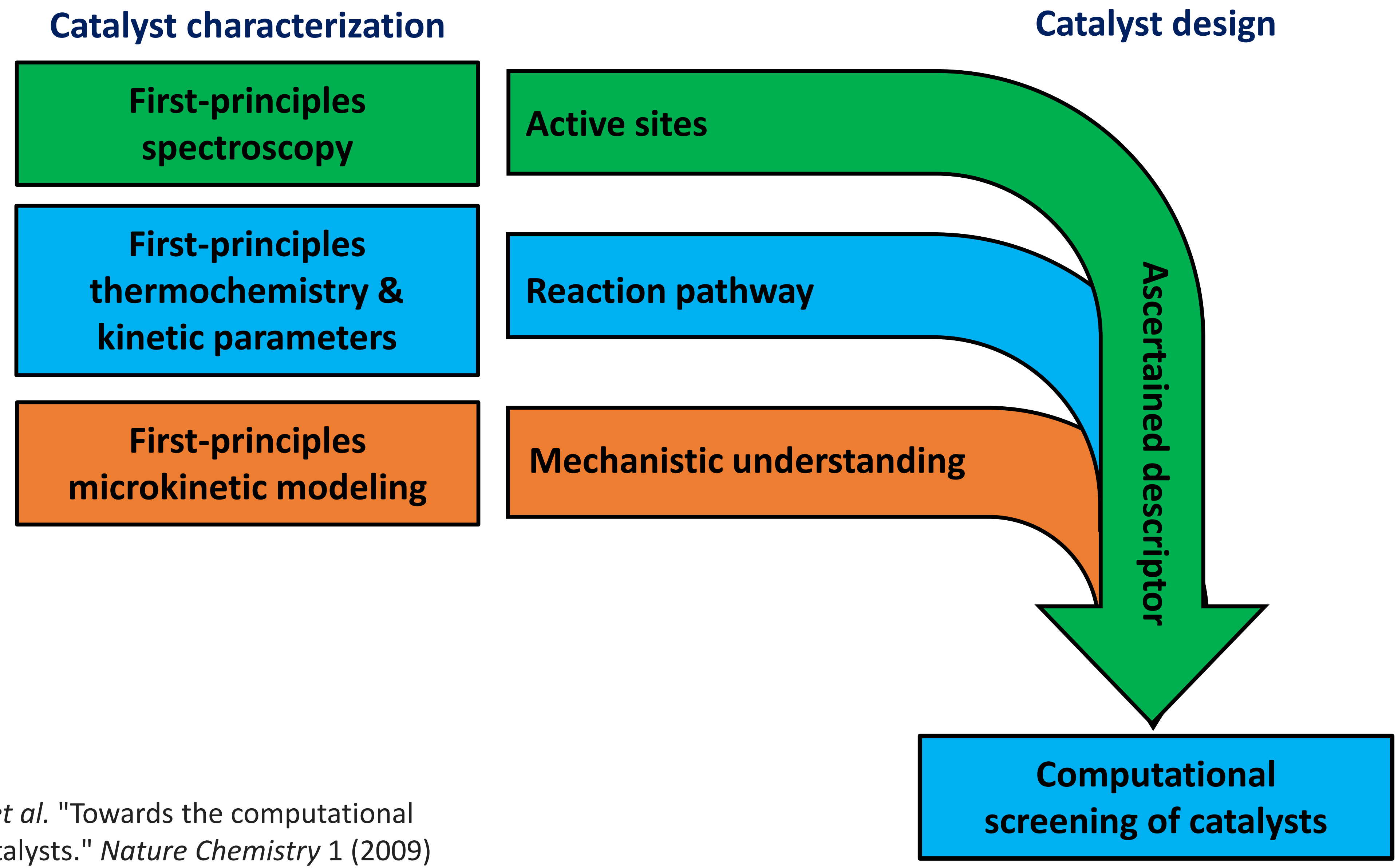
Richard Schrock
Boston, MA, 2005

”For the development of the
metathesis method in organic synthesis”

Gerhard Ertl
Fritz-Haber-Institut, Berlin
“For his studies of chemical processes
on solid surfaces”, 2007

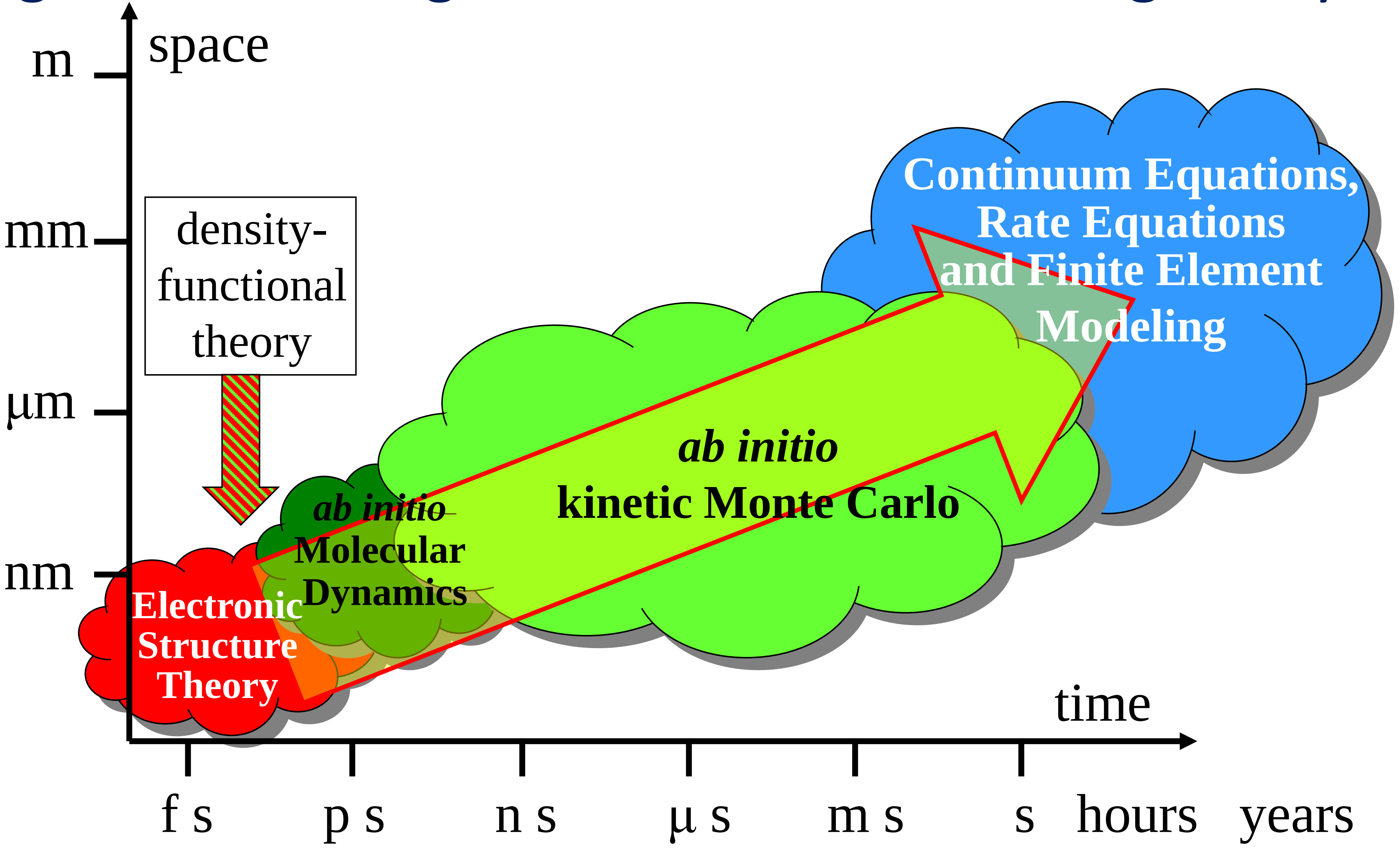
Martin Karplus, Michael Levitt, and Arieh Warshel successfully developed methods that *combined quantum and classical mechanics to calculate the courses of chemical reactions* using computers. **(2013 Nobel Prize in Chemistry)**

Computational catalysis can aid catalyst characterization and design



Nørskov, Kehlet, *et al.* "Towards the computational design of solid catalysts." *Nature Chemistry* 1 (2009)

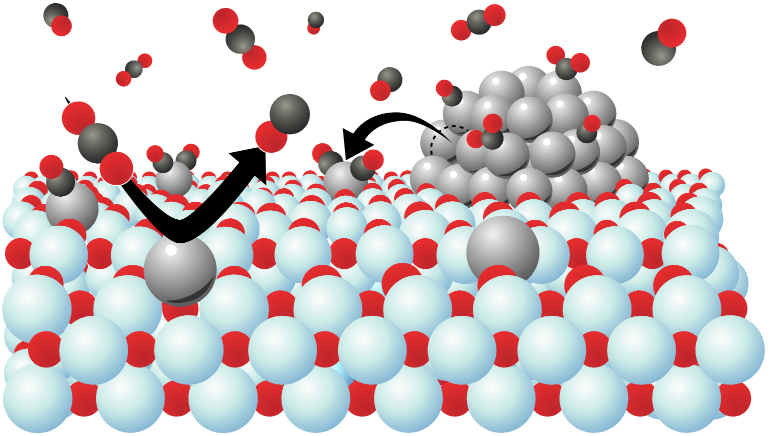
Bridging time and length scales when modeling catalysts



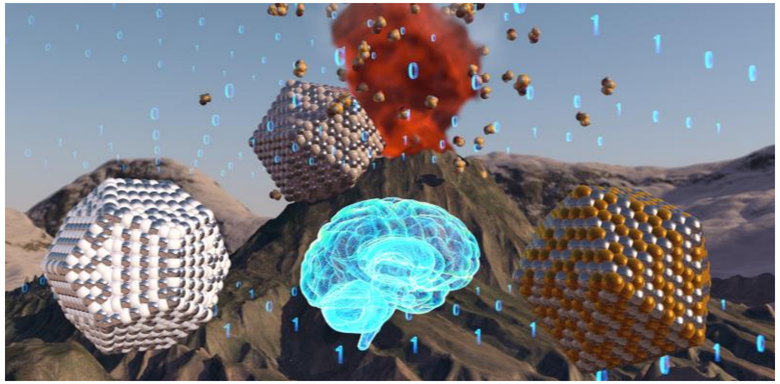
Adapted from slides of Karsten Reuter and Kristen Fichthorn

Overview of research areas in my lab

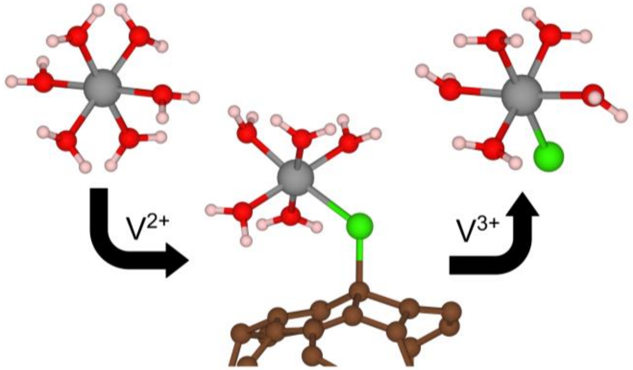
Area 1: Heterogeneous Catalysis for Chemical Conversion and Pollution Reduction



Area 2: Machine Learning to Accelerate Catalyst and Materials Design



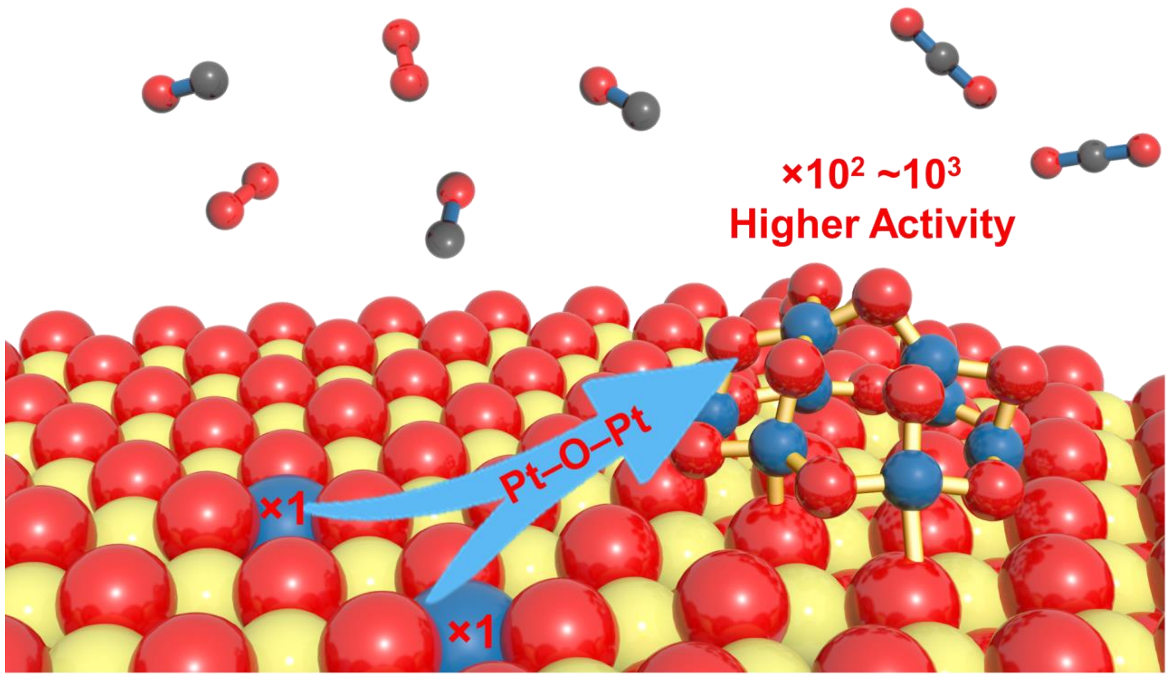
Area 3: Renewable Energy Generation, Use, & Storage

