Catalysis on High Entropy Materials

Jan Rossmeisl
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CHEAC
Department of Chemistry
University of Copenhagen

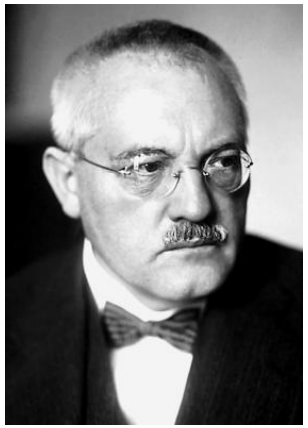
Danmarks Grundforskningsfond
Danish National Research Foundation

erc
European Research Council
Established by the European Commission

CHEAC

Haber-Bosch

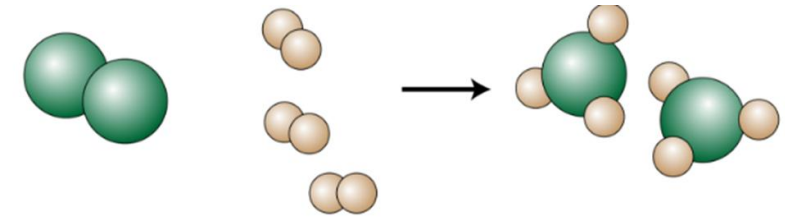
Fritz Haber 1909
Nobel prize 1918



Carl Bosch 1910
Nobel prize 1931

Alwin Mittasch
After ~20.000 experiments
Fe_3O_4, K_2O, CaO, Al_2O_3, SiO_2

Gerhard Ertl
Nobel prize 2007

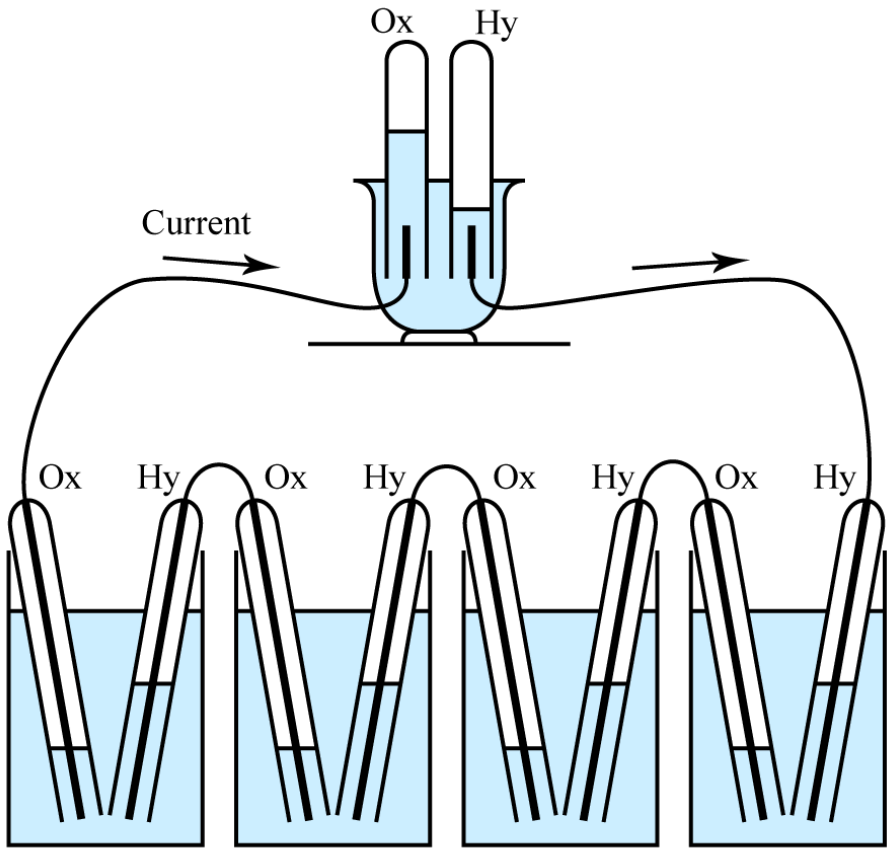


1 molecule **N_2**
1 mol **N_2**
28.02 g **N_2**

3 molecules **H_2**
3 mol **H_2**
3 x 2.02 g = 6.06 g **H_2**

2 molecules **NH_3**
2 mol **NH_3**
2 x 17.04 g = 34.08 g **NH_3**

Fuel cell

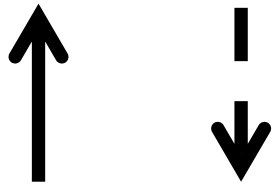


Gas-battery

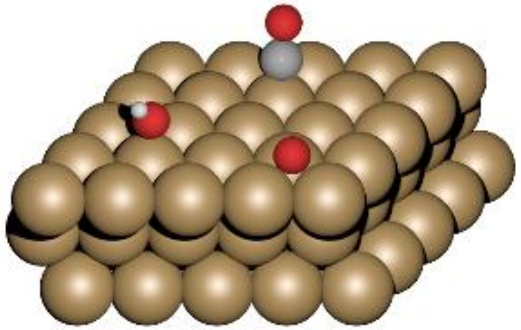
William R. Grove
1838

Discovery - From consequences to course

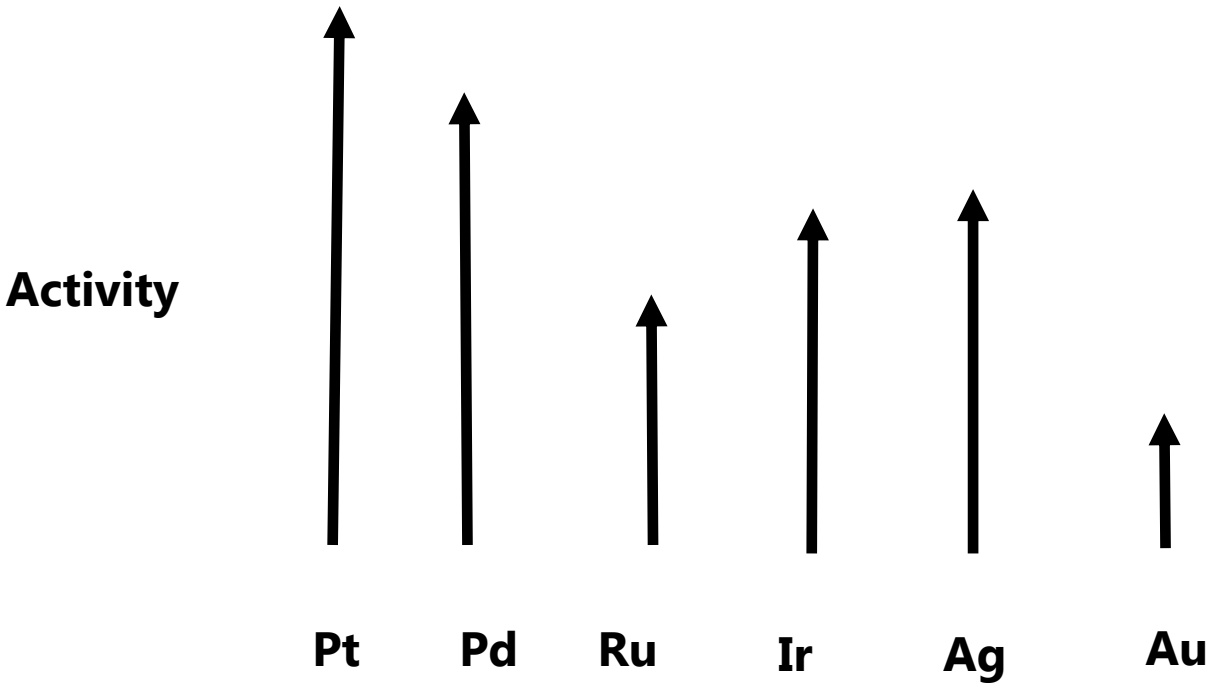
Catalytic Properties

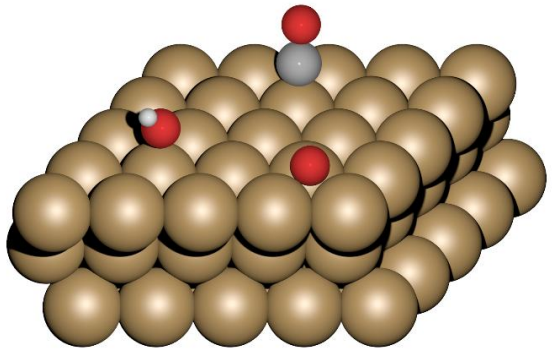


Material, surface

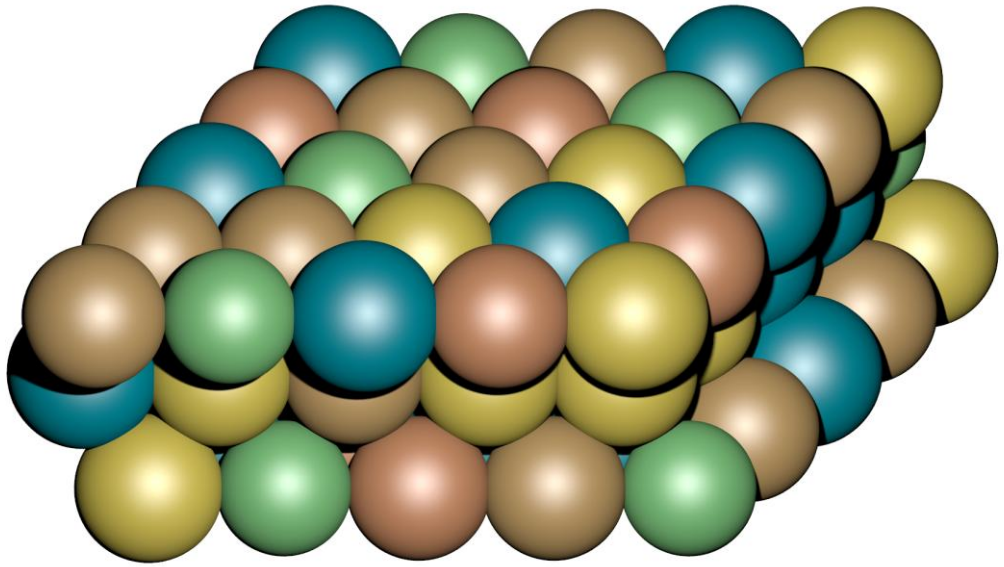


Screening



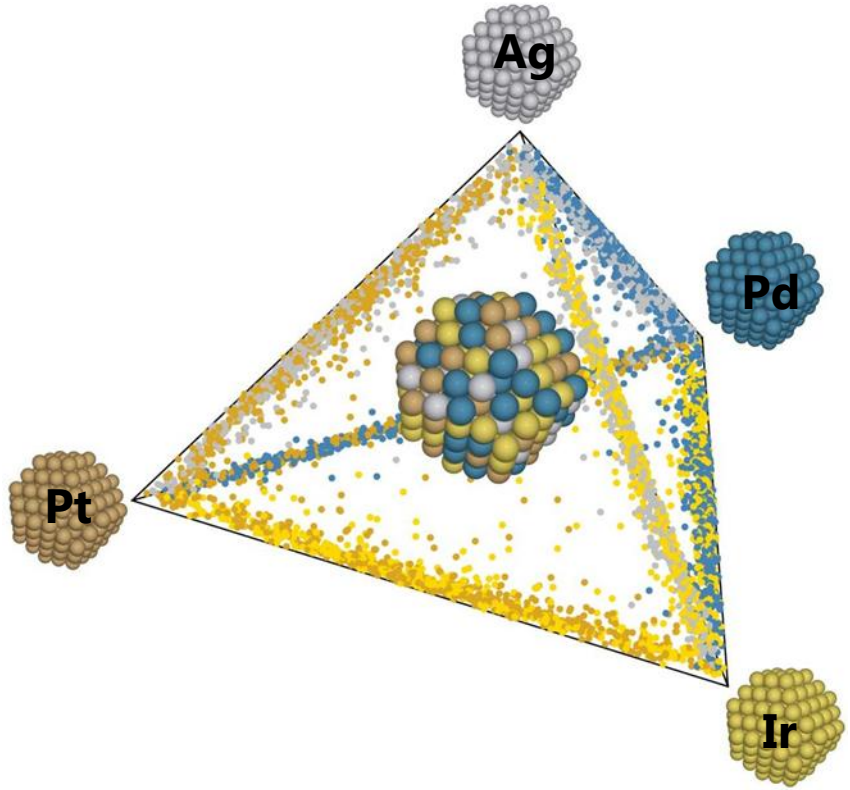


High Entropy Alloys

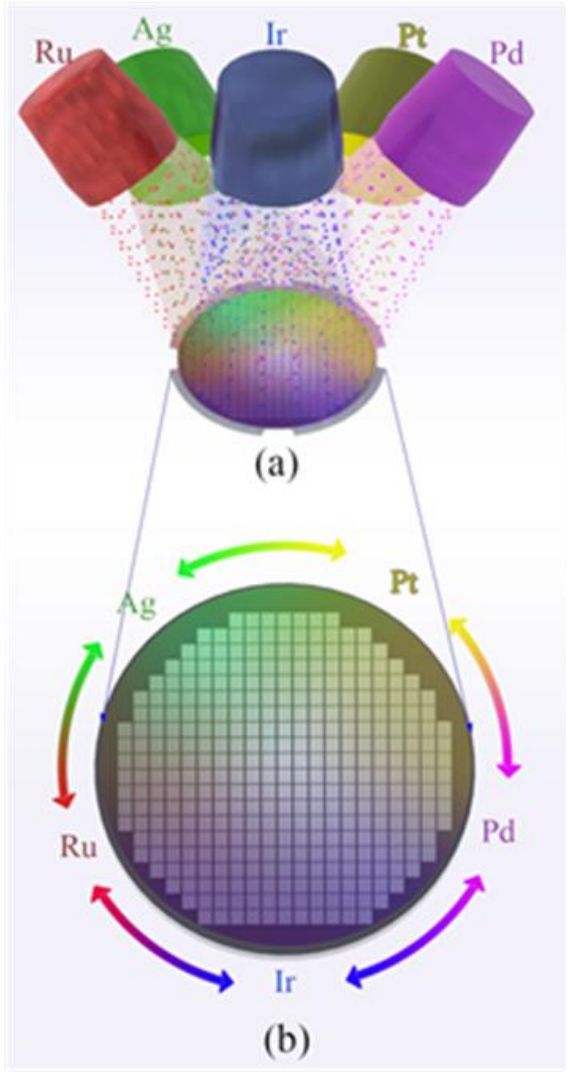


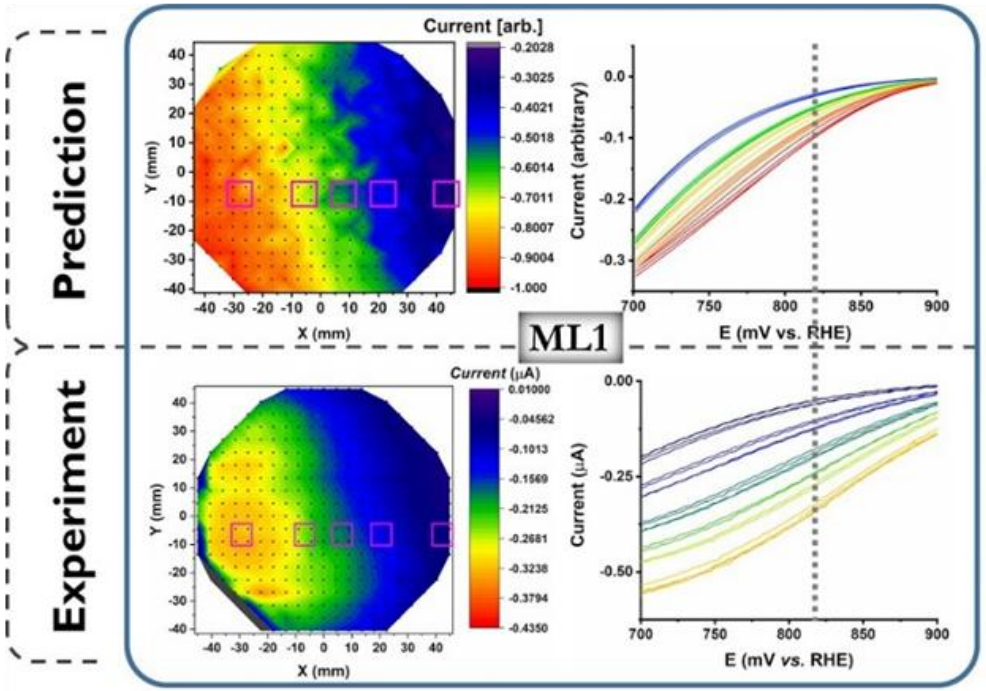
B Cantor et al, Materials Science and Engineering, 2004
J.W. Yeh, et al, Adv. Eng. Mater. 2004

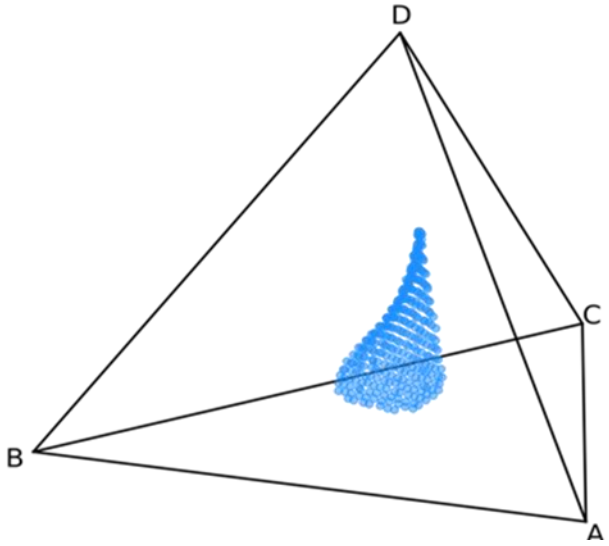
The material space becomes continuous rather than discrete



