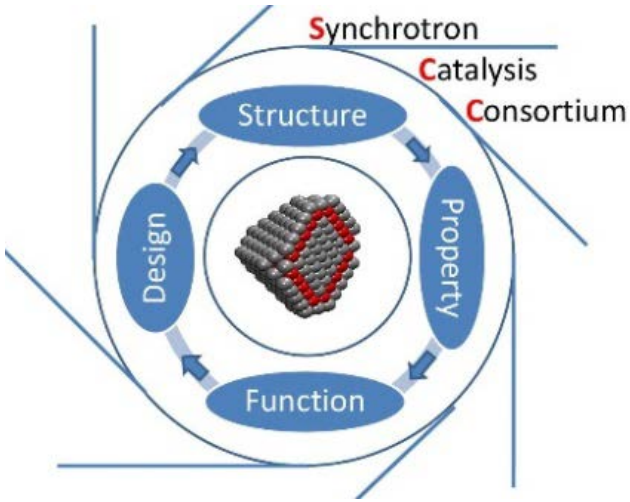
In situ and operando experiments in catalysis research



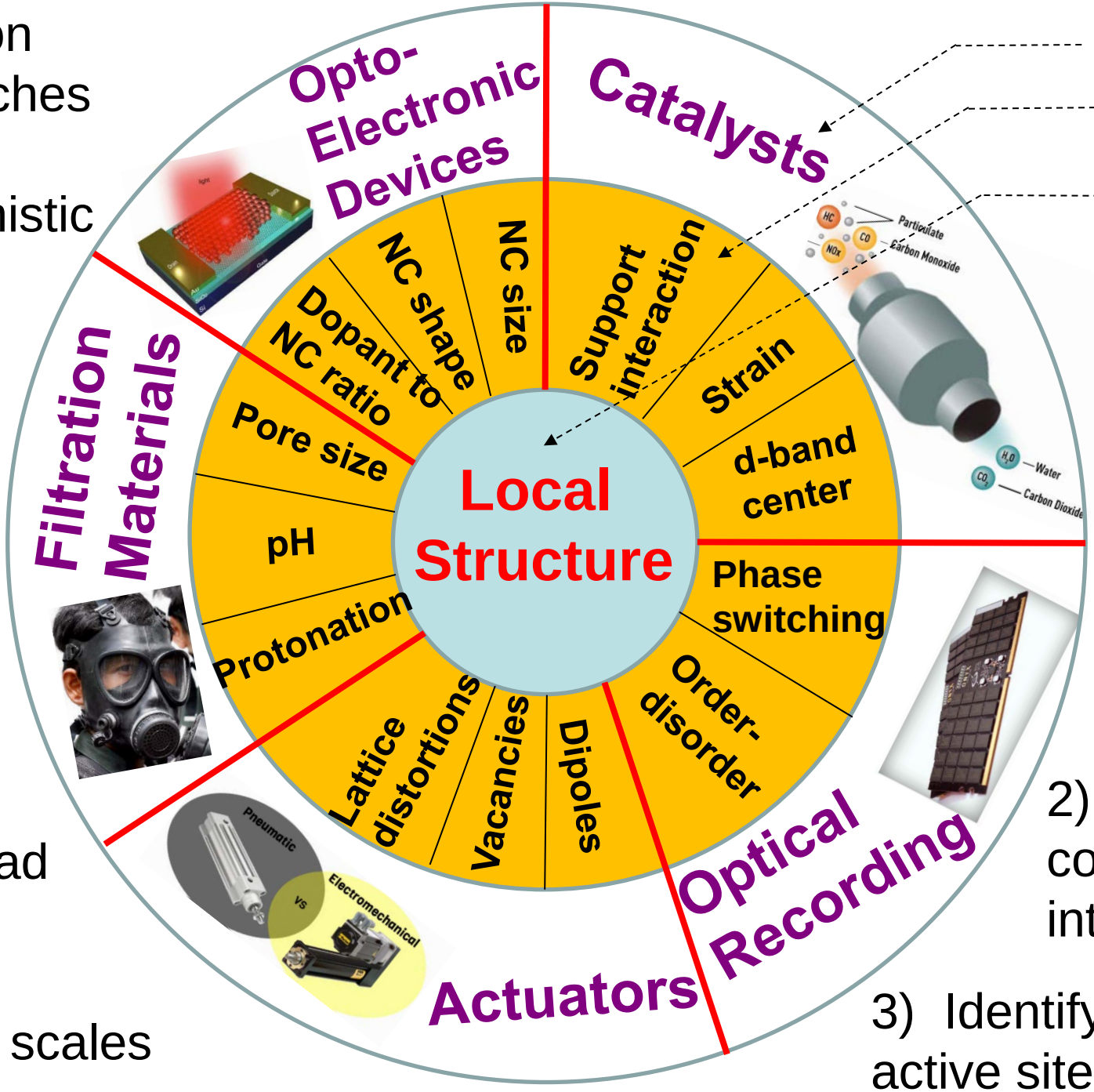
Anatoly Frenkel

Department of Materials Science and Chemical Engineering, SBU

Department of Chemistry, BNL

Synchrotron Catalysis Consortium at BNL

Common approaches to mechanistic studies:

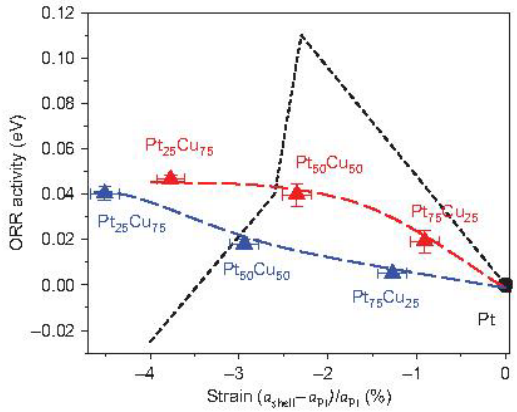


1) Broad length/ time/ energy scales

2) Solving complex interactions

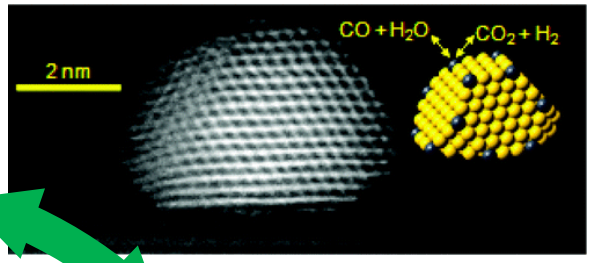
3) Identifying active sites

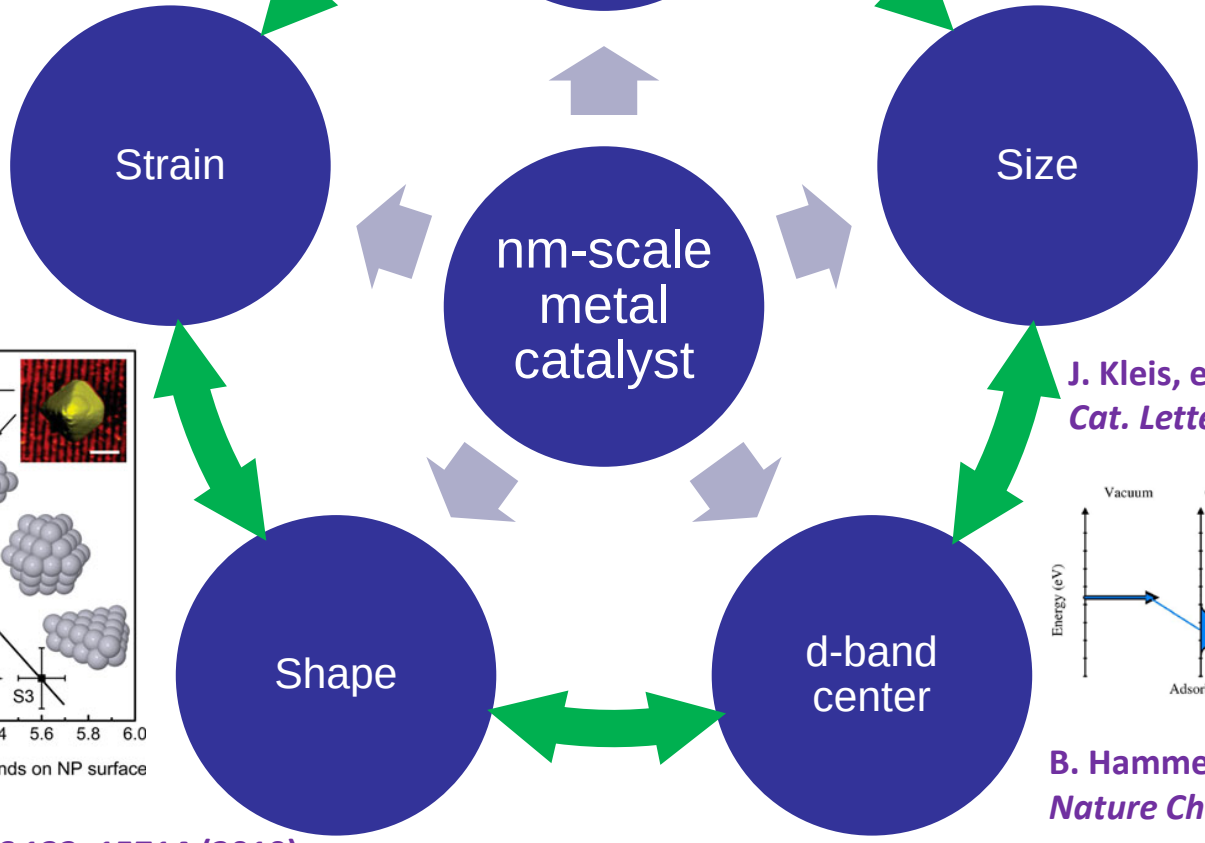
Catalytic Descriptors

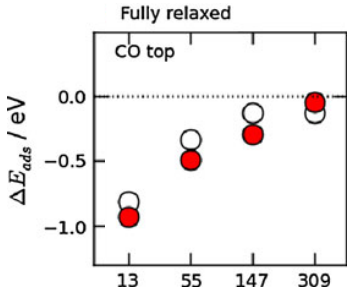


P. Strasser, et al, *Nature Chem.* 2, 454, 2010

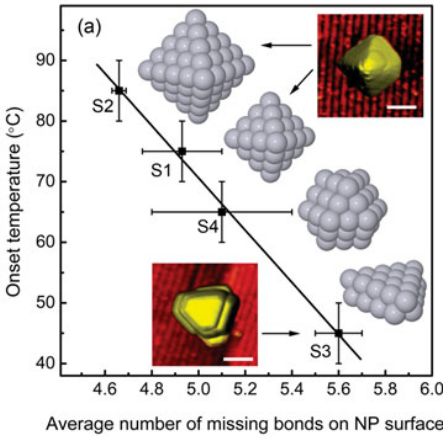
M. Cargnello, et al., *Science* 341, 771, 2013
W. Williams, et al., *JACS*, 132, 14018, 2010



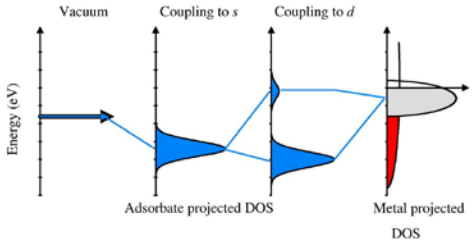




J. Kleis, et al, *Cat. Letters* 141, 1067 (2011)



S. Mostafa et al, *JACS* 132, 15714 (2010)



B. Hammer and J. Nørskov *Nature Chem.* 1, 37, 2009

J. Nørskov, et al, *Nature Chem.* 1, 37, 2009

To explain catalytic mechanisms:

Capturing effects at different length, times, energy scales

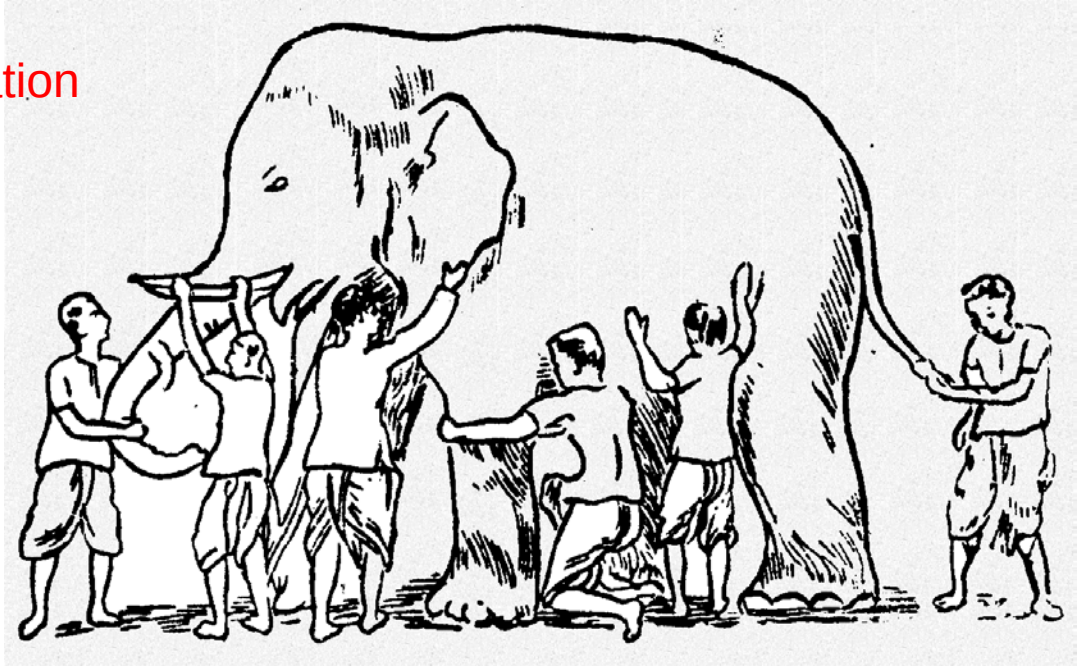
- Need multiple complementary probes

Resolving between multiple descriptors of activity (e.g., size, structure, shape)

- Need multiple complementary probes

Determining active sites

- Need *operando* characterization



In situ vs operando

"*in-situ*" ("in place"): a method of data collection without exposing the sample to external environment e.g., removing a catalyst from the reaction mixture

In situ: I suppose it's working…

?

… and I can determine reaction mechanism

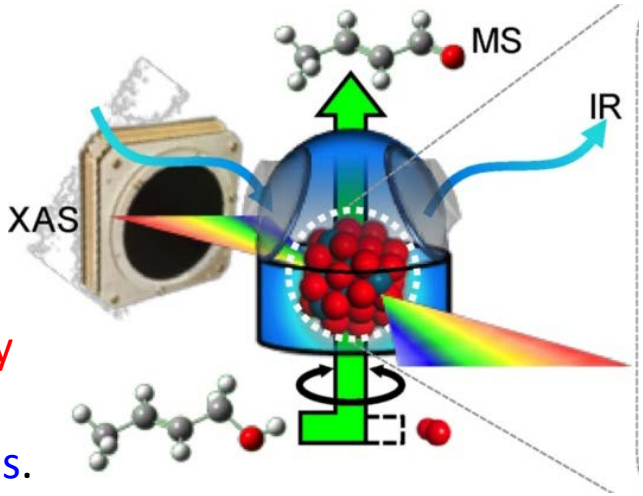
Operando: I know it's working…

… and I can determine reaction mechanism

(M. Bañares)

"*Operando* methodology: Combination of in situ spectroscopy and simultaneous activity measurements under catalytic reaction conditions".