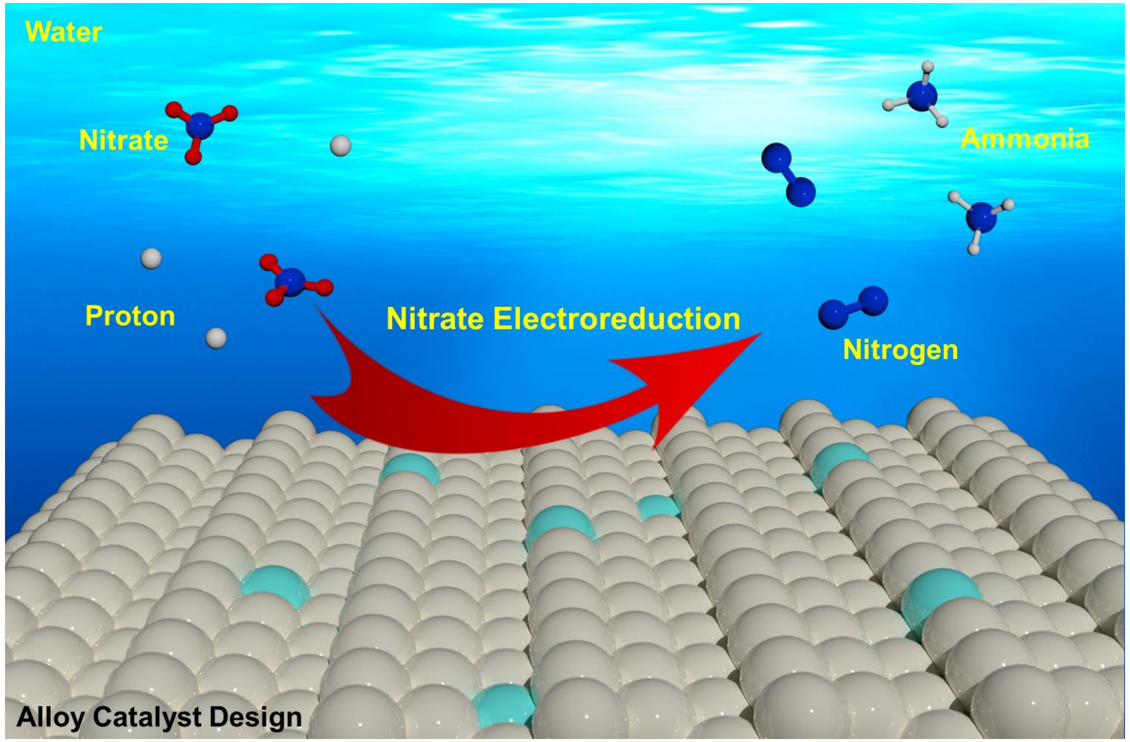


Topics of my talk today: Converting CO and NO_3^-

(1) Low temperature CO oxidation using Pt single atoms and nanoclusters

(2) Electrocatalytic reduction of nitrate (NO_3^-) in wastewater

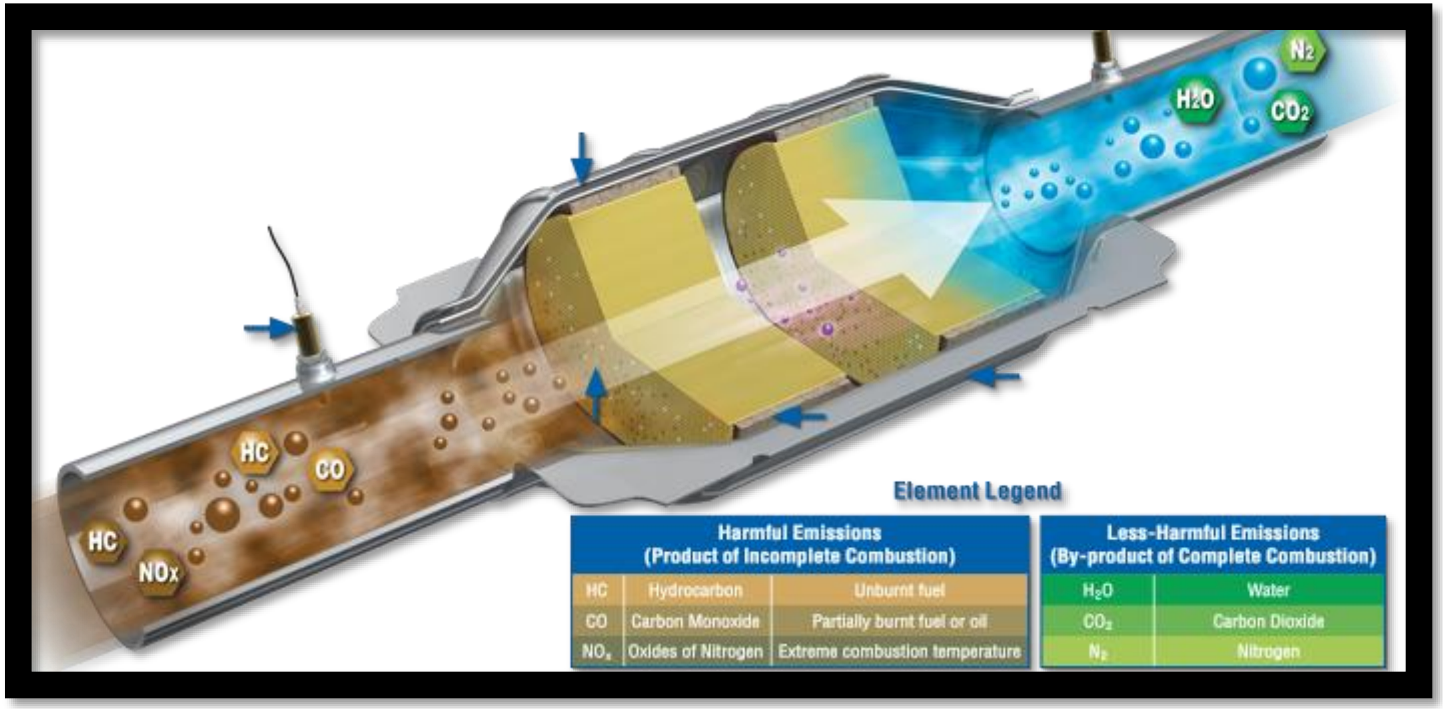


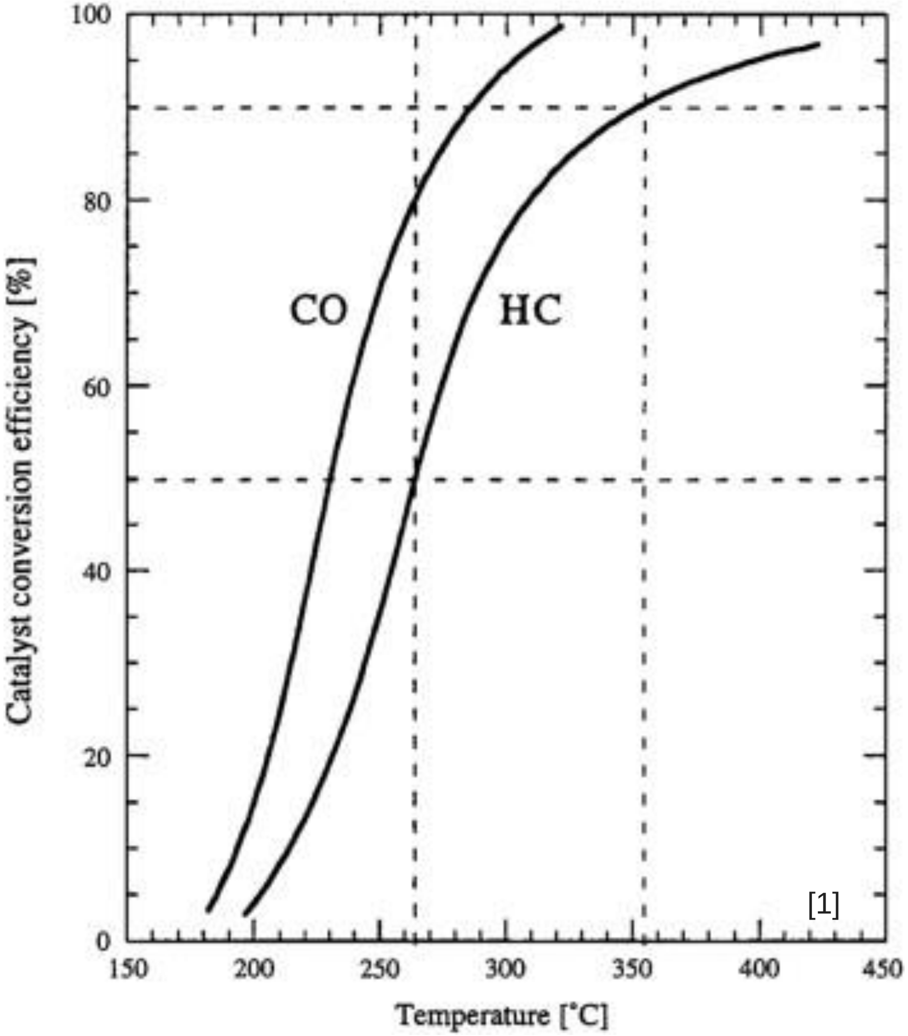


Low-temperature CO oxidation in catalytic converters

Platinum group metals (PGM) dispersed on ceria need to be more active in eliminating CO emissions below 150 °C during engine cold start.

Especially crucial for automotive emissions control

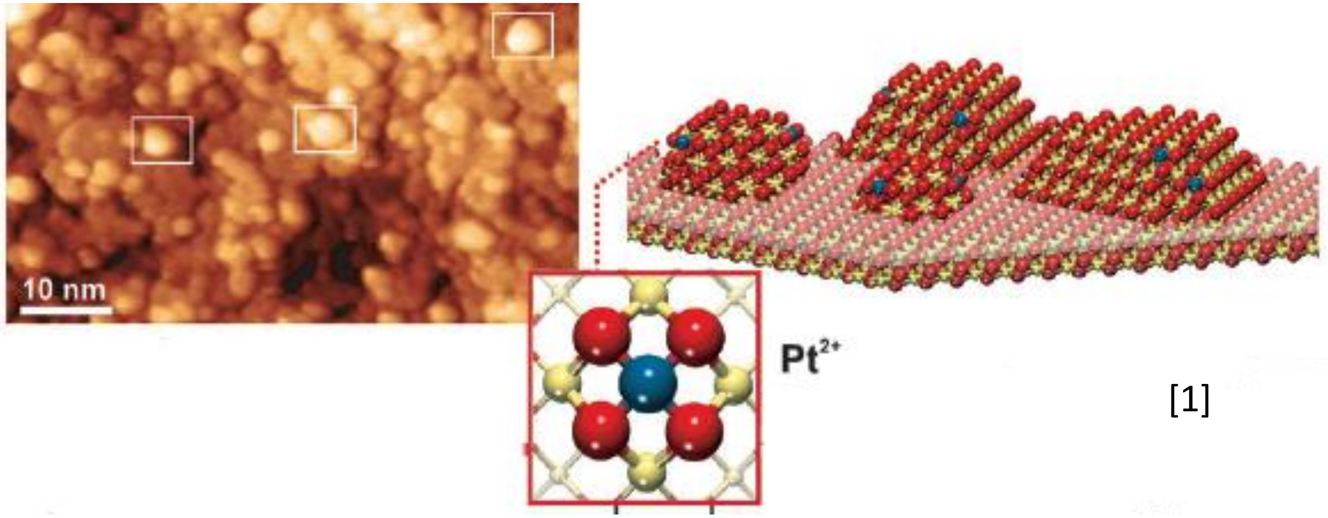




[1]. A. Roberts, R. Brooks, P. Shipway. *Energy Conversion and Management* 82 (2014)

Pt_1 single-atoms supported on oxides are of interest for low-temperature CO oxidation

Single atom catalysts are desired because they make optimal use of rare and expensive metals.



[1]

Unfortunately, Pt_1 single atom catalysts c
to or worse than conventional Pt particle

<u>At 150 °C priorly reported</u>

Pt_1/CeO_2: TOF of 0.0005–0.092 s^{-1}

Pt particle/CeO_2: TOF of 0.004–0.35 s^{-1}

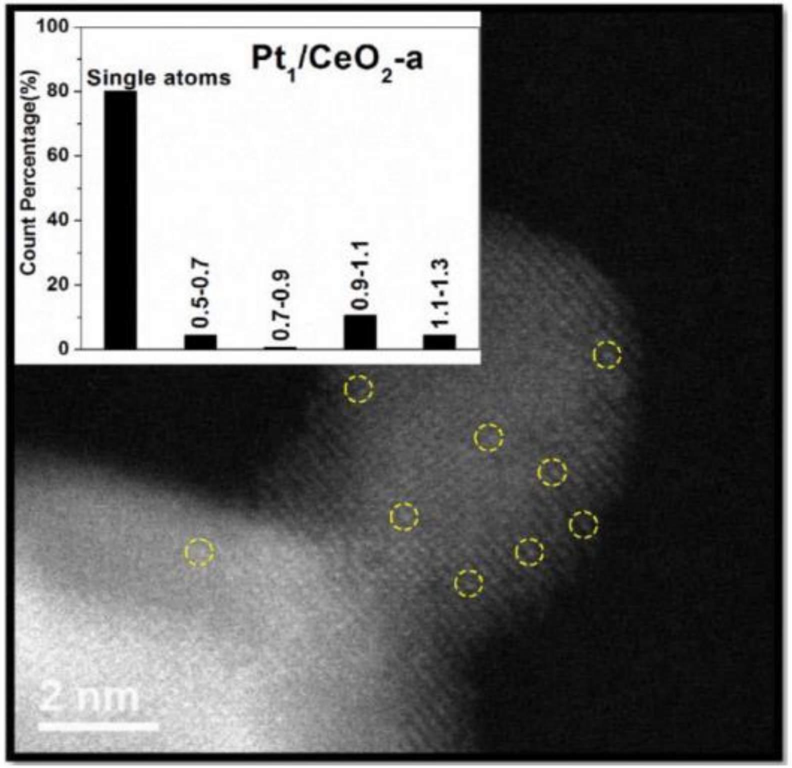
Our goal: Understand the activity difference between Pt_1 and well-defined Pt nanoclusters under oxygen rich conditions.

[1]. A. Bruix, Y. Lykhach *et al. Angew. Chem.* 53 (2014)

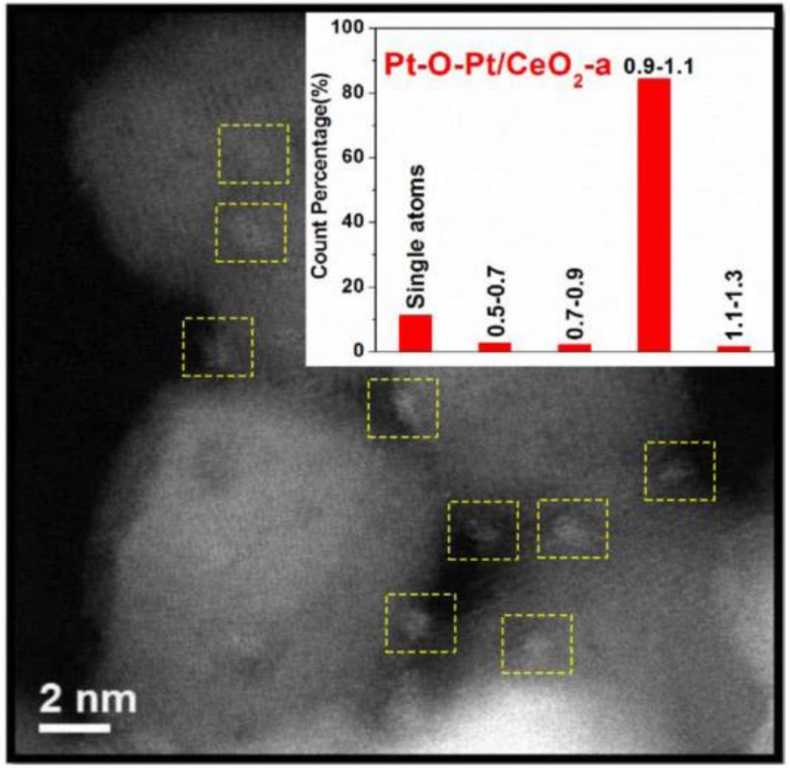
Experimental synthesis of Pt_1/CeO_2 and Pt-O-Pt/CeO_2

ceria support (10-30 nm particles)

Pt_1 single-atom catalyst

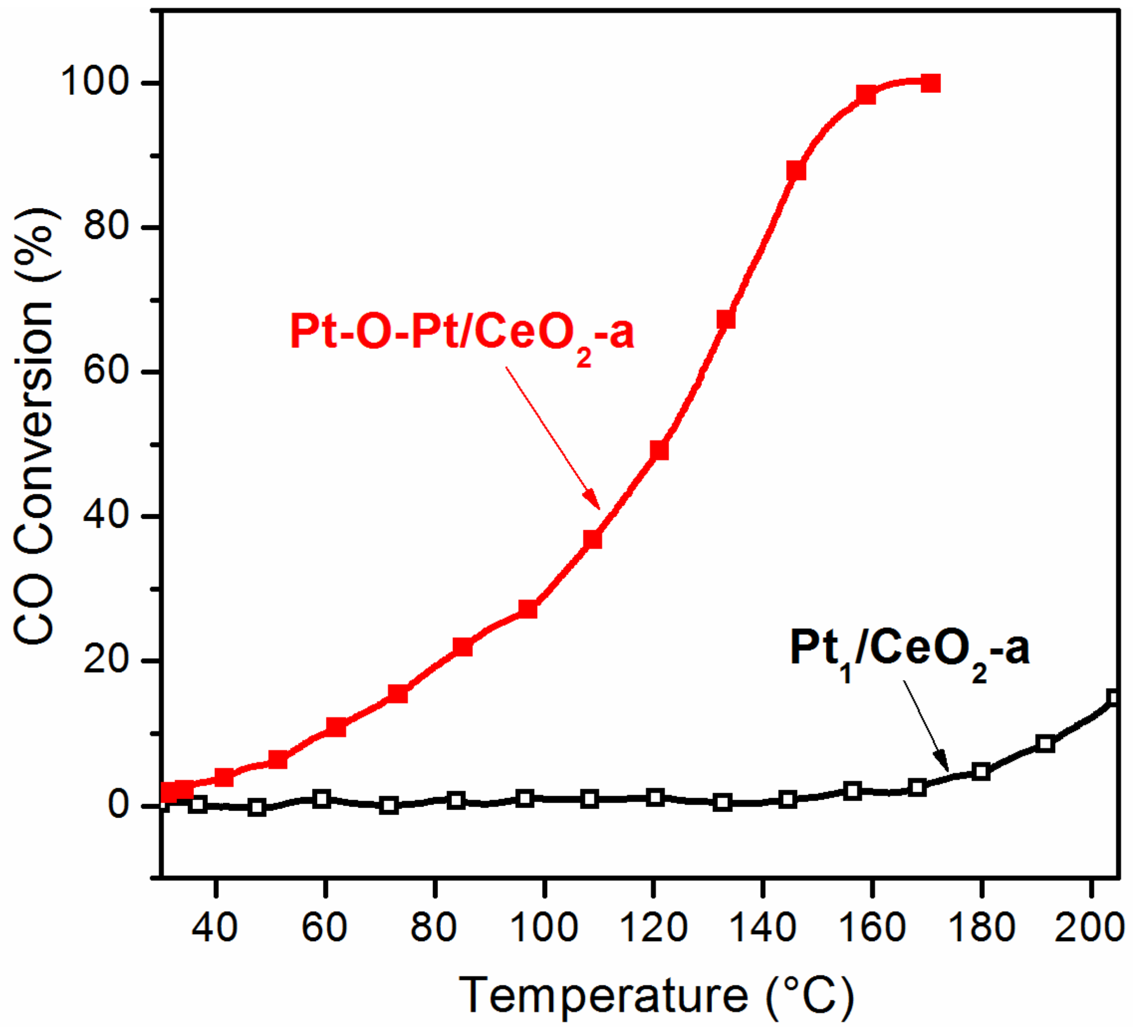


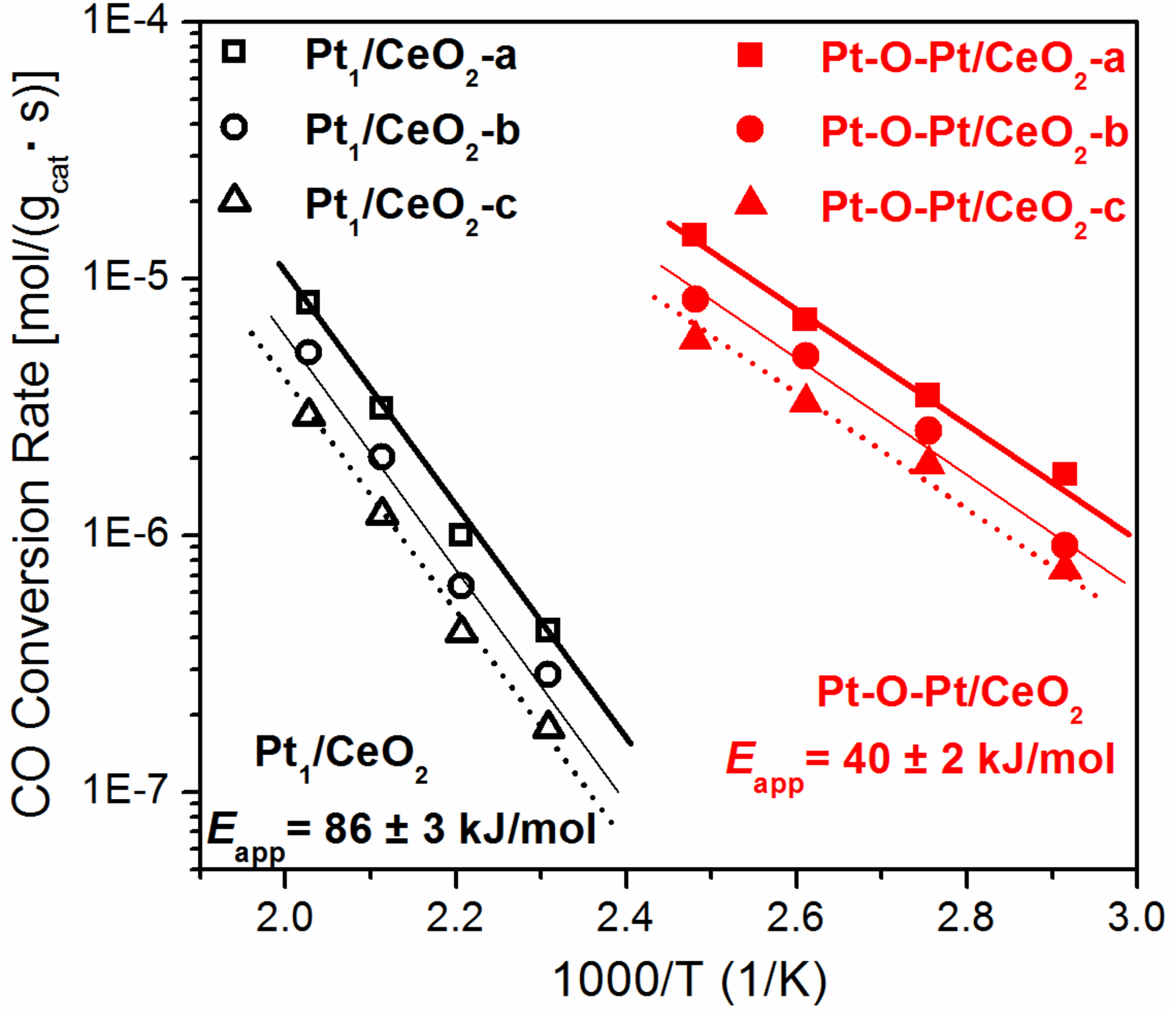
0.9 - 1.1 nm Pt-O-Pt catalyst



H. Wang, J.-X. Liu, W. Li, L. F. Allard, S. Lee, J. Wang, H. Li, J. Wang, X. Cao, M. Shen, B. R. Goldsmith, M. Yang, *Nat. Commun.* 10 (2019)