Combinatorial co-sputtering

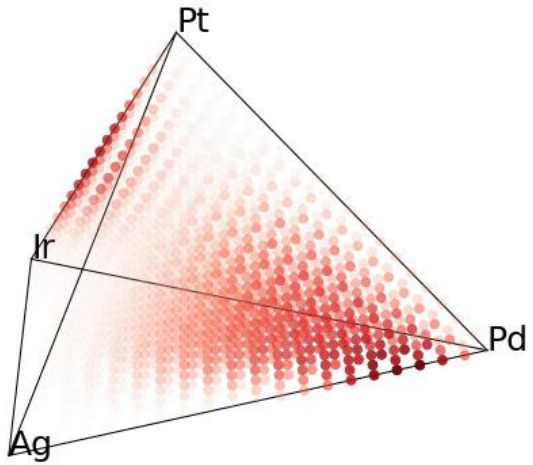


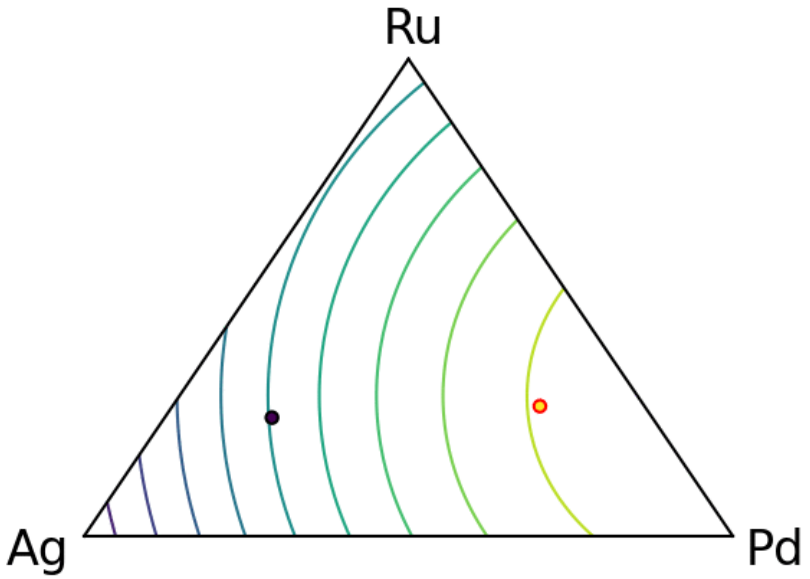




Complex-Solid-Solution Electrocatalyst Discovery by Computational Prediction and High-Throughput Experimentation
Batchelor, Löffler, Xiao, Krysiak, Strotkötter, Pedersen, Clausen, Savan, Li, Schuhmann, Rossmeisl, Ludwig, **Angewandte Chemie Int. Edt 2021**

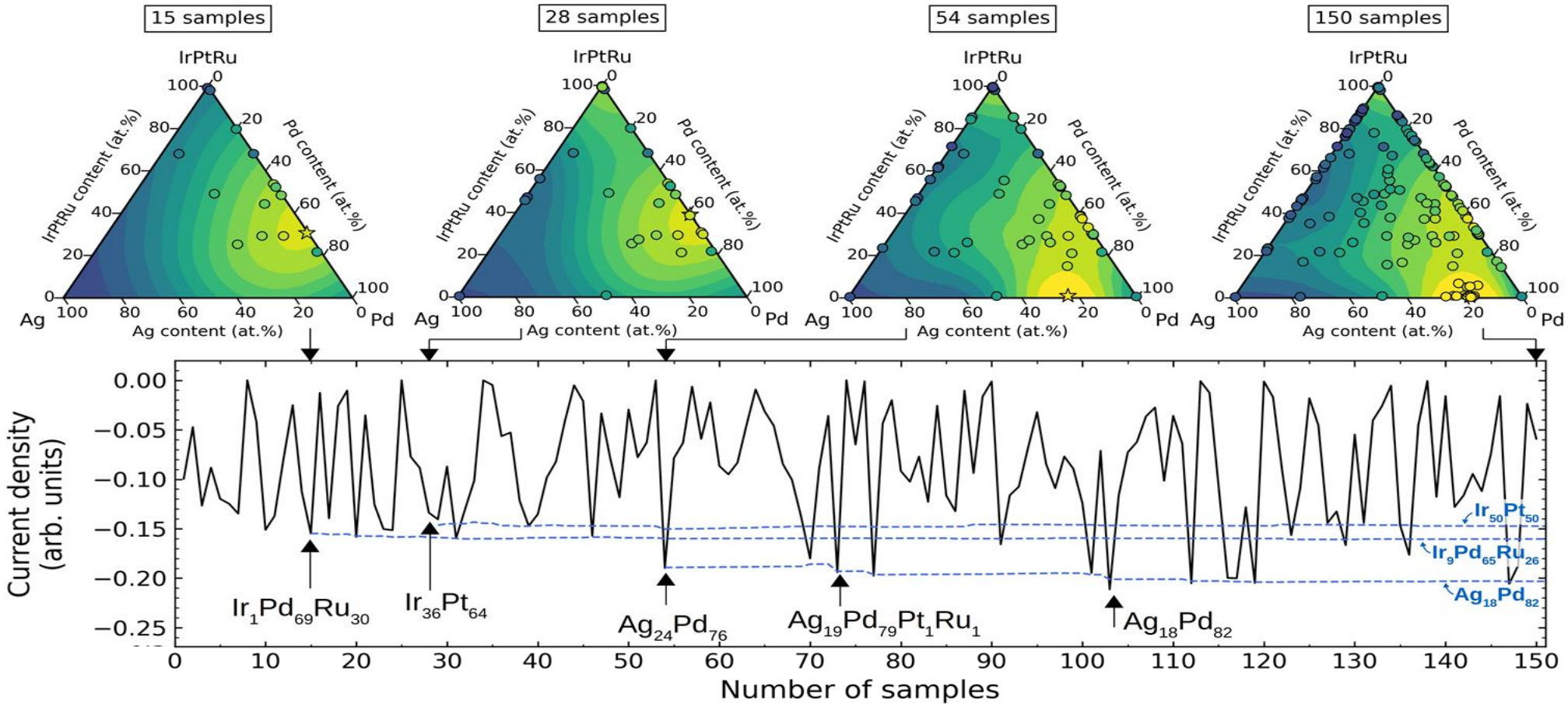
How many experiments are needed? Exploration/exploitation





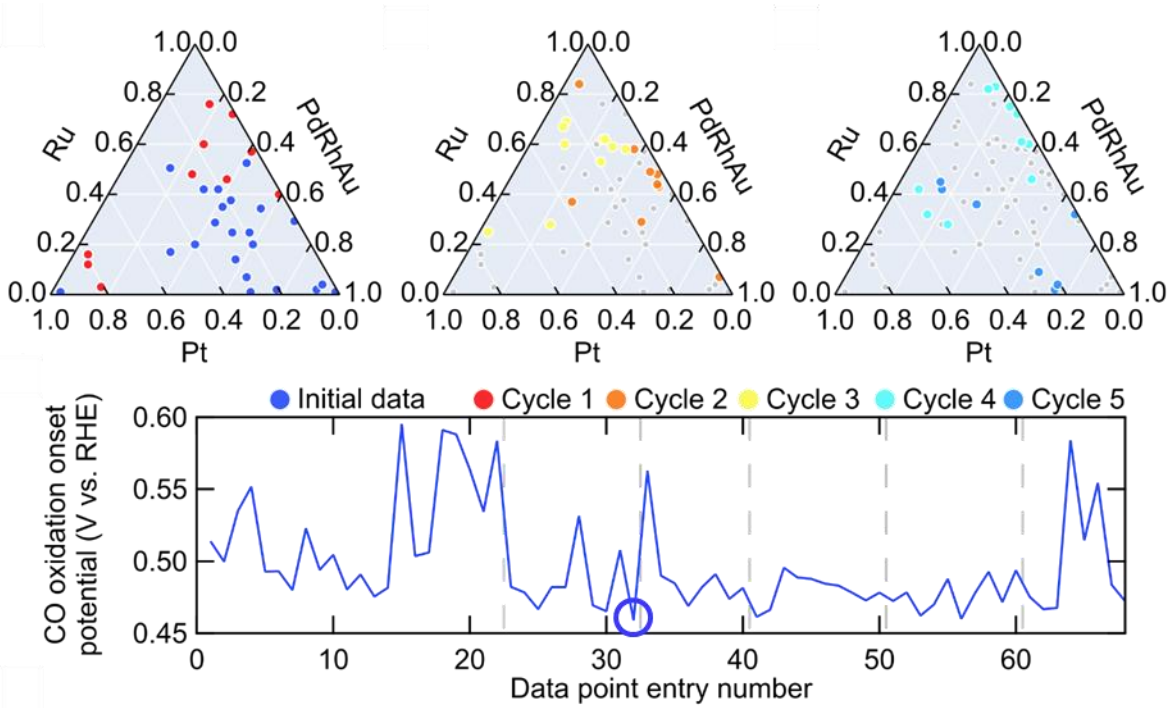
Bayesian Optimization of High-Entropy Alloy Compositions for Electrocatalytic Oxygen Reduction
Pedersen, Clausen, Krysiak, Xiao, Batchelor, Löffler, Mints, Banko, Arenz, Savan, Schuhmann, Ludwig, Rossmeisl **Angewandte Chemie Int. Edt 2021**

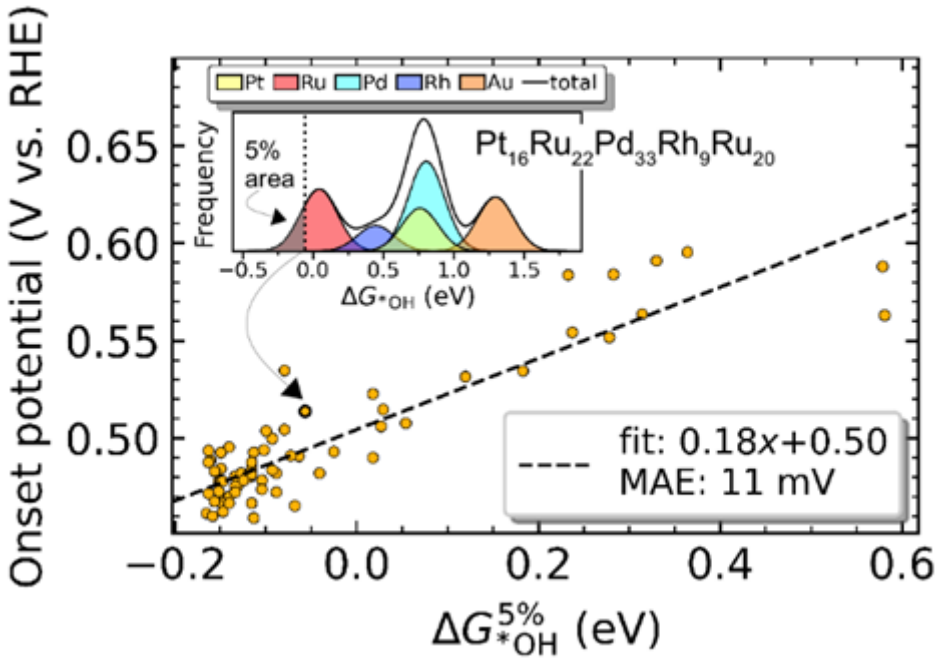
Bayesian optimization of high-entropy alloy compositions



PtRuPdRhAu

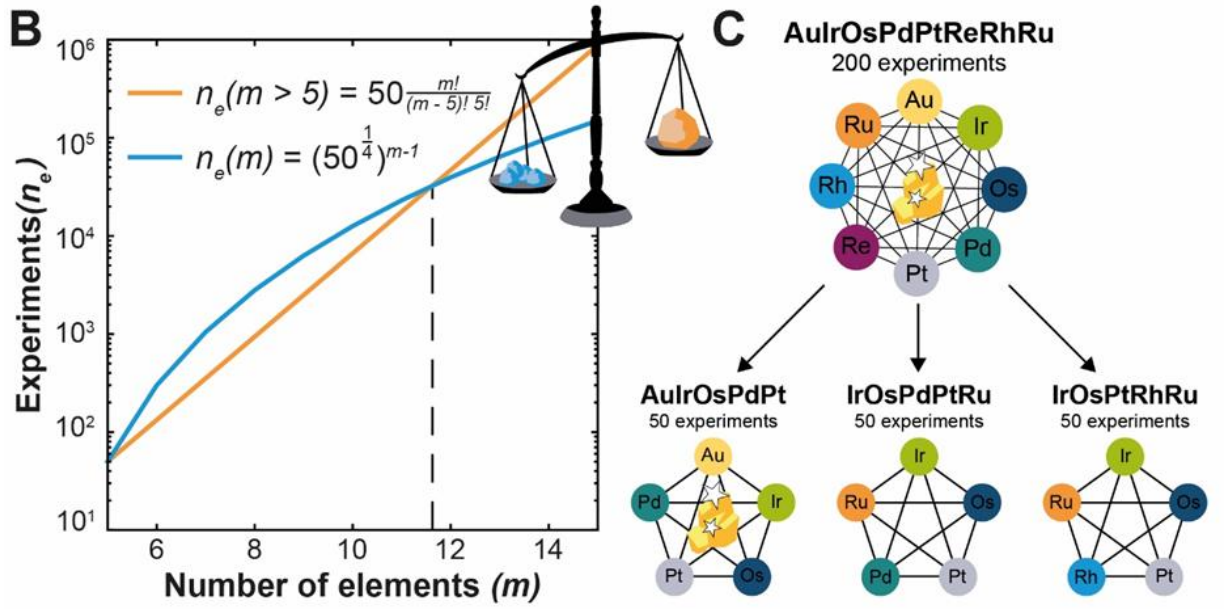
- Hydrogen Oxidation Reaction + CO Tolerant Catalyst
- Optimum HEA composition at 32nd entry:
  $Pt_{12}Ru_{38}Pd_8Rh_{41}Au_1$

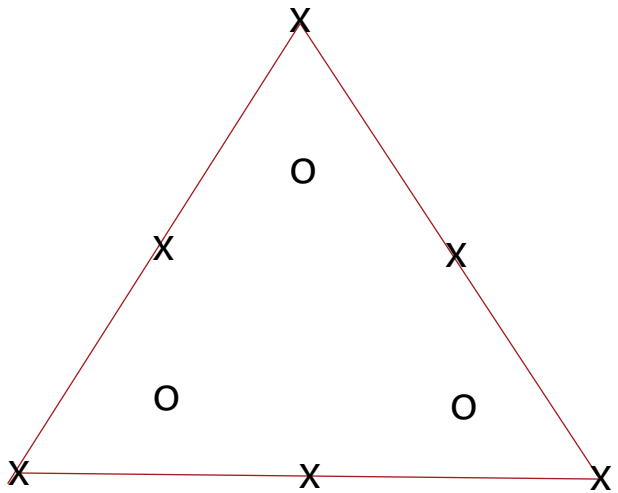




Exploring the Composition Space of High-Entropy Alloy Nanoparticles for the Electrocatalytic H2/CO Oxidation with Bayesian Optimization
Mints, Pedersen, Bagger, Quinson, Anker, Jensen, Rossmeisl and Arenz
ACS catalysis 2022

