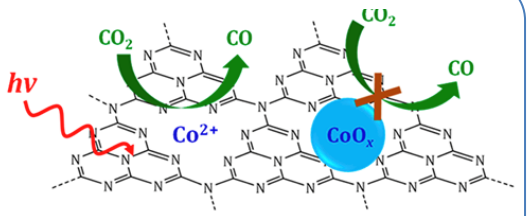
Application of EXAFS to Nanomaterials

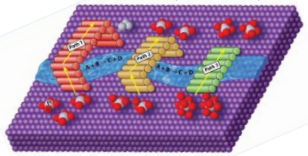
Structure and Dynamics of Applied Nanomaterials (SBU and BNL)

Applied nanomaterials → Nature of active species and active sites? → Mechanisms?

"Single-atom" catalysts

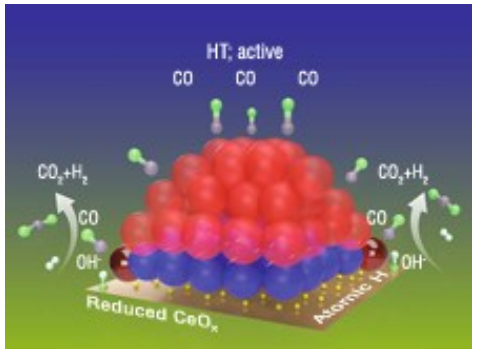


JACS 2018, 140, 16042



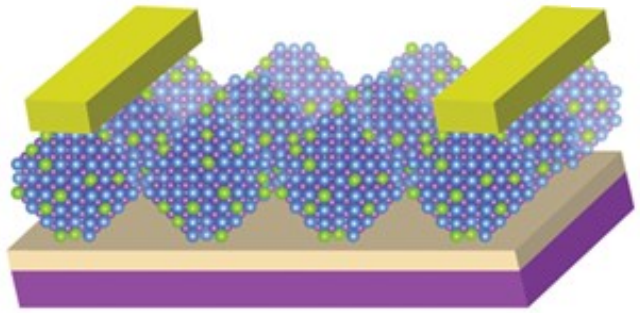
Acc. Chem. Res. 2021, 54, 2660

Nanoparticle catalysts



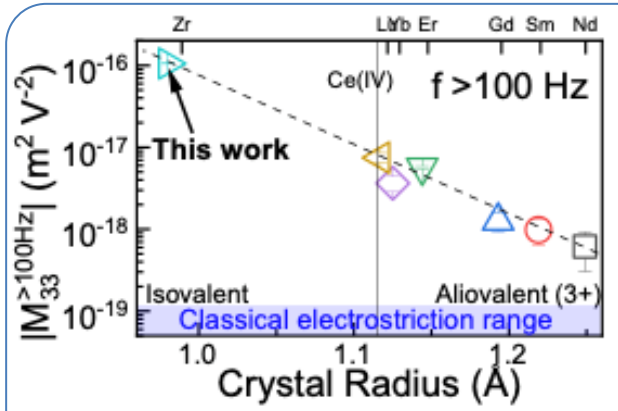
Nature Commun. 2023, 12, 914

Doped quantum dots



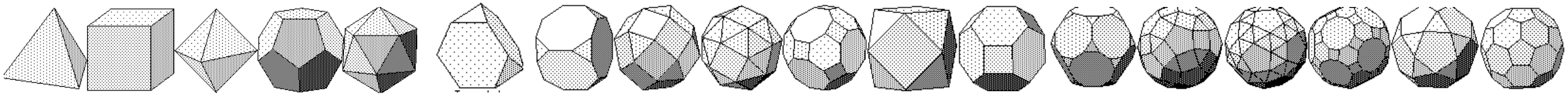
Adv. Mater. 2023, 35, 220832

Electromechanical materials

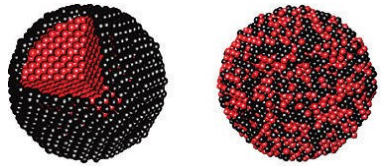


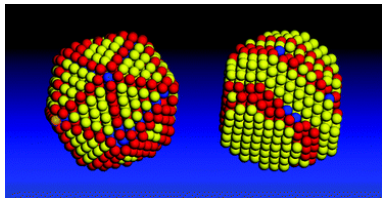
Nature Commun. 2023, in press

Finite size effects (an incomplete list)



Lattice Constants	Laplace's Law (~18th century)	$\frac{\Delta a}{a} \sim \frac{1}{d}$
Melting Points	Gibbs-Thomson relation (1871)	$\frac{T_t - T_{m,\infty}}{T_{m,\infty}} \sim \frac{1}{d}$
Electronic properties	Kubo gap	$\Delta E \sim \frac{1}{d}$
Mechanical Properties	Hall-Petch relationship	$\sigma_y = \sigma_y + \frac{k_y}{\sqrt{d}}$
Phase Diagrams		



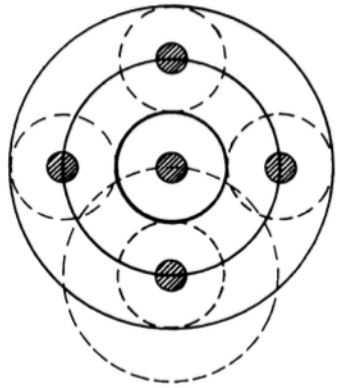


1968-
1978

"For study of the chemistry of catalysts and other noncrystalline systems this technique XAS may have a role comparable to that of X-ray and electron diffraction in crystalline systems."

van Nordstrand, Adv. Catal. 1960, **12**, 149

Sayers, Lytle and Stern, 18th Denver X-ray Conf, 1970: Model of EXAFS
Sayers, Ph.D. Thesis, 1971;
Sayers, Stern, Lytle, *PRL*, 1971, 27, 1204: Fourier transform
Stern, *PRB*, 1974, 10, 3027: EXAFS theory

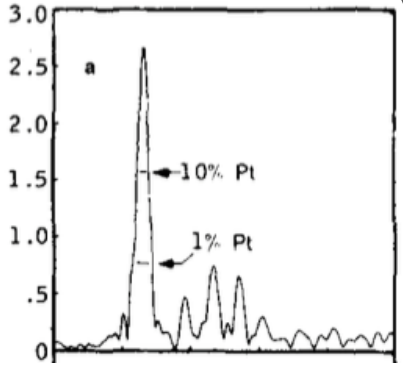


F. Lytle, *JSR* 1999, **6**, 123
E. Stern, *JSR*, 2001, 8, 49

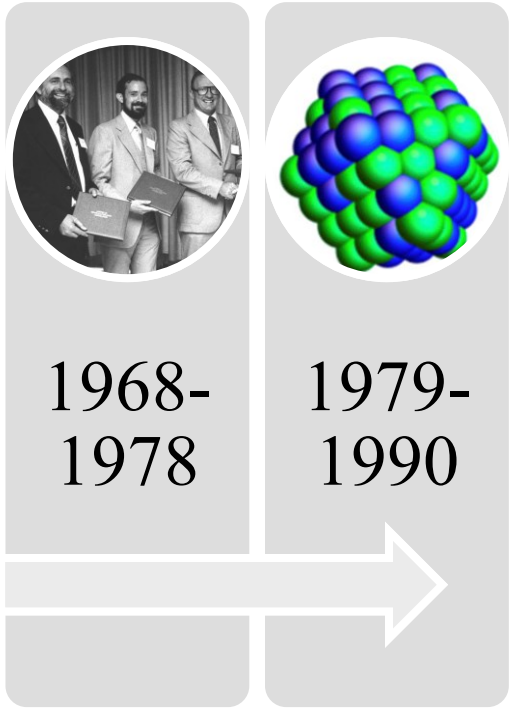
Lytle, Sayers, Moore, *APL*, 1974, 24, 45:
First application to catalysis

These results demonstrate that the EXAFS technique can be a powerful tool for studying catalysts in order to determine the precise structural relationships between catalytically active sites and the surrounding atoms.

Sinfelt, Via, Lytle, *JCP*, 1978, 68, 2009:
First application to nanoparticles;
Coordination numbers



In summary, the EXAFS data of this investigation illustrate the potential of the method for highly dispersed metal catalysts. The results have a special significance when one considers the technological importance of catalysts of this type.



Bunker, *Nucl. Instr. Meth.*, 1983, 207, 3027:
Log-ratio method

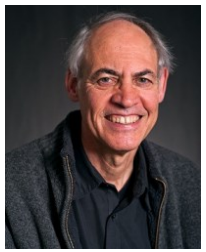
Sinfelt, Via, Lytle, *JCP*, 1980, 72, 4832:
First application to bimetallic nanoparticles

TABLE I. Structural parameters of silica supported Ru–Cu clusters derived from EXAFS data.[a]

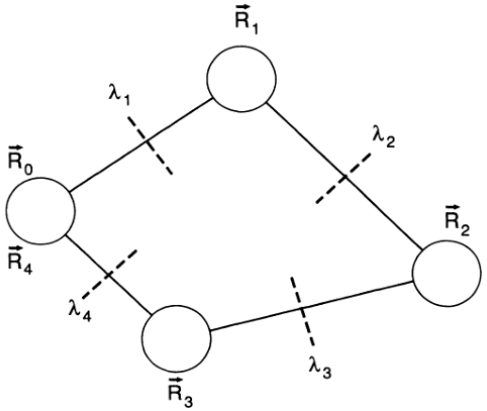
Composition of first coordination shell, % Ru[b]:	
about Ru	93, 92
about Cu	53, 52
Nearest neighbor distances, Å[b]:	
RuRu	2.654, 2.653
CuCu	2.586, 2.582
RuCu (from Ru edge data)	2.586, 2.595
CuRu (from Cu edge data)	2.648, 2.636

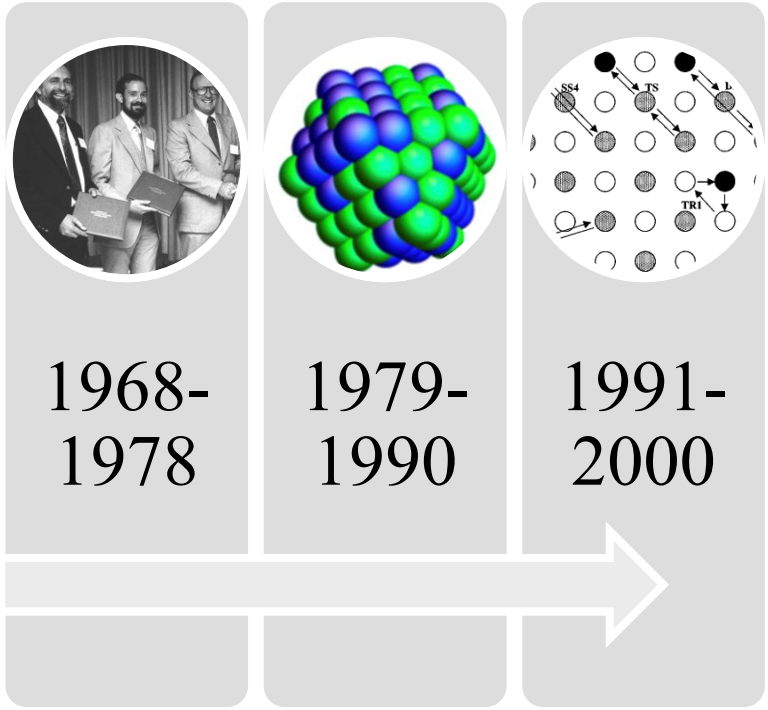
$$N^{ab} = (X_b/X_a)N^{ba}$$

[1] J.H. Sinfelt, G.H. Via and F.W. Lytle, Catalysis Reviews-Science and Engineering 26 (1984) 81.
[2] J.H. Sinfelt, *Bimetallic Catalysts: Discoveries, Concepts, and Applications* (John Wiley and Sons, New York, 1983).
[3] J.H. Sinfelt, G.H. Via and F.W. Lytle, J. Chem. Phys. 72 (1980) 4832.
[4] J.H. Sinfelt, G.H. Via, F.W. Lytle and R.B. Greegor, J. Chem. Phys. 75 (1981) 5527.
[5] G. Meitzner, G.H. Via, F.W. Lytle and J.H. Sinfelt, J. Chem. Phys. 78 (1983) 882.
[6] G. Meitzner, G.H. Via, F.W. Lytle and J.H. Sinfelt, J. Chem. Phys. 78 (1983) 2533.
[7] G. Meitzner, G.H. Via, F.W. Lytle and J.H. Sinfelt, J. Chem. Phys. 83 (1985) 353.
[8] G. Meitzner, G.H. Via, F.W. Lytle and J.H. Sinfelt, J. Chem. Phys. 83 (1985) 4793.
[9] G. Meitzner, G.H. Via, F.W. Lytle and J.H. Sinfelt, J. Chem. Phys. 87 (1987) 6354.