Experiments show the 1 nm Pt-O-Pt/CeO_2 clusters are much more active than Pt_1/CeO_2 at low temperatures

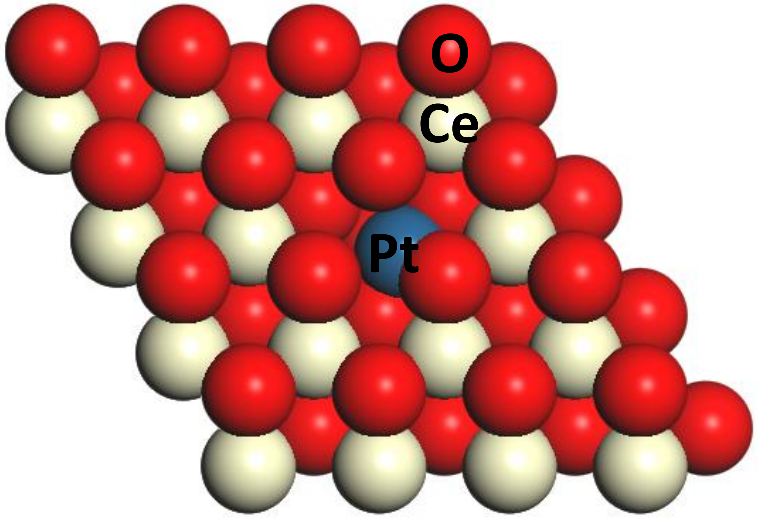




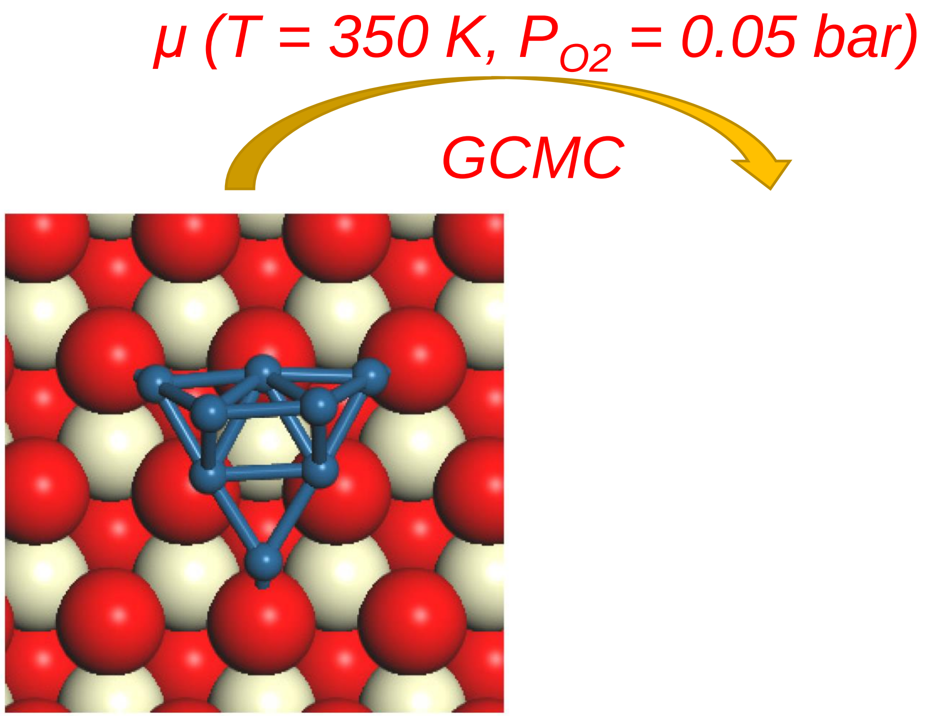
CO oxidation light-off performance ([CO] = 0.1%, [O_2] = 5 %, balanced with N_2)

Perform DFT modeling to understand the structure and activity of Pt_1/CeO_2 and Pt_xO_y/CeO_2

- Cluster structure search using genetic algorithm + grand canonical Monte-Carlo (GA+GCMC)[1]
- $CeO_2(111)$ used as the model support
- Use a model Pt_8O_y cluster as a representative cluster (~ 1 nm)



Stable $Pt_1/CeO_2(111)$ configuration

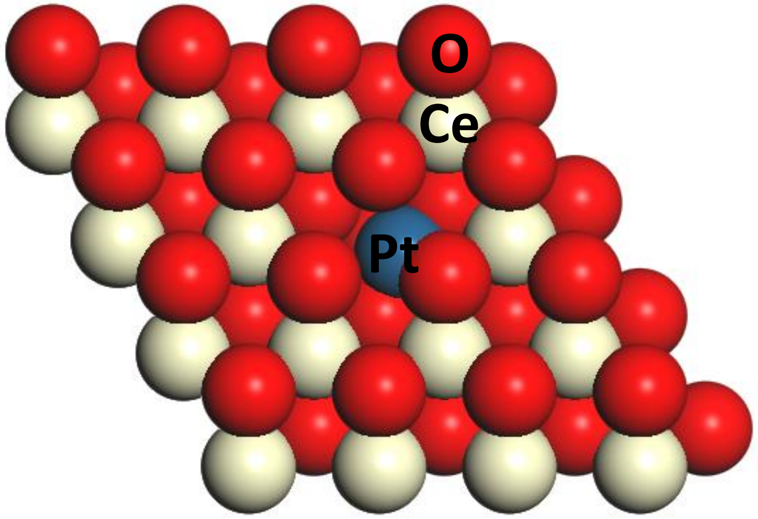


Pt_8/CeO_2

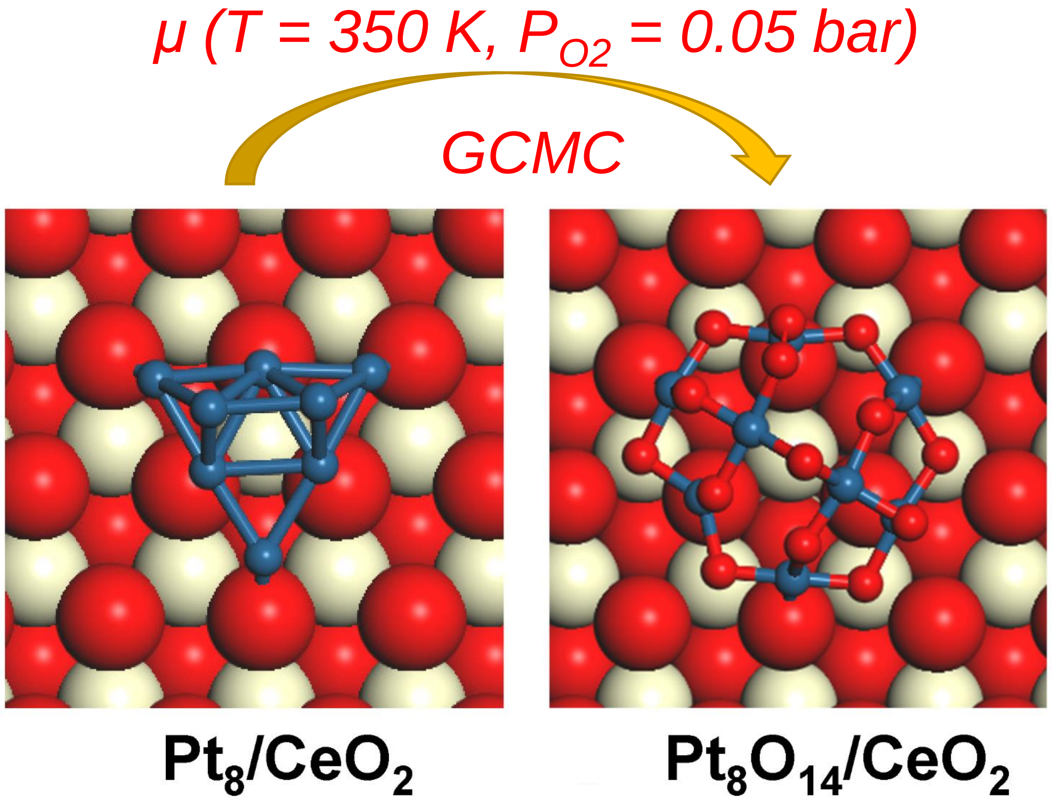
[1] J-X. Liu,… E. J. Hensen *JACS* 140 (2018)

Perform DFT modeling to understand the structure and activity of Pt_1/CeO_2 and Pt_xO_y/CeO_2

- Cluster structure search using genetic algorithm + grand canonical Monte-Carlo (GA+GCMC)[1]
- $CeO_2(111)$ used as the model support
- Use a model Pt_8O_y cluster as a representative cluster (~ 1 nm)

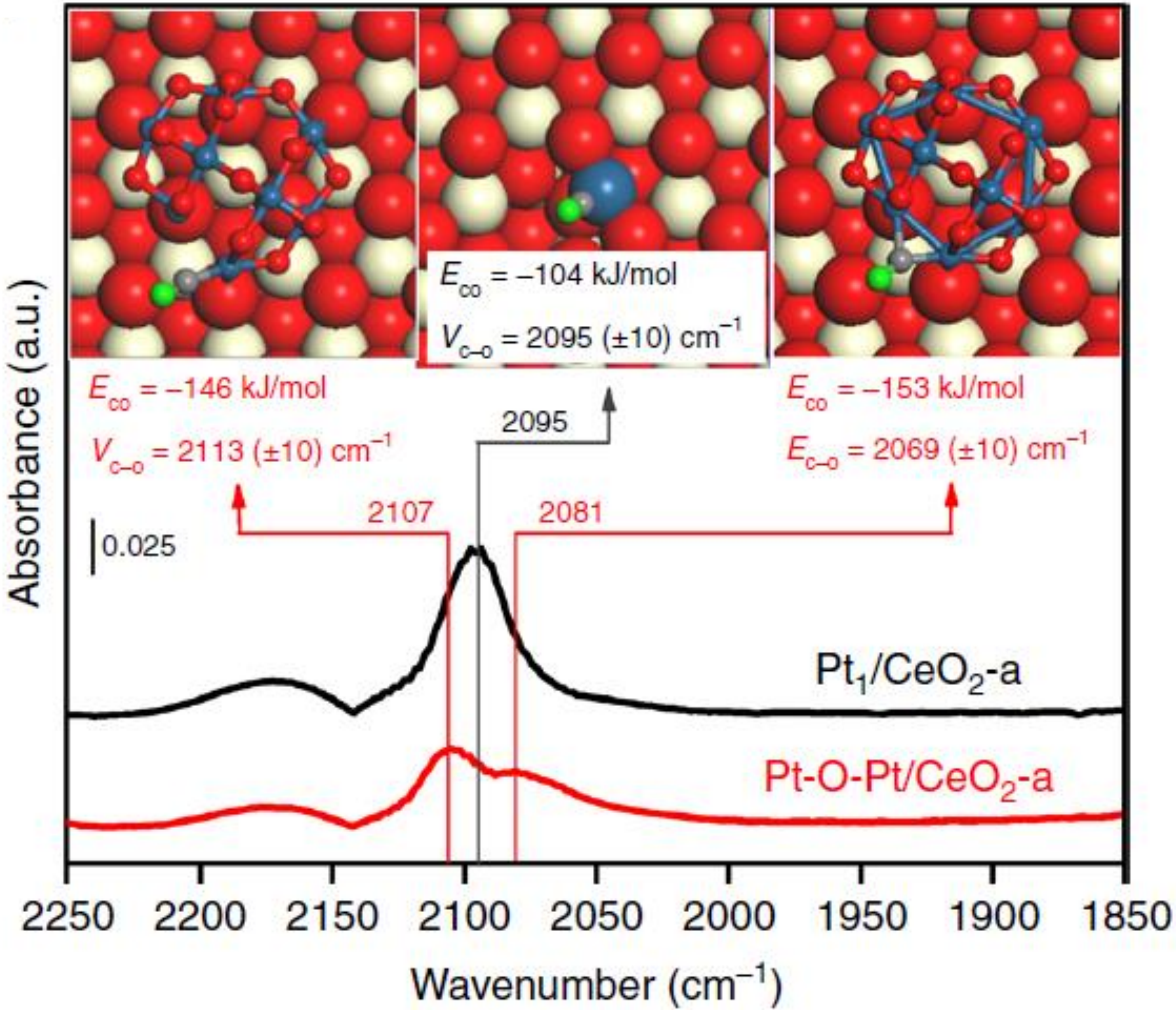


Stable $Pt_1/CeO_2(111)$ configuration

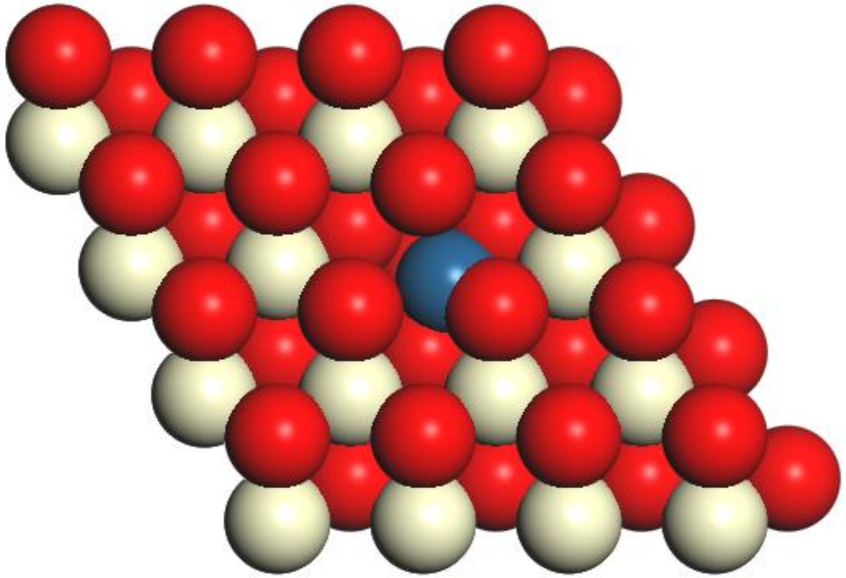


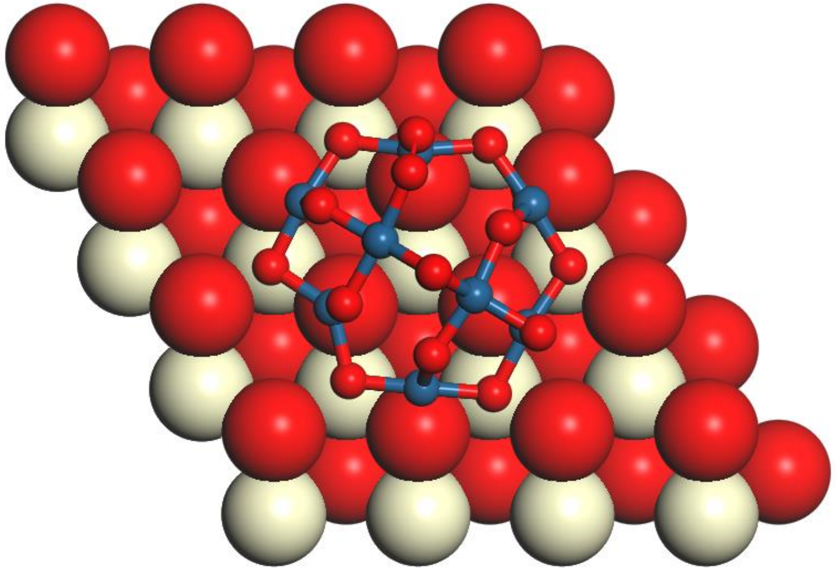
[1] J-X. Liu,… E. J. Hensen *JACS* 140 (2018)

Pt_1/CeO_2 and Pt_8O_{14}/CeO_2 models are consistent with DRIFTS



Study the mechanism of CO oxidation on $Pt_1/CeO_2(111)$ and $Pt_8O_{14}/CeO_2(111)$ under oxygen-rich conditions





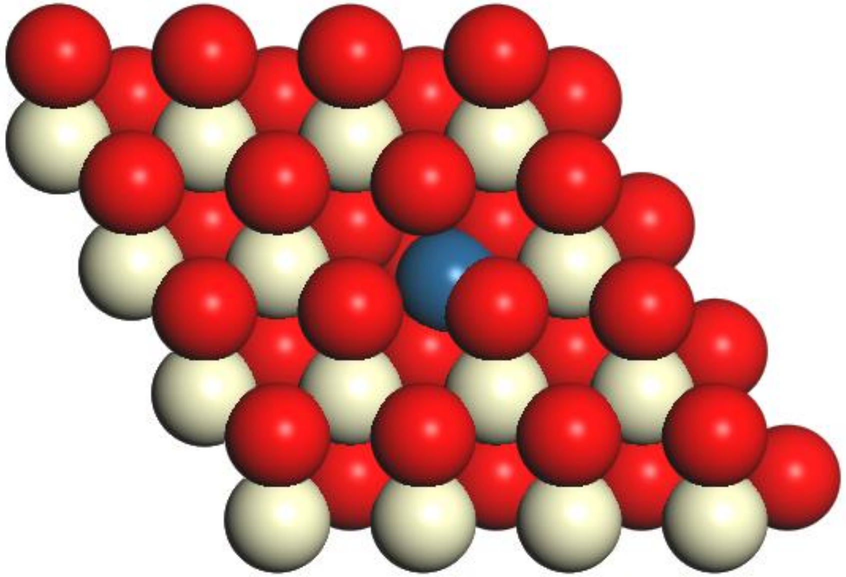
→ Surface oxygen vacancies will be rapidly filled under our oxygen-rich conditions and low-temperature.[1-2]