Dimensionality

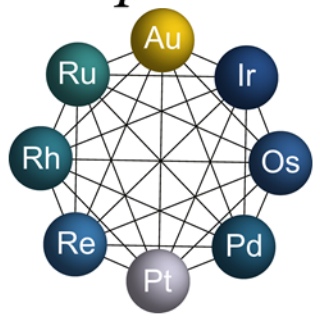




V Mints, JK Pedersen, GKH Wiberg, J Rossmeisl, M. Arenz **submitted 2023**

AuIrOsPdPtReRhRu

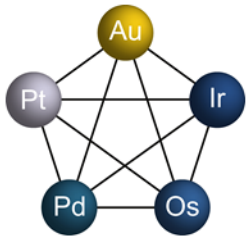
200 experiments



Oxygen Reduction Reaction

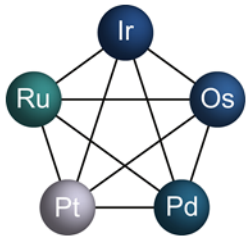
AuIrOsPdPt

50 experiments



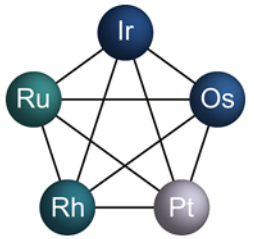
IrOsPdPtRu

50 experiments

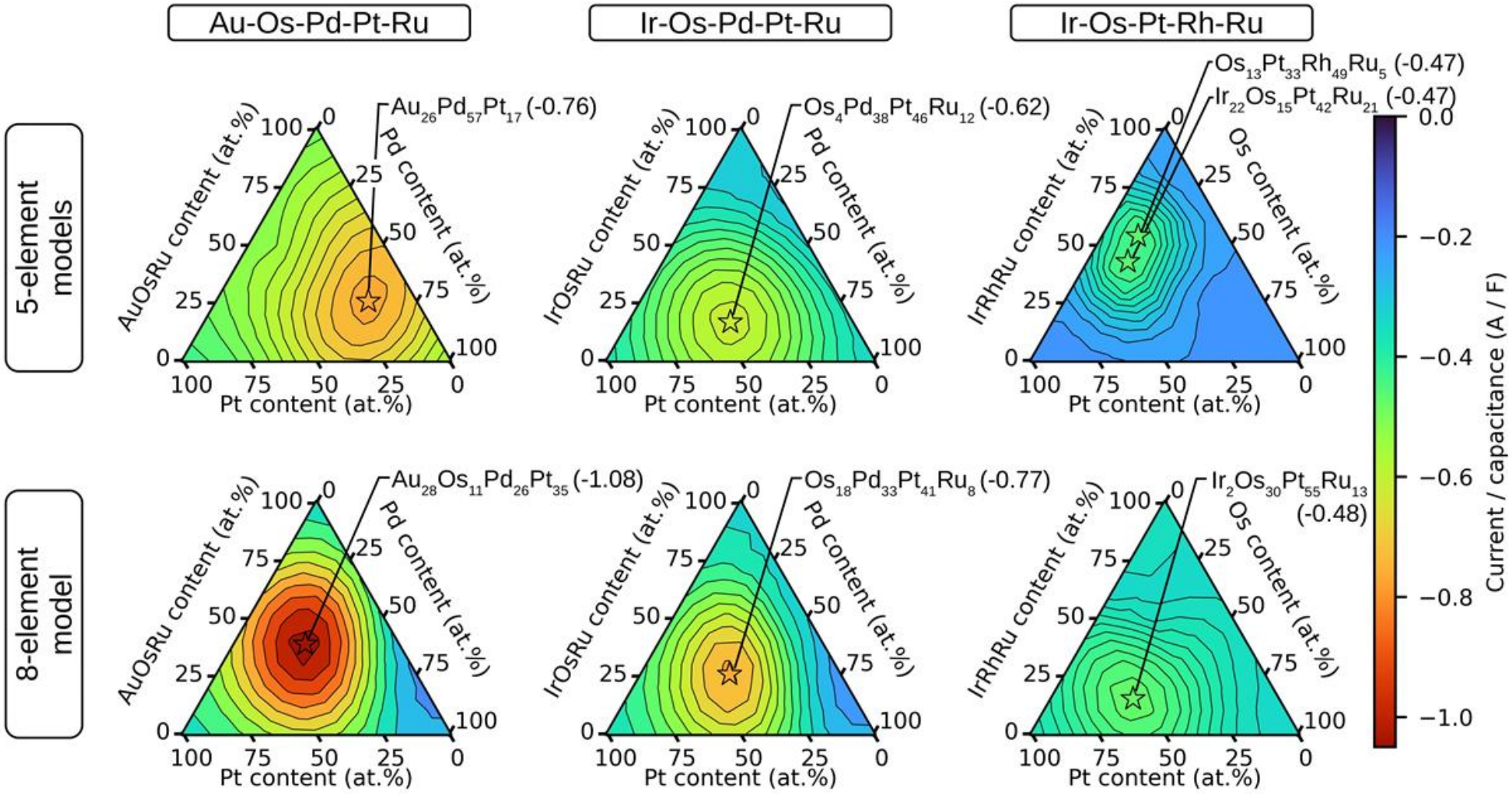


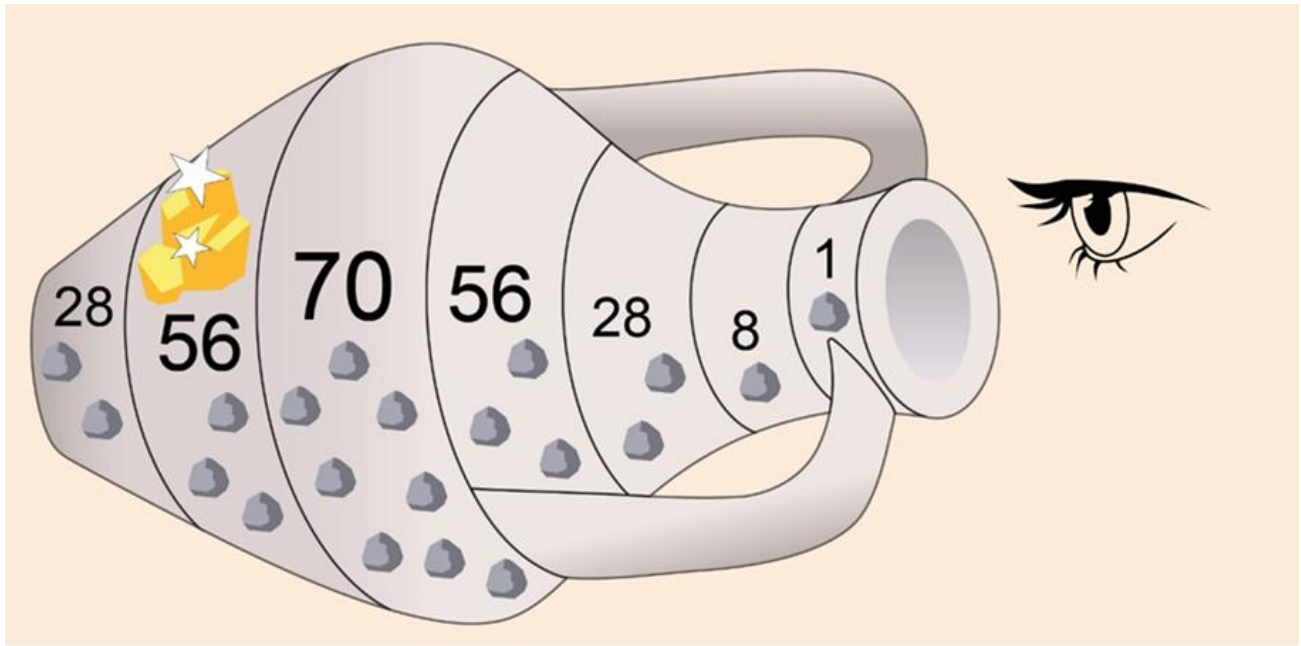
IrOsPtRhRu

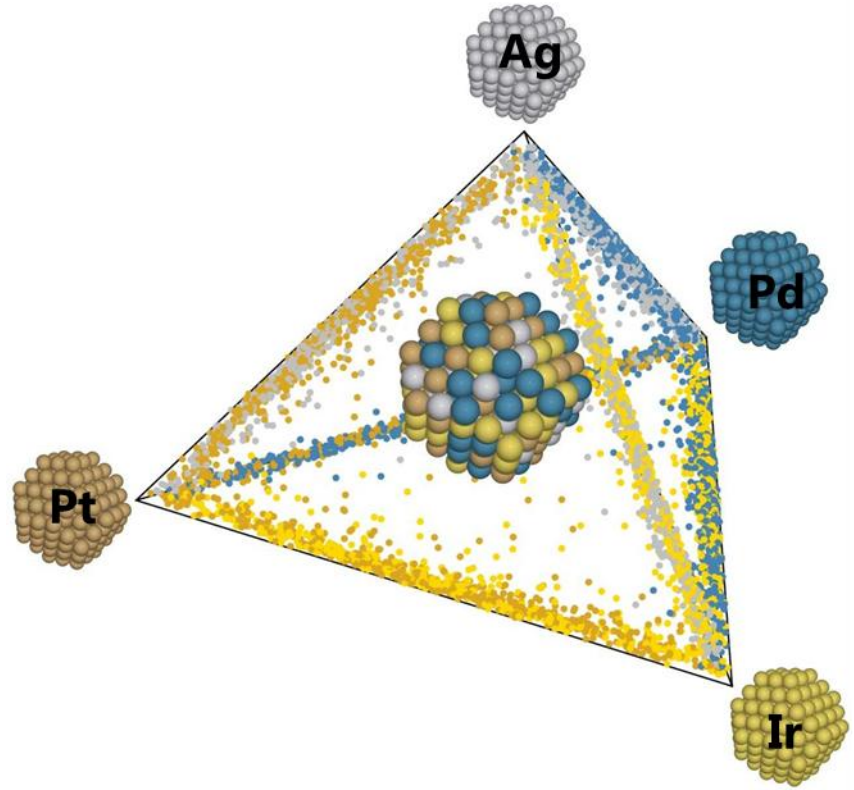
50 experiments



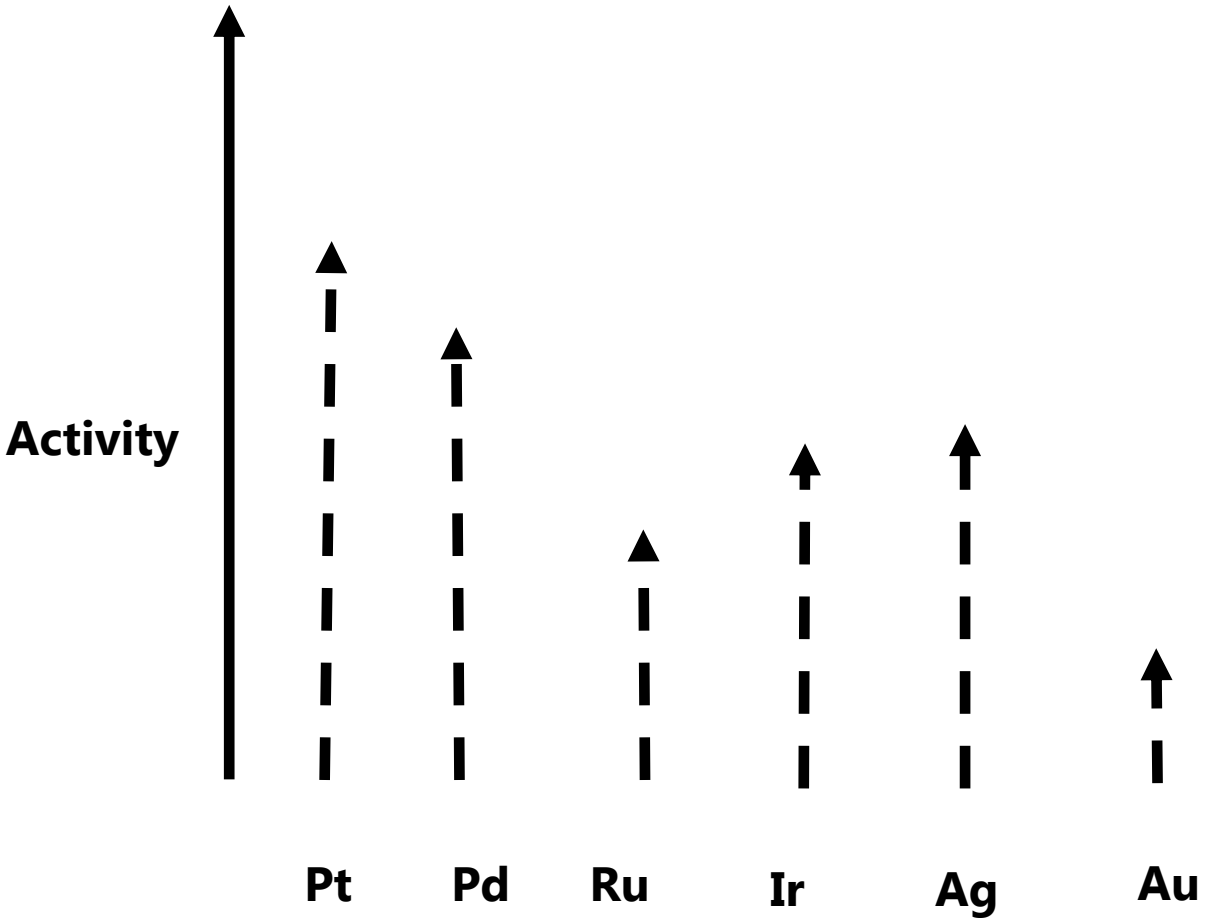
Dimensionality ORR

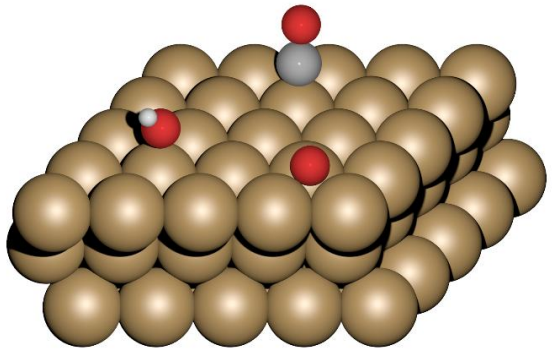



28
56
70
56
28
8
1

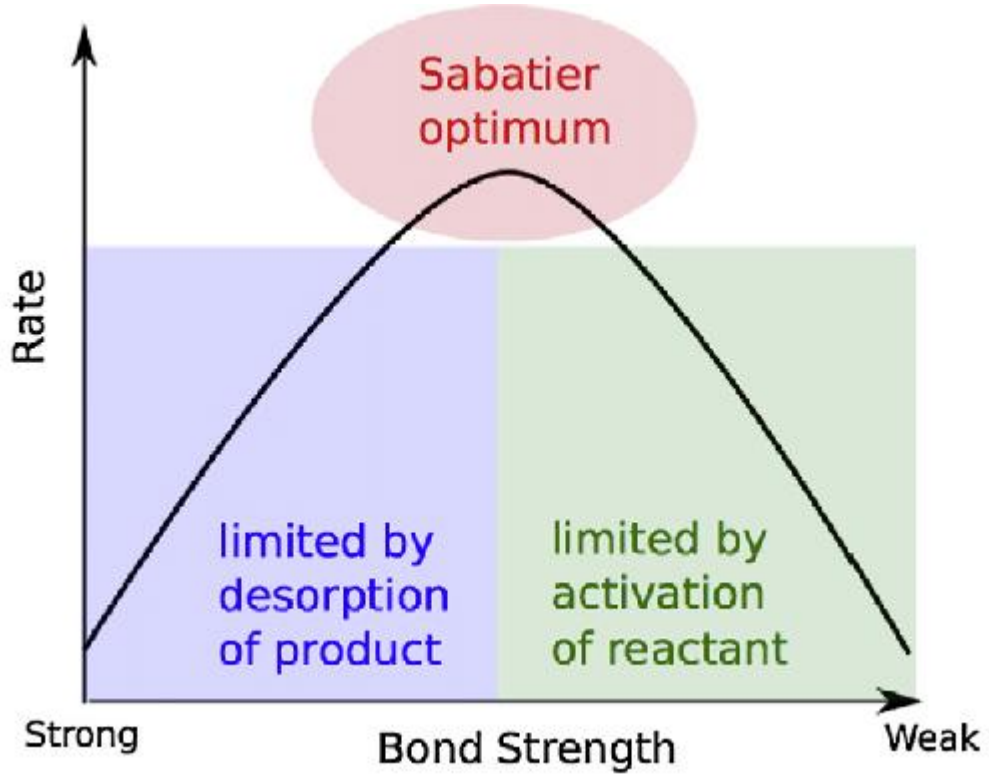

Ag
Pd
Pt
Ir

Screening





Model for Catalytic Activity



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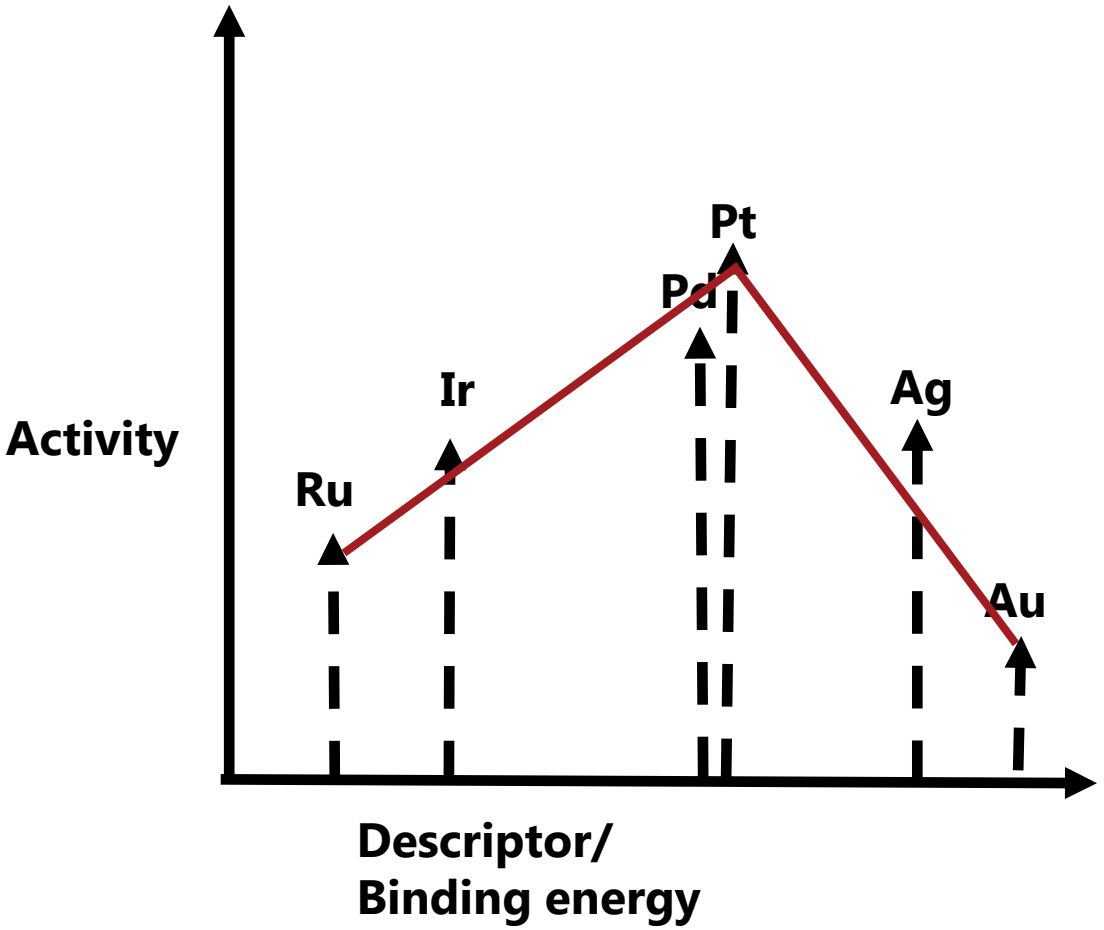