Rehr, Albers, PRB *1990*, 4
8139.
Multiple-scattering theory.
1990: Birth of FEFF codes
(FEFF3 etc.)

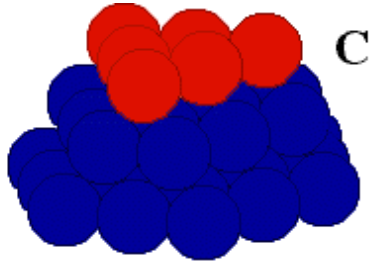


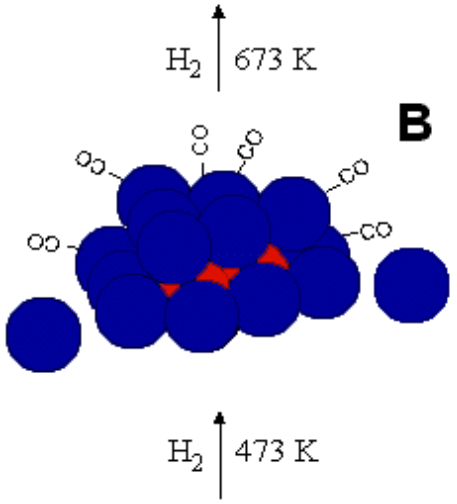


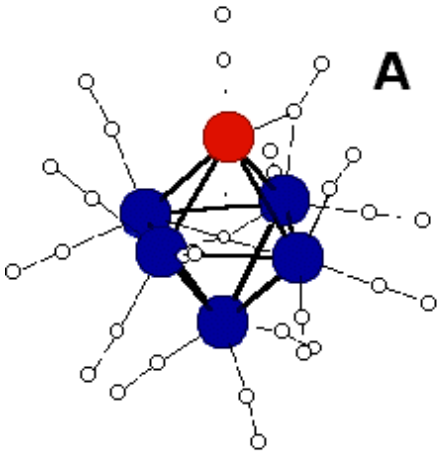
- FEFF5: Multiple scattering analysis in full swing;
- In situ/operando characterization of catalysts;
- UWXAFS, IFEFFIT:

Versatile modeling is now possible;

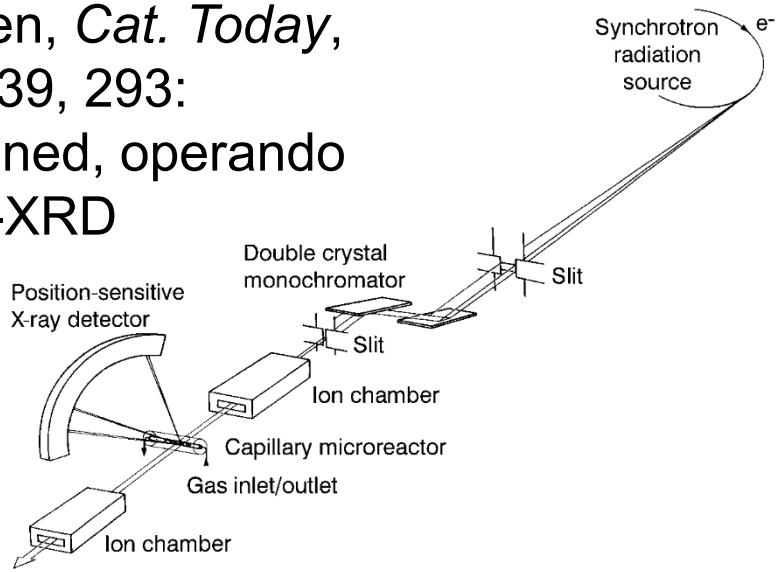
- Composition of NPs change with T, P and reaction conditions;



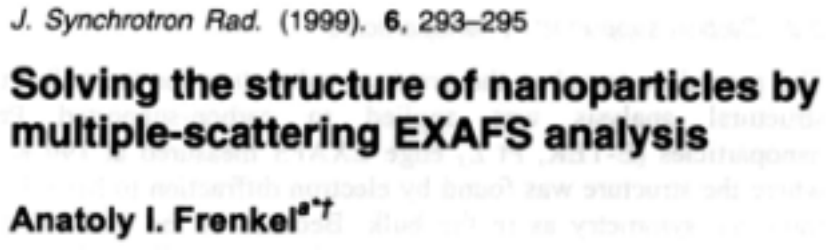




Clausen, *Cat. Today*, 1998, 39, 293: Combined, operando XAFS-XRD



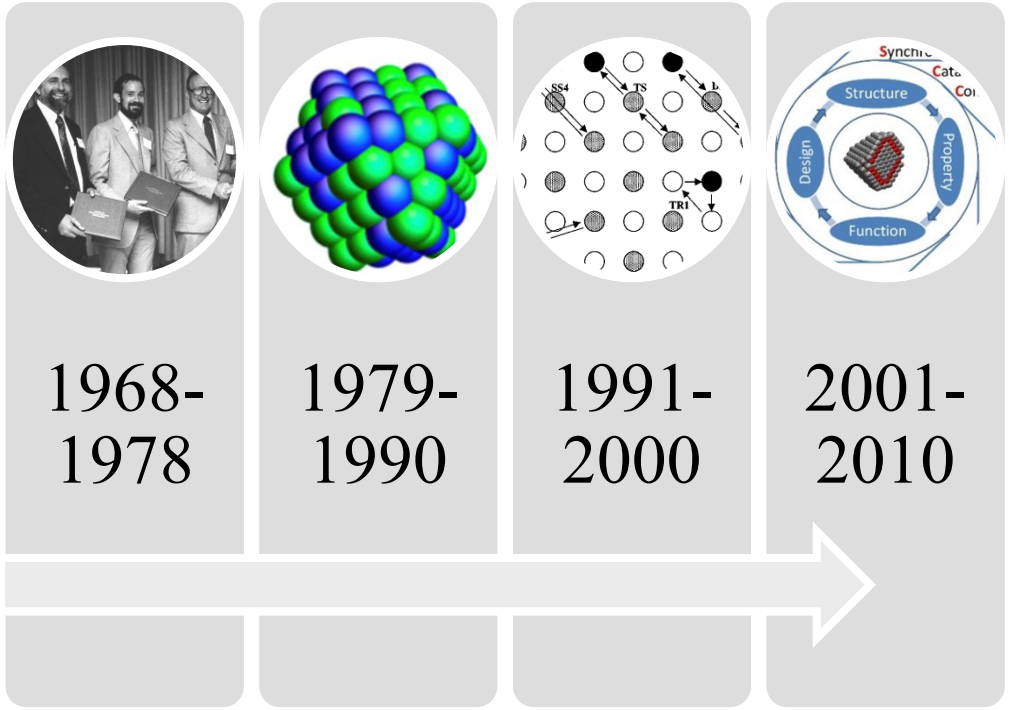
Nashner, Frenkel, et al, *JACS*, 1998, 120, 8093: In situ growth and restructuring of Pt-Ru bimetallic nanoparticles



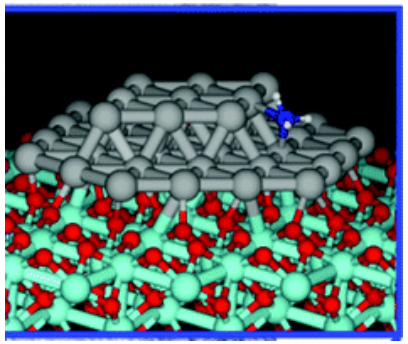
J. Synchrotron Rad. (1999). **6**, 293–295

Solving the structure of nanoparticles by multiple-scattering EXAFS analysis

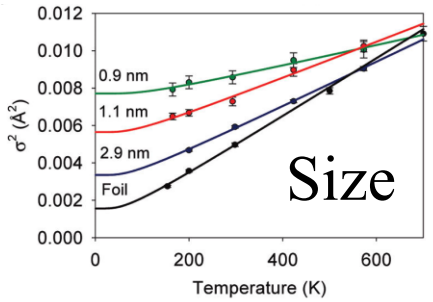
Anatoly I. Frenkel

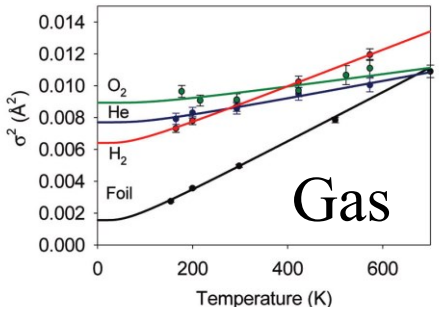


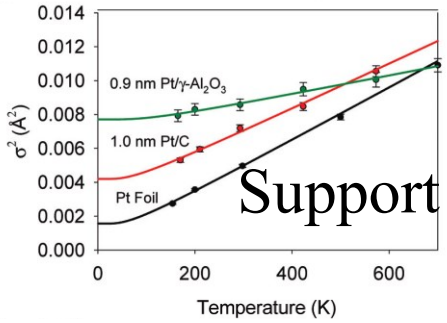
- Synthesis and control
- Synchrotron consortia
- Thermal properties
- Effects of support, adsorbates



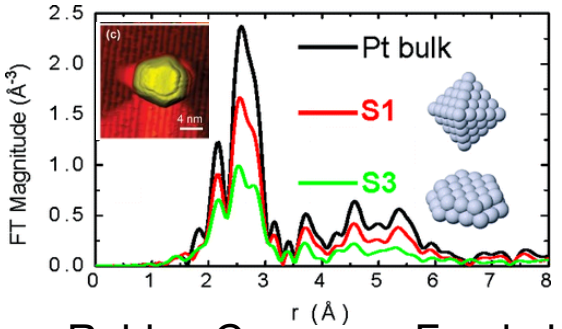
Karim, Frenkel, et al
JACS 2009, 131, 12230