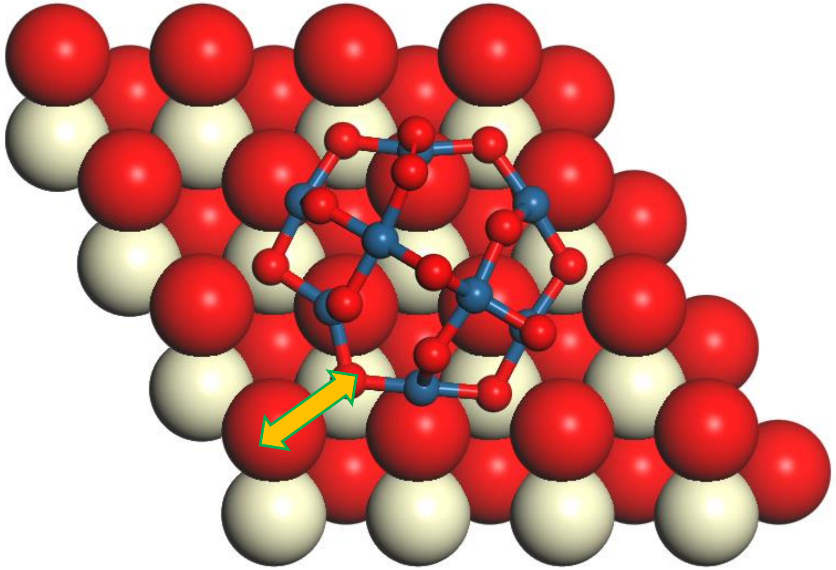
Three CO oxidation pathways:

1. **At the metal-support interface**
2. **At the Pt_8O_{14} cluster edge**
3. **On Pt_8O_{14} cluster**

[1] M. Fronzi *et al. J. Chem. Phys.* 131 (2009)
[2] V. Botu, R. Ramprasad, A. Mhadeshwar. *Surf. Science* 619 (2014)

Study the mechanism of CO oxidation on $Pt_1/CeO_2(111)$ and $Pt_8O_{14}/CeO_2(111)$ under oxygen-rich conditions





→ Surface oxygen vacancies will be rapidly filled under our oxygen-rich conditions and low-temperature.[1-2]

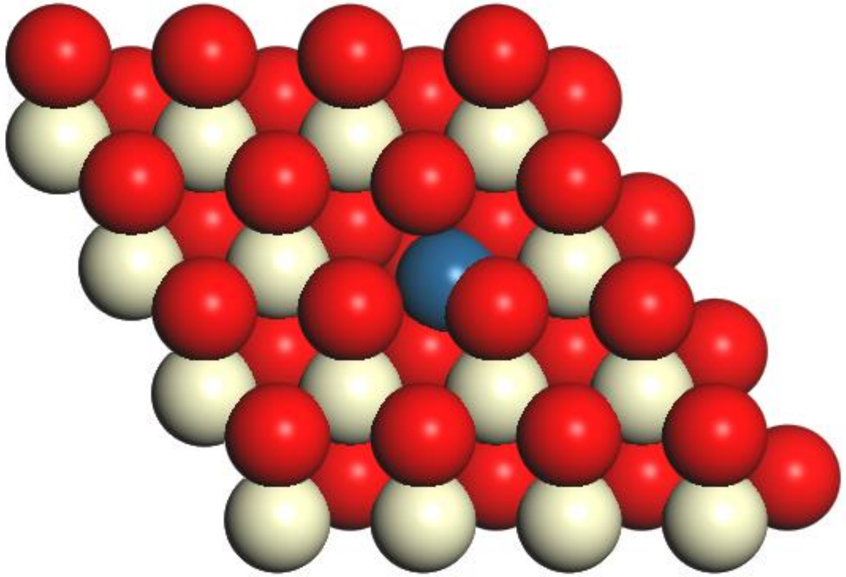
Three CO oxidation pathways:

1. **At the metal-support interface**
2. **At the Pt_8O_{14} cluster edge**
3. **On Pt_8O_{14} cluster**

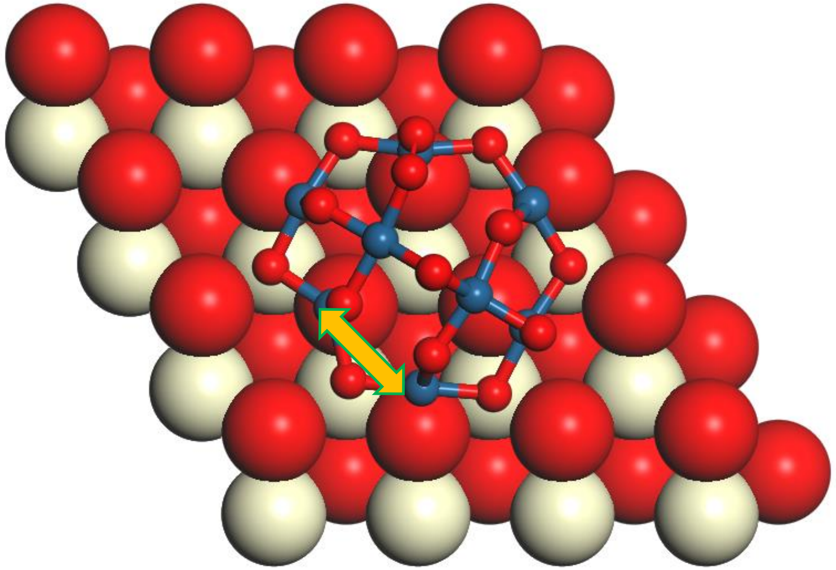
[1] M. Fronzi *et al. J. Chem. Phys.* 131 (2009)

[2] V. Botu, R. Ramprasad, A. Mhadeshwar. *Surf. Science* 619 (2014)

Study the mechanism of CO oxidation on $Pt_1/CeO_2(111)$ and $Pt_8O_{14}/CeO_2(111)$ under oxygen-rich conditions



→ Surface oxygen vacancies will be rapidly filled under our oxygen-rich conditions and low-temperature.[1-2]



Three CO oxidation pathways:

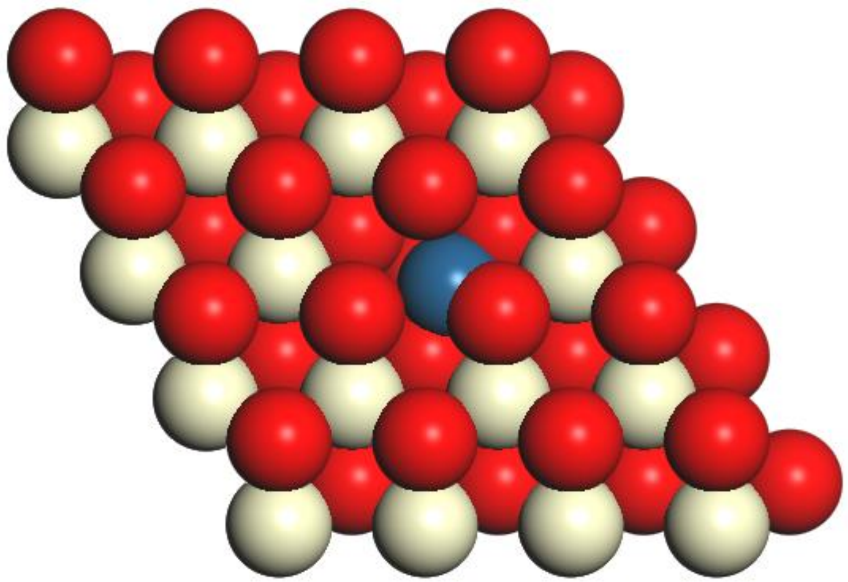
1. At the metal-support interface

2. At the Pt_8O_{14} cluster edge

3. On Pt_8O_{14} cluster

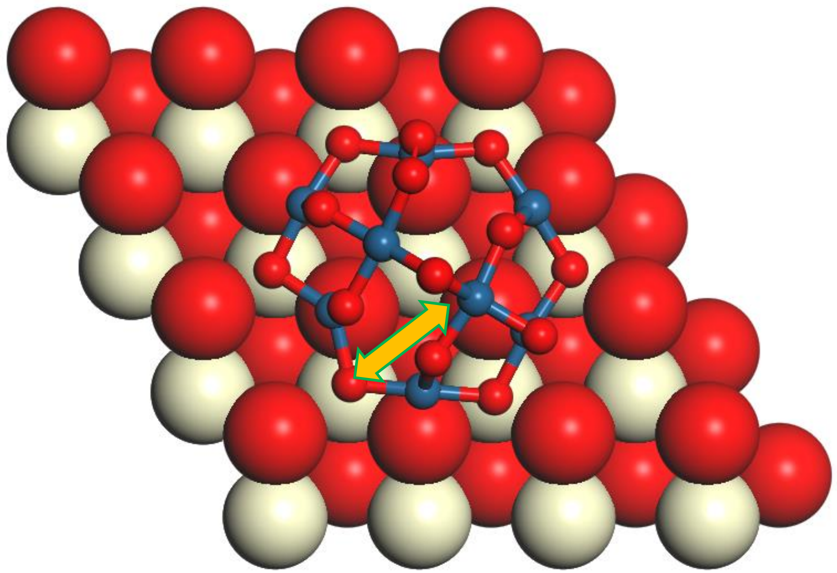
[1] M. Fronzi *et al. J. Chem. Phys.* 131 (2009)
[2] V. Botu, R. Ramprasad, A. Mhadeshwar. *Surf. Science* 619 (2014)

Study the mechanism of CO oxidation on $Pt_1/CeO_2(111)$ and $Pt_8O_{14}/CeO_2(111)$ under oxygen-rich conditions



→ Surface oxygen vacancies will be rapidly filled under our oxygen-rich conditions and low-temperature.[1-2]

[1] M. Fronzi *et al. J. Chem. Phys.* 131 (2009)
[2] V. Botu, R. Ramprasad, A. Mhadeshwar. *Surf. Science* 619 (2014)



Three CO oxidation pathways:

1. At the metal-support interface

2. At the Pt_8O_{14} cluster edge

3. On Pt_8O_{14} cluster

Microkinetic modeling for mechanistic hypothesis testing of CO oxidation by Pt_1 /CeO_2(111) and Pt_8O_{14}/CeO_2(111)

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

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

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

Use MKMCXX[1] mean-field microkinetic modeling software.

<u>Inputs to software</u>

✓ Adsorption energies of reactant, intermediates, and product

✓ Forward and backward reaction barriers

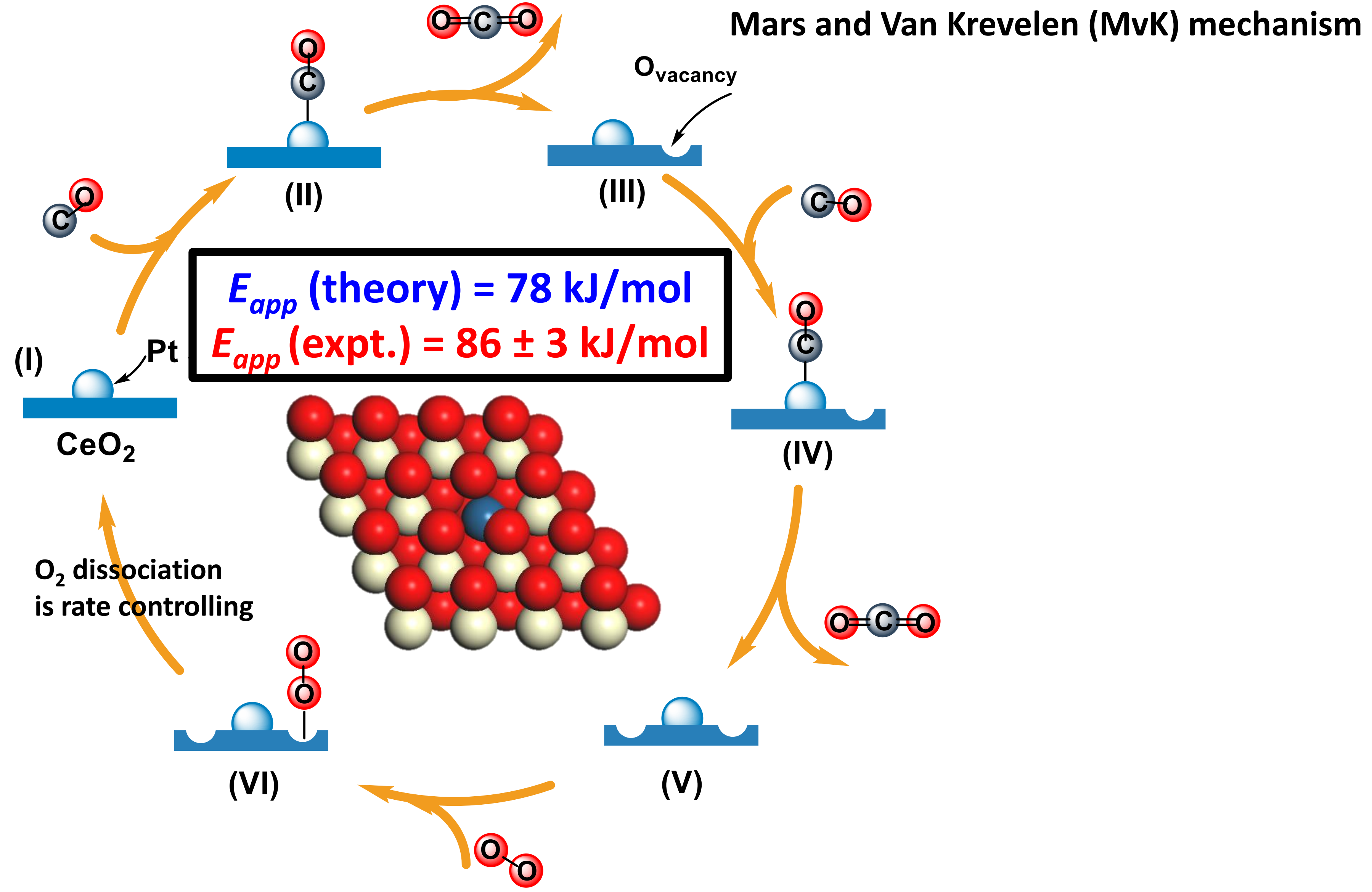
✓ Temperature, pressure

<u>Output:</u>

✓ Reaction rate, coverages, apparent activation barrier

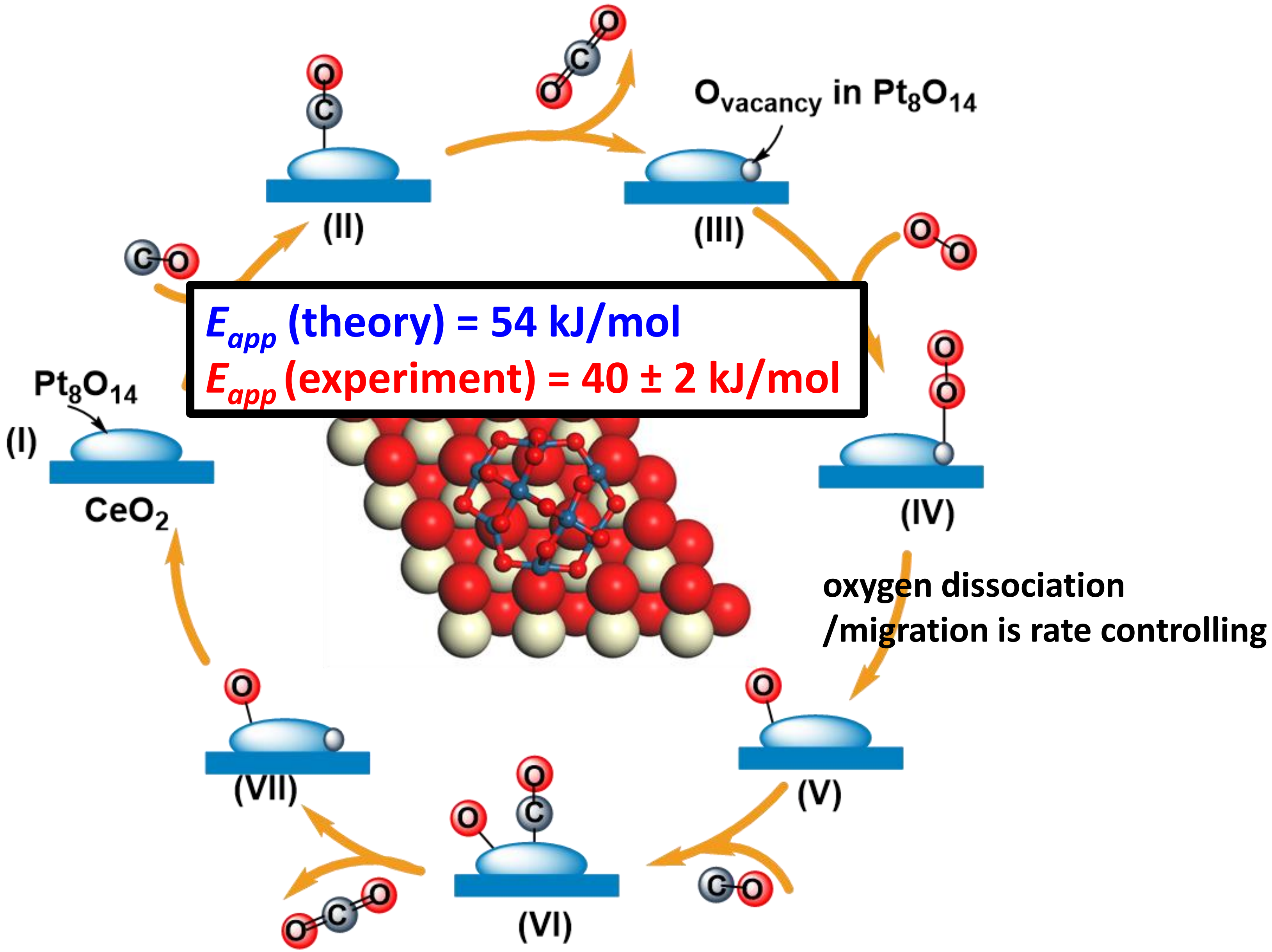
[1] https://www.mkmcxx.nl/, I. Filot, van Santen Rutger, E. Hensen, *Angew. Chem. Int.* 53 (2014)

CO oxidation on $Pt_1/CeO_2(111)$ follows MVK mechanism



H. Wang, J.-X. Liu, W. Li, L. F. Allard, S. Lee, J. Wang, H. Li, J. Wang, X. Cao, M. Shen, B. R. Goldsmith, M. Yang, *Nat. Commun.* 10 (2019)