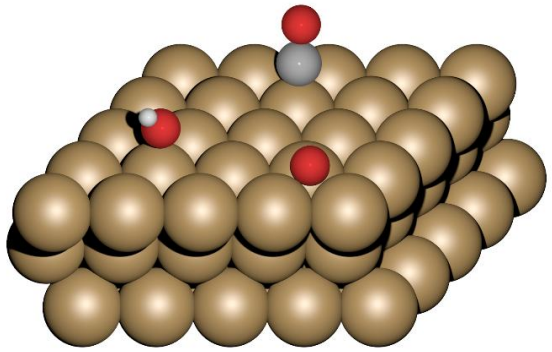

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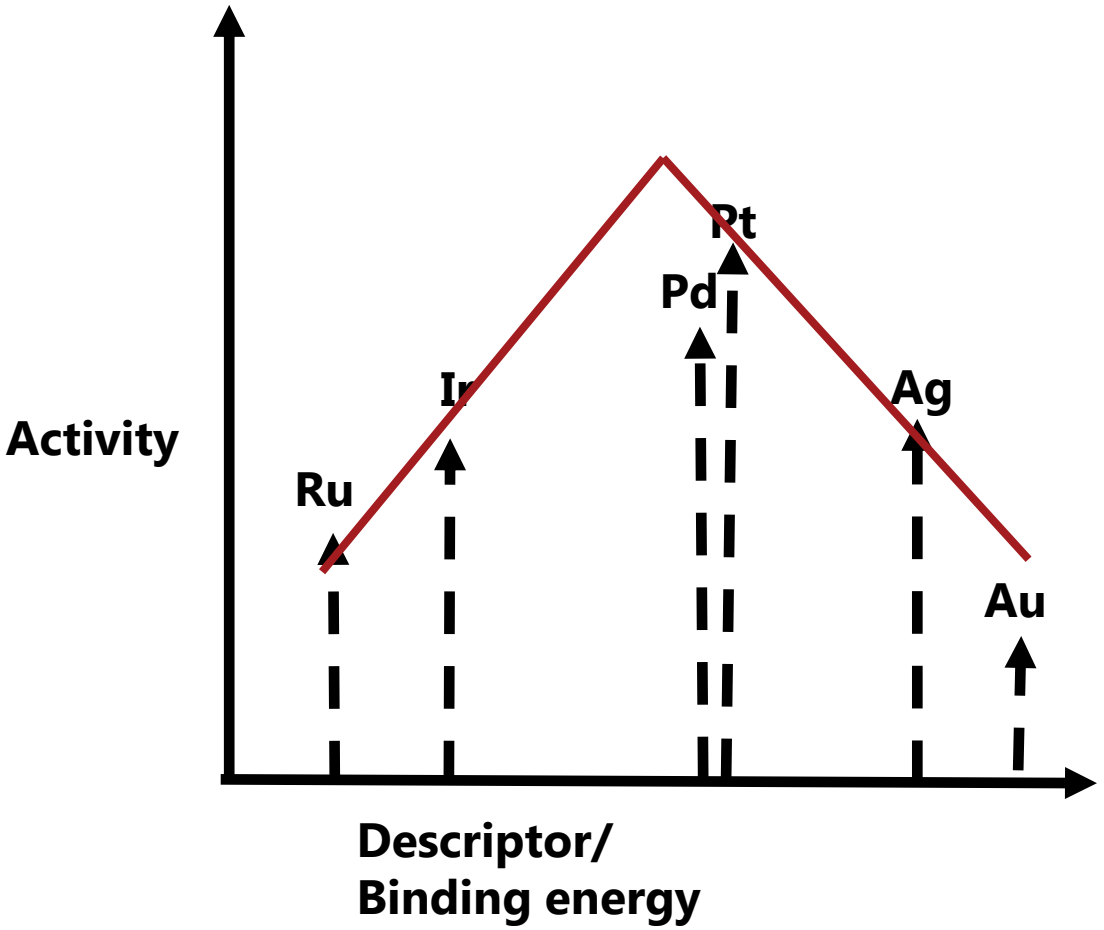
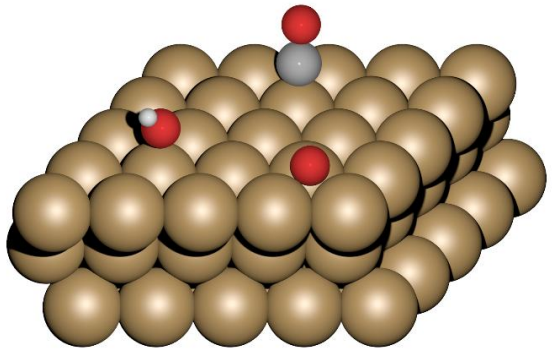
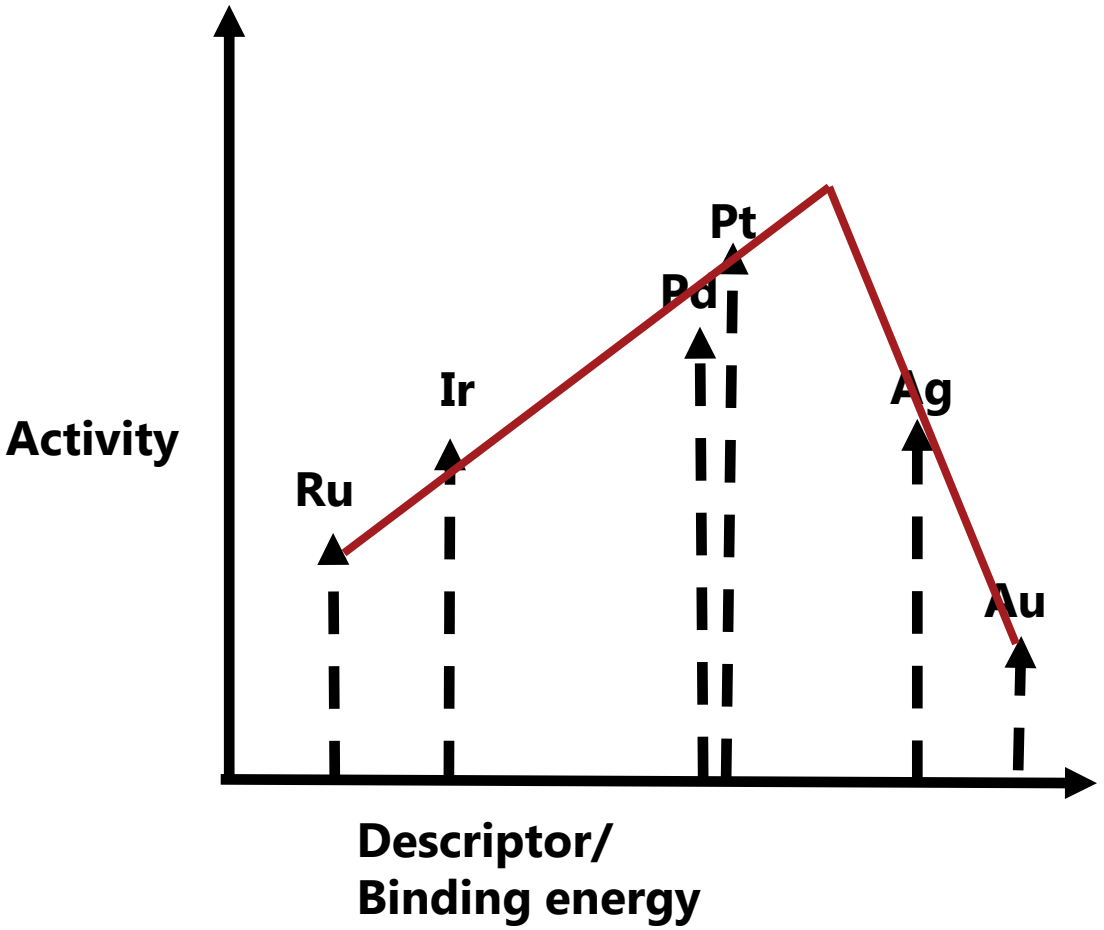
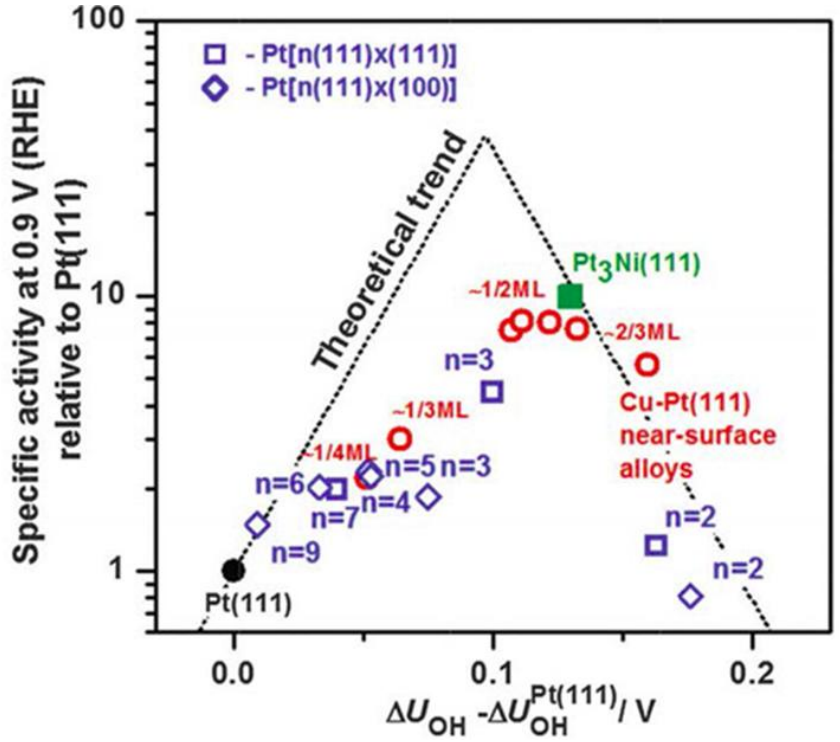




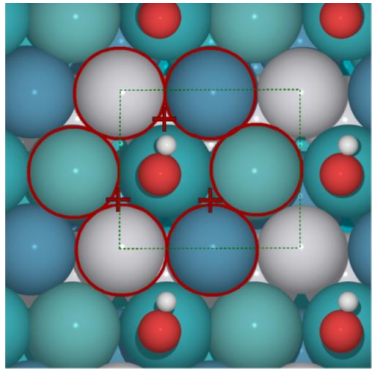
Model for Catalytic Activity

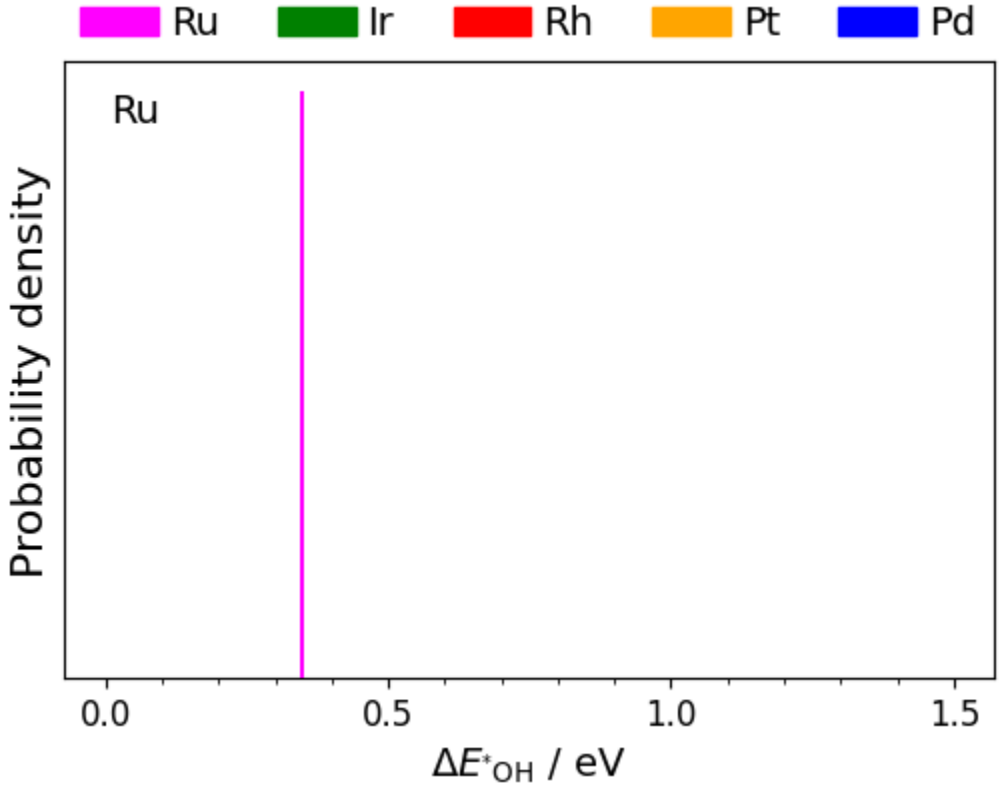




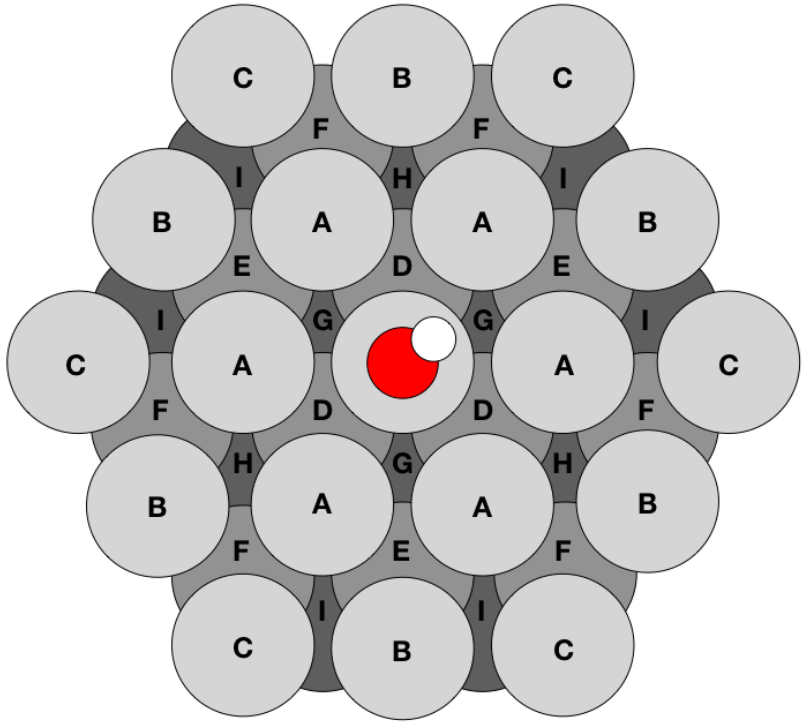
Bandarenka, Hansen, Rossmeisl, Stephens, PCCP. 2014

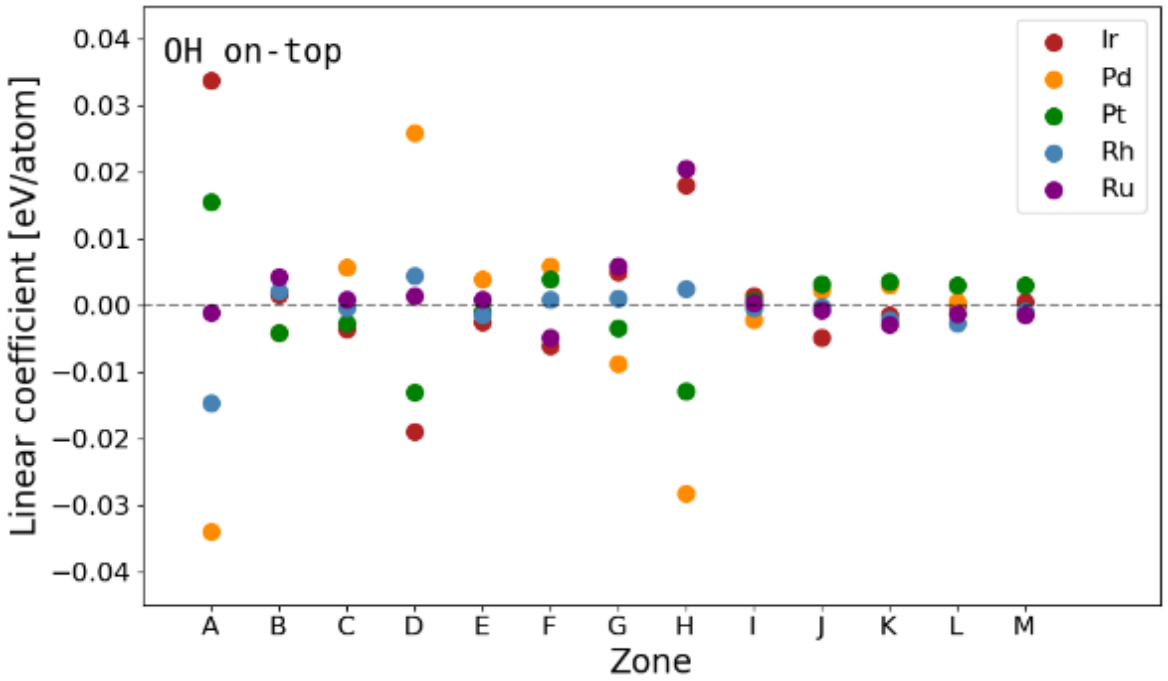
Ensemble and Ligand effect





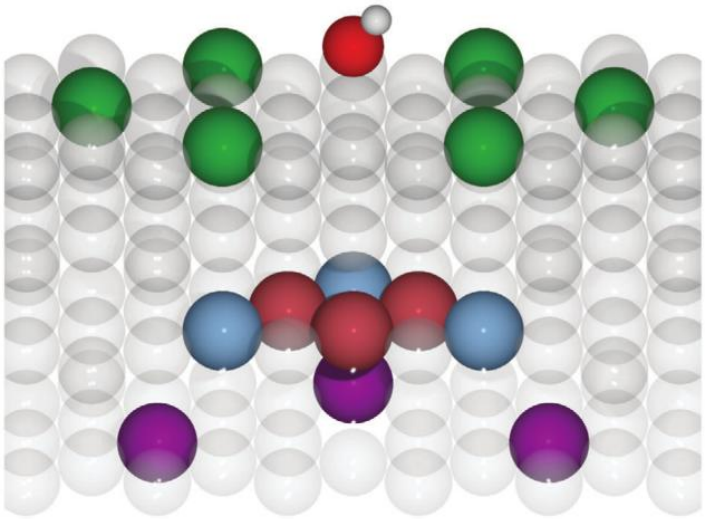
Which are the important atoms for the ligand effect?

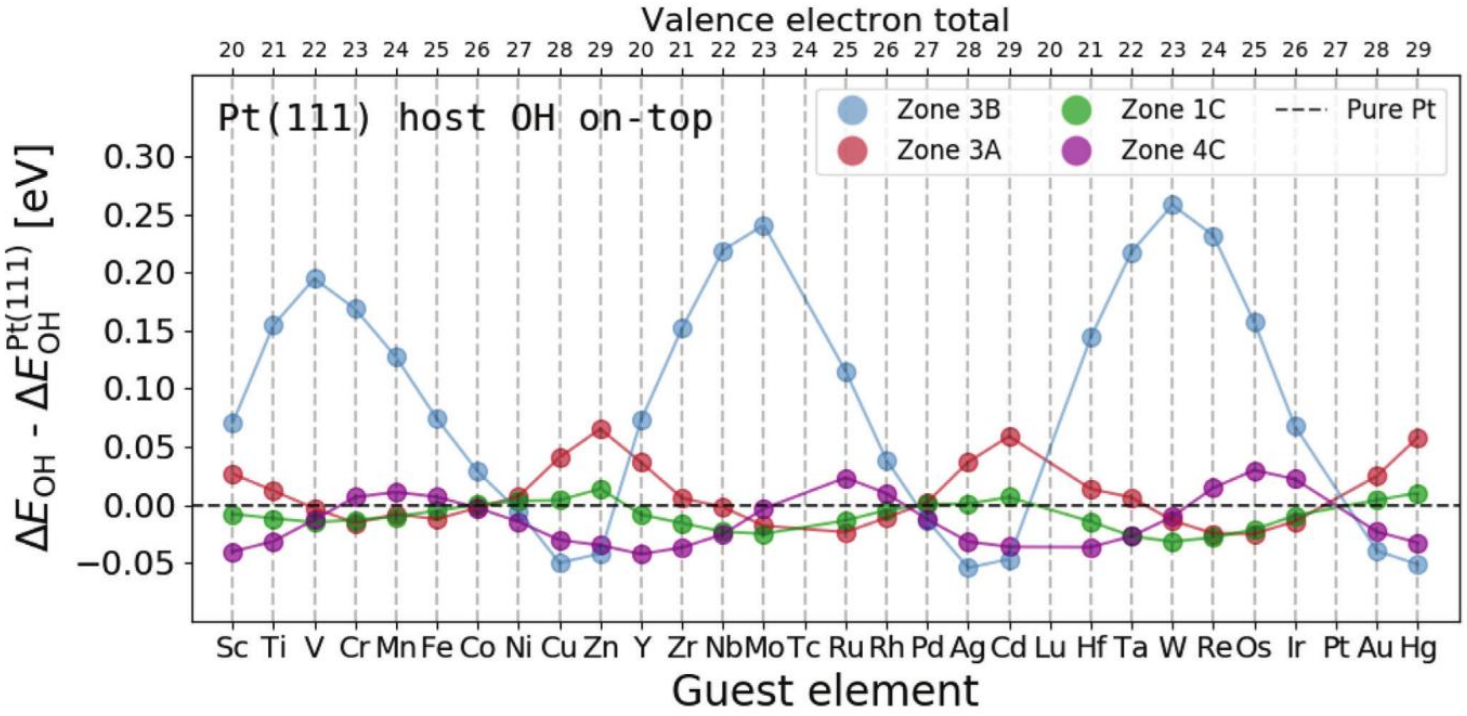




C.M. Clausen, T.A.A. Batchelor, J.K. Pedersen and J.Rossmeisl, **Advanced Science 2021**

Improving the model: Which atoms matter?