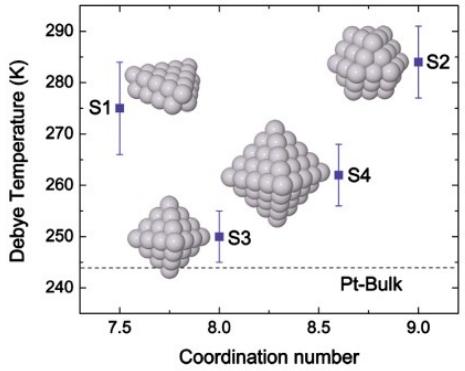




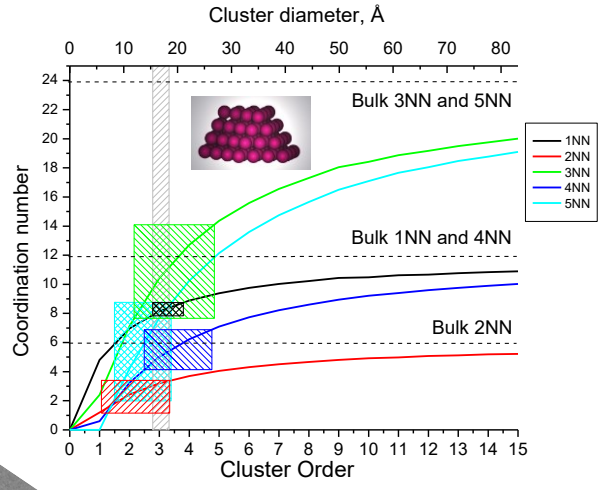
Sanchez, … Frenkel,
JACS, 2009, 131, 7040

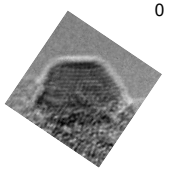


Roldan Cuenya,…Frenkel
JACS 2010, 132, 8747

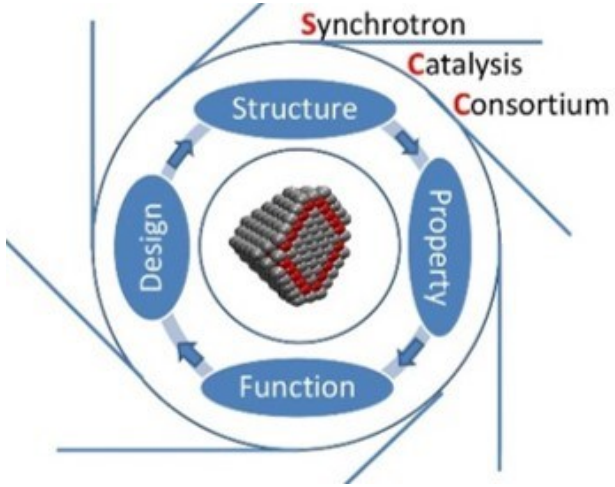


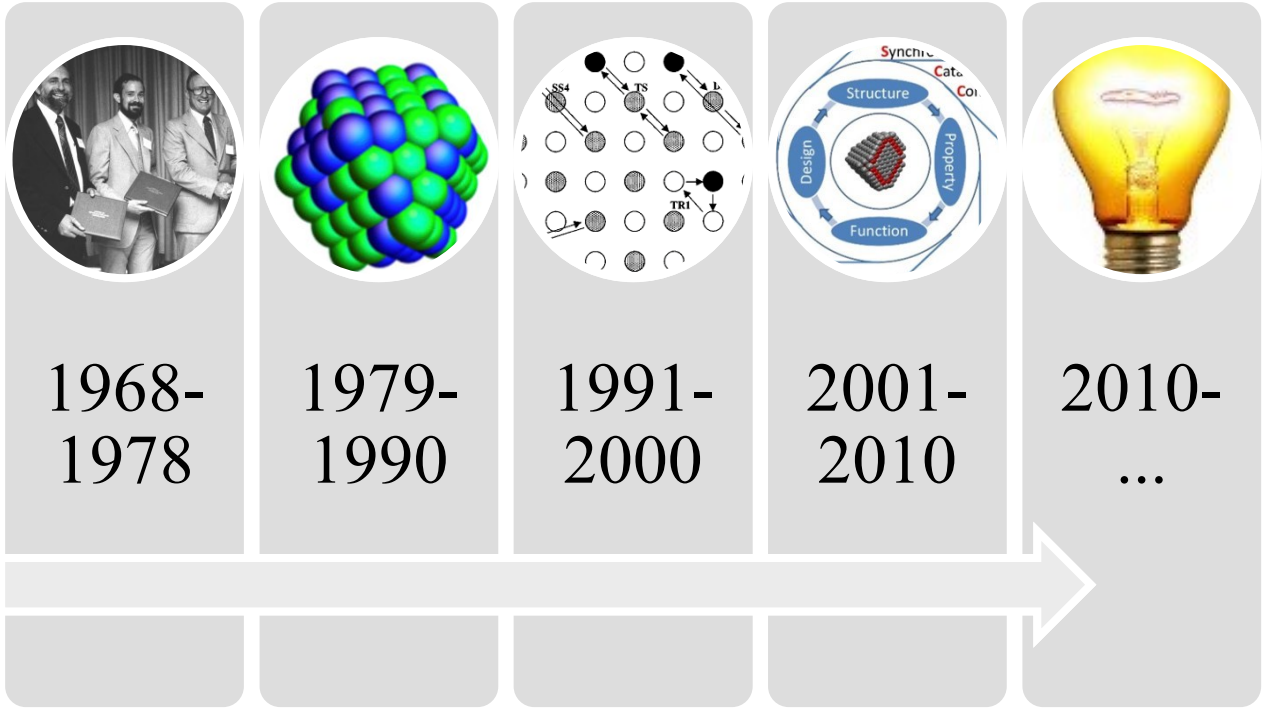
Roldan Cuenya, … Frenkel
PRB 2010, 82, 155450





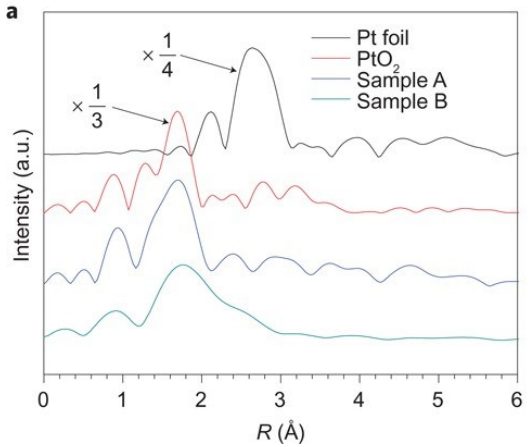
Frenkel, Hills, Nuzzo,
JPCB 2001, 105, 12689



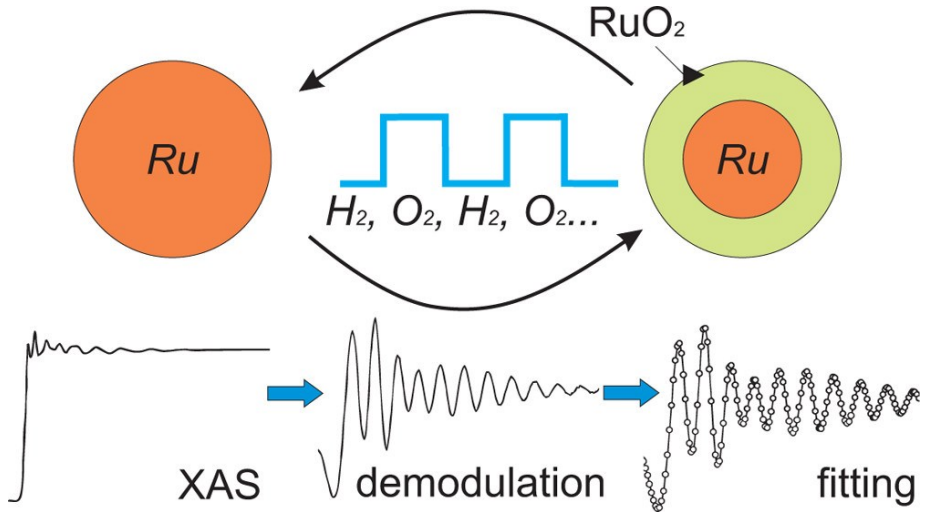


- New materials:
  - Single atom catalysts
  - Size-selective clusters
- New experiments:
  - HERFD and RIXS
  - Modulation excitation spectroscopy
- New analysis methods:
  - Supervised machine learning

…



Zhang et al,
Nature Chem. 2011, 3, 634



Koenig et al,
JPCC 2012,116, 19857

SDAN group at SBU/BNL, 2017-…

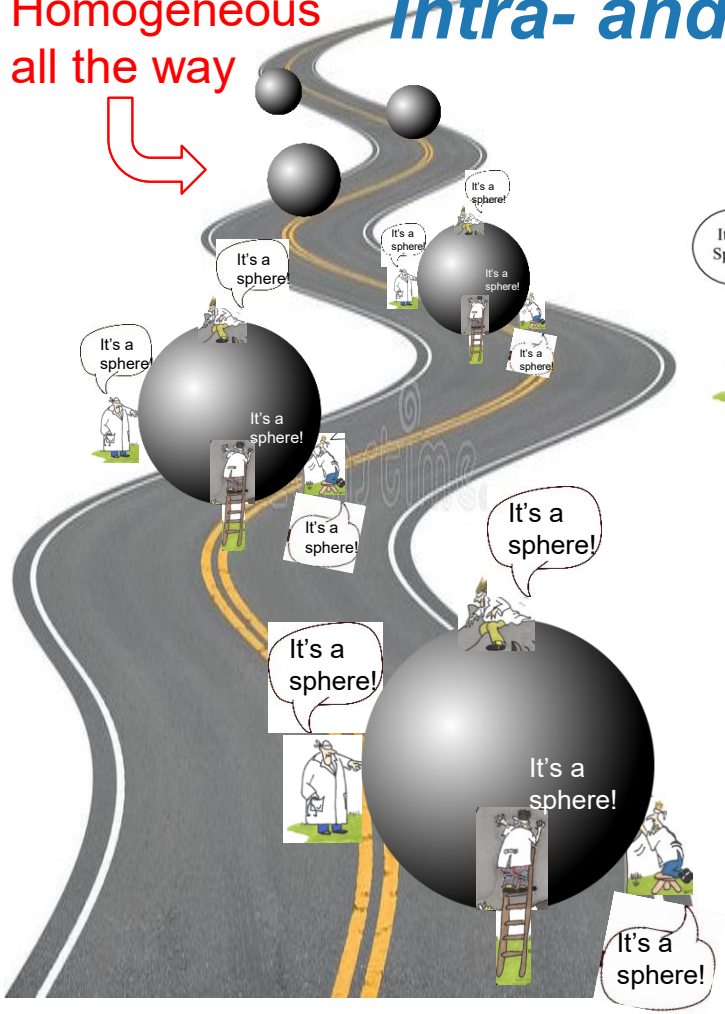
"You are blind without an experiment but you are deaf without modeling"

"You are blind without an experiment … and you remain blind with it"