CO oxidation at Pt-O-Pt in Pt_8O_{14} is favored

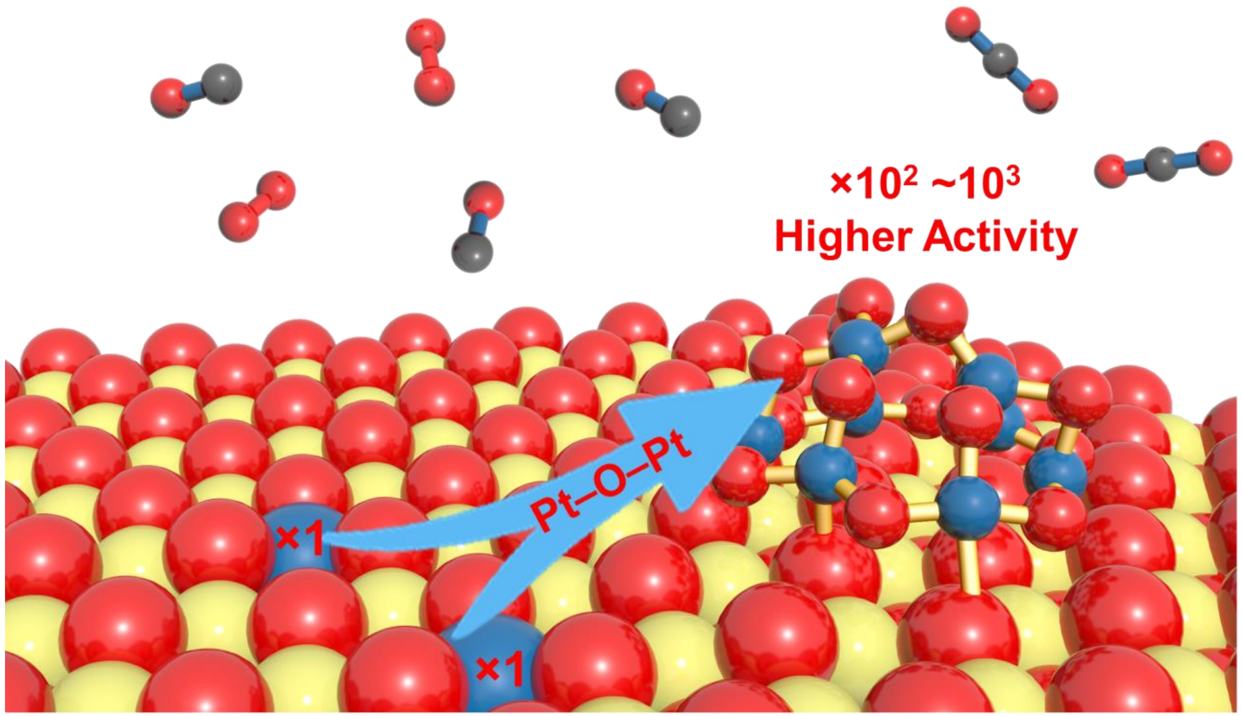


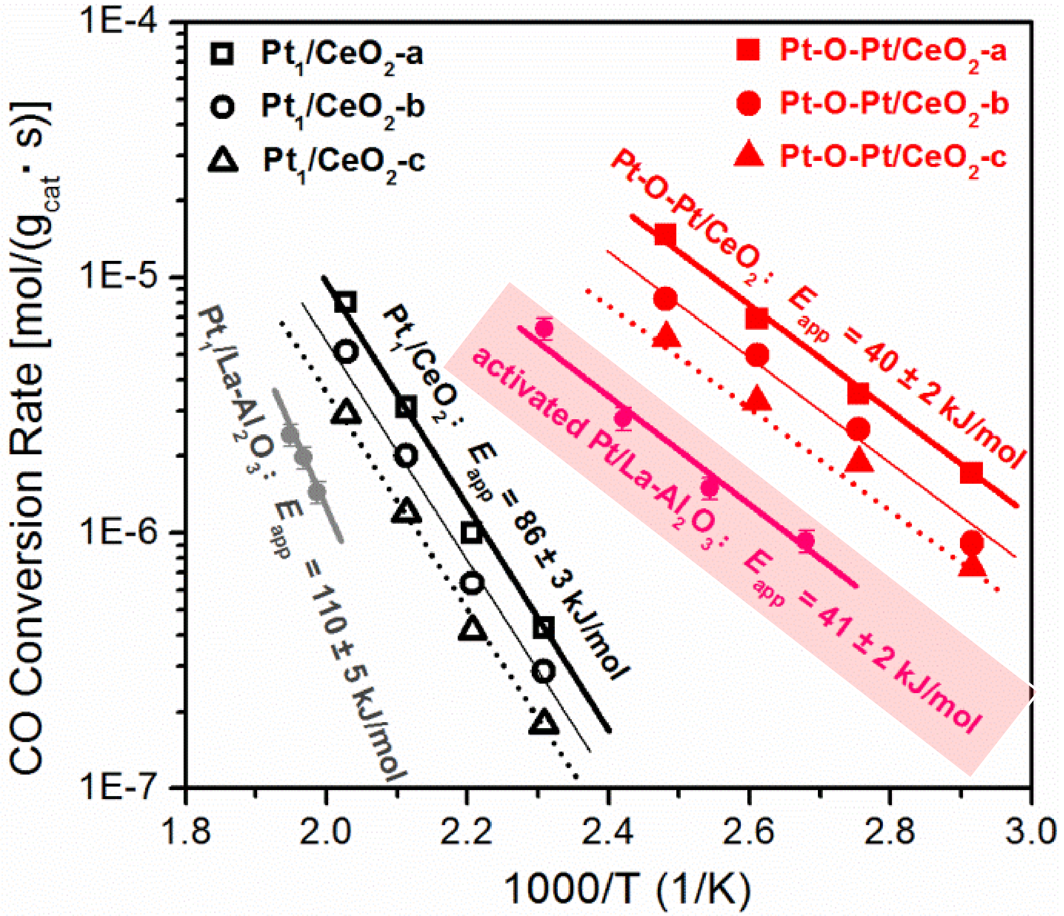
H. Wang, J.-X. Liu, W. Li, L. F. Allard, S. Lee, J. Wang, H. Li, J. Wang, X. Cao, M. Shen, B. R. Goldsmith, M. Yang, *Nat. Commun.* 10 (2019)

Pt-O-Pt/CeO_2 has 100-1000× higher TOF than Pt_1/CeO_2 for low-temperature CO oxidation

1) Semi-quantitative structural and kinetic agreement found between experiment and models for both the Pt-O-Pt/CeO_2 and Pt_1/CeO_2 systems.

2) High catalytic activity may arise from the Pt-O-Pt unit in Pt-O-Pt/CeO_2 under these O_2-rich conditions.

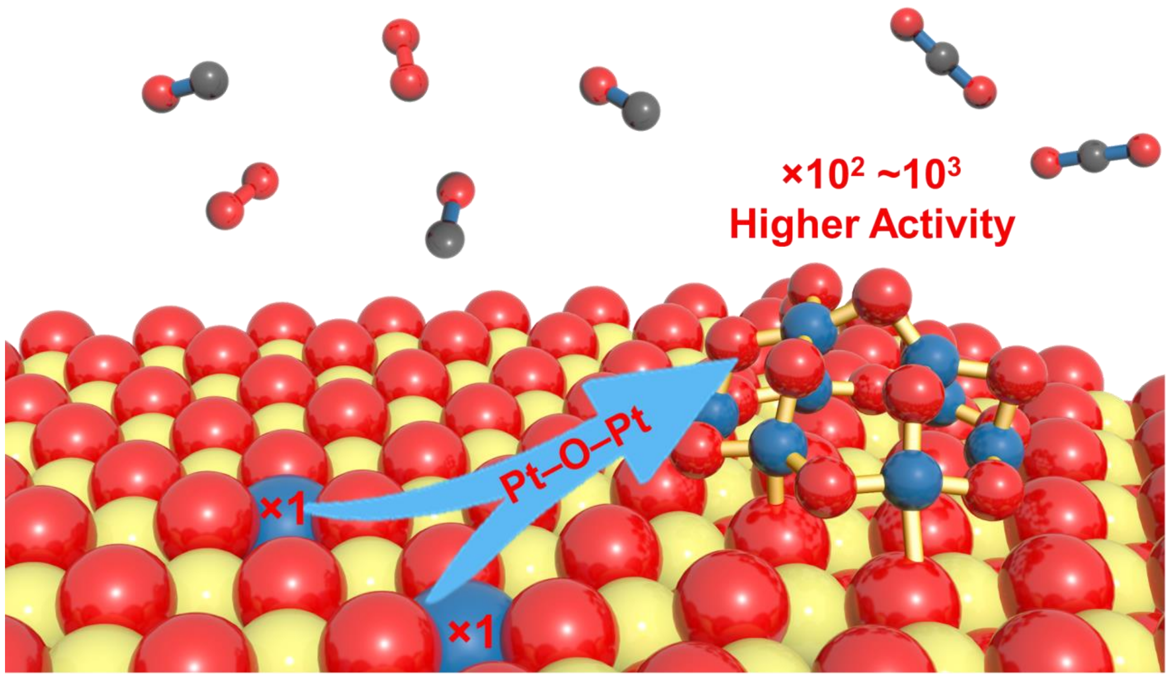




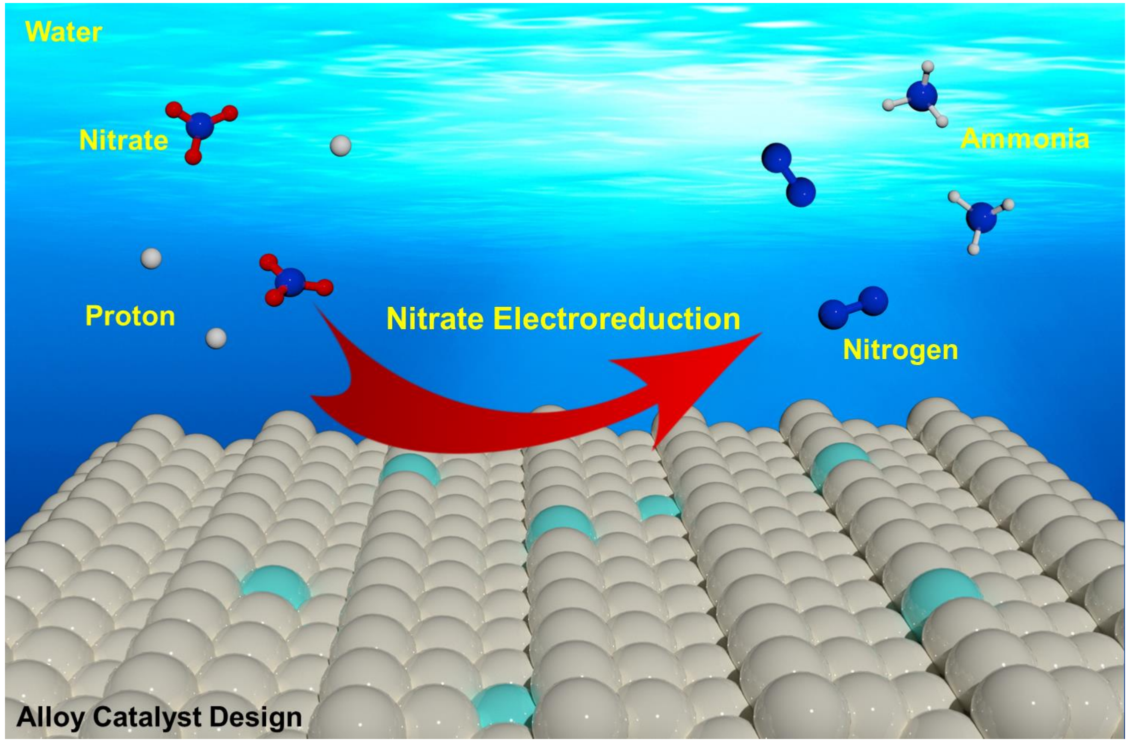
H. Wang *et al.*, *Nat. Commun.* 10 (2019)

Topics of my talk today: Converting CO and NO_3^-

(1) Low temperature CO oxidation using Pt single atoms and nanoclusters



(2) Electrocatalytic reduction of nitrate (NO_3^-) in wastewater



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

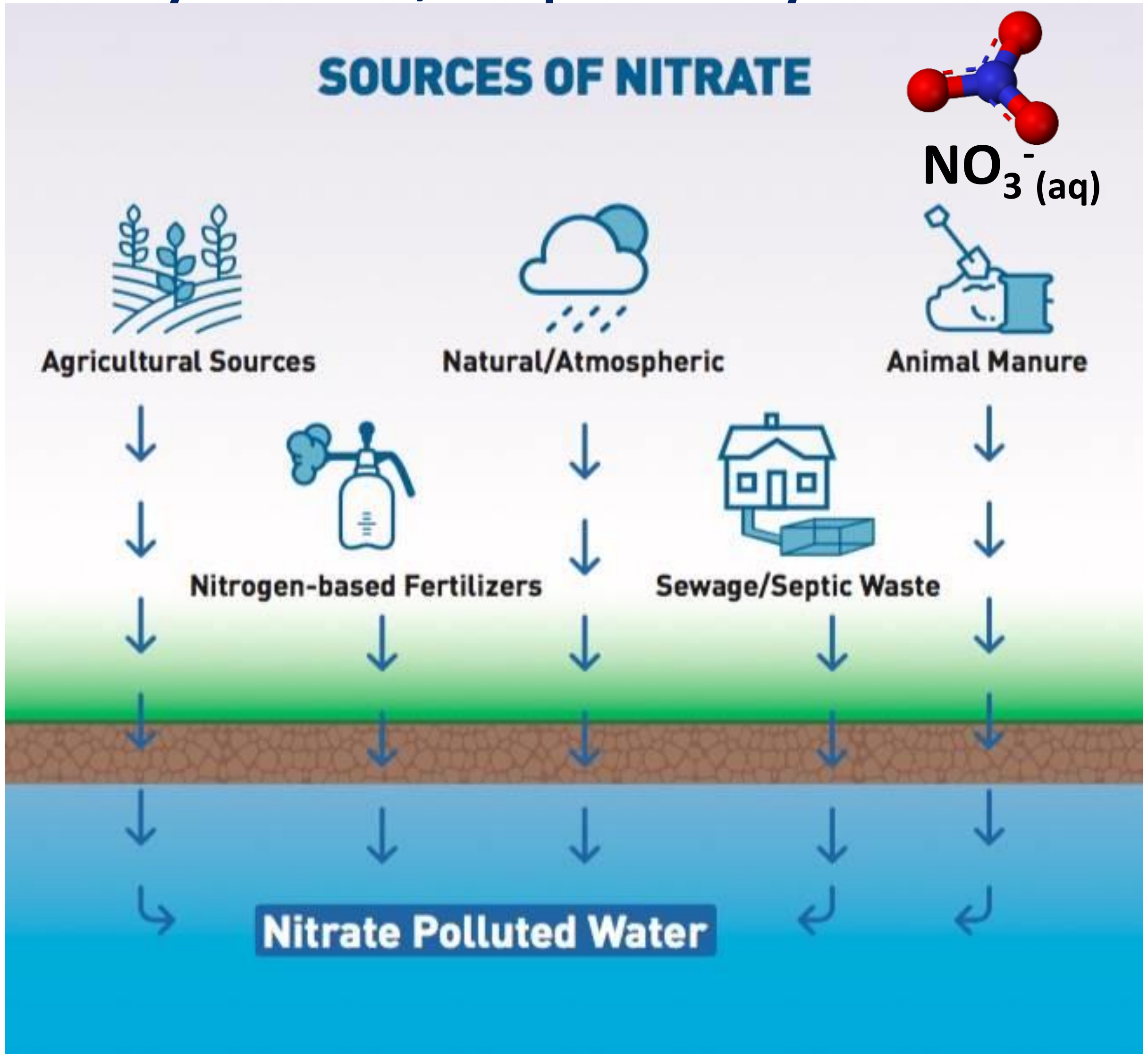
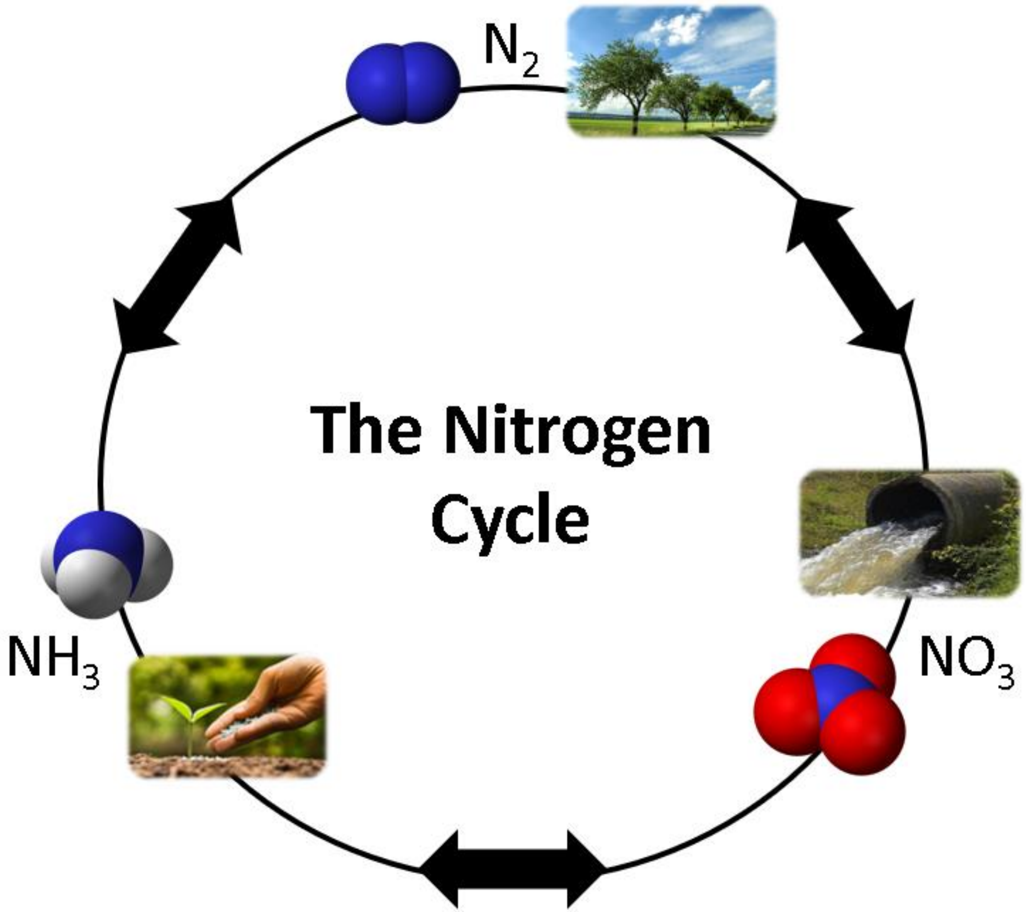