M. Bañares, *Catalysis Today* **100**, 71 (2005)

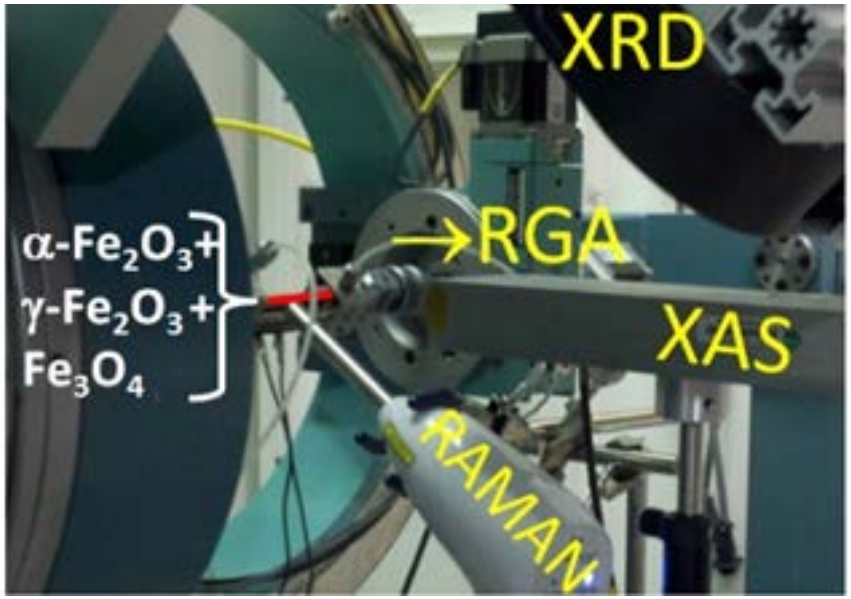


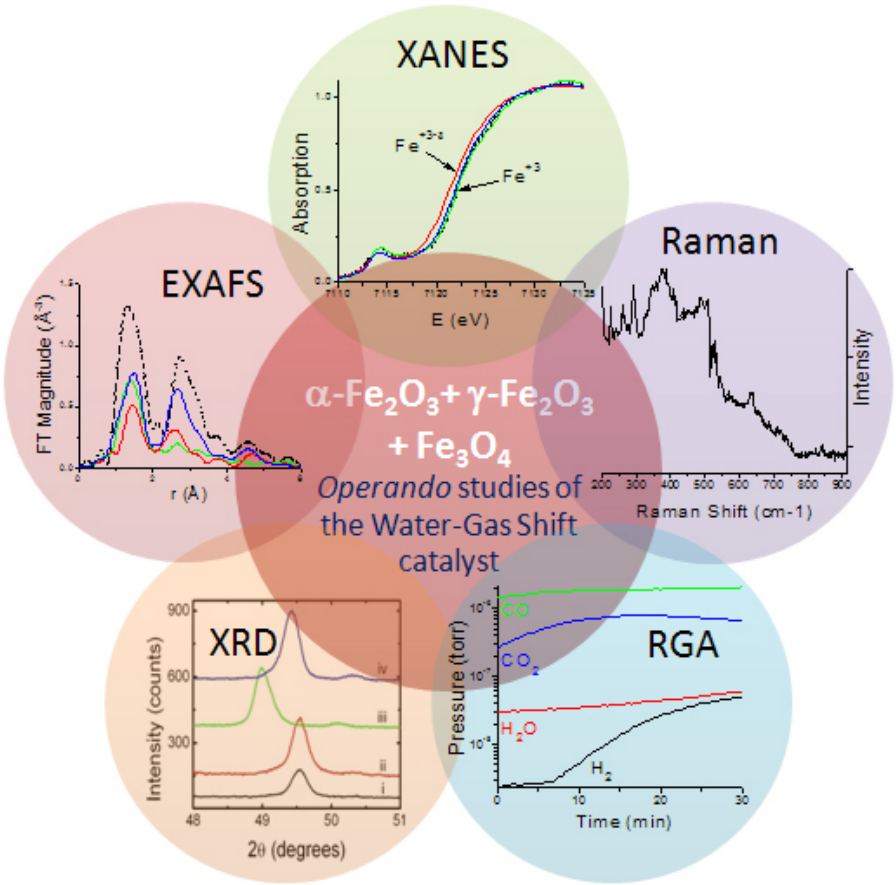
The fact that, strictly speaking, the active state of a catalyst only exists during the catalysis further emphasizes the need for performing *operando* studies under relevant reaction conditions.

Henrik Topsøe, J. Catal. 216, 155 (2003)

C. M. A. Parlett, et al.
Catalysis Today, 205, 76 (2013)

EXAMPLE 1: Operando studies of active sites in Water-Gas-Shift catalysts by combined XAFS, XRD and Raman measurements

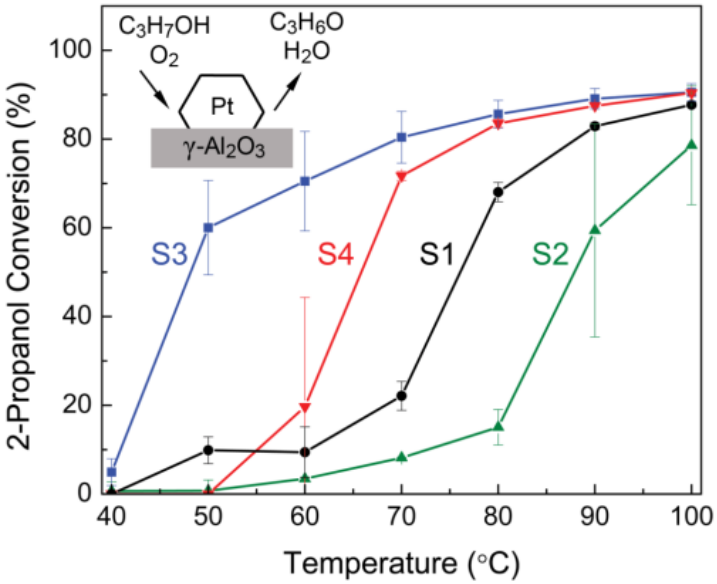




A. Patlolla, E. V. Carino, S. Ehrlich,
E. Stavitski, A. I. Frenkel
(invited) ACS Catalysis **2**, 2216-2223 (2012)

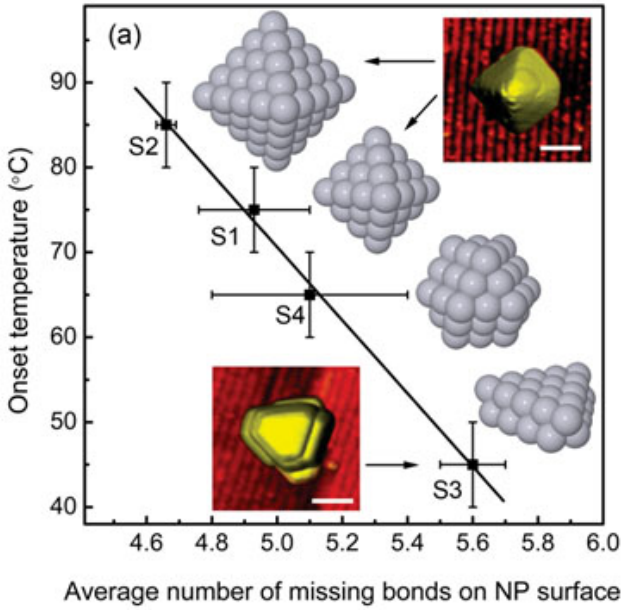
Beamline: X18A

Example 2: Shape dependent nanocatalysis



Reaction temperature correlates with the number of under-coordinated sites (<u>number of missing bonds on NP surface)</u>

S. Mostafa, F. Behafarid, J. R. Croy, L. K. Ono, L. Li, J. C. Yang, A. I. Frenkel, B. Roldan Cuenya, *J. Am. Chem. Soc.*, **132**, 15714 (2010)