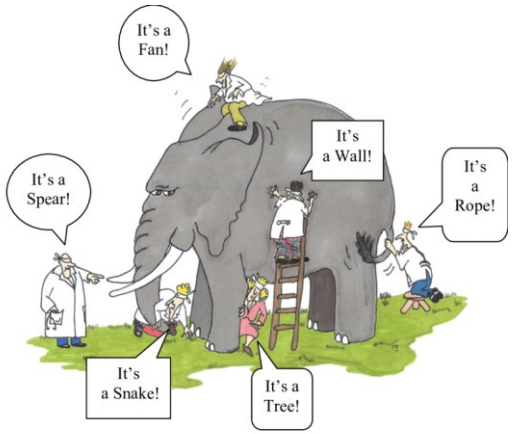
AIF

Intra- and inter-particle heterogeneity: A hot topic

Homogeneous all the way

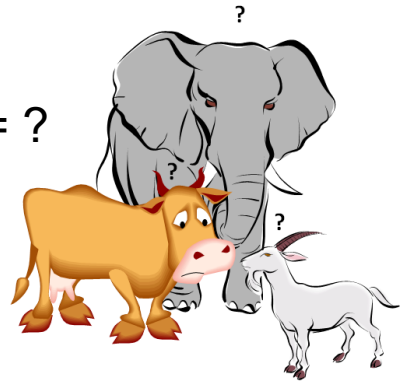


= Sphere ⊗ Sphere ⊗ Sphere … = Sphere



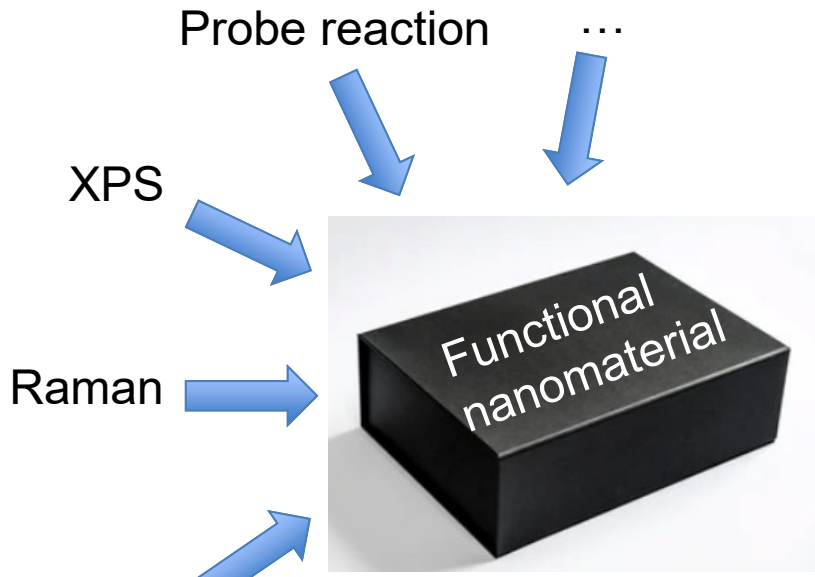
Intra-particle heterogeneity

= Spear ⊗ Wall ⊗ Fan … = ?



Inter-particle heterogeneity

= Spear ⊗ Wall ⊗ Horns … = ?



= Descriptor1 ⊗ Descriptor2 ⊗ Descriptor3 … = ?

Spectroscopy of heterogeneous mixtures

THE JOURNAL OF PHYSICAL CHEMISTRY C
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

pubs.acs.org/JPCC Perspective

Speciation of Nanocatalysts Using X-ray Absorption Spectroscopy Assisted by Machine Learning

Prahlad K. Routh,* Nicholas Marcella,* and Anatoly I. Frenkel*

Cite This: J. Phys. Chem. C 2023, 127, 5653–5662 Read Online

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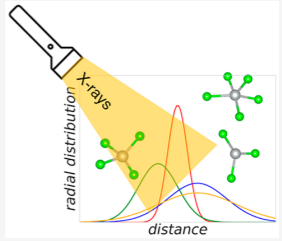
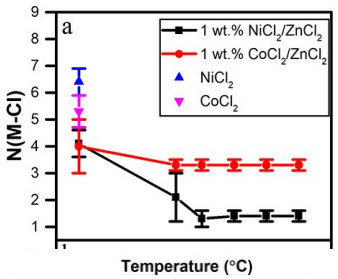
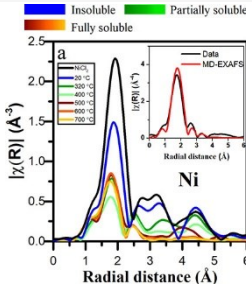
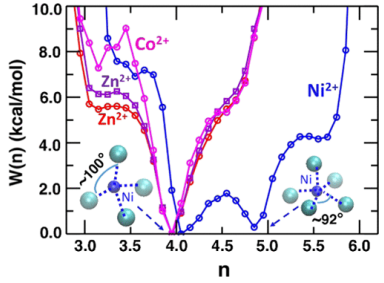
ABSTRACT: The structure and morphology of supported nanoparticle catalysts play important roles in many industrial reactions. Recent progress has identified key aspects of structure−activity relationships at the nanoscale and novel methods to study the local environment of the active sites. X-ray absorption fine structure (XAFS) spectroscopy, despite being a leading technique for this purpose, is hampered significantly by its ensemble-averaging nature which often leads to a bias toward a single "representative" structure. Learning heterogeneous distributions of nanostructures at the inter- and intraparticle levels from the average XAFS spectrum is a formidable challenge that can be overcome in some cases described in this Perspective. We also discuss emerging machine learning techniques for extracting the information about the heterogeneity of metal species from XAFS data.