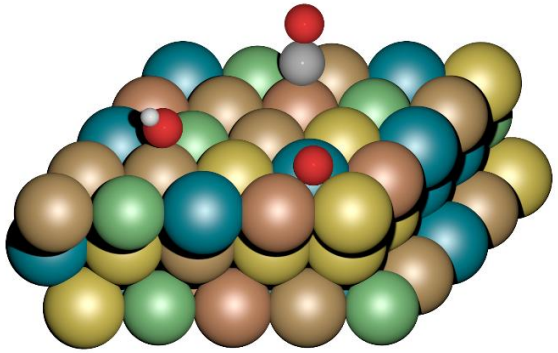


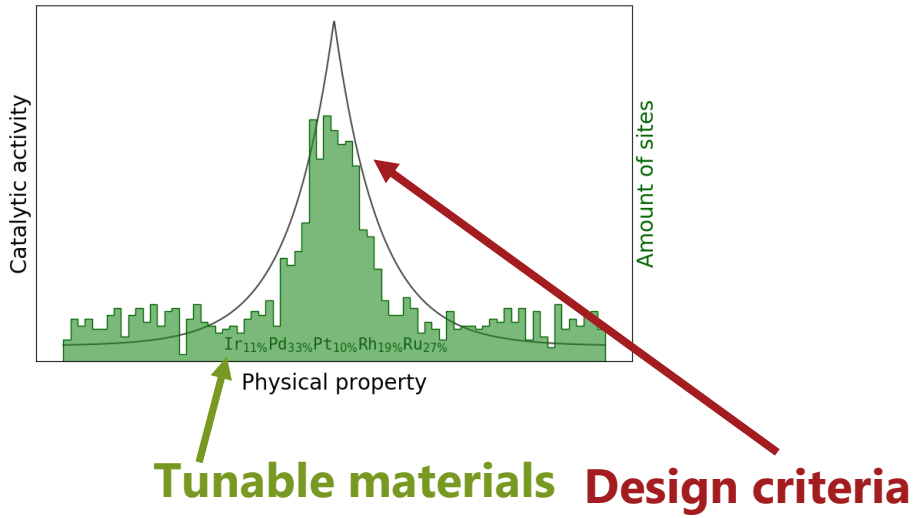


Particularly strong ligand effect from 3rd atomic layer

C.M. Clausen, T.A.A. Batchelor, J.K. Pedersen and J.Rossmeisl, **Advanced Science 2021**

Design criteria and tunable material

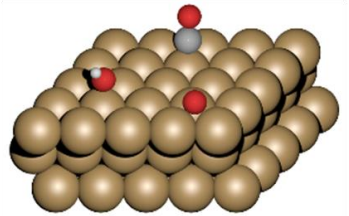




Catalytic Properties

↑ ↓

Material, surface

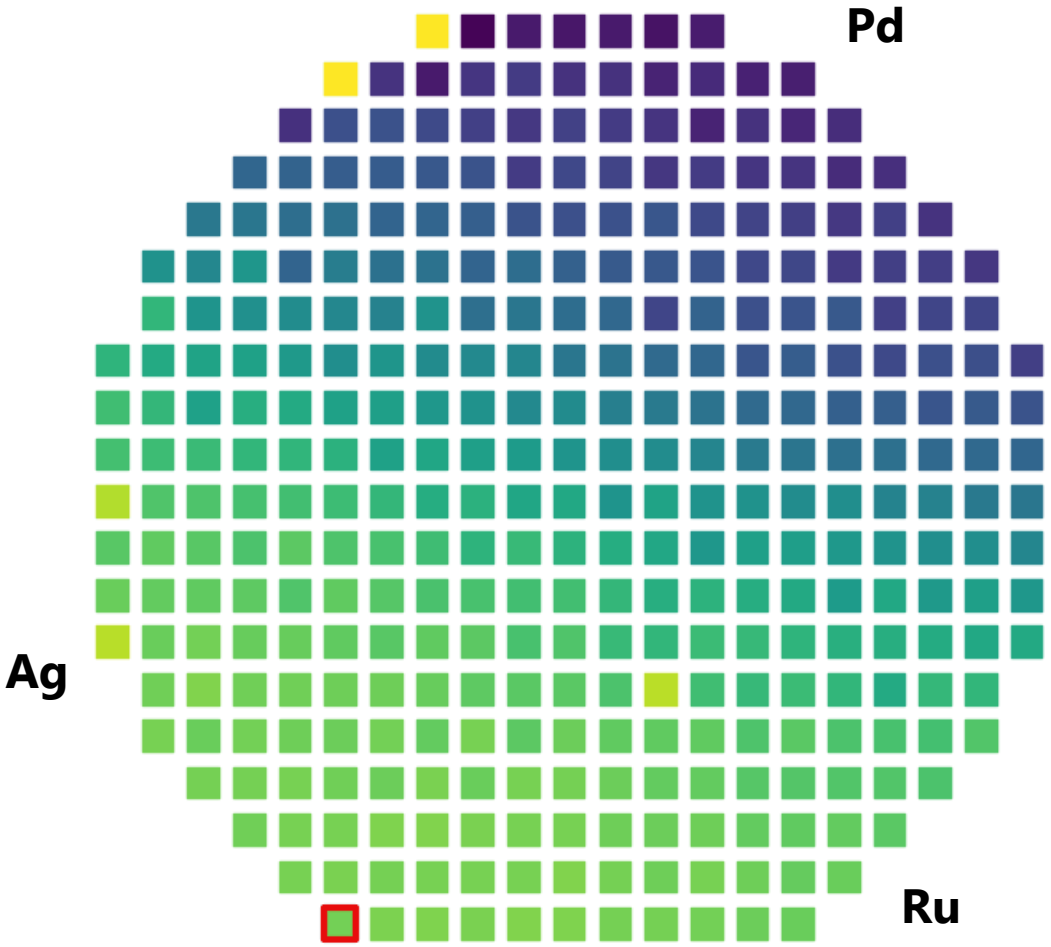


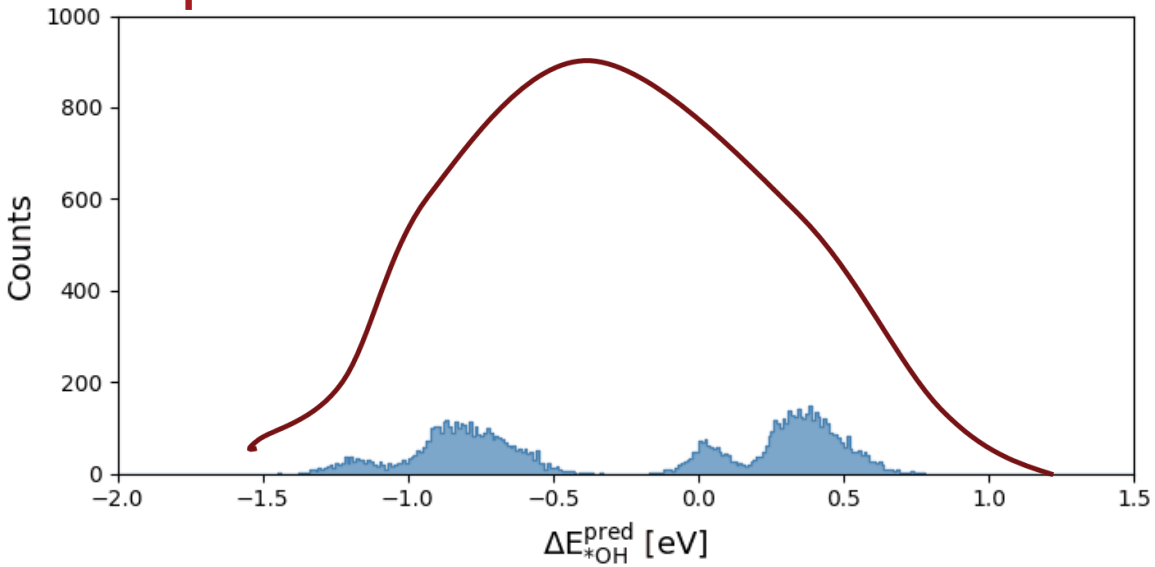
$$Experimental\ activity = a \int D(\Delta E) A(\Delta E) d\Delta E$$

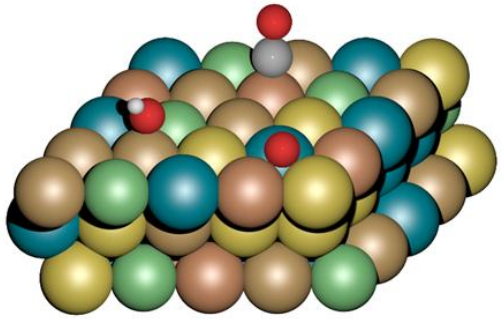
From ”calculating properties of materials”
to ”calculate materials of properties”

High-Entropy Alloys as a Discovery Platform for Electrocatalysis,
TAA Batchelor, JK Pedersen, SH Winther, IE Castelli, KW Jacobsen, J Rossmeisl, **Joule 2019** 3

Learn a theoretical model from experiments

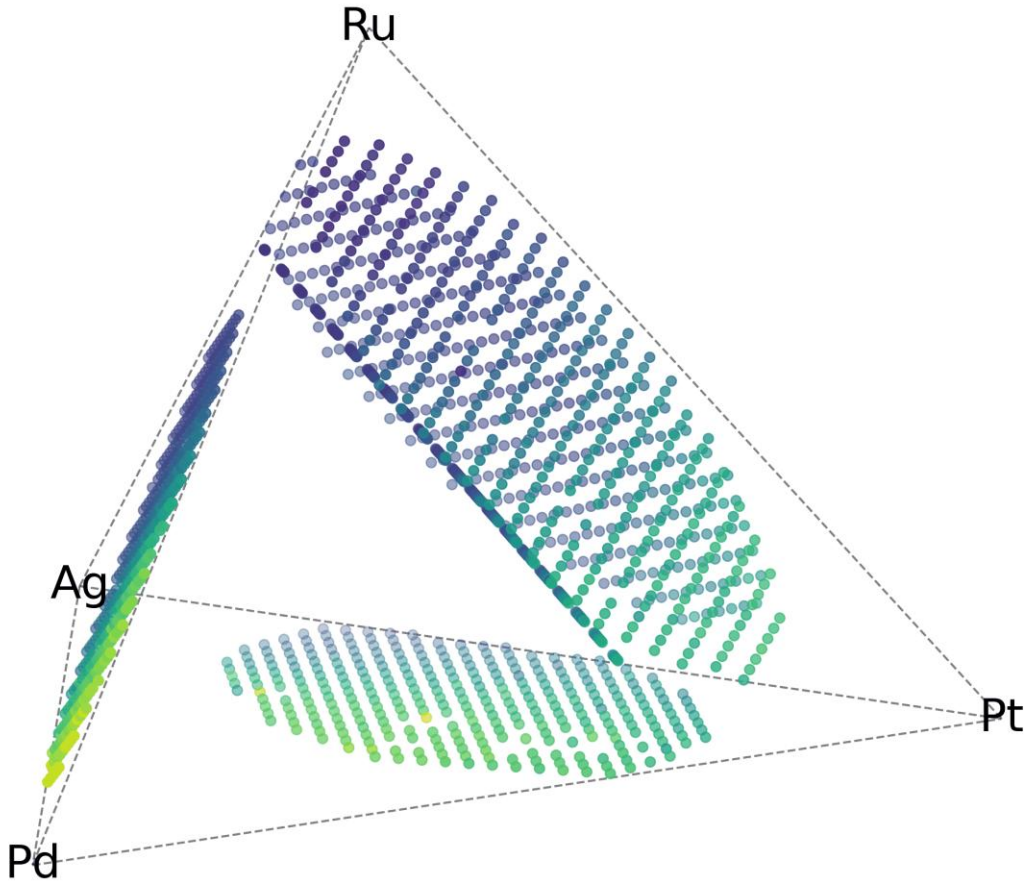




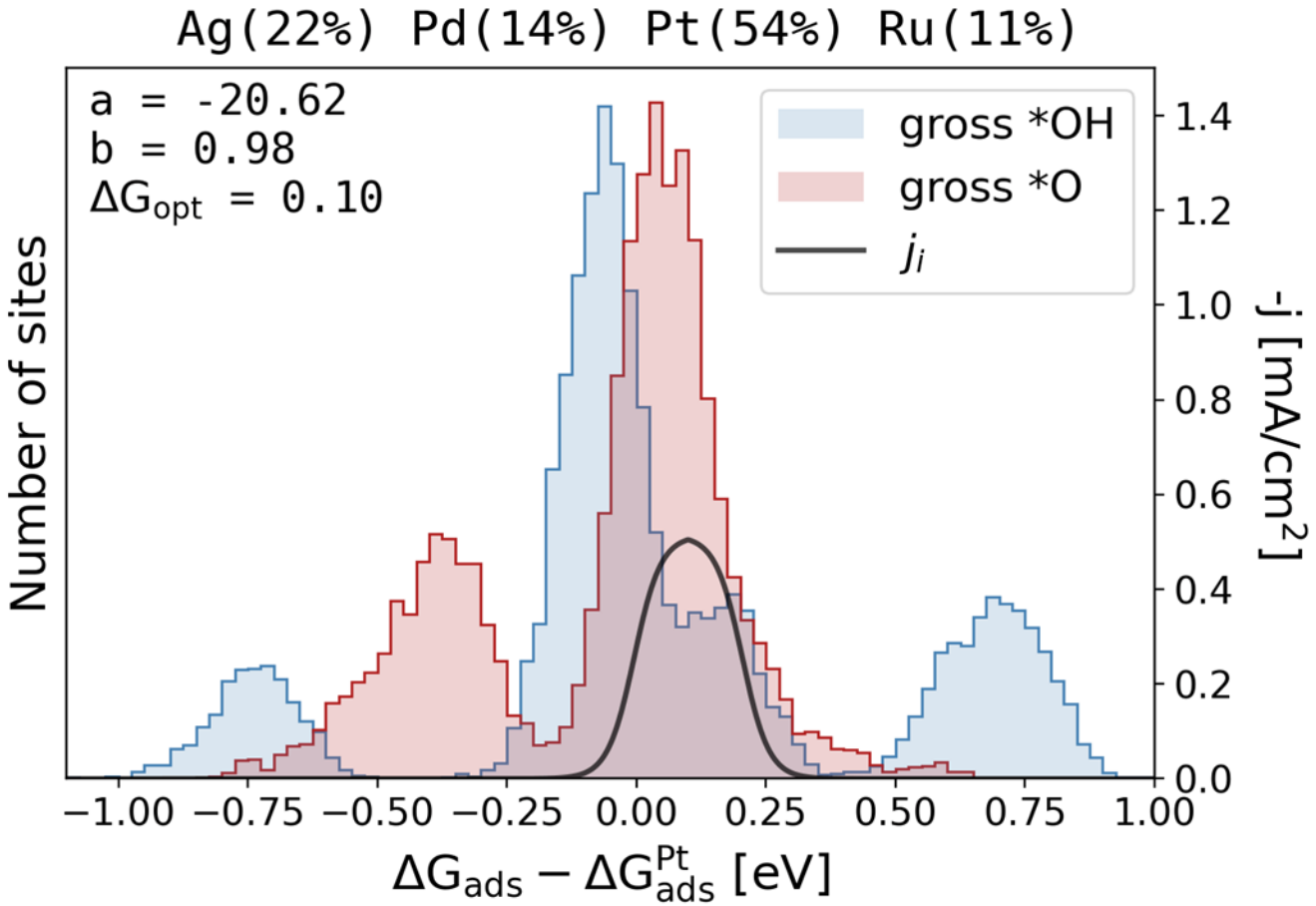


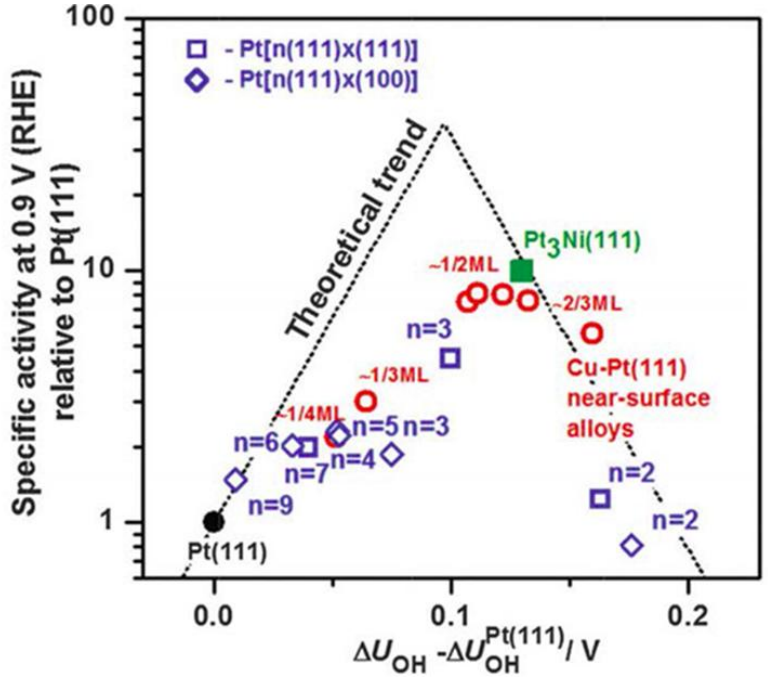
A Flexible Theory for Catalysis: Learning Alkaline Oxygen Reduction on Complex Solid Solutions within the Ag− Pd− Pt− Ru Composition Space
Clausen, Banko, Krysiak, Pedersen, Schuhmann, Ludwig, Rossmeisl
Angewandte (2023)

Experiments



Theory-derived model





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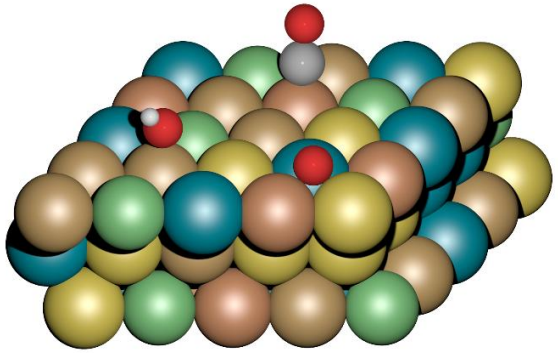
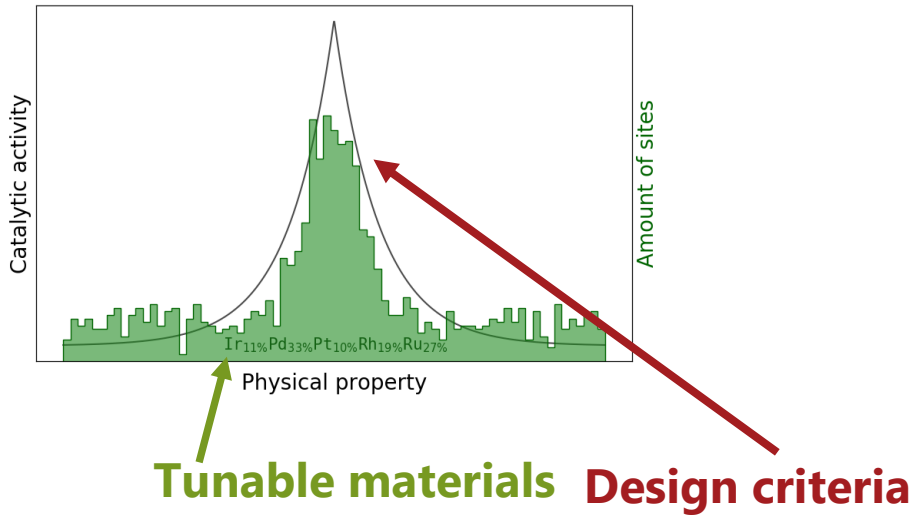
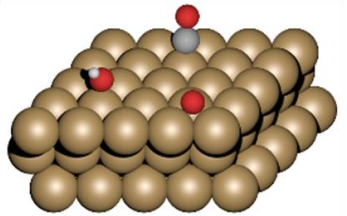