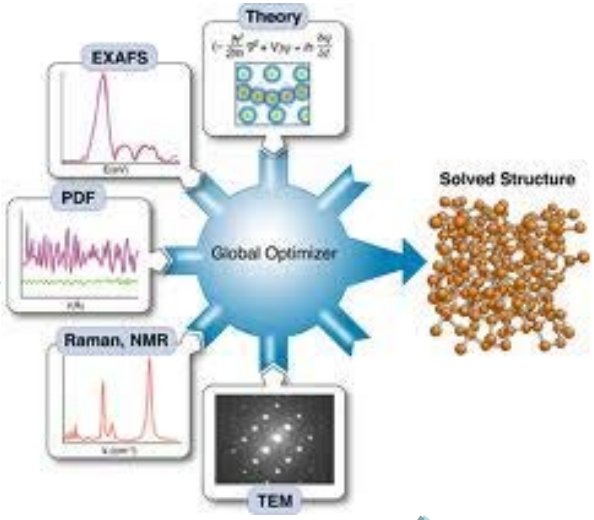


<u>Other factors?</u> Size? Morphology of the particle-support interface? Disorder? Strain?

<u>How to deconvolute them?</u>

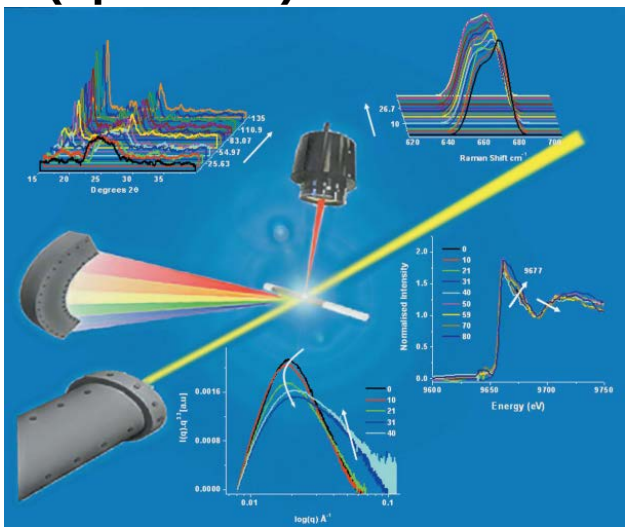
How to resolve complex interactions in heterogeneous systems at multiple length scales in working conditions (operando)?

S. Billinge, I. Levin, Science **2007**, 316, 561.

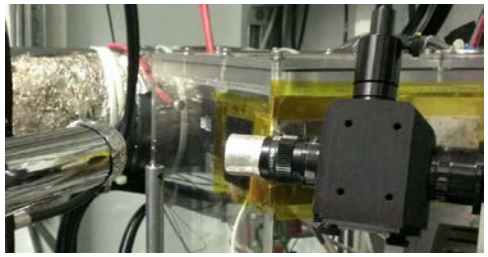


Gaps:

- Pressure
- Materials
- Instrument
- Complexity

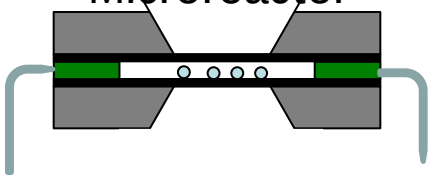


XAS/SAXS/WAXS/UV-Vis/Raman
A. Iglesiaz-Juez et al, SRN, **2009**, v.22

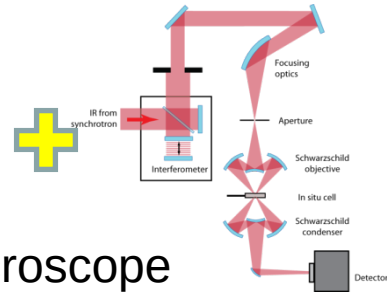


XAS

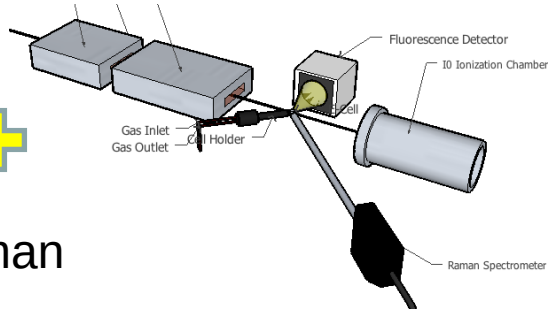
Microreactor



TEM

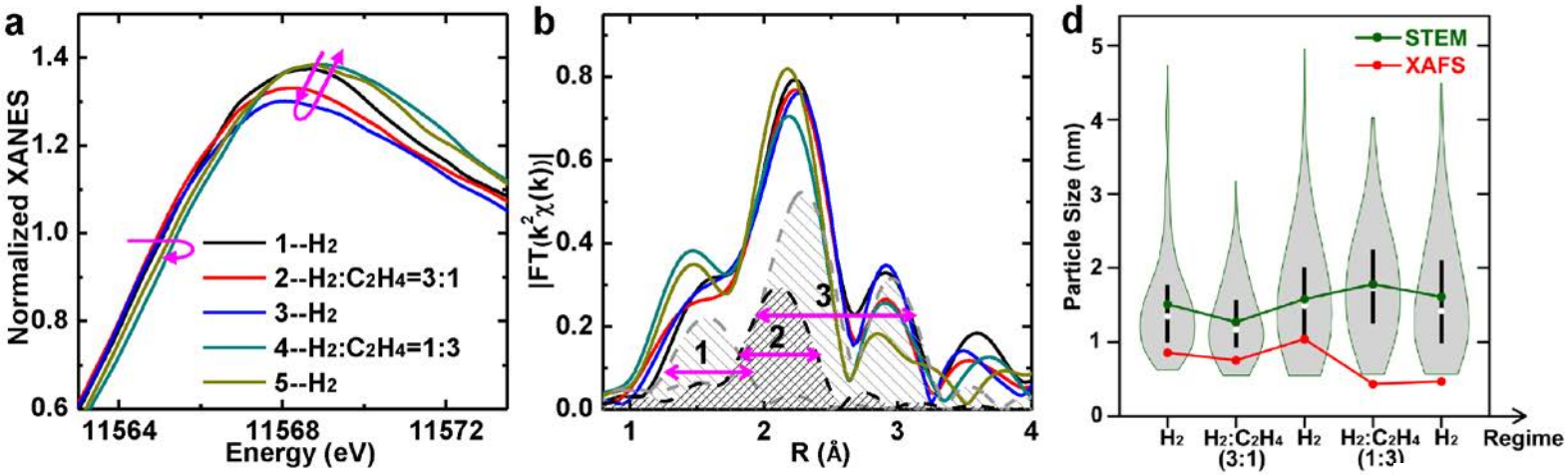


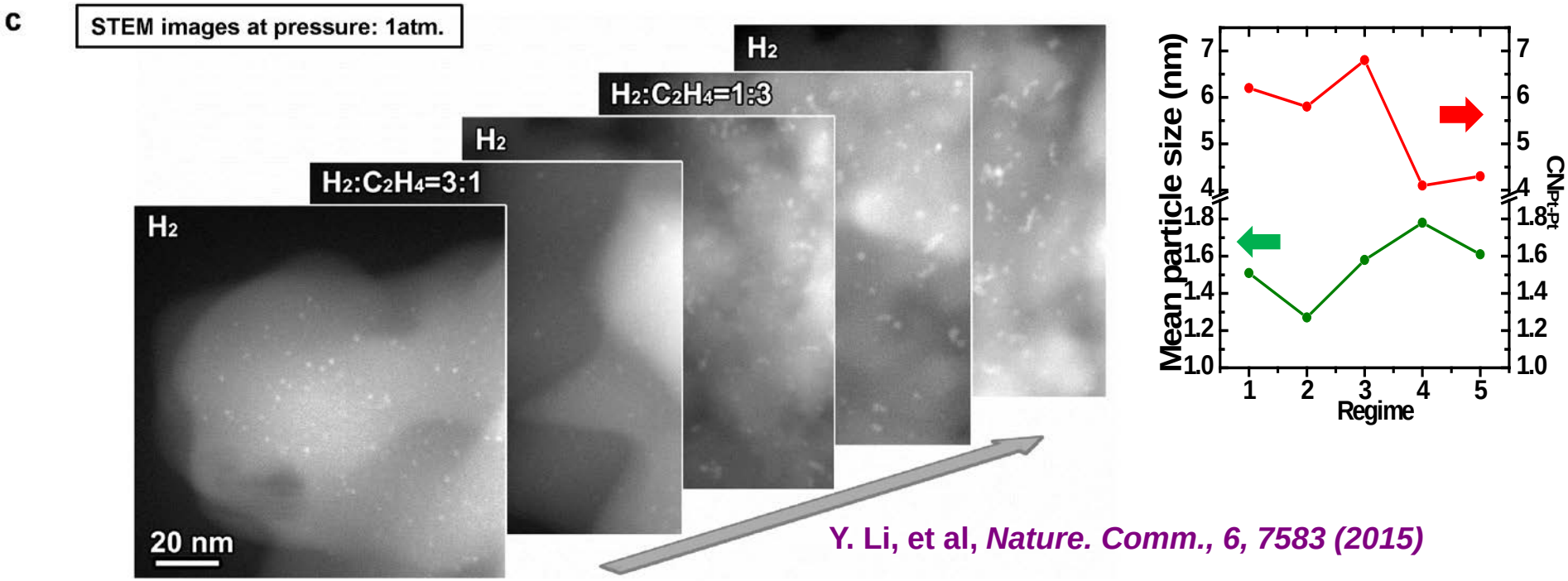
IR Microscope



Raman

Ethylene hydrogenation over Pt/SiO_2





Y. Li, et al, *Nature. Comm., 6, 7583 (2015)*

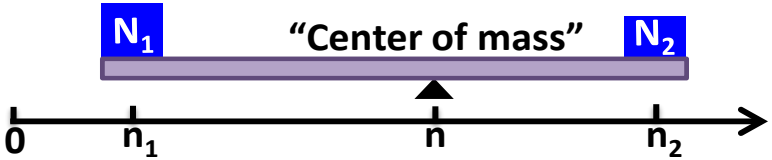
The Seesaw

Undetectable parts in STEM:
the number of atoms and bonds
"that are left behind the curtain"

STEM-derived quantities: number of atoms and bonds in measured distribution

$$n = \frac{2m_1 + \sum_{L=L_{\min}} \rho(x_L) 2m(L)\Delta x}{N_1 + \sum_{L=L_{\min}} \rho(x_L) N(L)\Delta x}$$

EXAFS-derived quantity



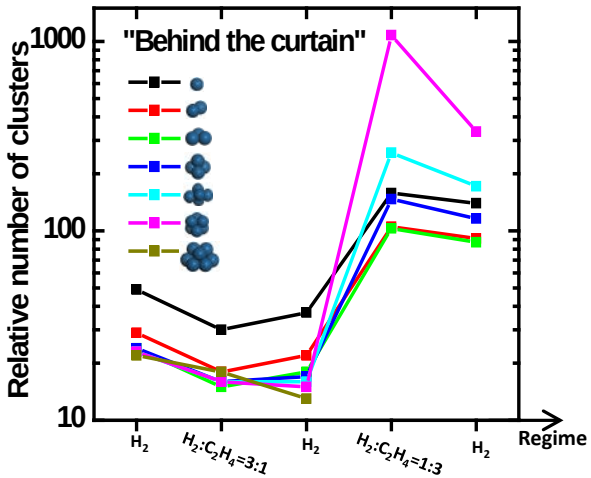
The outcome:

Counting clusters ***of all sizes***, including those ***"behind the resolution curtain"***