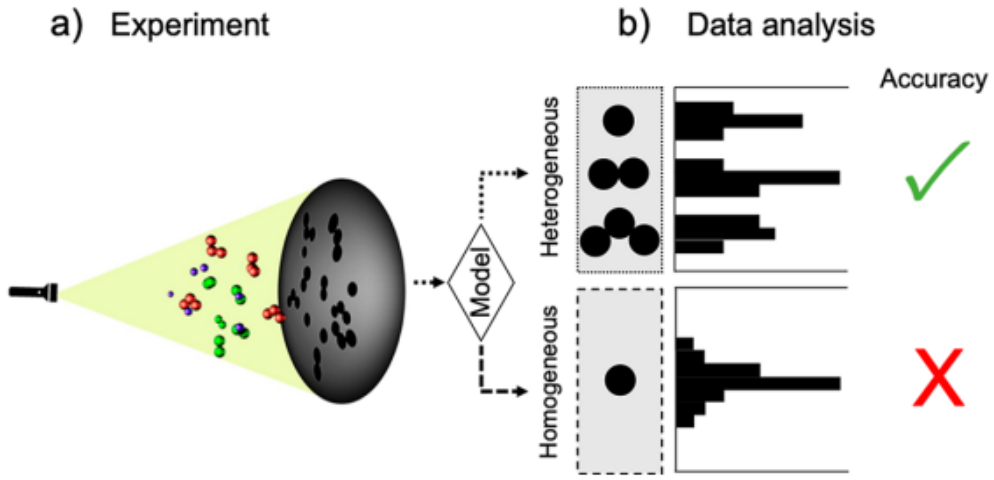


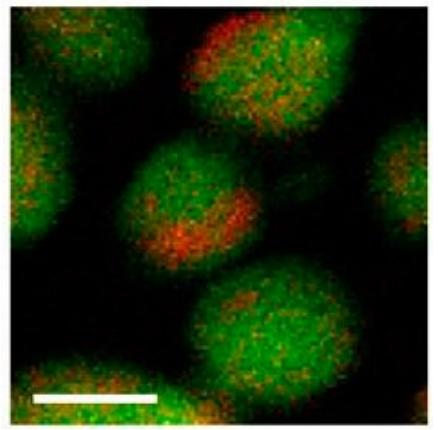




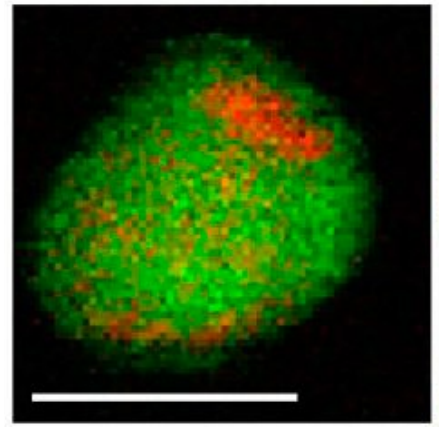


S. Gill, … AIF, J. Phys. Chem. B 2020, 124, 1253-1258





10 nm

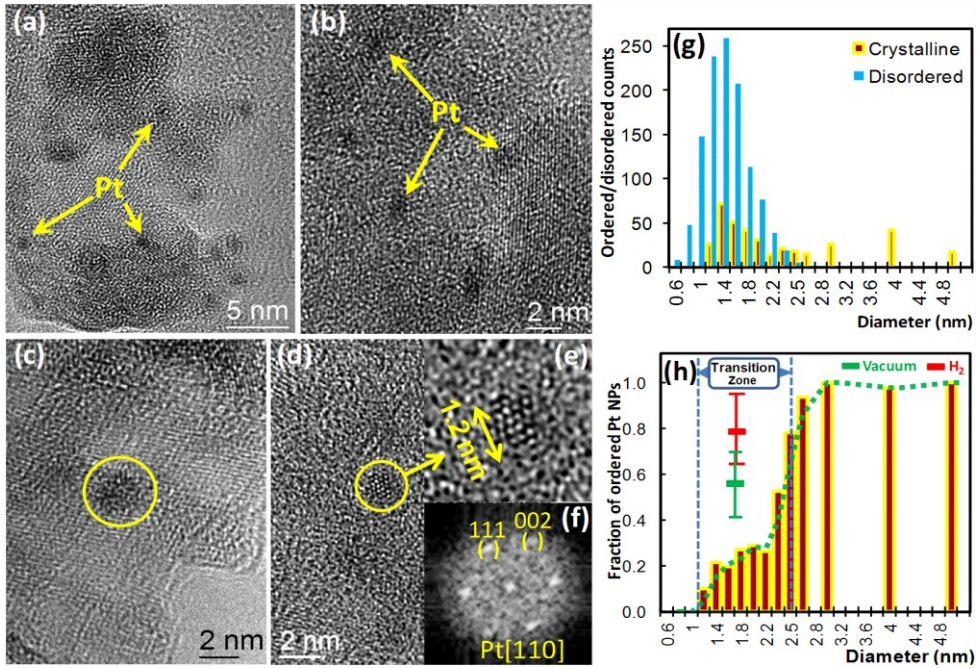


10 nm

E. Guan, … AIF, ChemCatChem 2020, 12, 717– 721

Inter-cluster heterogeneity under in-situ/operando conditions

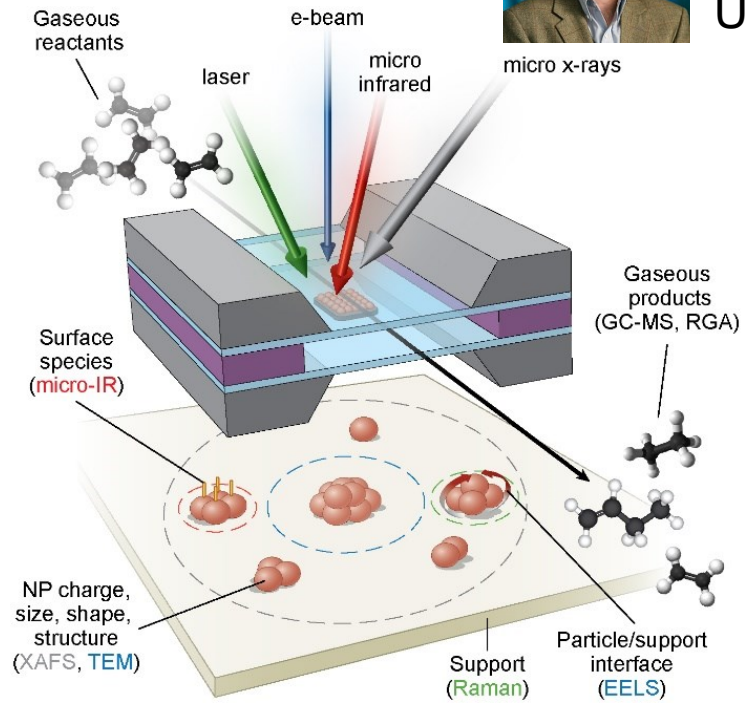
Judy Yang
CFN



Coexistence of order and disorder in nanocatalysts

J. Am. Chem. Soc. 135, 13062 (2013)

Eric Stach
U. Penn

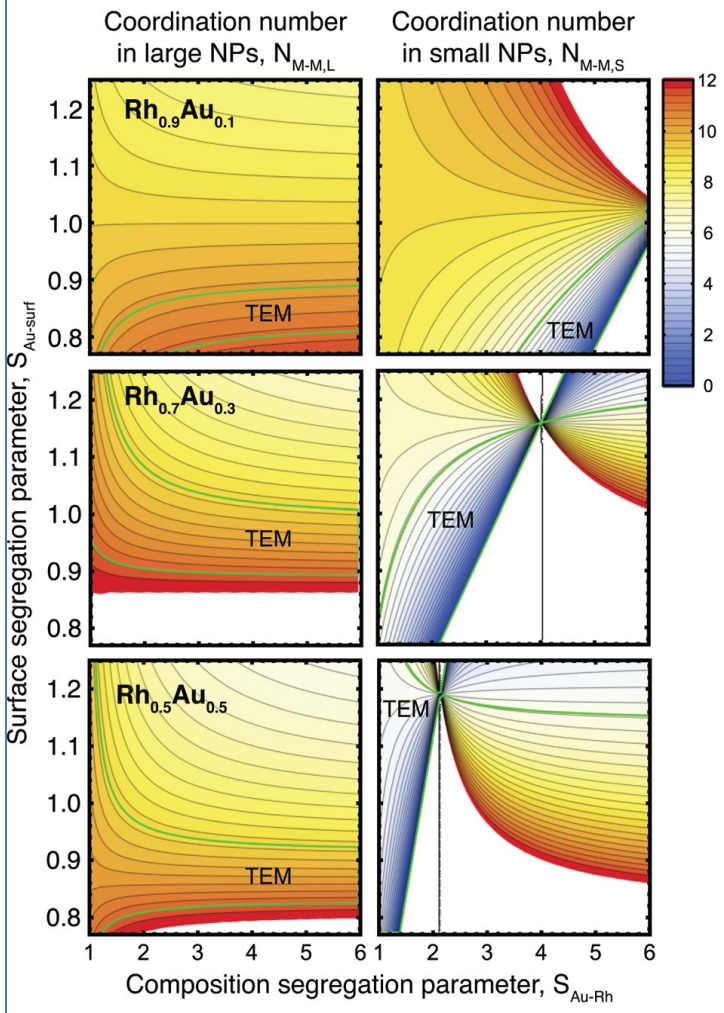


Coexistence of unreduced species, single atoms, ultra-small and large clusters in reaction conditions

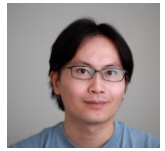
Li, … AIF, Nature Commun.., 6, 7583 (2015)

Zhao, … AIF, Stach, ChemCatChem., 7, 3683 (2015)

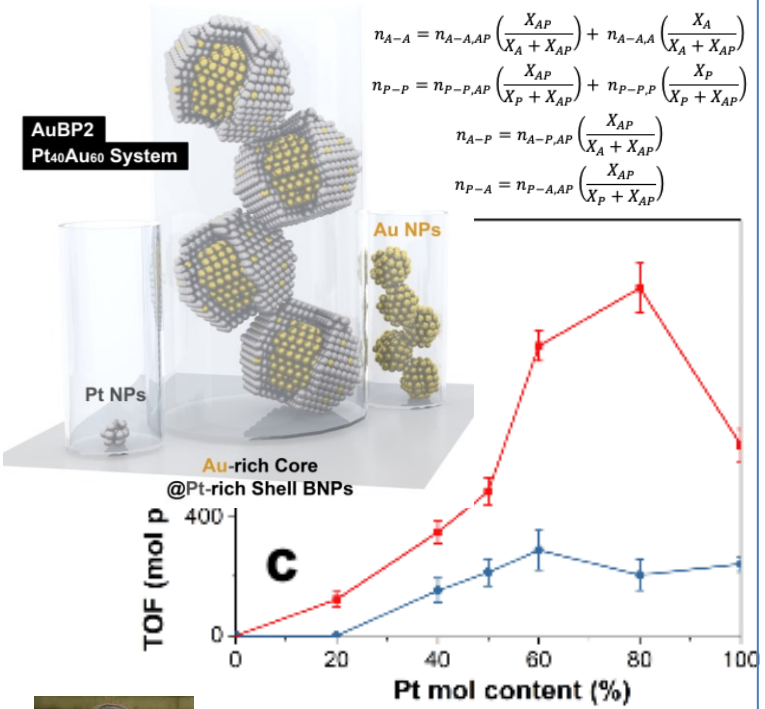
J. Timoshenko
Rh-Au



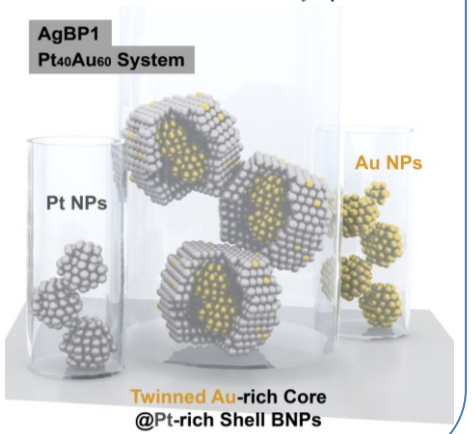
Nanoscale 10, 22520 (2018)



R. Shimogawa
Y. Liu

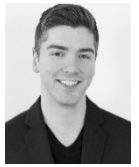


M. Knecht
(U. Miami)



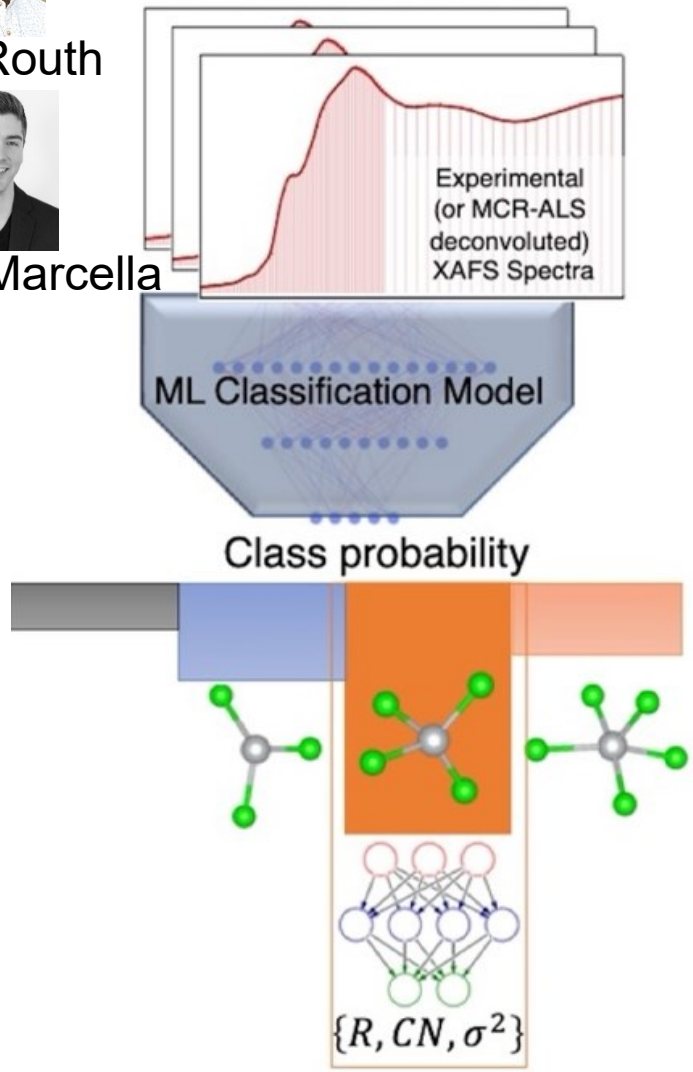
In review

P. Routh



N. Marcella

More accurate speciation, if series of spectra is used:

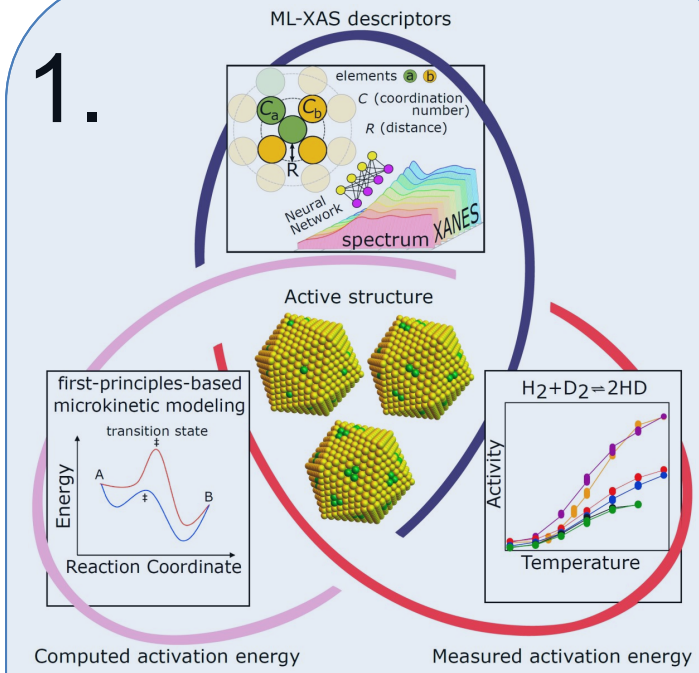


J. Phys. Chem. C (Perspective) 127, 5653 (2023)


N. Marcella
P. Routh

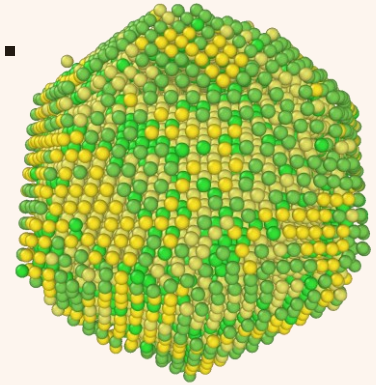
Intra-particle heterogeneity

1.

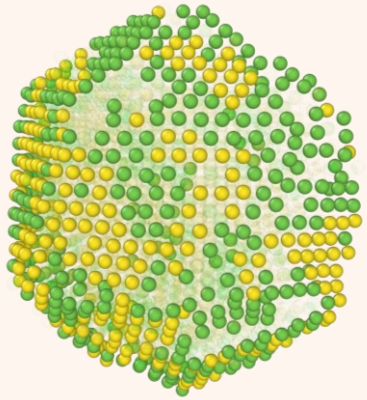


Q: Structure – function?
A: Descriptors

2.