Catalytic Properties

↑ ↓

Material, surface



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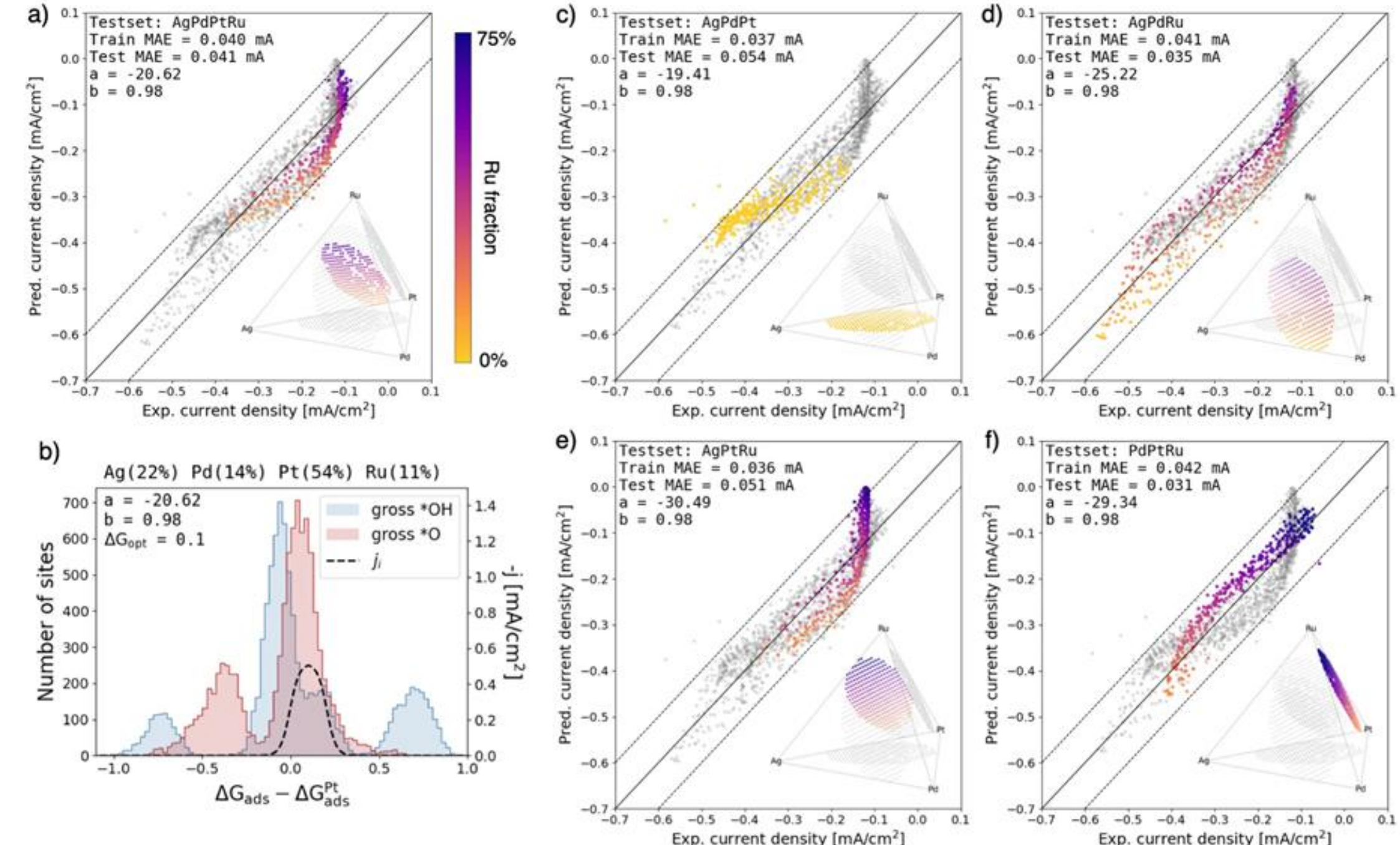
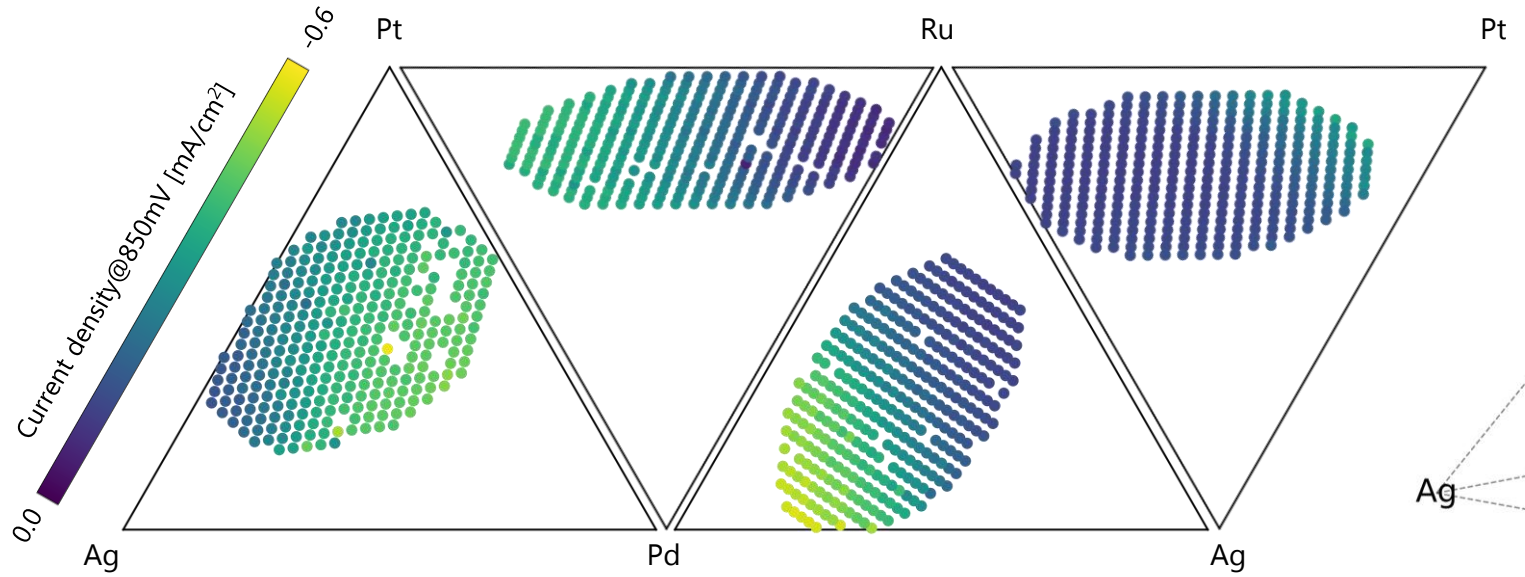
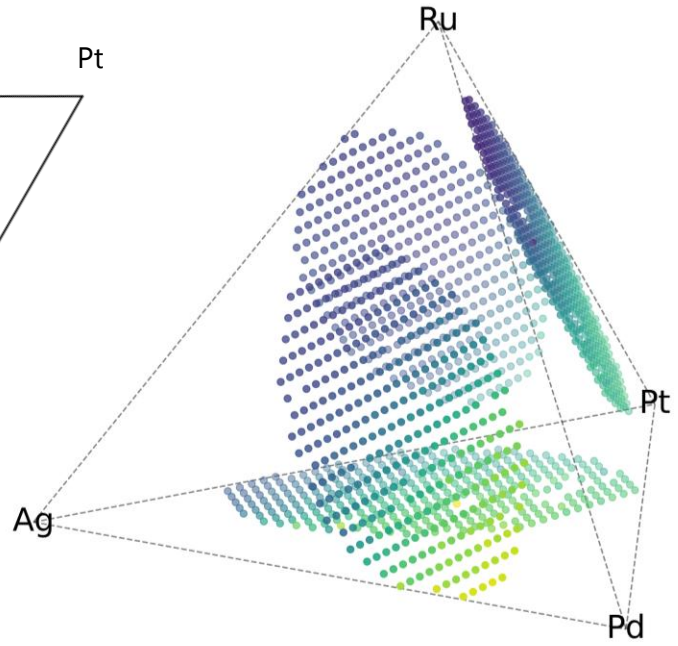
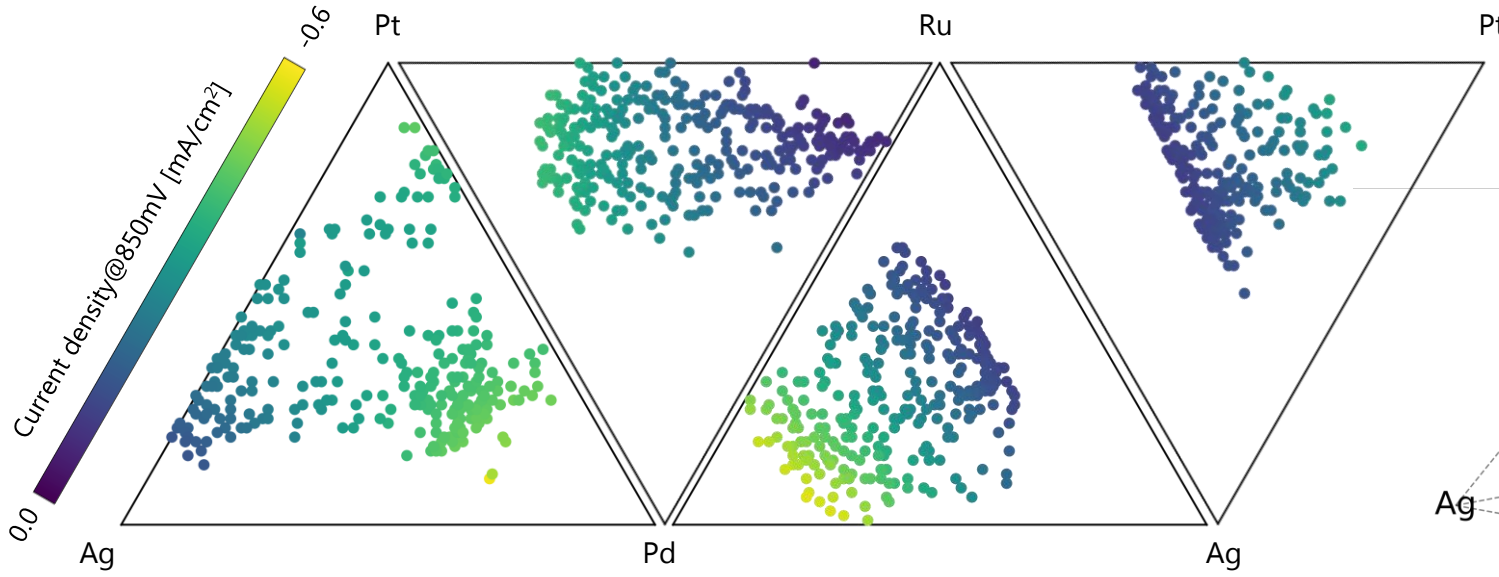
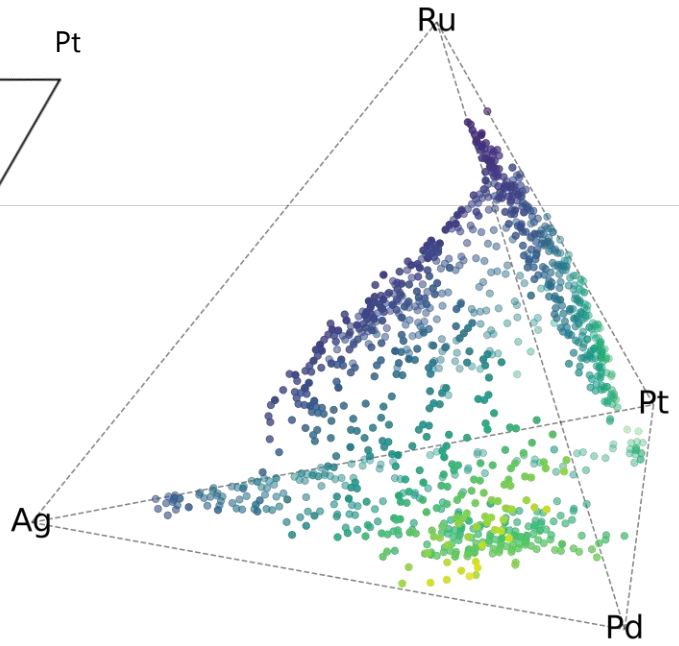
High-Entropy Alloys as a Discovery Platform for Electrocatalysis,
TAA Batchelor, JK Pedersen, SH Winther, IE Castelli, KW Jacobsen, J Rossmeisl, **Joule 2019** 3


a)
Testset: AgPdPtRu
Train MAE = 0.040 mA
Test MAE = 0.041 mA
a = -20.62
b = 0.98
75%
Ru fraction
0%
Pred. current density [mA/cm²]
Exp. current density [mA/cm²]
b)
Ag(22%) Pd(14%) Pt(54%) Ru(11%)
a = -20.62
b = 0.98
ΔG_opt = 0.1
gross *OH
gross *O
j_i
Number of sites
-j [mA/cm²]
ΔG_ads − ΔG^Pt_ads
c)
Testset: AgPdPt
Train MAE = 0.037 mA
Test MAE = 0.054 mA
a = -19.41
b = 0.98
d)
Testset: AgPdRu
Train MAE = 0.041 mA
Test MAE = 0.035 mA
a = -25.22
b = 0.98
e)
Testset: AgPtRu
Train MAE = 0.036 mA
Test MAE = 0.051 mA
a = -30.49
b = 0.98
f)
Testset: PdPtRu
Train MAE = 0.042 mA
Test MAE = 0.031 mA
a = -29.34
b = 0.98
Ag
Pd
Pt
Ru