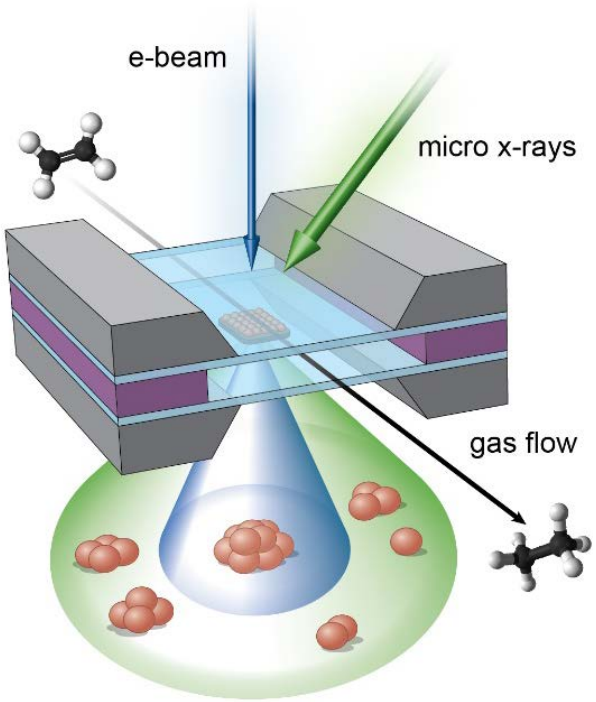
$$n = \frac{n_1 N_1 + n_2 N_2}{N_1 + N_2}$$

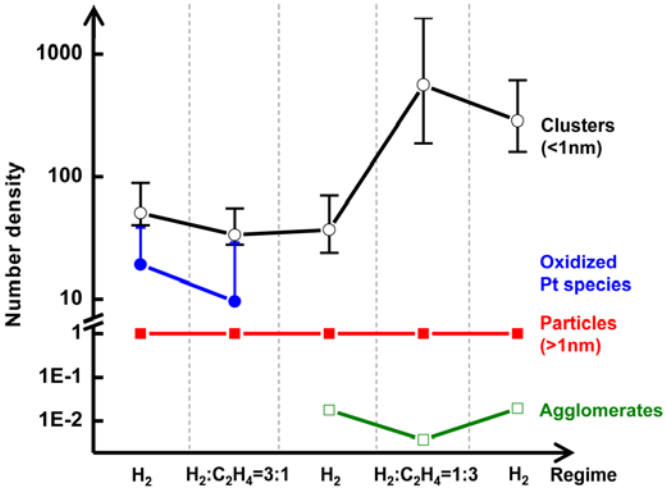
Y. Li, et al, *Nature. Comm., 6, 7583 (2015)*

The Summary: Reaction-driven restructuring of Pt nanoparticles during catalytic hydrogenation of ethylene

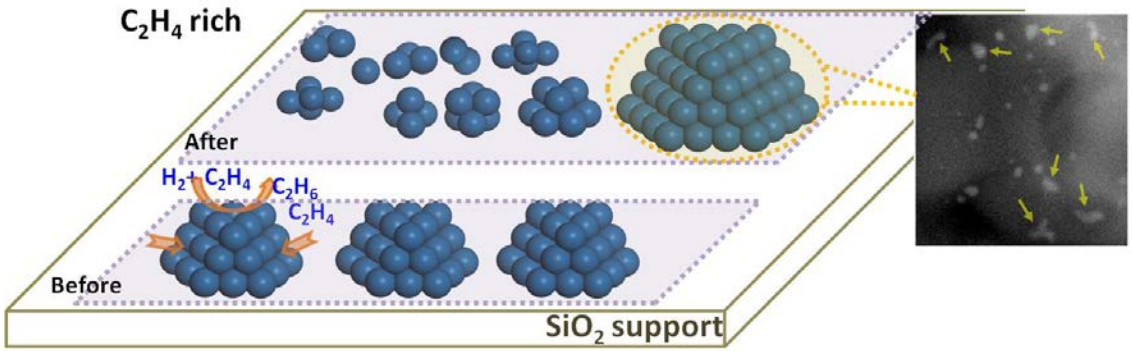


A peek "behind the curtain"