Active species and spectators

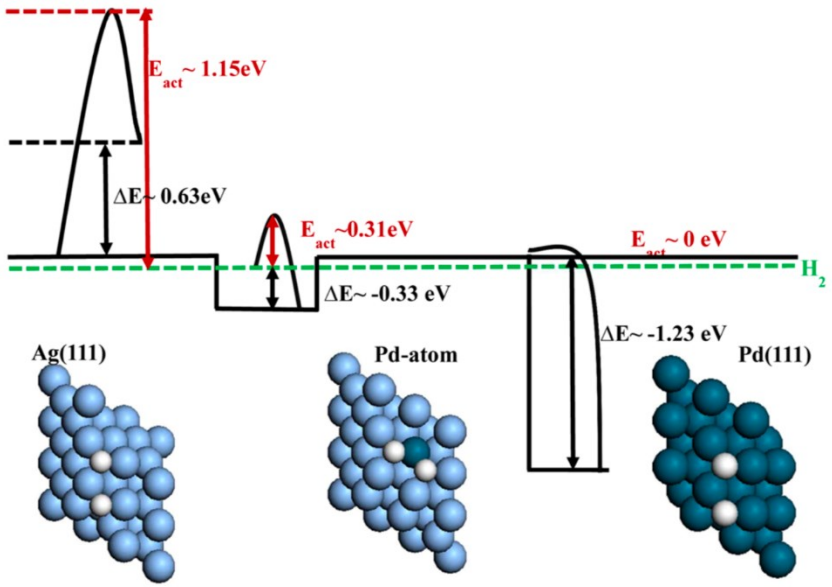


Active species

Q: Active species?
A: Modulation Excitation Spectroscopy

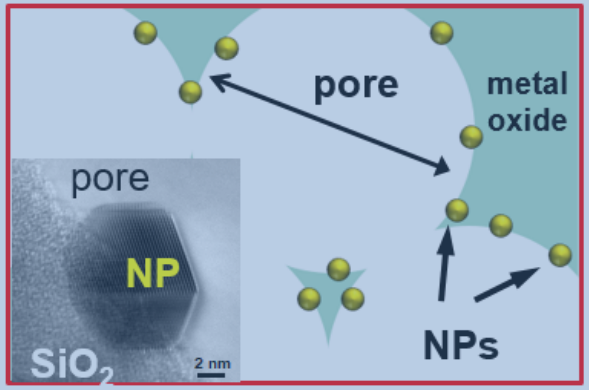
Decoding Reactive Structures in Dilute Alloy Nanocatalysts

Too inert **Bifunctional** **Too reactive**



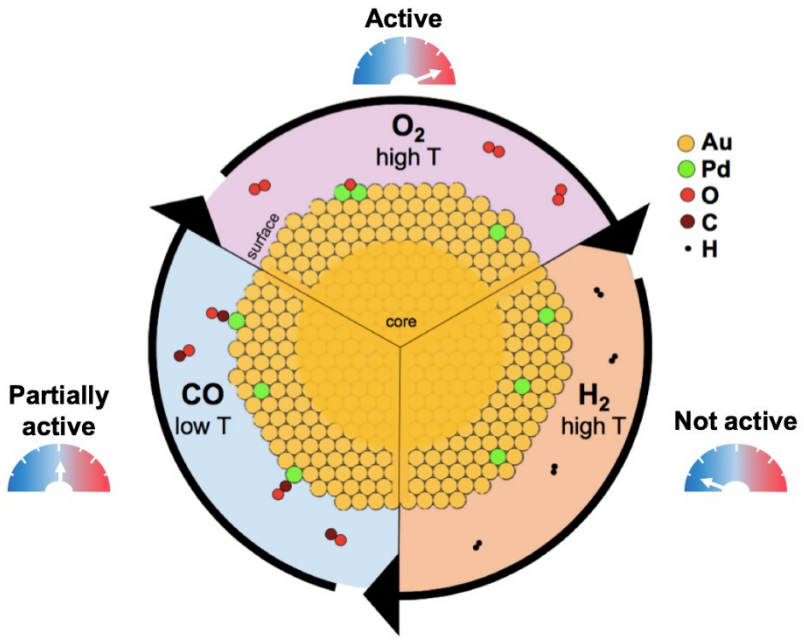
Aich… Meyer, J. Phys. Chem. C 119, (2015) 18140.

Raspberry Colloid Template



E. Shirman, …, J. Aizenberg, *Adv. Funct. Mater.* 28, 1704559 (2018)

Alloy surfaces are highly dynamic



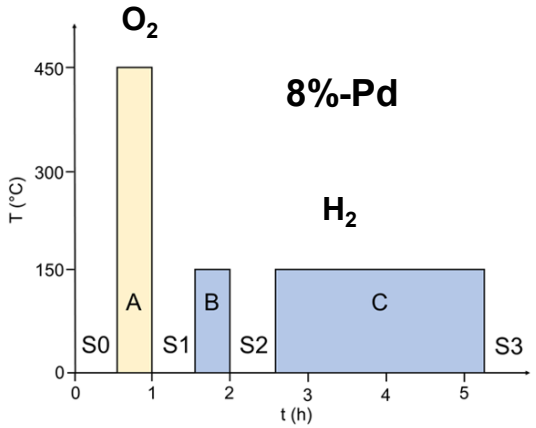
Questions:
- *Active species and active sites?*
- *Reaction mechanism?*

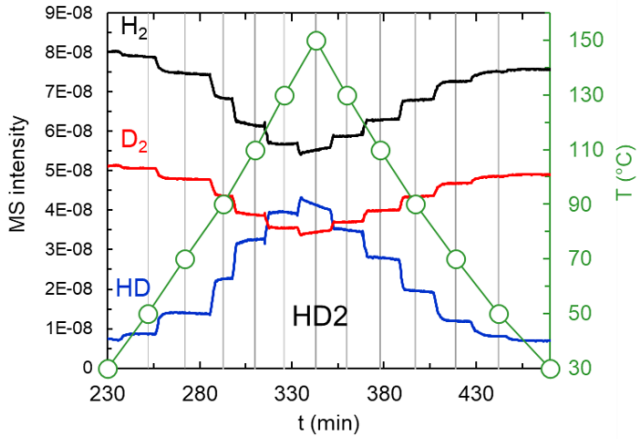
Challenges:
Restructuring, dependence on treatment

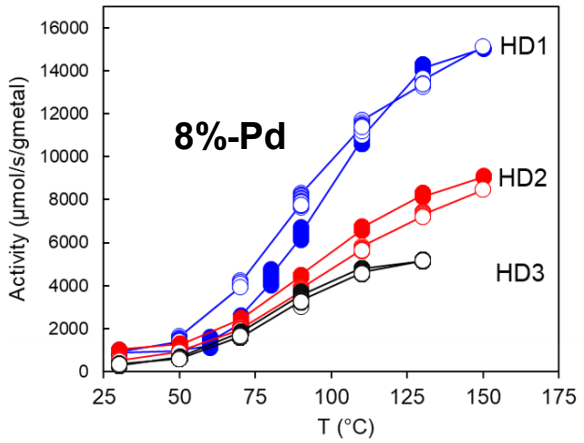
Idea:
Activation energy *of the reaction network is a link between theory and experiments*

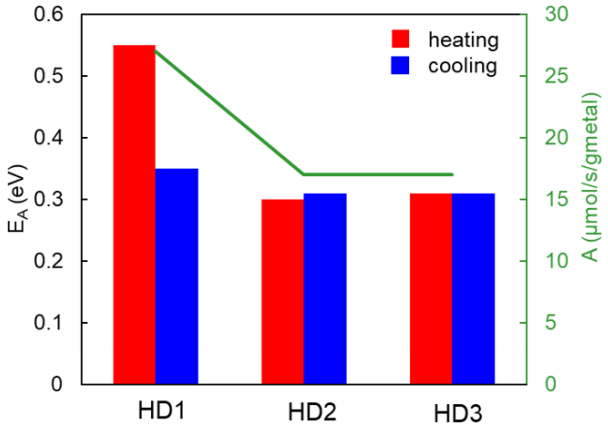
H_2 dissociation over Pd-Au on RCT@SiO_2: Activity


A. Plonka,
N. Marcella (SBU)

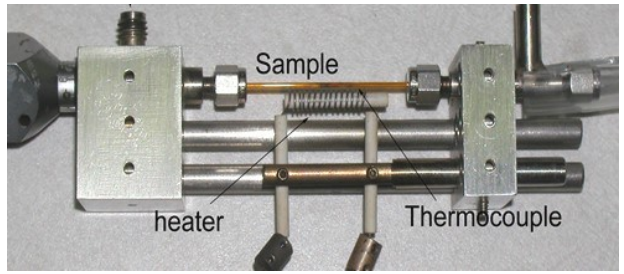








QAS beamline at NSLS-II

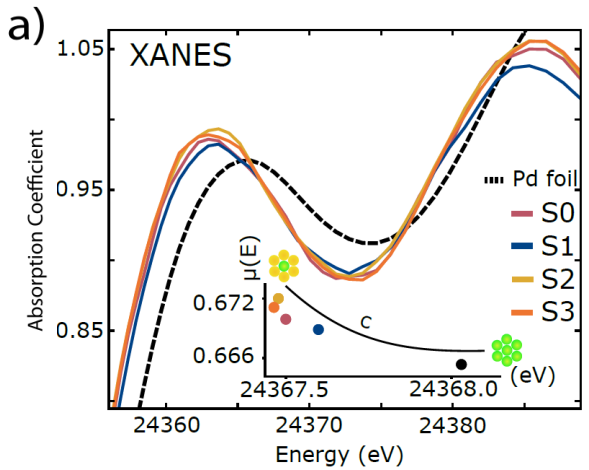


- Catalyst is activated by O_2 treatment
- Both the activity and kinetic parameters decrease upon H_2 treatment
- That means that the number and the nature of active species present in S1 have changed in S2 and S3

N. Marcella, … AIF, *Nature Commun.* 13, 832 (2022)

H_2 dissociation over Pd-Au on RCT@SiO_2


A. Plonka,
N. Marcella (SBU)

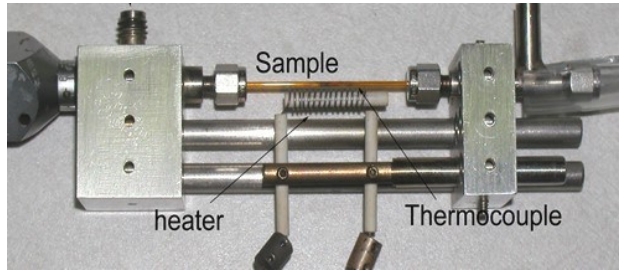


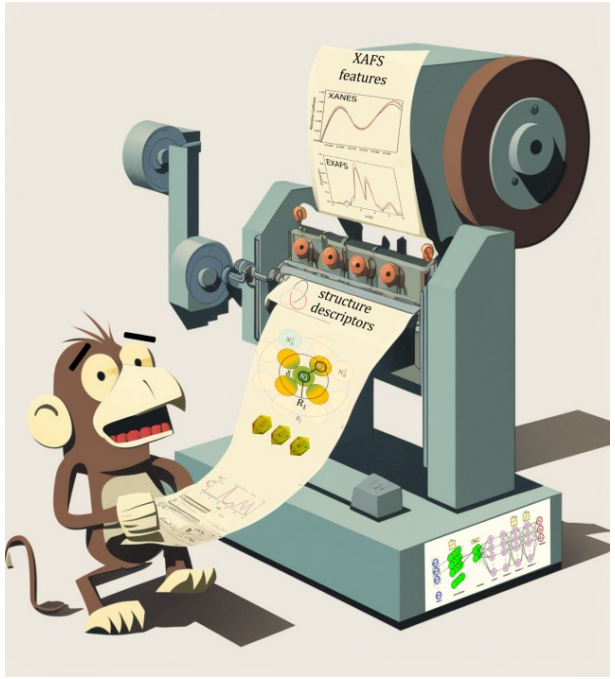
Raw data:

Hypothesis:
Rearrangement of Pd environment in response to conditions

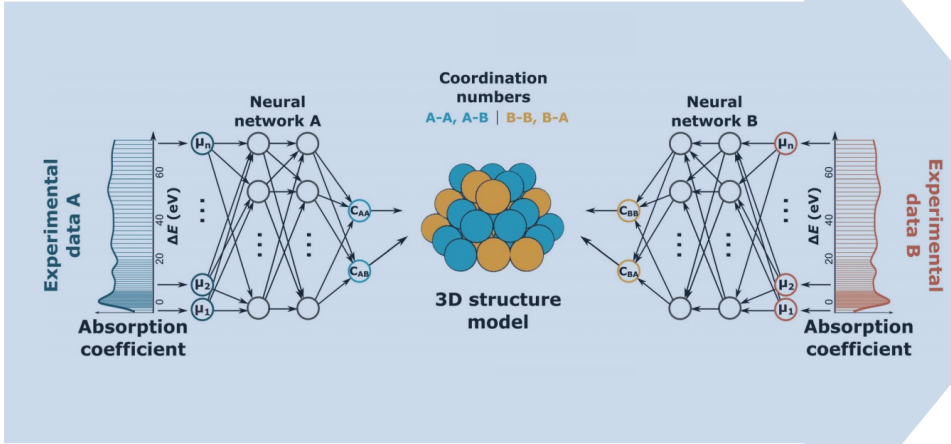
QAS beamline at NSLS-II

8% Pd in Au



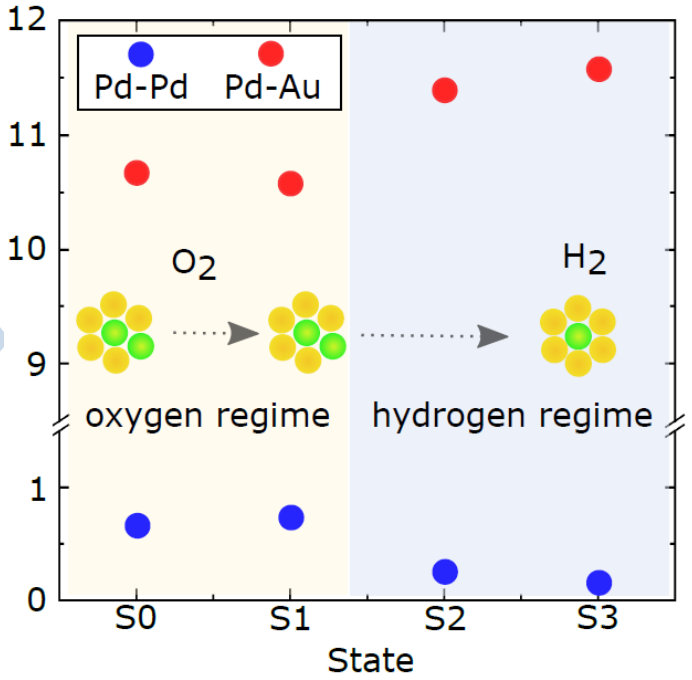


Q: Spectrum – structure?
A: Machine Learning



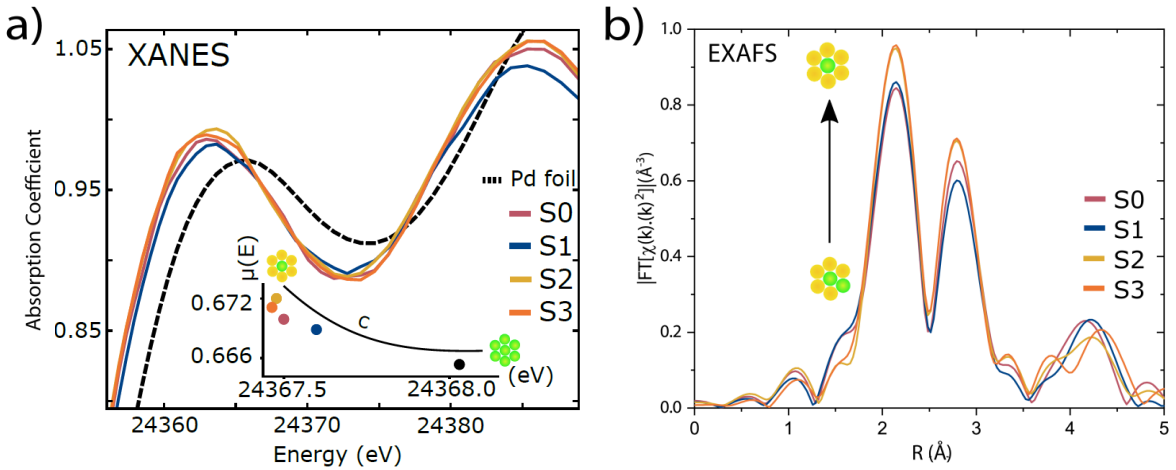
XANES: Machine learning methods

CN



H_2 dissociation over Pd-Au on RCT@SiO_2


A. Plonka,
N. Marcella (SBU)

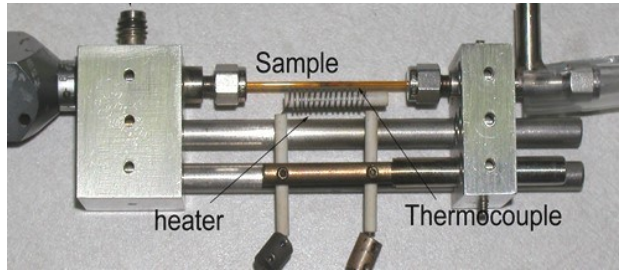


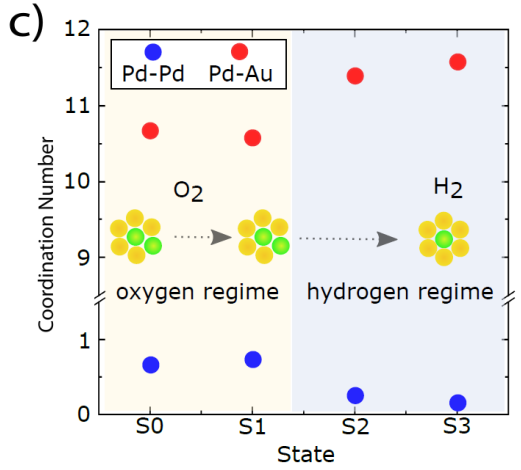
Raw data:

Hypothesis:

Rearrangement of Pd environment in response to conditions

QAS beamline at NSLS-II





Results:

Pd rearranges, but how – not clear…

Thermodynamic modeling:

Initially: Pd in subsurface –most stable

After O_2: large Pd ensembles are favored.

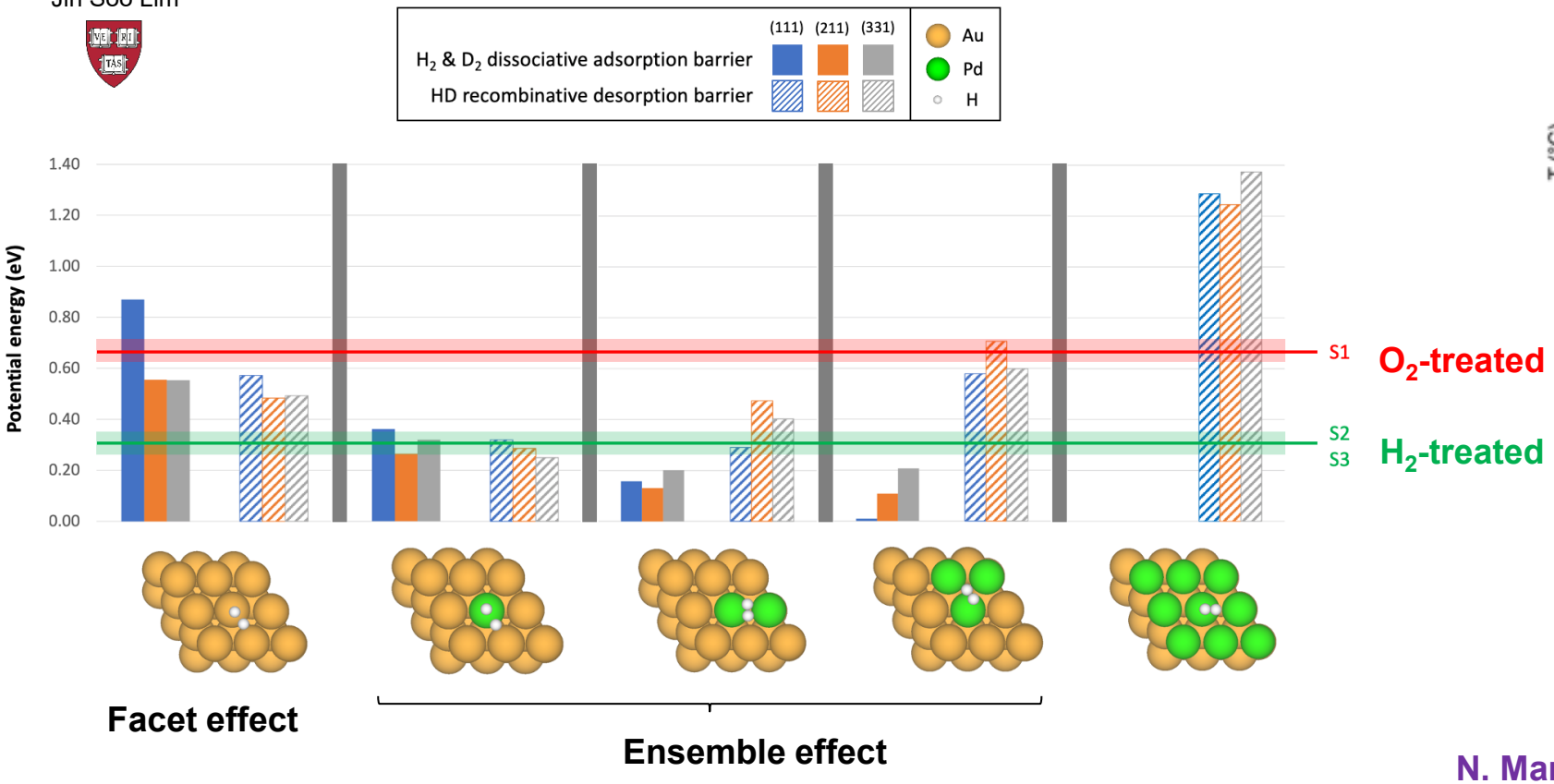
Once O_2 is removed: small Pd ensembles

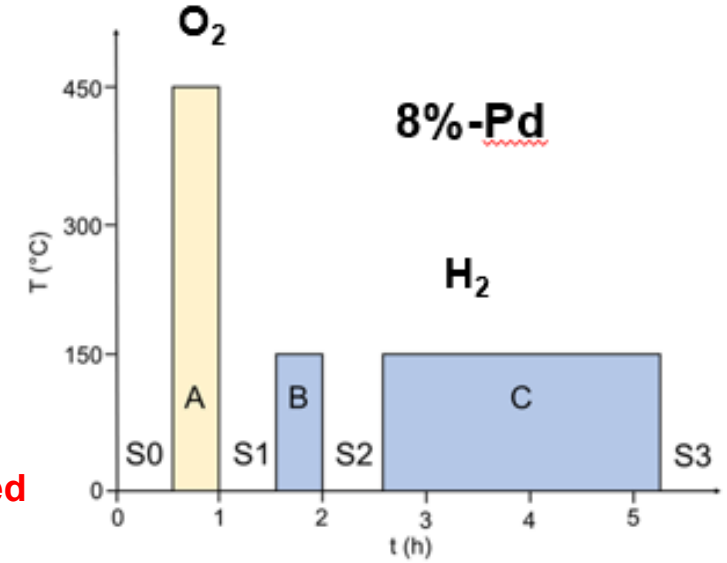
N. Marcella, … AIF, *Nature Commun.* 13, 832 (2022)