Current density@850mV [mA/cm²]
-0.6
0.0
Pt
Ru
Pt
Ag
Pd
Ag

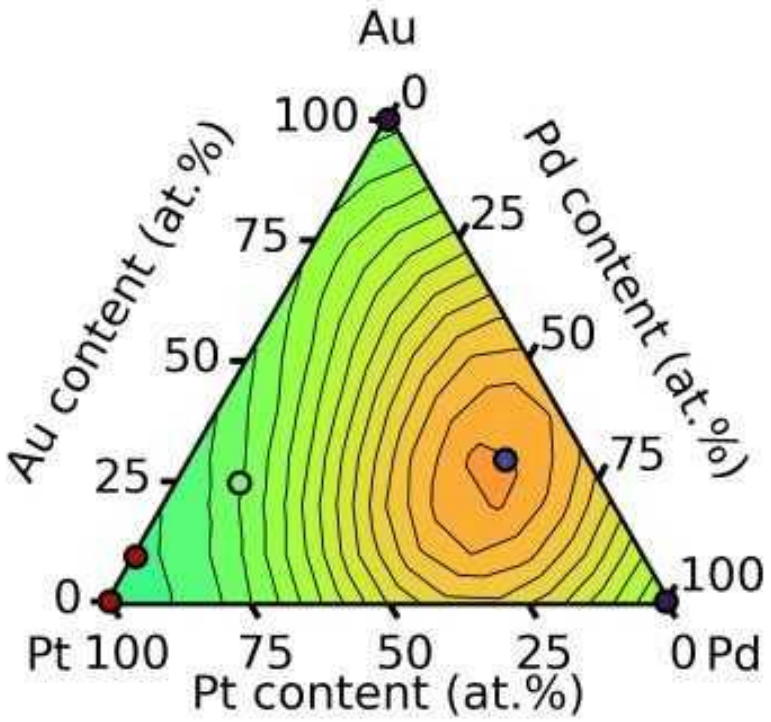

Ru
Pt
Ag
Pd


Current density@850mV [mA/cm²]
-0.6
0.0
Pt
Ru
Pt
Ag
Pd
Ag

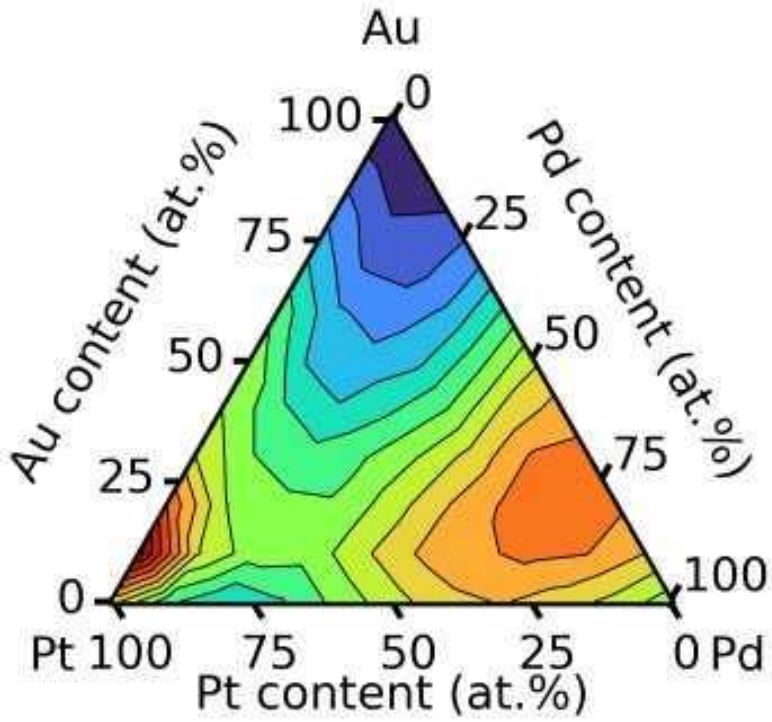

Ru
Pt
Ag
Pd

False negatives

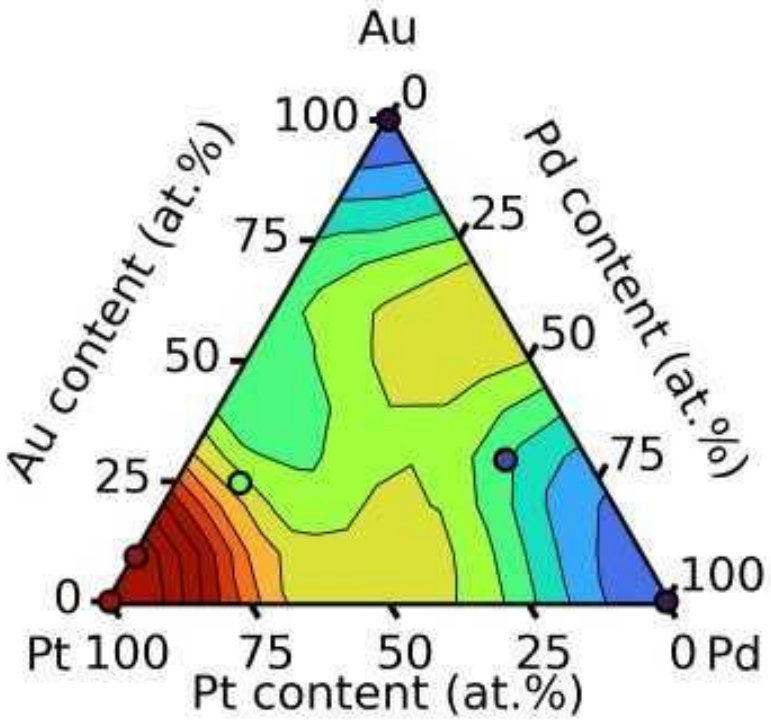
Experiments 1



Theory



Experiments 2



V Mints, JK Pedersen, GKH Wiberg, J Rossmeisl, M. Arenz **submitted 2023**

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GDCh
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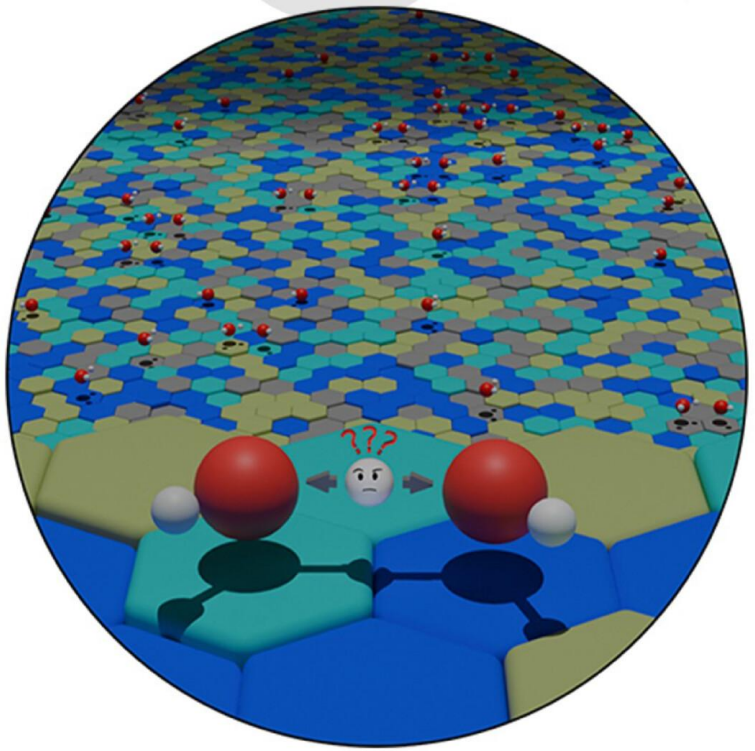
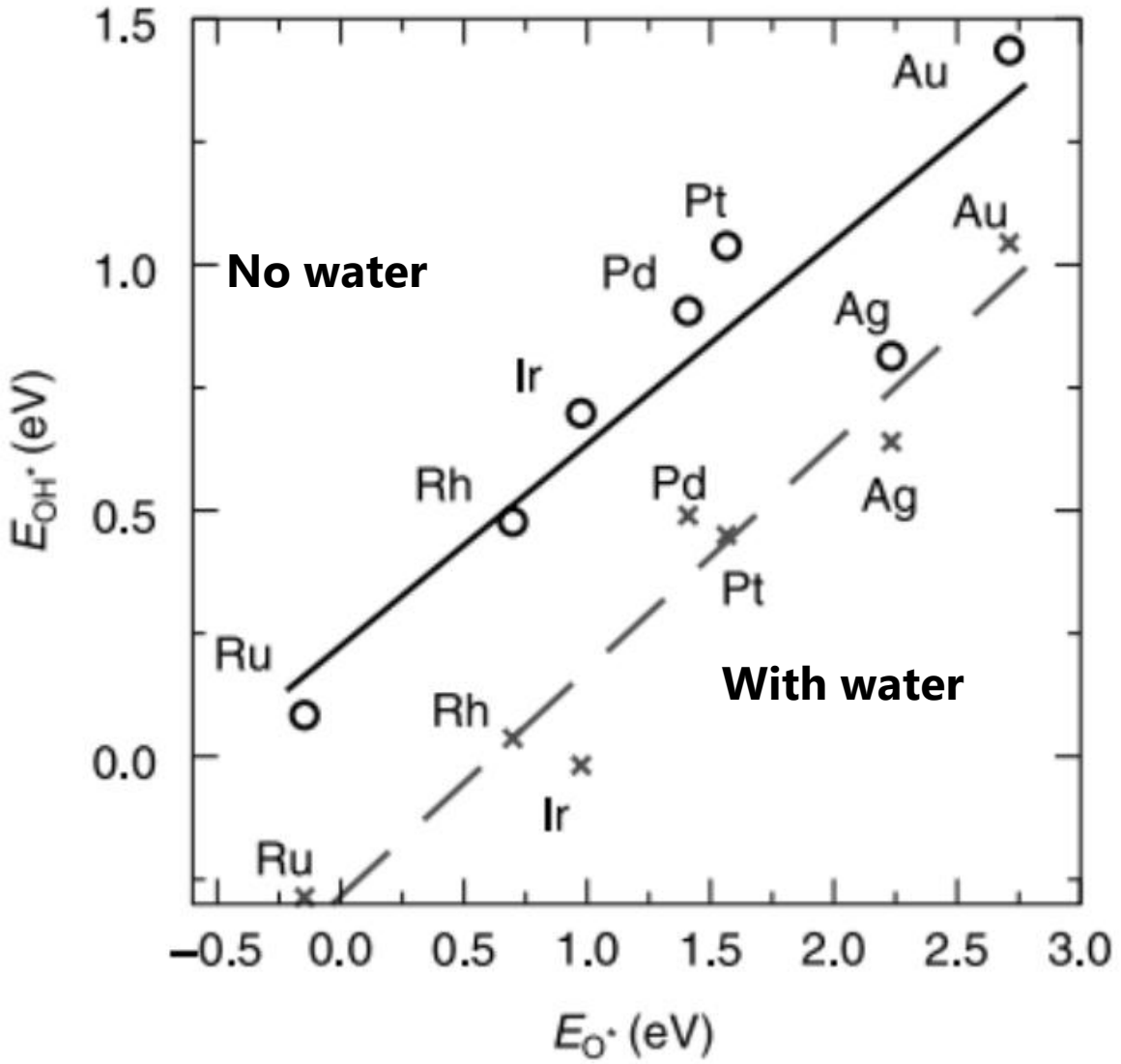
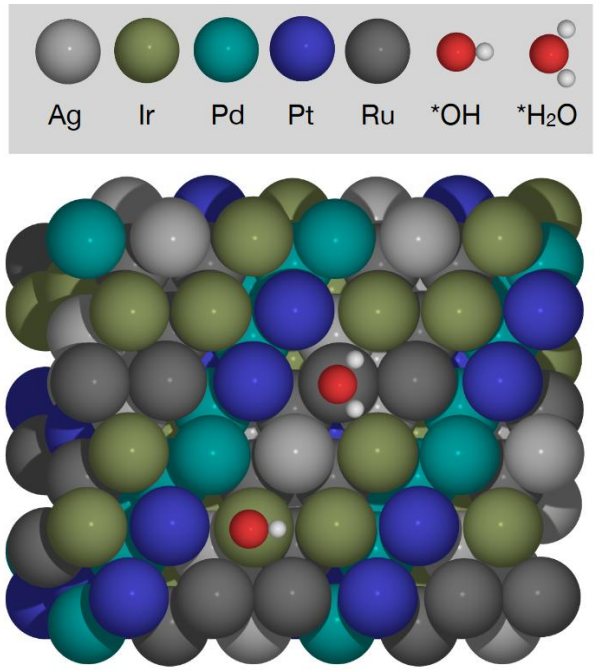


The intricate interactions between surface-near species, OH and water are illustrated in the cover picture. While water and OH form hydrogen bonds, this does not fully capture the interaction. Electrons can delocalize across adjacent adsorbates, leading to a more complex electronic structure than anticipated. The cover displays the dilemma of a hydrogen atom situated between two oxygen atoms, as is the case with adjacent OH and water. Which oxygen atom will hydrogen form a bond with? The answer is both, as detailed by Jan Rossmeisl et al. in their Research Article (e202417308).

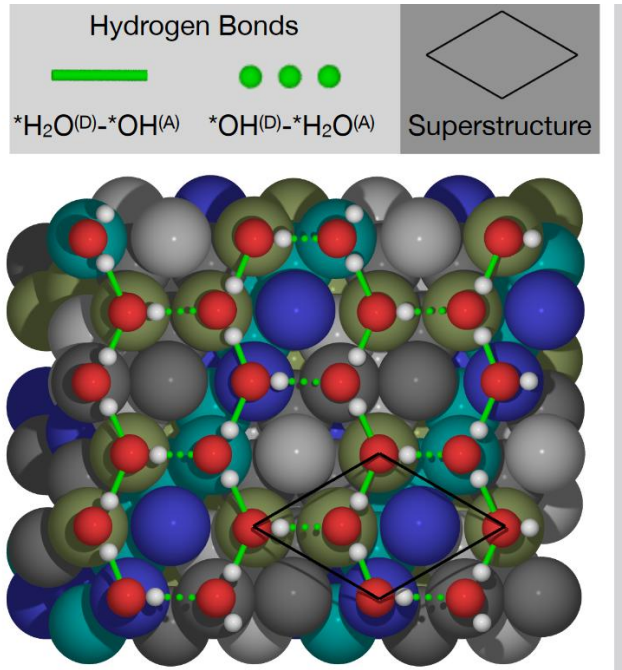
WILEY VCH

Interaction between water and HO*



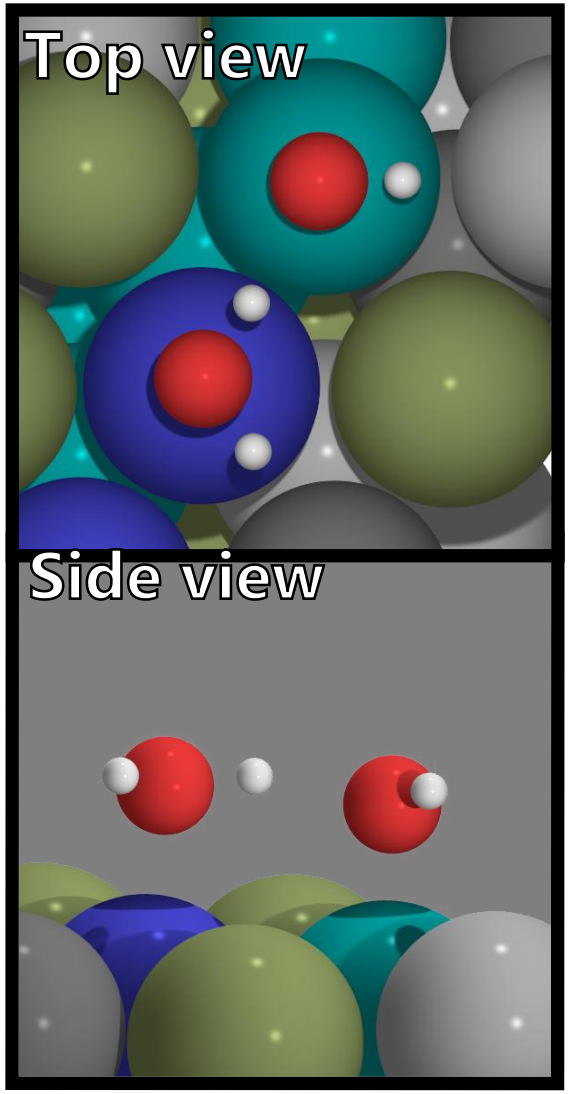


HEA with two adsorbates: *OH and $*H_2O$



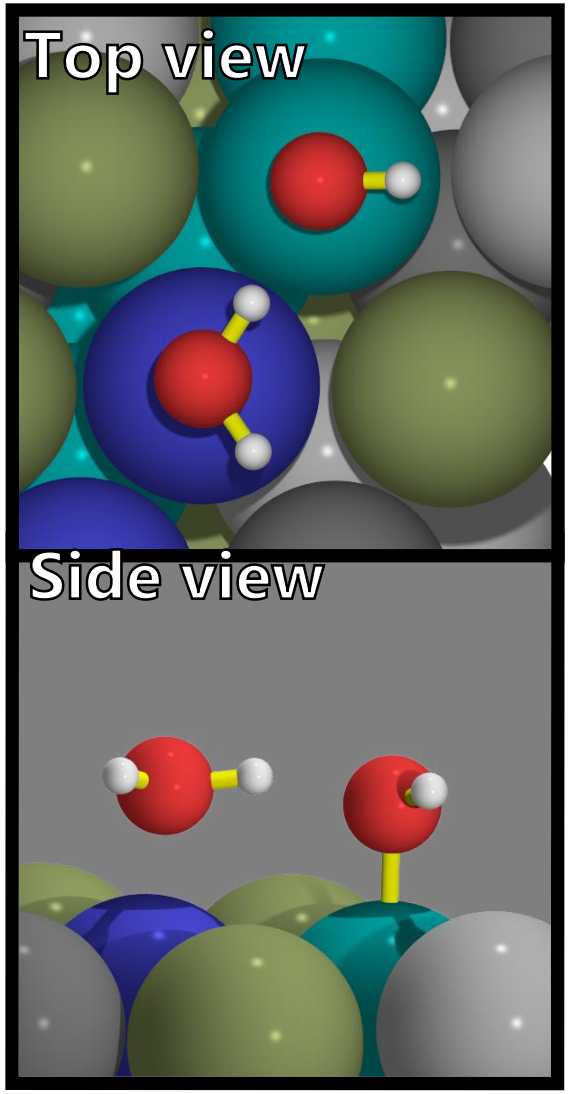
HEA with a hexagonal adlayer *(OH-H_2O)

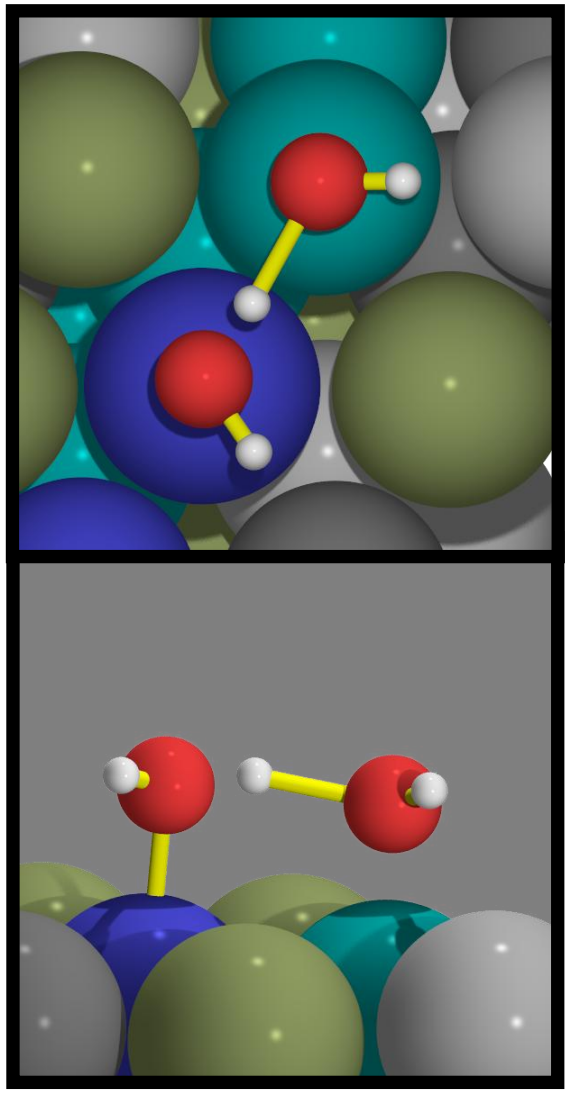
*OH and *H_2O coadsorption

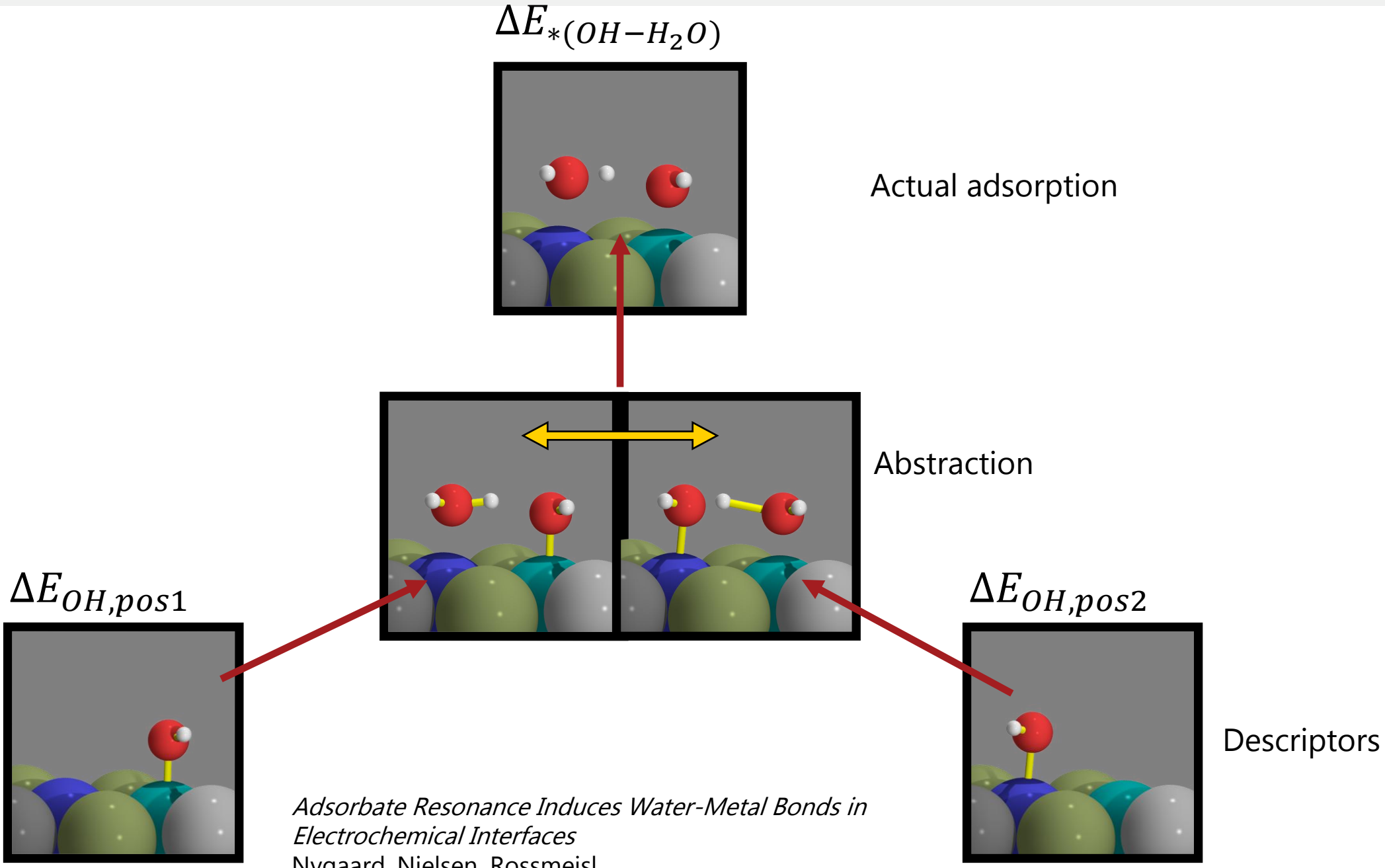


Which atoms form bonds?