Image credit: https://www.betalabservices.com/nitrate-test/



Nitrate accumulation has detrimental environmental and health effects

Algal blooms and dead zones

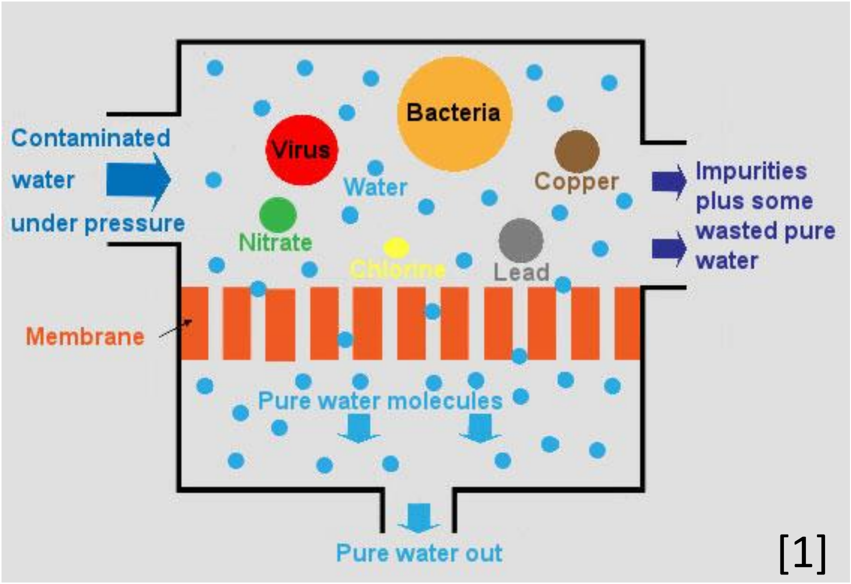
Lake Erie, Michigan (2017)

Northern Indian River Lagoon, Florida (2016)

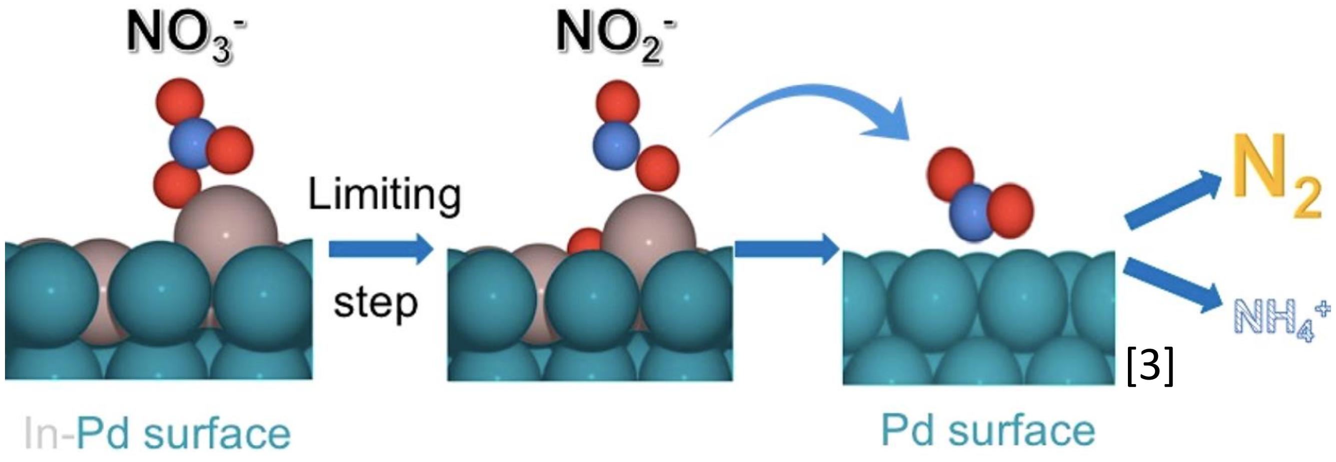
[1] Image from Aerial Associates Photography, Inc. by Z. Haslick

Overview of competing methods for nitrate remediation

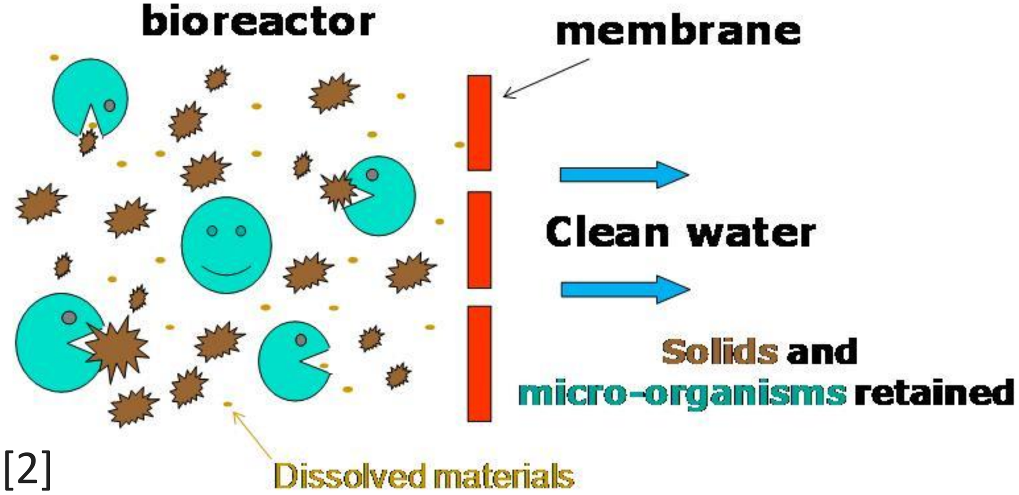
Physical



Thermocatalytic



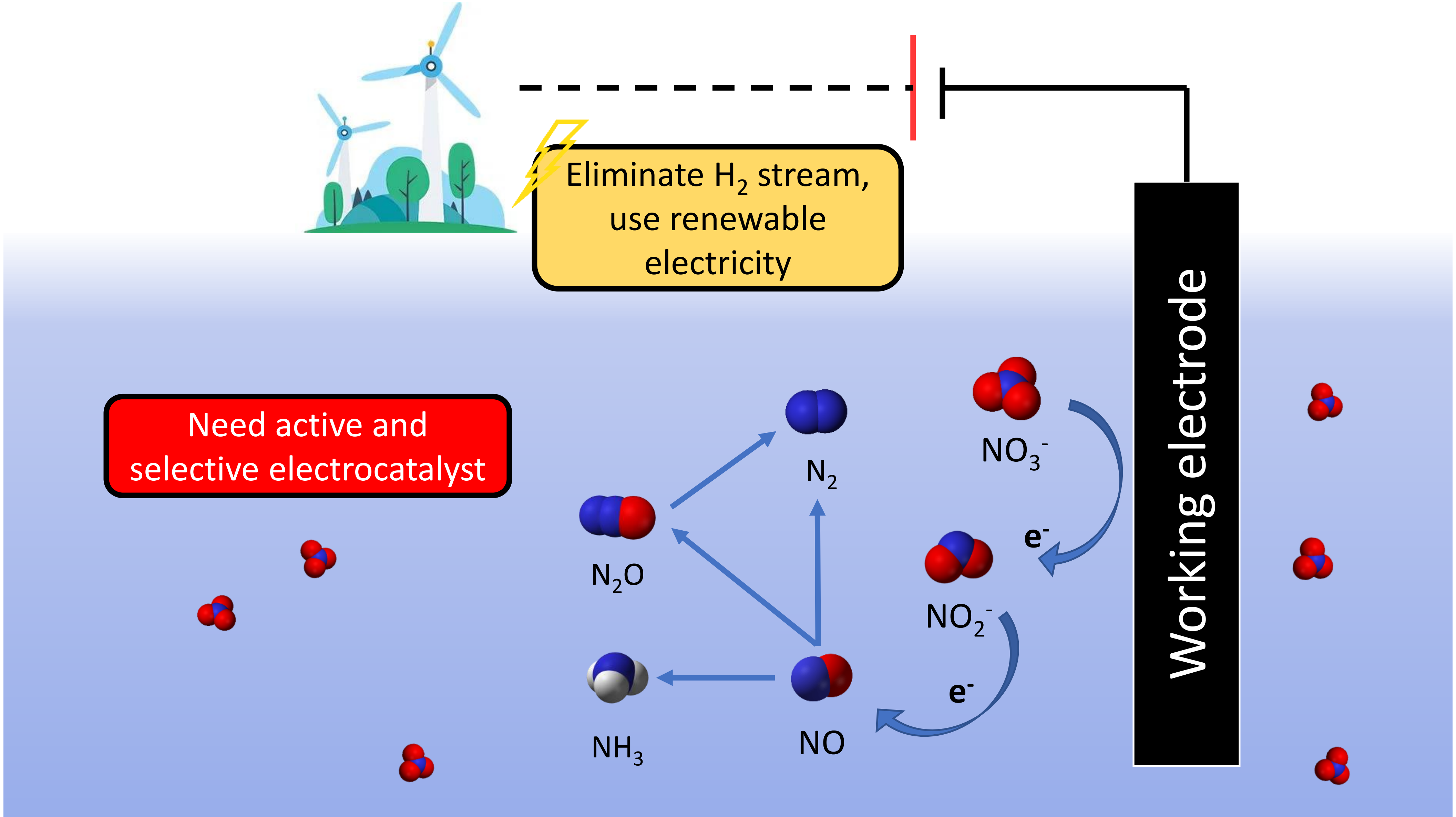
Biological



[2]

[1] https://www.ampac1.com/reverse-osmosis
[2] R. L. Smith, M. L. Ceazan, M. H. Brooks, *Appl. Environ. Microbiol.* 60 (1994)
[3] Guo et al. *ACS Catal.* 8 (2017)

Electrocatalytic nitrate reduction (NO_3RR)



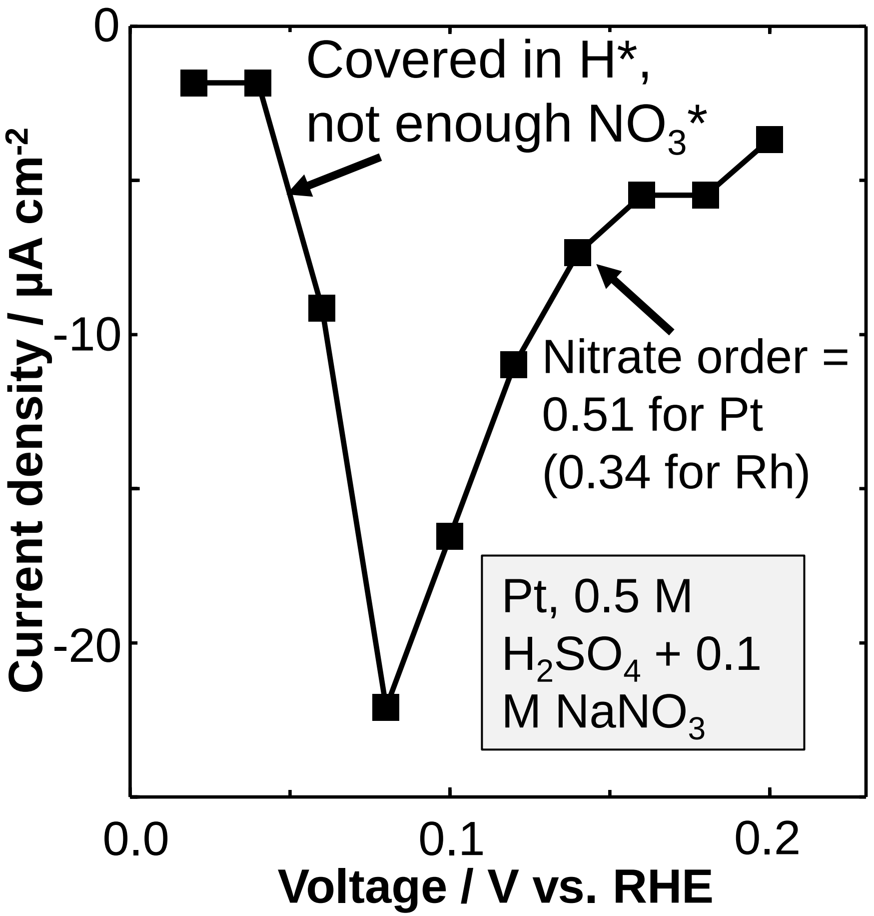
Xu, Dong, et al. Frontiers of Environmental Science & Engineering **2018**, 12, 9

The use of NO_3RR is hindered because no sufficiently active, selective, and stable electrocatalyst is known.

Measured NO_3RR activity trends[1]

- Platinum group metals: Rh > Ru > Ir > Pd ≈ Pt.
- Coinage metals less active than PGMs for NO_3RR, with the exception of Cu.
- Alloys can have superior activity and selectivity

Nitrate reduction on Pt [1]



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

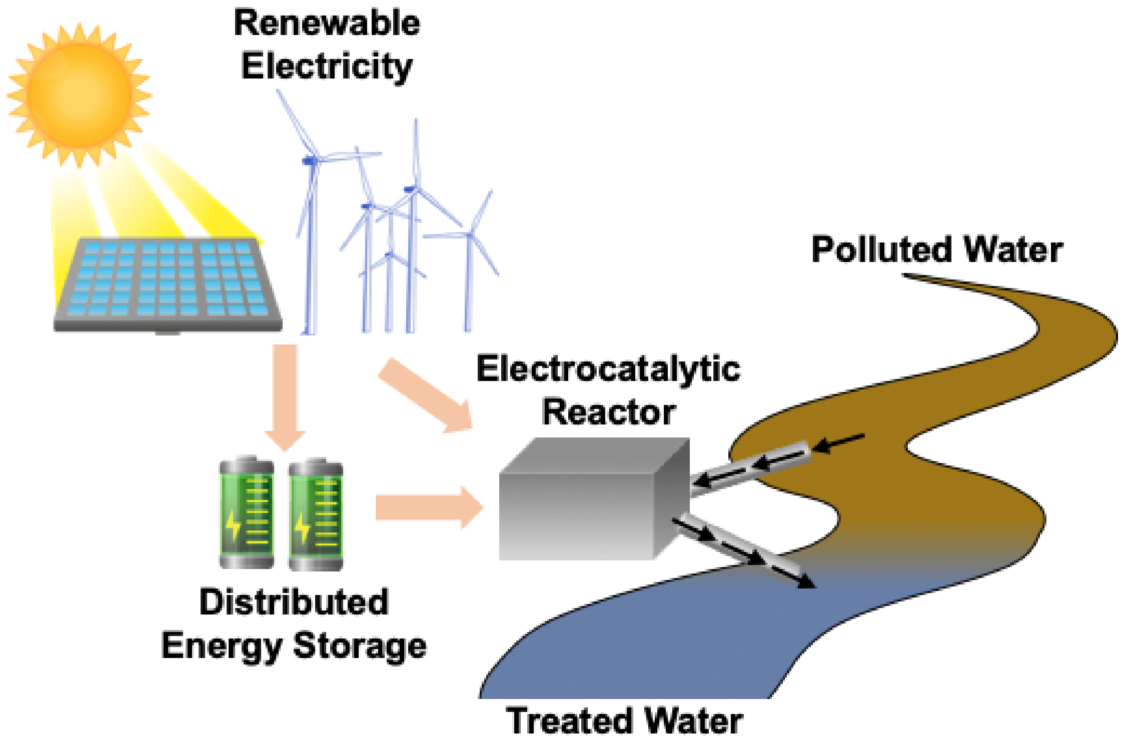
For nitrate reduction on metals and alloys, we show:

(i) Nitrate reduction electrocatalyst activity and selectivity trends across metals and bimetallic alloys

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

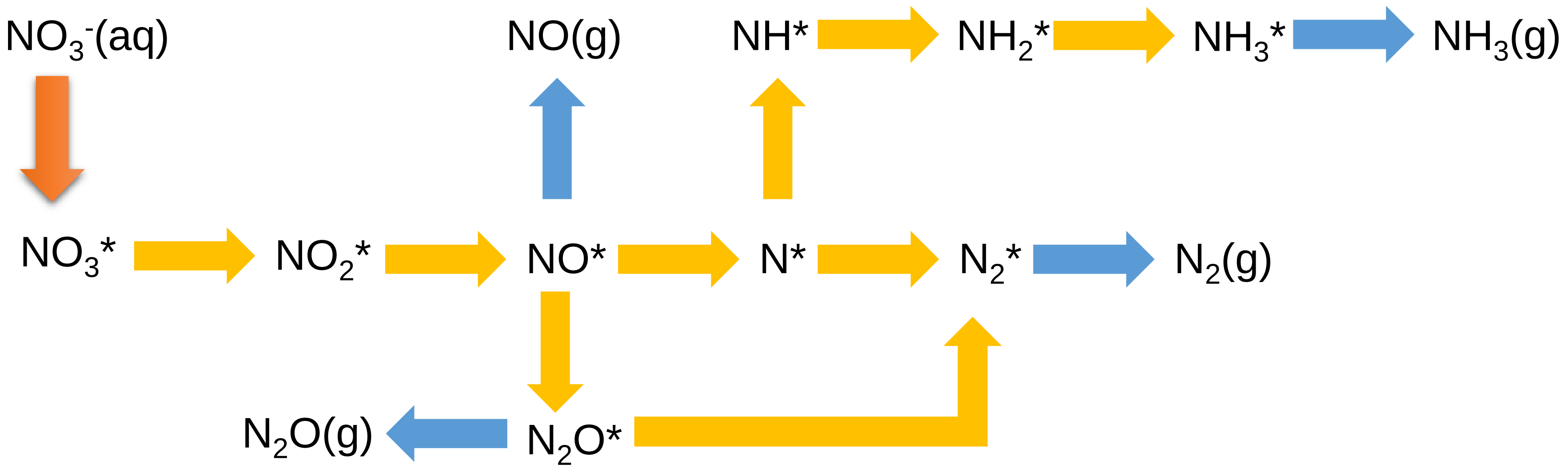
(iii) Predict a volcano activity plots for NO_3RR on metals

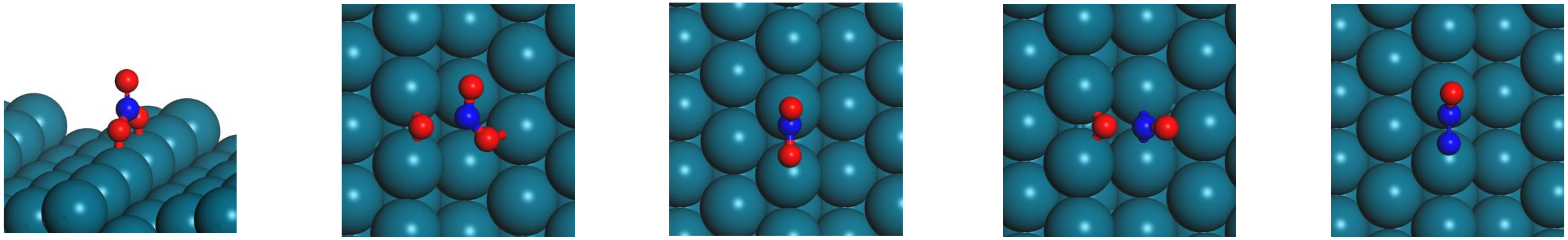
(iv) Predict, synthesize and test alloy catalysts