U.S. DEPARTMENT OF ENERGY | Office of Science | Lawrence Livermore National Laboratory | Tufts University | Stony Brook University | UCLA | UF University of Florida | Brookhaven National Laboratory | IMASC

DFT energetics: H_2 dissociation vs. desorption

Jin Soo Lim





Key idea:

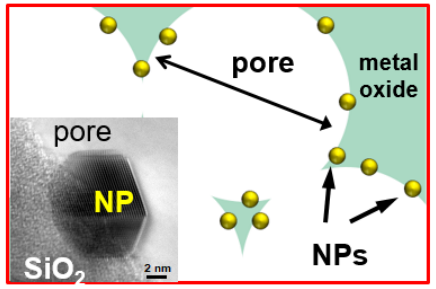
Activity measurements help determine reactive structures

N. Marcella, … AIF, *Nature Commun.* 13, 832 (2022)

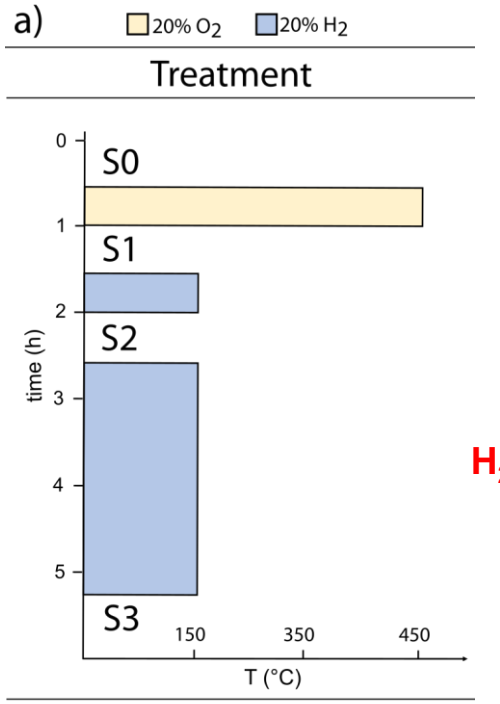
H_2 dissociation over Pd-Au on RCT@SiO_2: Reactive Structures

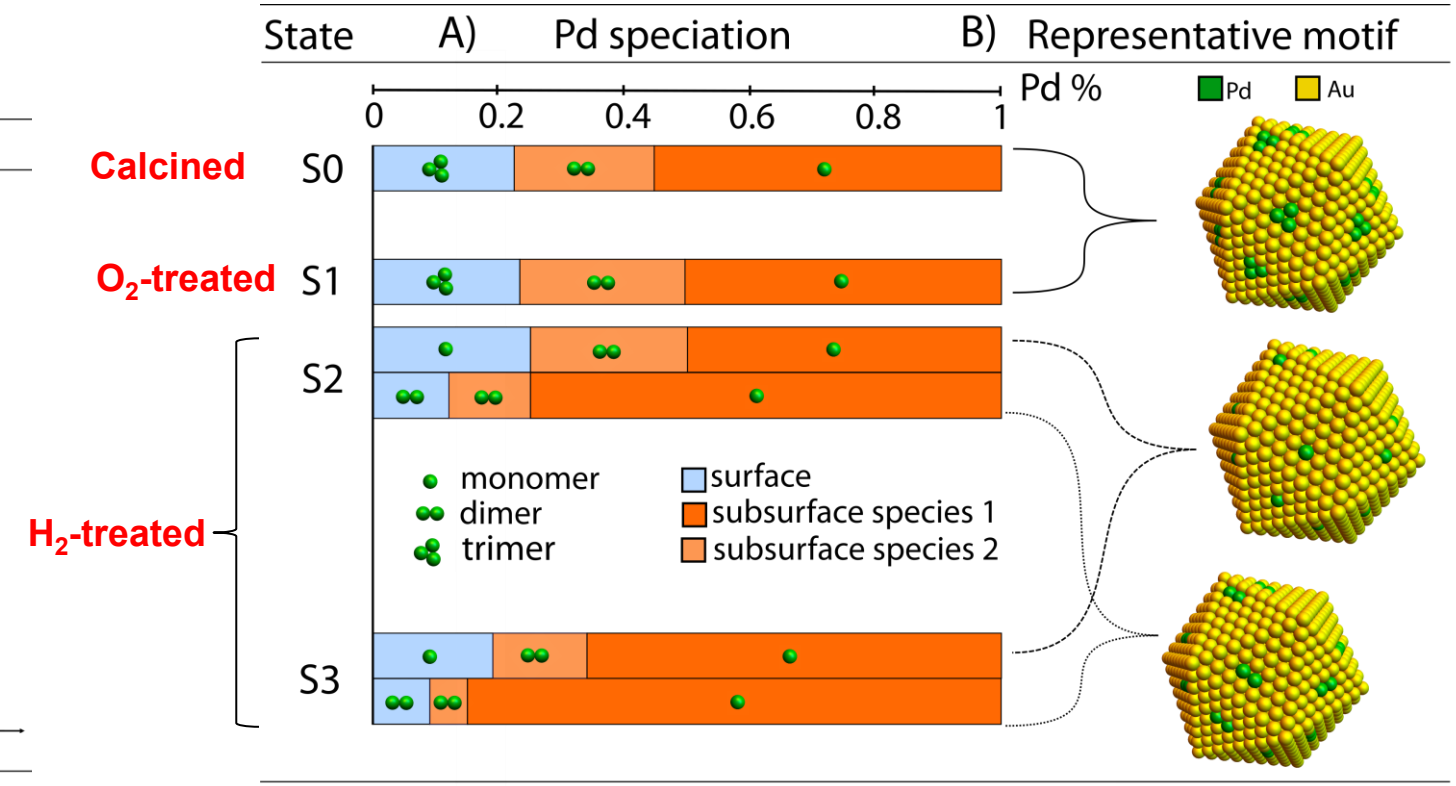
N. Marcella

Raspberry Colloid Template



E. Shirman, …, J. Aizenberg, *Adv. Funct. Mater.* 28, 1704559 (2018)





Reactive structures are obtained; They are responsive to the environment; Reactivity mechanisms explained

N. Marcella, … AIF, *Nature Commun.* 13, 832 (2022)

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Stony Brook University

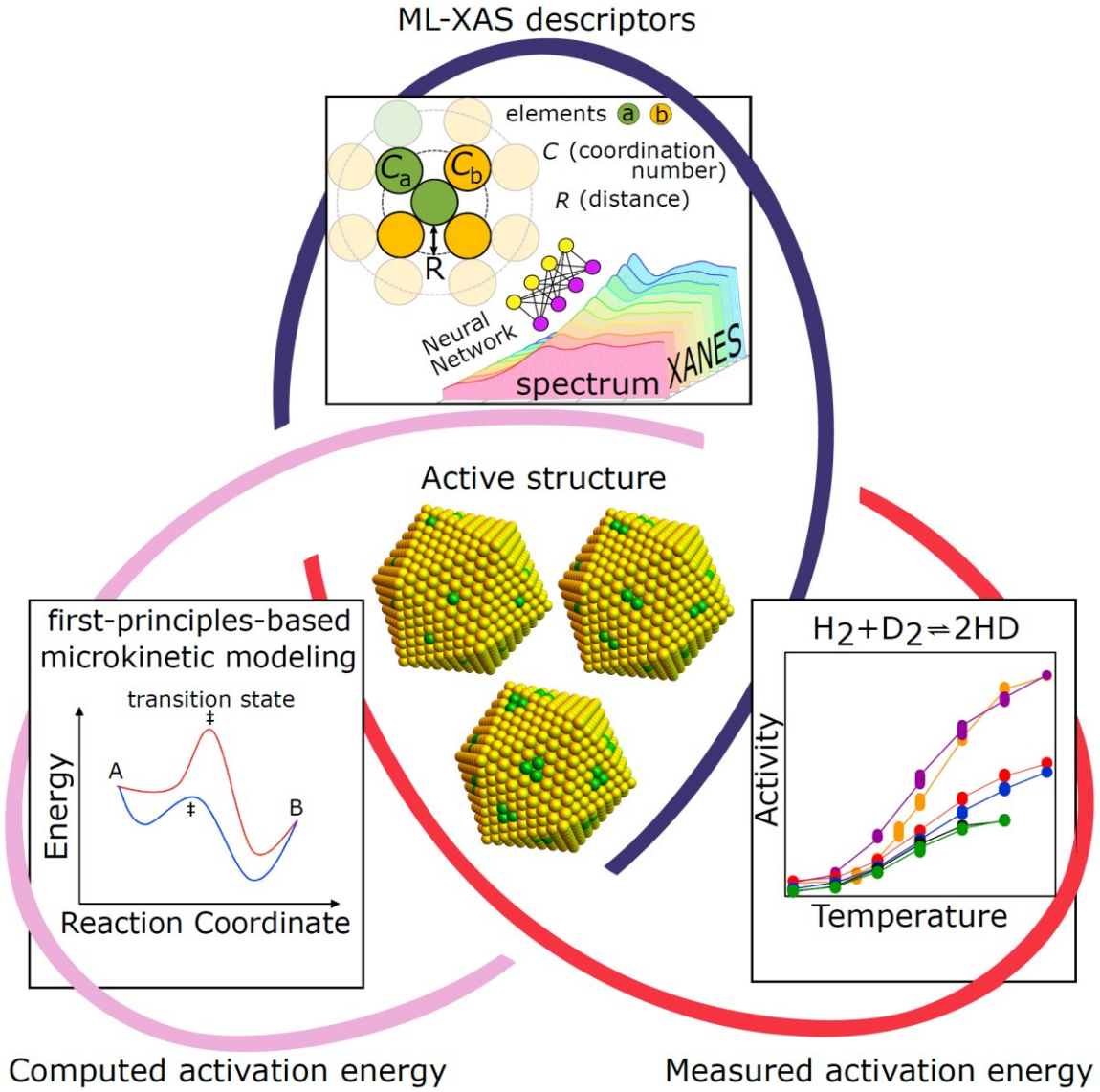
Conclusions

- For dilute Pd-in-Au catalyst, O_2- and H_2-treated samples are dominated by Pd_3 and Pd_{1-2}, respectively

- Catalytic activity and selectivity are controlled by pretreatment

Unanswered questions:

1) How to isolate unique ensembles (monomers, dimers or trimers)?
2) What are the mechanisms responsible for forming surface ensembles?
3) What is the kinetics of structural transformations in reaction conditions?



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https://www.bnl.gov/chemistry/SDAN/
http://you.stonybrook.edu/frenkel

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