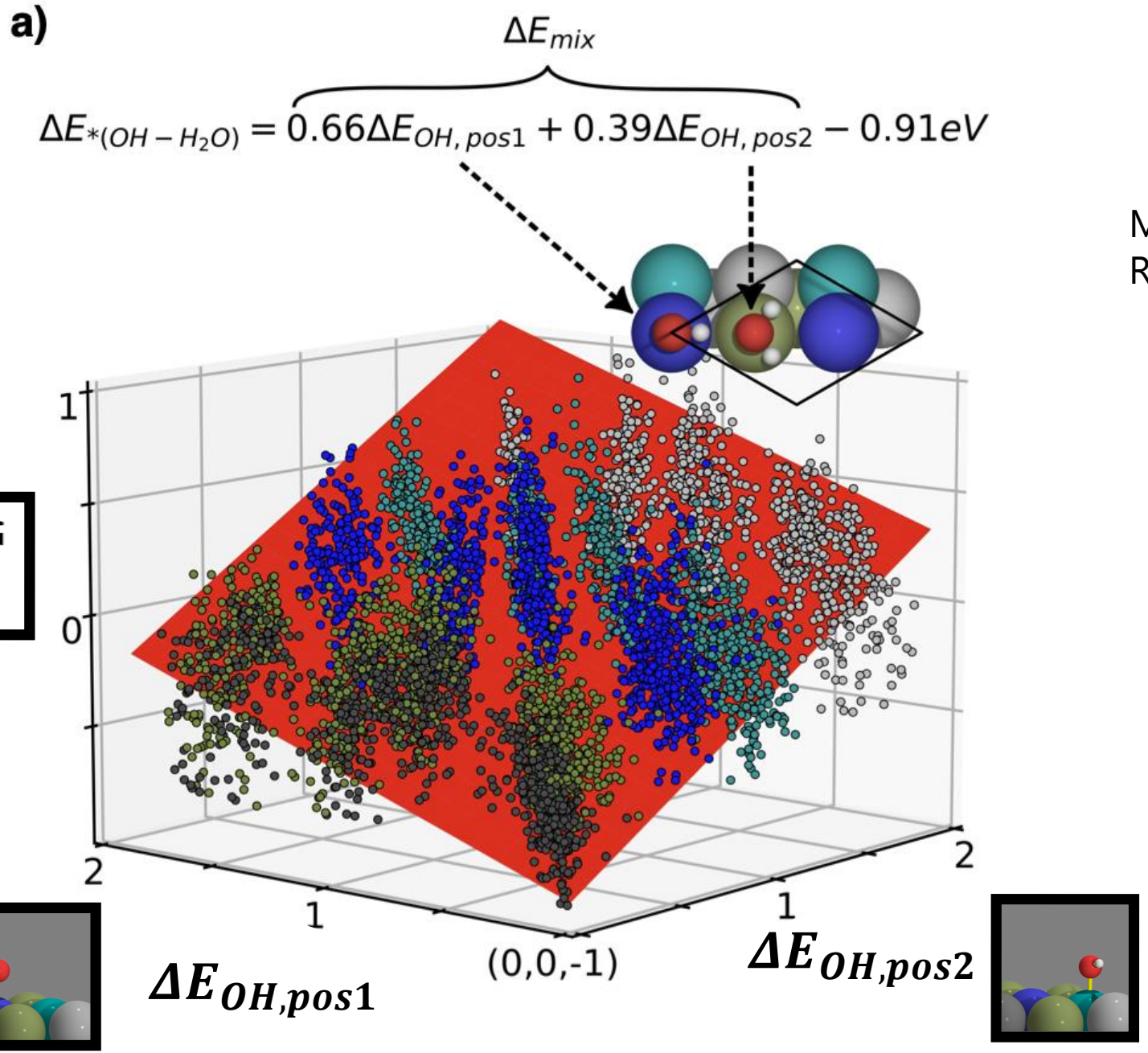
*OH and *H_2O coadsorption





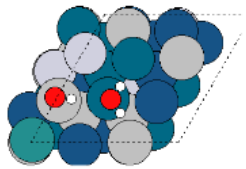
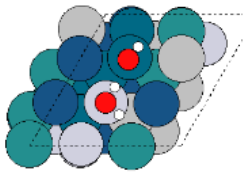
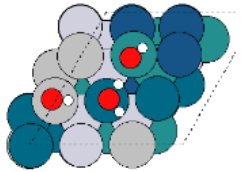
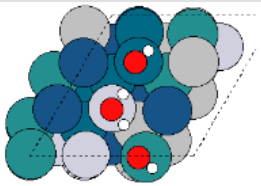
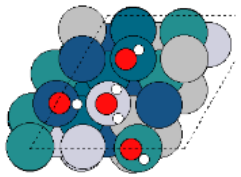


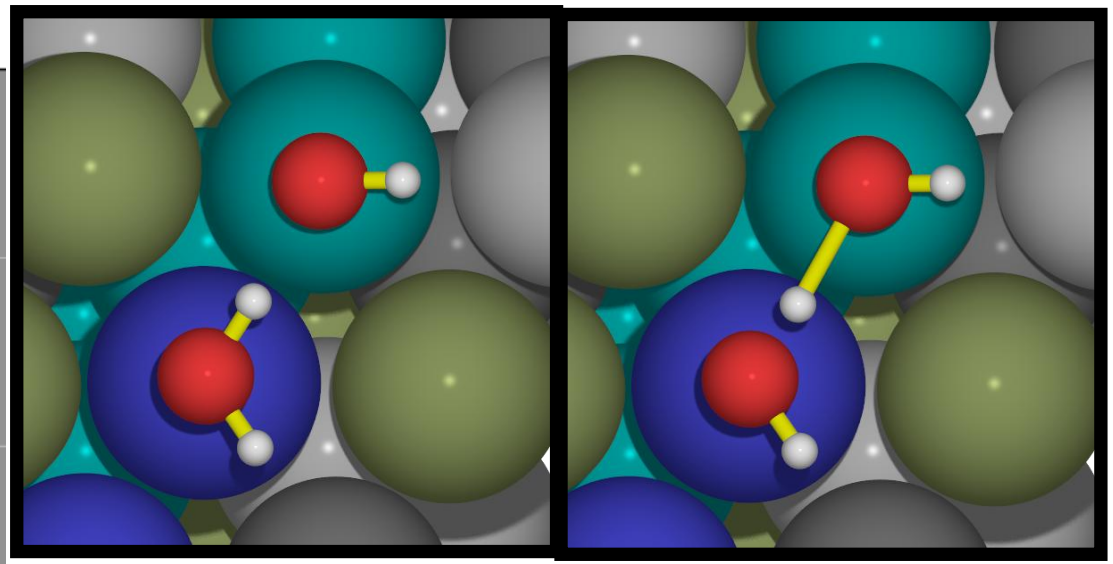
Adsorbate Resonance Induces Water-Metal Bonds in Electrochemical Interfaces
Nygaard, Nielsen, Rossmeisl
Angewandte Chemie (2024)

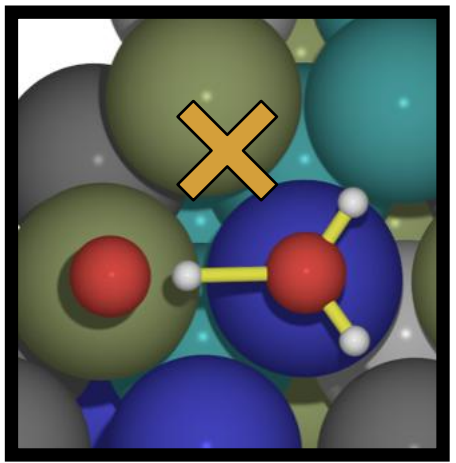


MAE: 0.083eV
R2: 0.91

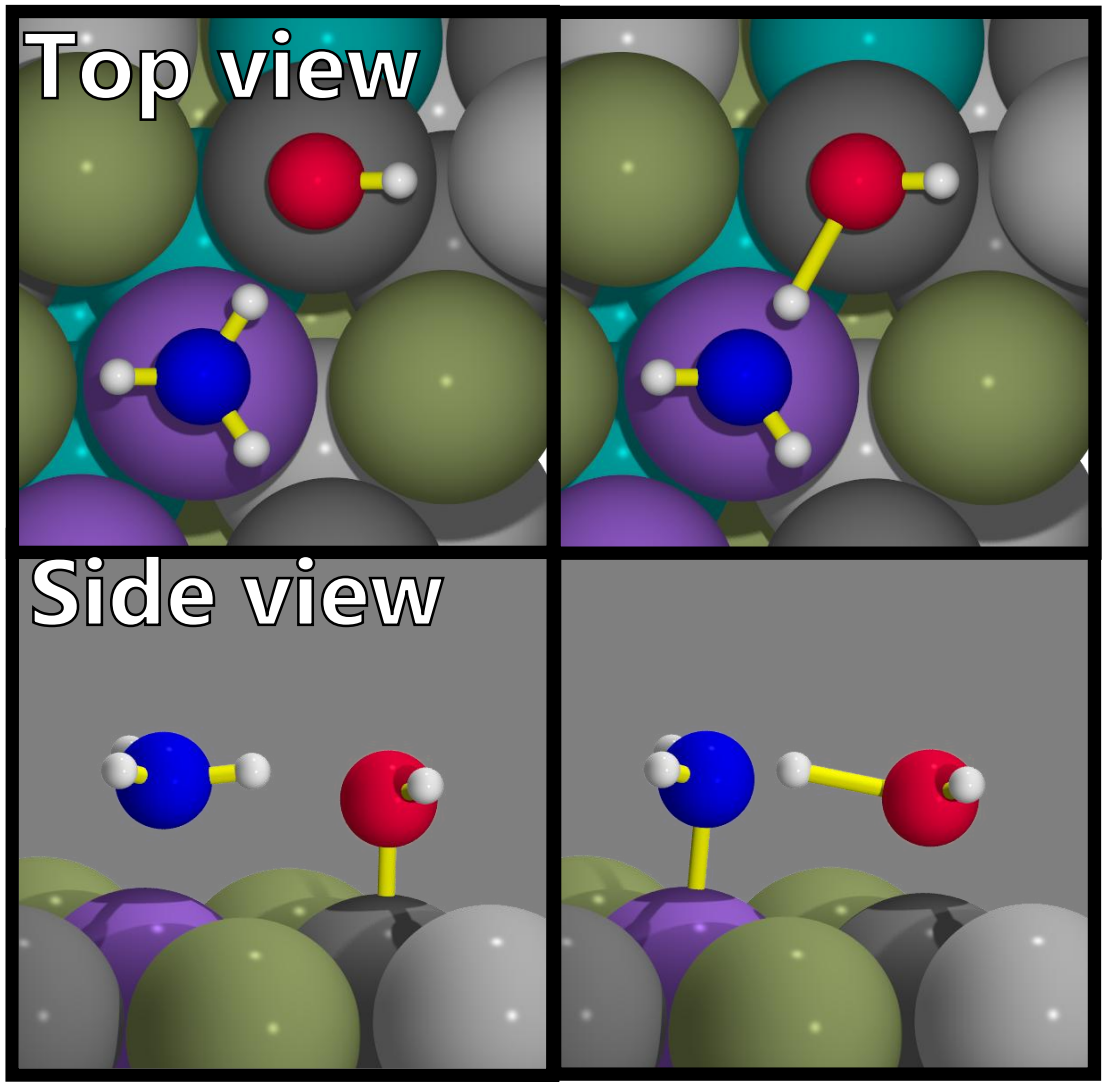
Adsorbate Resonance

Adsorbed species (Figure)	Adsorbed species (Text)	H_2O	$OH^{(D)}$	$OH^{(A)}$
	$OH^{(D)}$-$H_2O^{(A)}$	0.06	0.89	*N/A*
	$H_2O^{(D)}$-$OH^{(A)}$	**0.16** 1/6	*N/A*	0.79
	$OH^{(D)}$-$H2O^{(A+D)}$-$OH^{(A)}$	0.10	0.96	0.80
	$H_2O^{(DD)}$-2x$OH^{(A)}$	**0.36** 2/6=1/3	*N/A*	0.82, 0.79
	$OH^{(D)}$-$H_2O^{(A+DD)}$-2x$OH^{(A)}$	0.19	0.91	0.79, 0.75

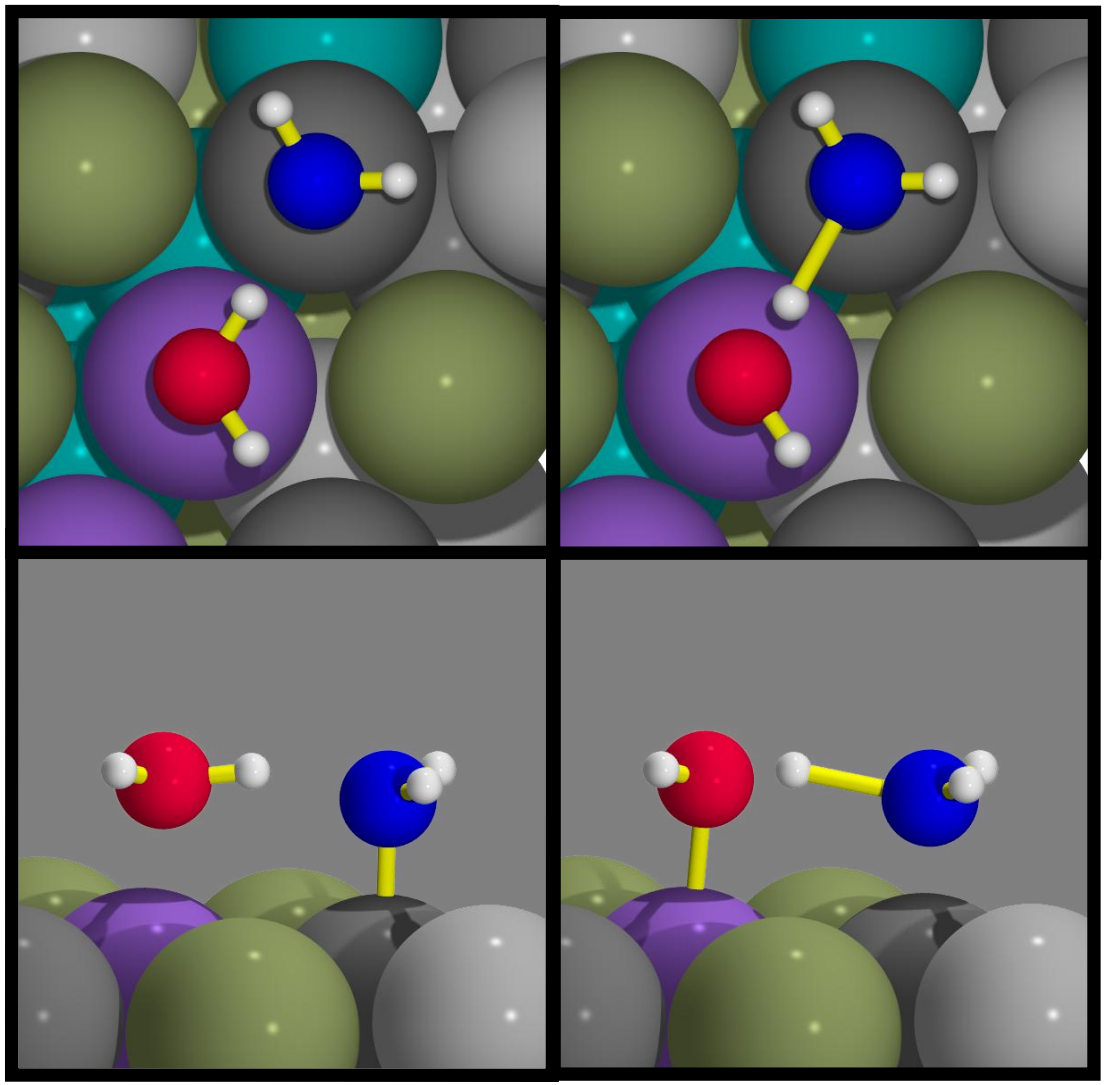




*(NH_3-OH) Resonance



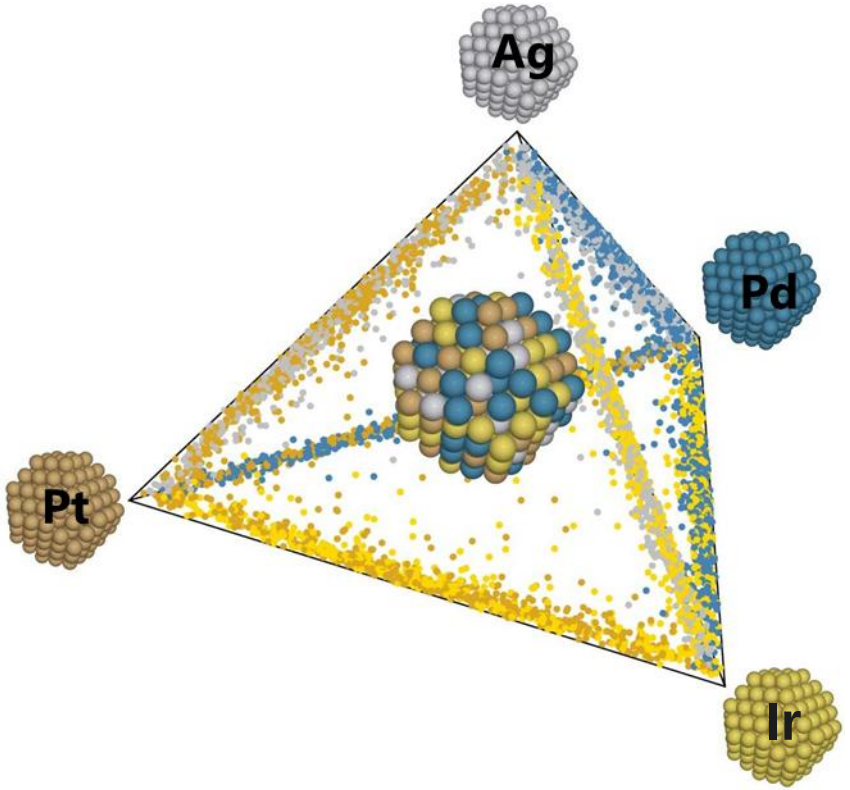
*(NH_2-H_2O) Resonance



Summary

It is not just a new class of materials
it is a new approach to catalysis

A platform for discovering catalysis
and catalysts



Three Reasons for High Entropy Materials

- An efficient platform to discover new catalyst materials
- Learning design criteria and falsify hypothesizes
- Revealing fundamental understanding previously buried in the mean field