[1] J.-X. Liu, D. Richards, N. Singh, B. R. Goldsmith, *ACS Catal.* 9 (2019)
[2] N. Singh, B. R. Goldsmith, *ACS Catal.* 10 (2020)

Studied 19 elementary steps for electrocatalytic nitrate reduction on the eight metals (Co, Cu, Rh, Pd, Pt, Ag, Au, and Fe)

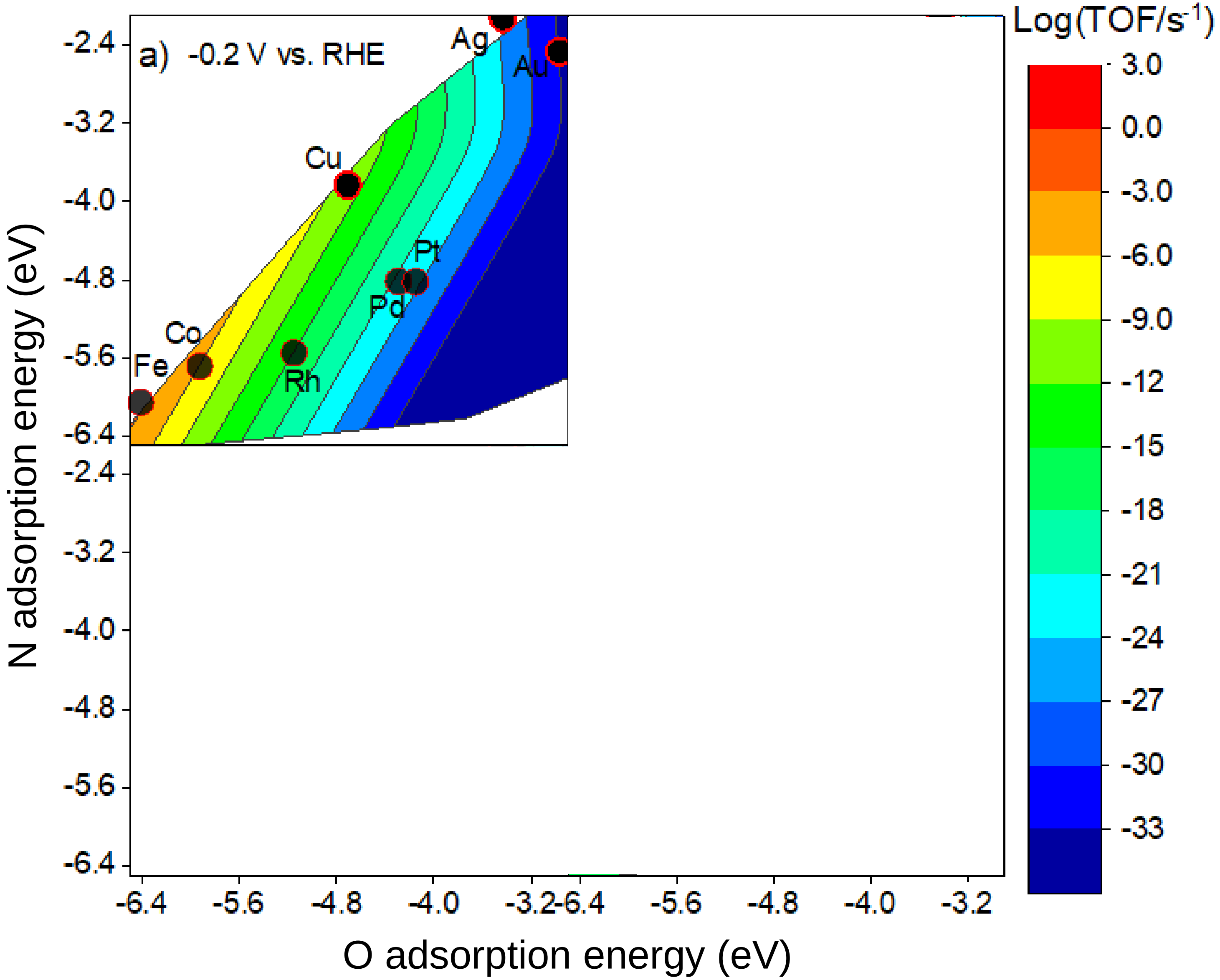




NO_3^* | $NO_3^* \rightleftarrows NO_2^*+O^*$ | NO_2^* | $NO_2^* \rightleftarrows NO^*+O^*$ | N_2O^*

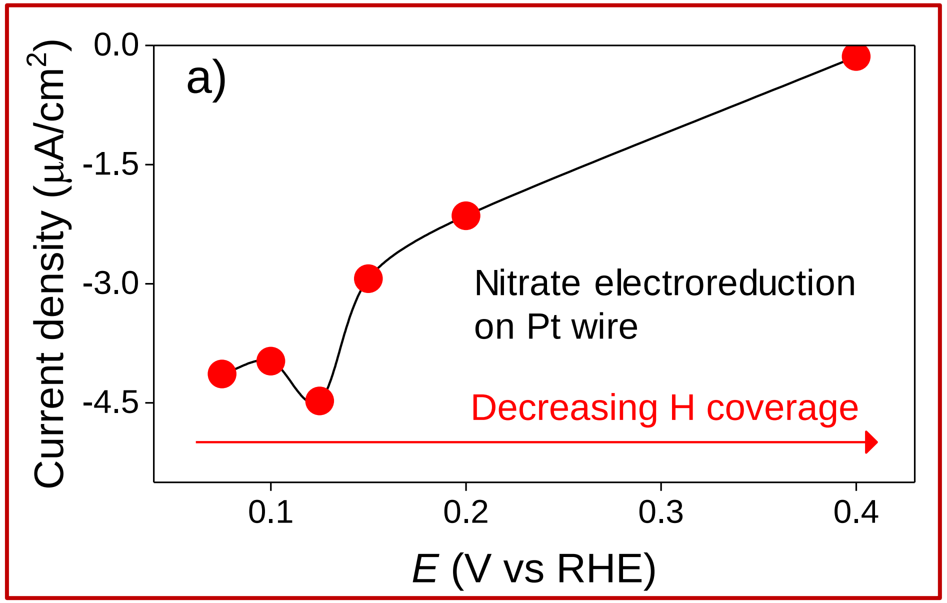
- Hydroxylamine formation not considered

Theoretical volcano plots as a function of applied 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

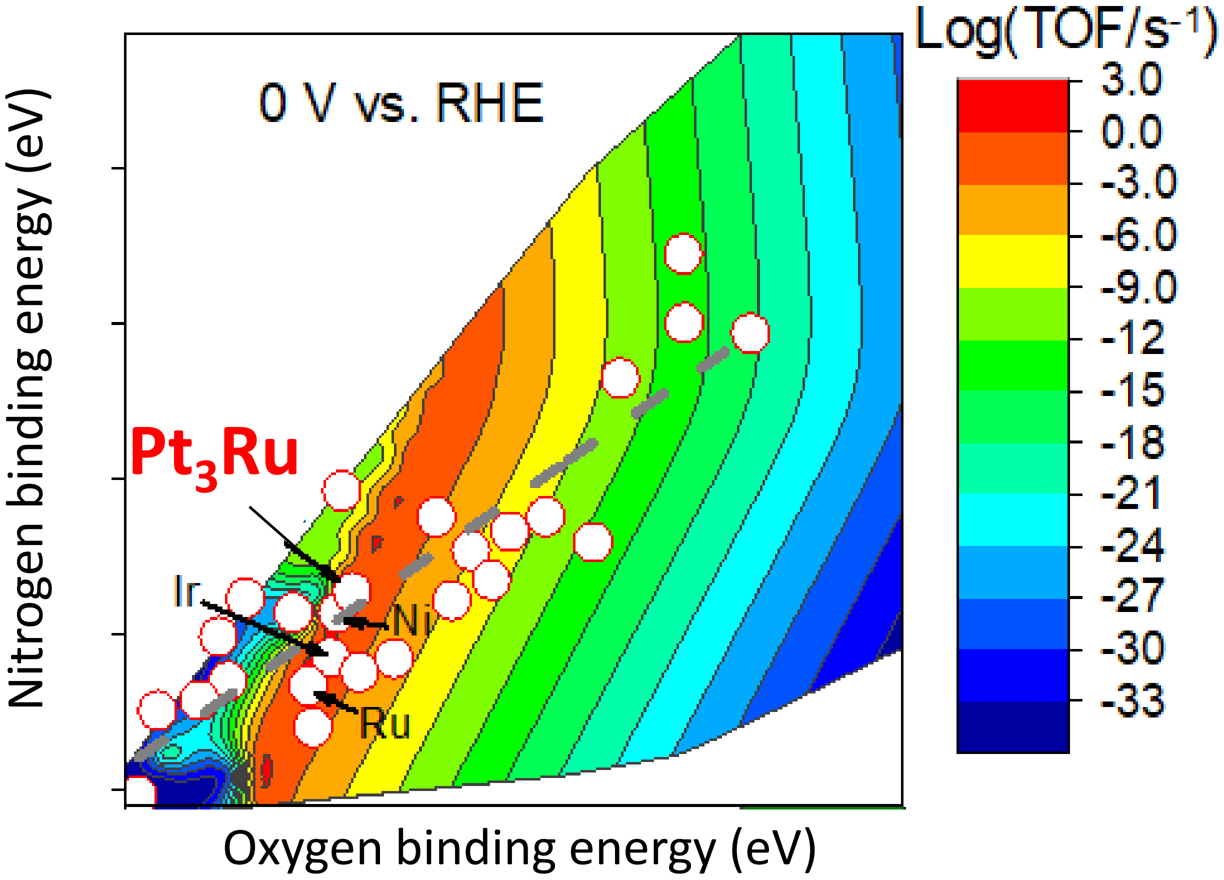


Activity ordering agrees with experimental observations in acidic solution. [1]

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

Studied the NO_3RR activity and selectivity of 22 Fe_3M, Pt_3M, and Rh_3M alloys.

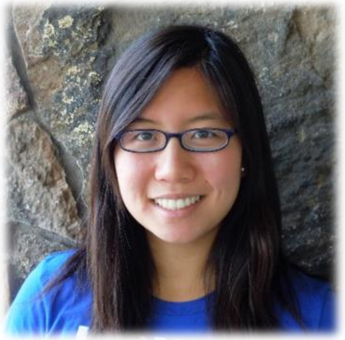
Predicted Pt_3Ru is a promising catalyst

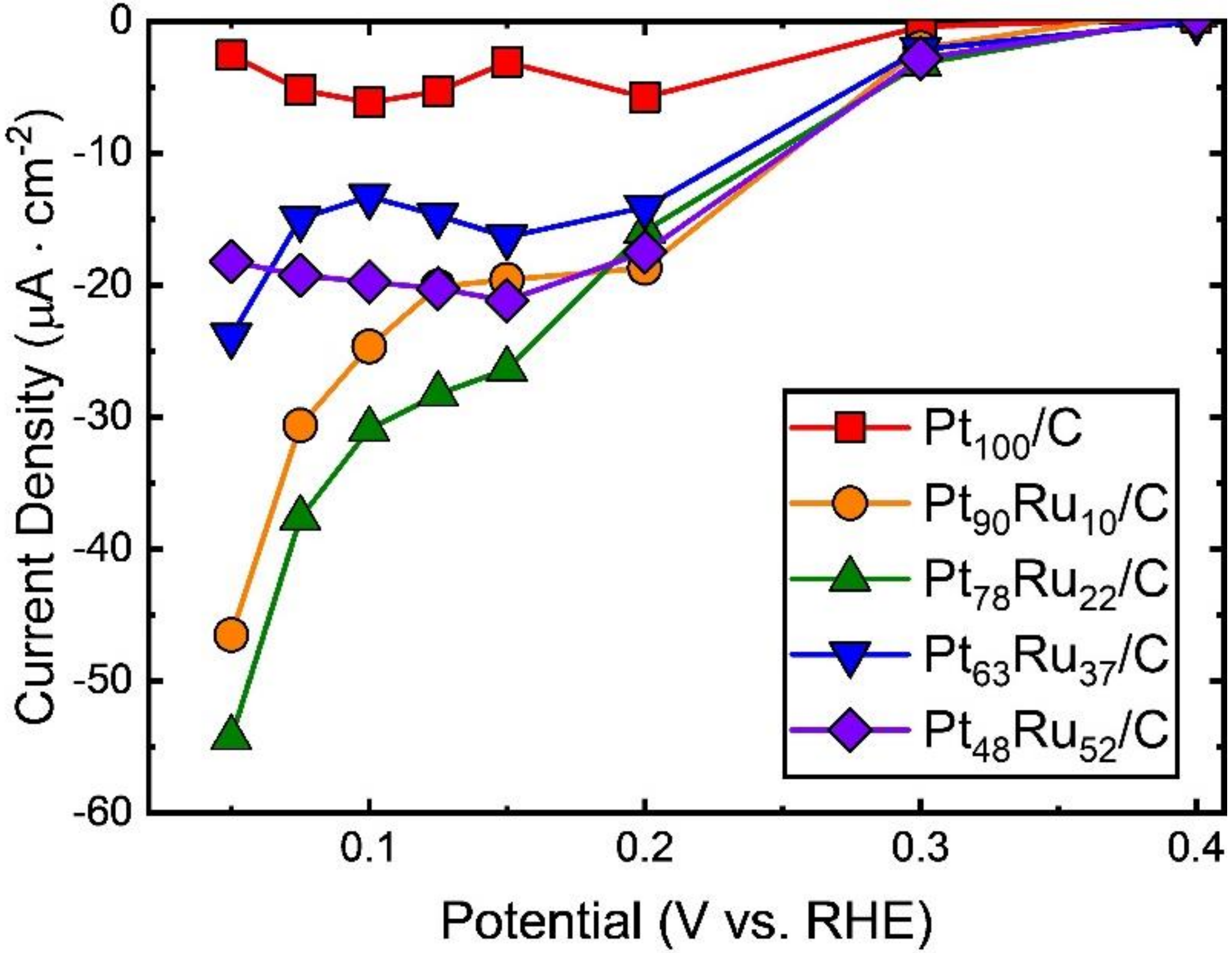


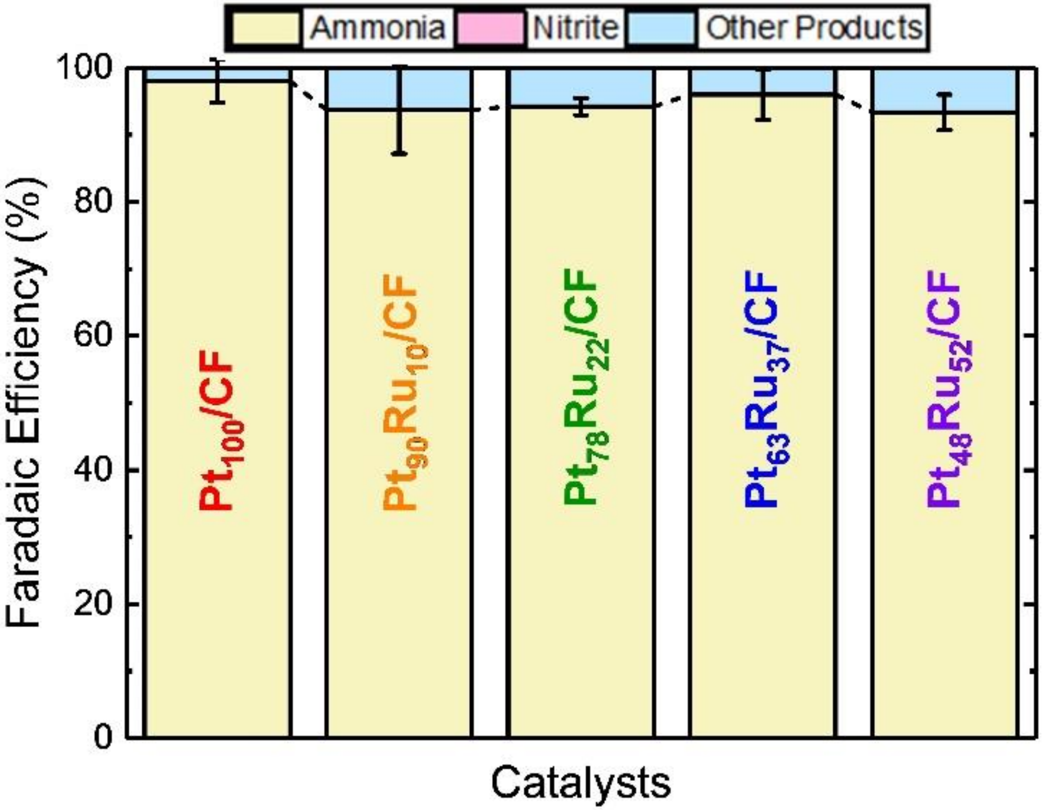
[1] J.-X. Liu, D. Richards, N. Singh, B. R. Goldsmith, *ACS Catal.* 9 (2019)

[2] N. Singh, B. R. Goldsmith, *ACS Catal.* 10 (2020)

Synthesized and tested PtRu alloys.
→ found to be more active than pure Pt.

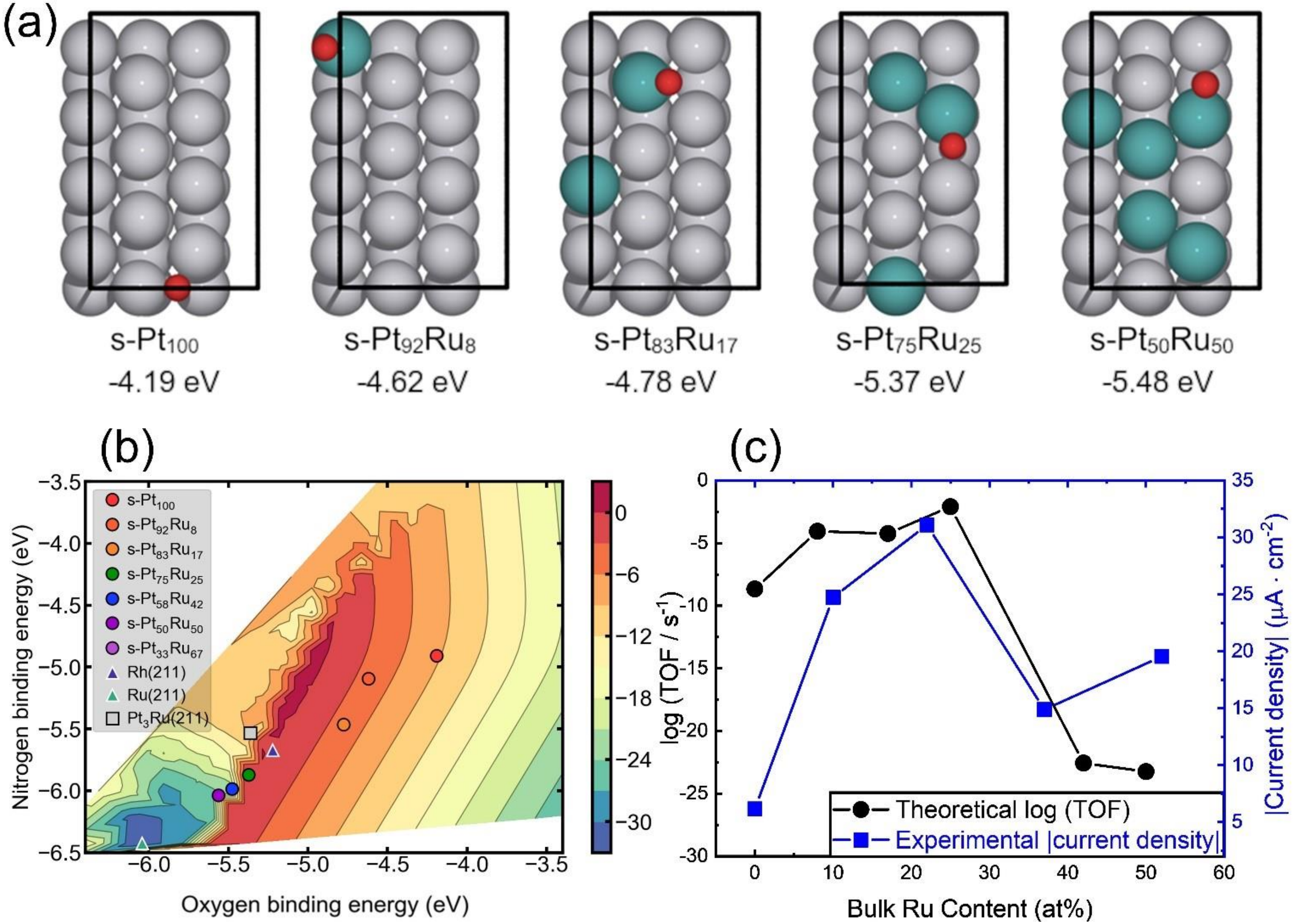






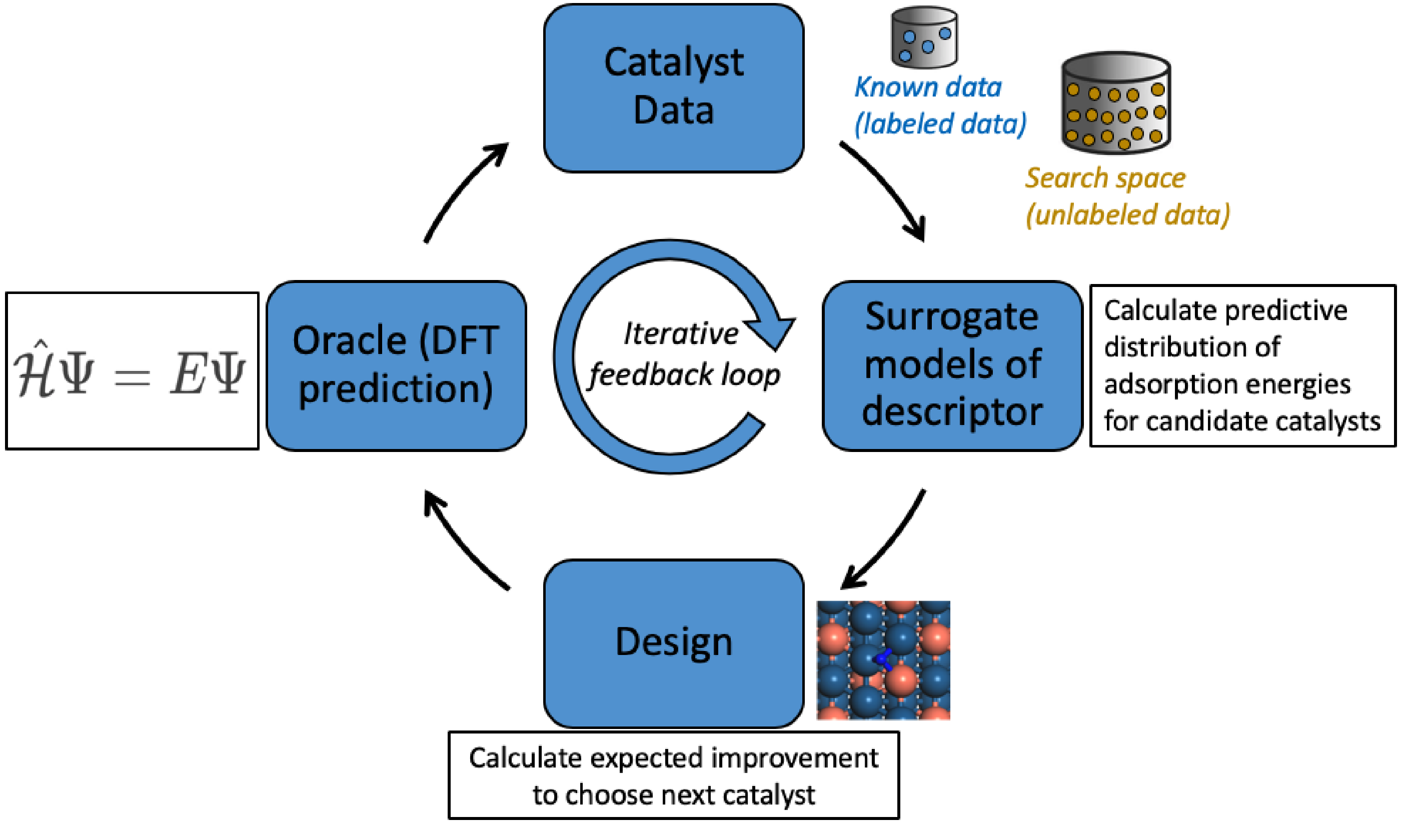
Z. Wang, S. Young, B. Goldsmith, N. Singh (In review)

Increasing Electrocatalytic Nitrate Reduction Activity by Controlling Adsorption Strength through PtRu Alloying



Ongoing: Using high-throughput machine learning and data science tools to design catalysts (e.g., for nitrate reduction)

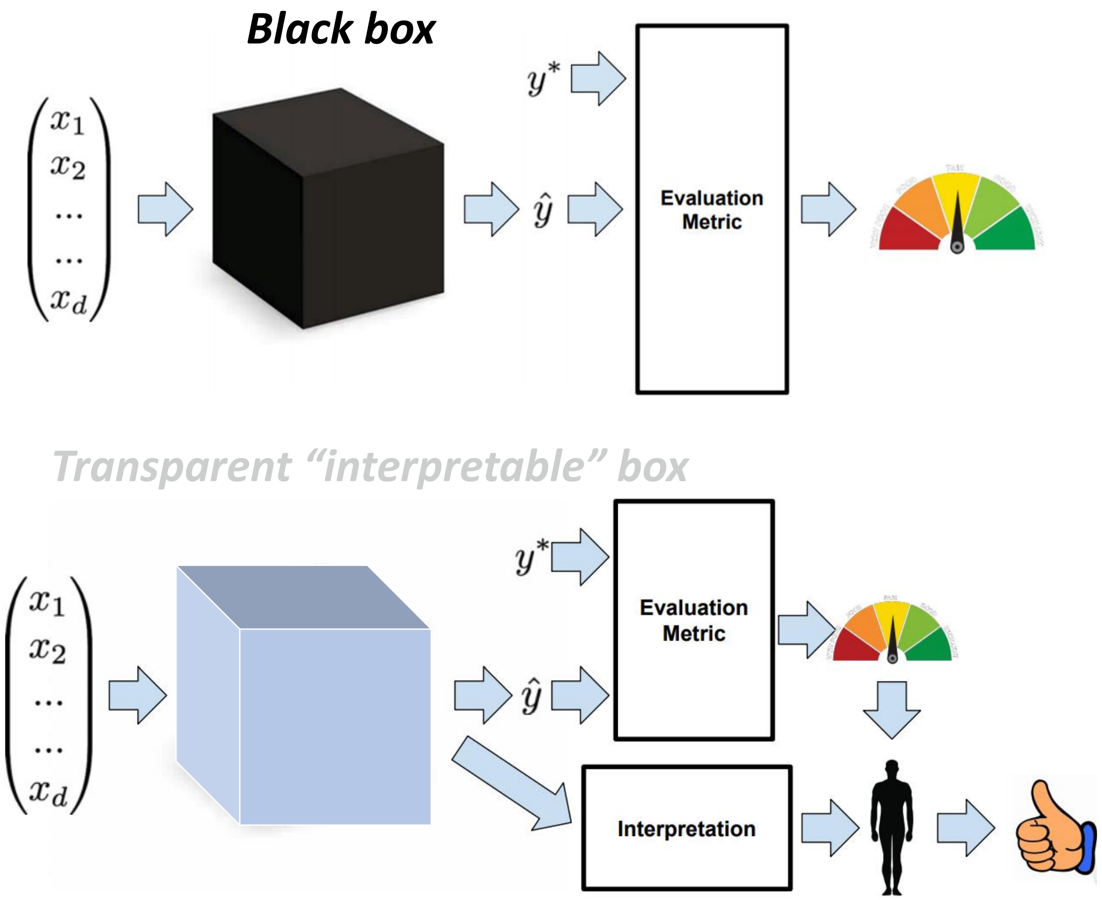
Combining DFT calculations with active learning for *screening* new alloys



B. R. Goldsmith *et al. AIChE J.* 64 (2018)

J. Esterhuizen, B. R. Goldsmith, S. Linic, *Chem* (2020)

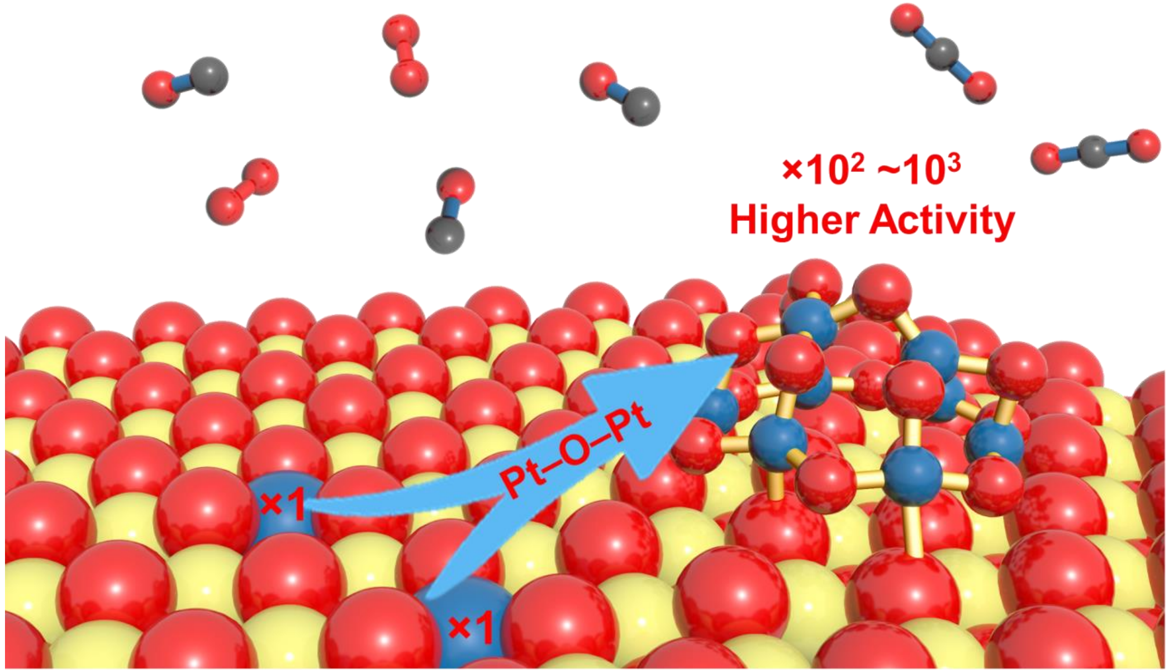
***Interpretable machine learning* to extract physical insight of catalysts**

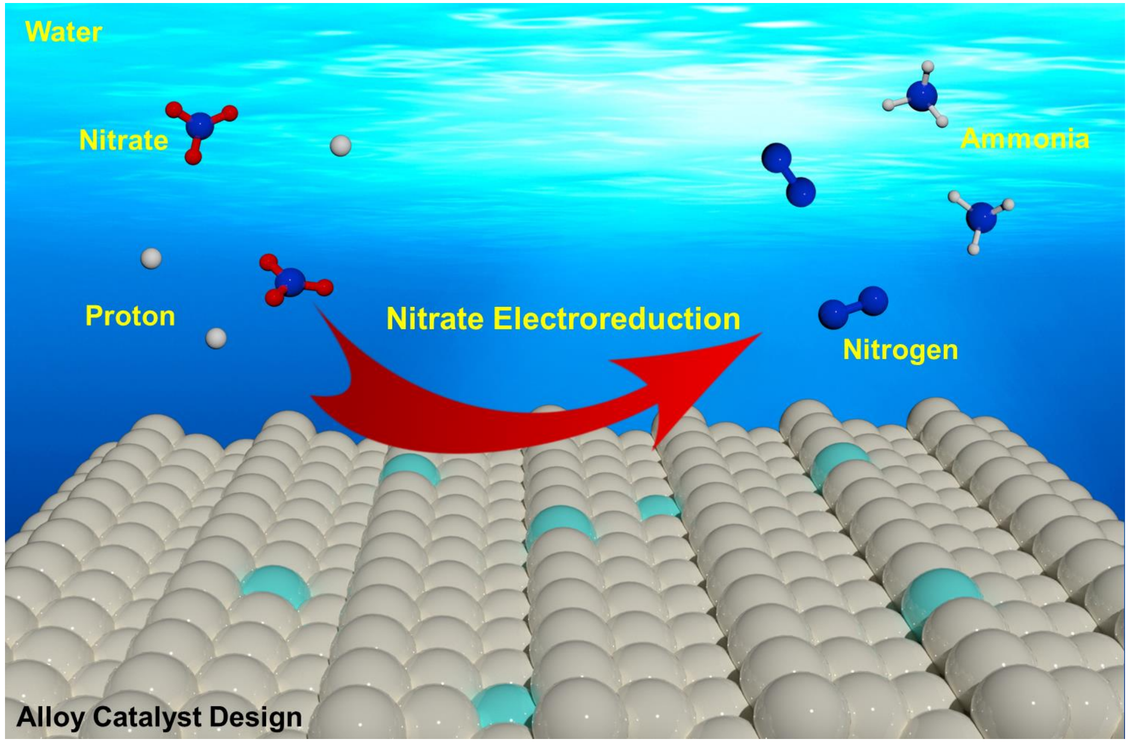


Combining theory with experiment can accelerate catalyst design and understanding for sustainable chemical conversion

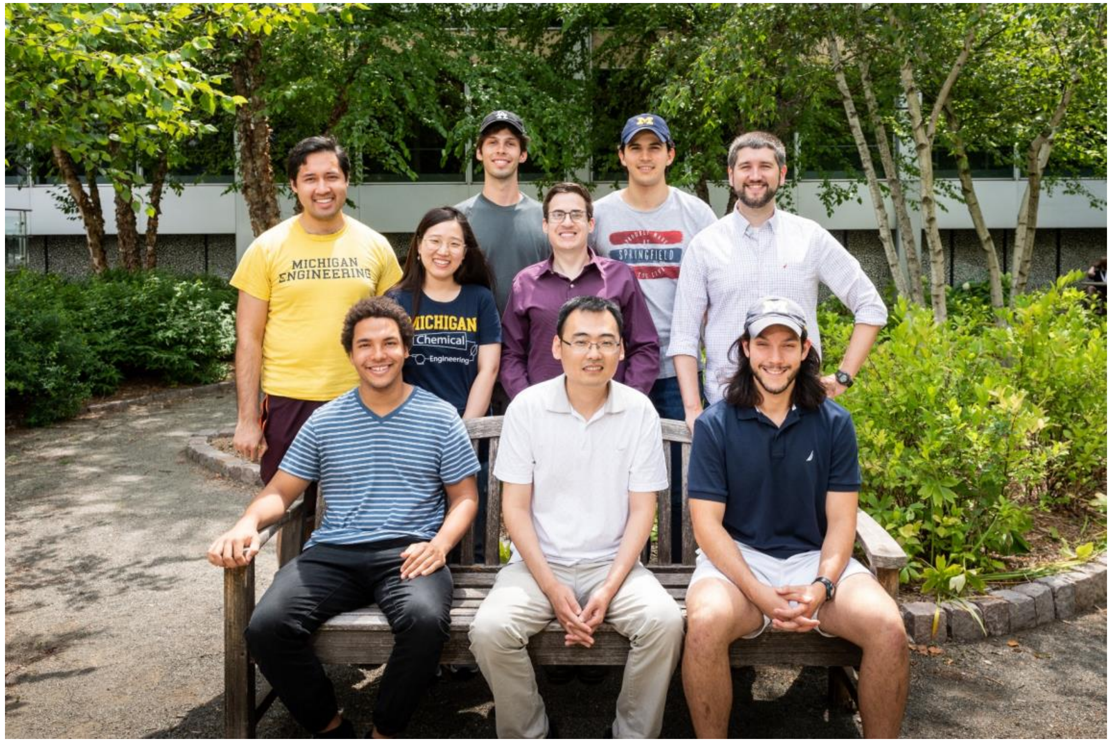
(1) Low temperature CO oxidation using Pt single atoms and nanoclusters

(2) Electrocatalytic reduction of nitrate (NO_3^-) in wastewater





Acknowledgements



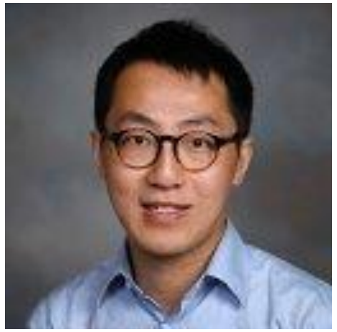
CHEMICAL ENGINEERING
UNIVERSITY OF MICHIGAN

Materials
Modeling
Data Science
Descriptors
Catalysis
Goldsmith Lab

Primary collaborators on these works

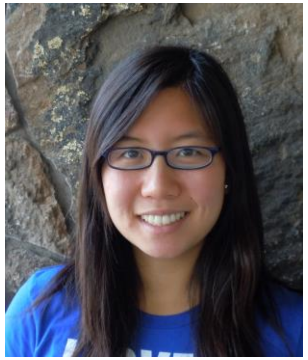
Prof. Nirala Singh
(UofM)

Prof. Ming Yang
(General Motors, now Clemson)



Dr. Jin-Xun Liu
(UofM)

Zixuan Wang
(UofM)



Samuel Young
(UofM)

Danielle Richards
(UofM)

Thank you to Dow for supporting my research and educational goals with a Dow Corning Assistant Professorship