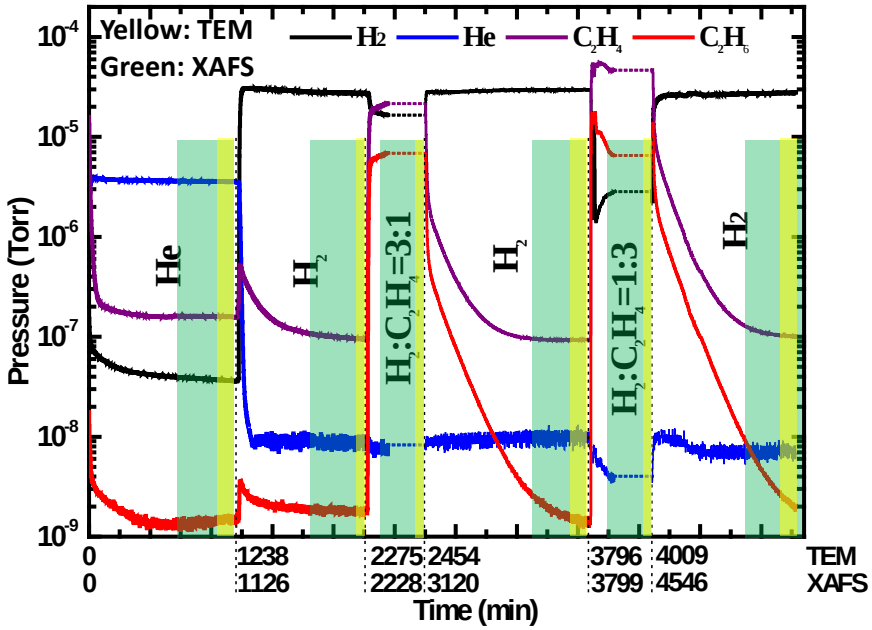


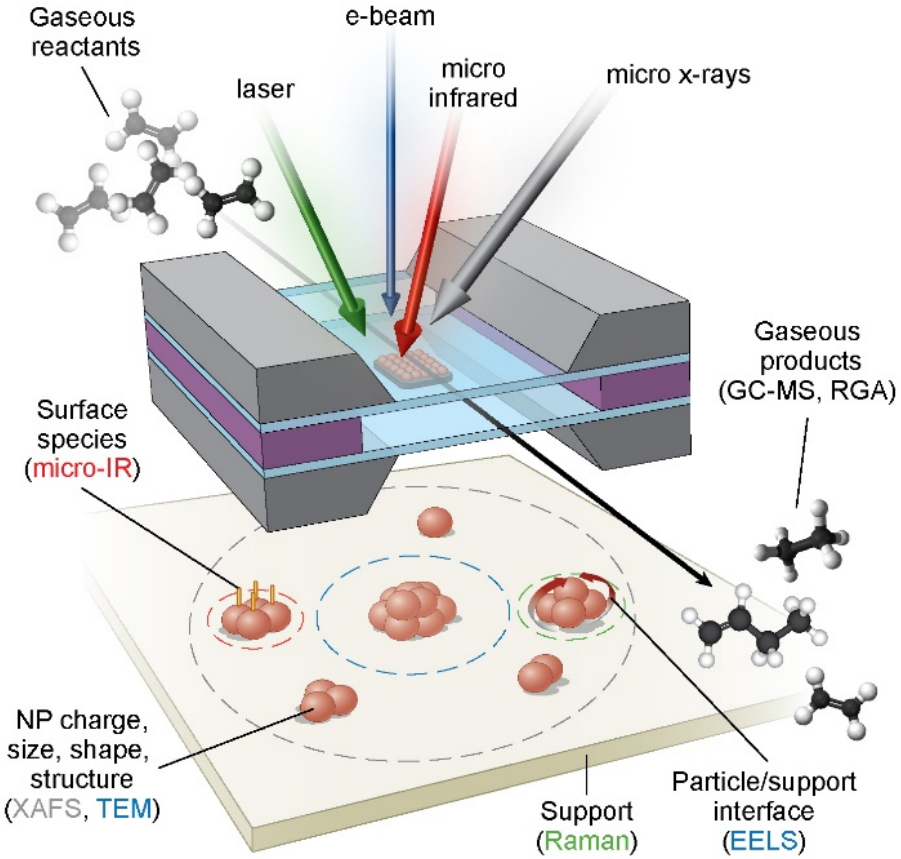
Complementary probes in nm-range



$$\nu_{total} = \nu_{ox} + \nu_{sub-nm\ clusters} + \nu_{larger\ particles} + \nu_{agglomerates}$$

EXAMPLE 3: Monitoring multiple components of a heterogeneous system by correlative use of operando XAS, TEM, IR and Raman





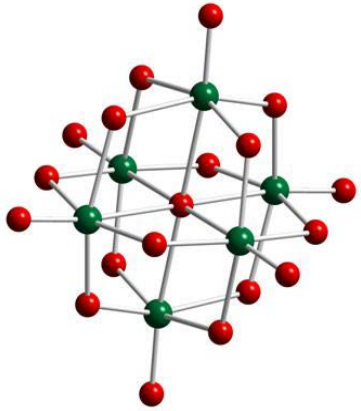
Coexistence of unreduced species, single atoms, ultra-small and large clusters in reaction conditions

Product formation is monitored at multiple facilities (NSLS-II, CFN and research labs) and correlated to each other – to correlate experimental data

Y. Li, et al, *Nature. Comm., 6, 7583 (2015)*

S. Zhao, et al, *Chem. Cat. Chem., 7, 3683 (2015)*

Application of in situ/operando methods to Filtration Materials



Questions:

- How do MOFs and POMs change structure under operational conditions?
- What are the molecular-level reaction mechanisms for agents?
- Where do agents bind during initial uptake?

Challenges:

-Identifying active sites in POMs and MOFs for the agent uptake;

-Structure, electronic & catalytic properties of MOFs and POMs in reaction conditions;

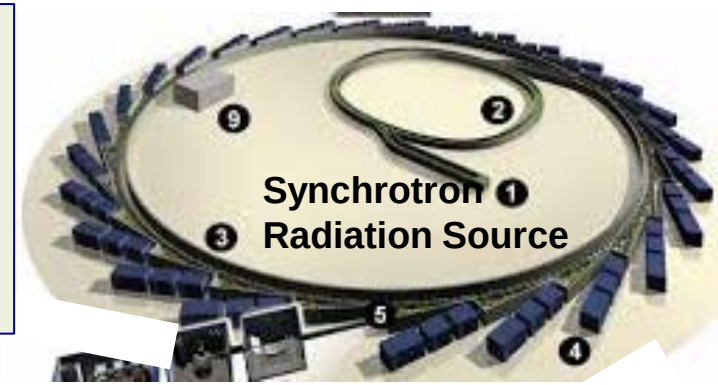
-Correlative studies by multiple techniques;

-Combination of characterization studies with theory

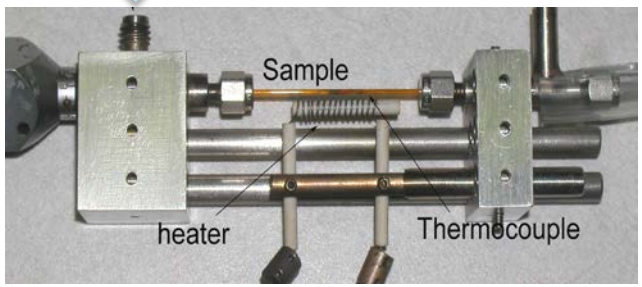
Methods:

- Local geometry of active sites in POMs and MOFs: XAFS/XANES/Raman
- Electronic charges of metal species in POMs and MOFs: XANES
- Long range order in MOFs: XRD
- In situ bond forming and breaking during agent uptake and decomposition: XAFS/XRD/Raman
- Correlation between multiple techniques using reactivity measurements and theoretical modeling

Correlative Multi-Technique *Operando* Characterization

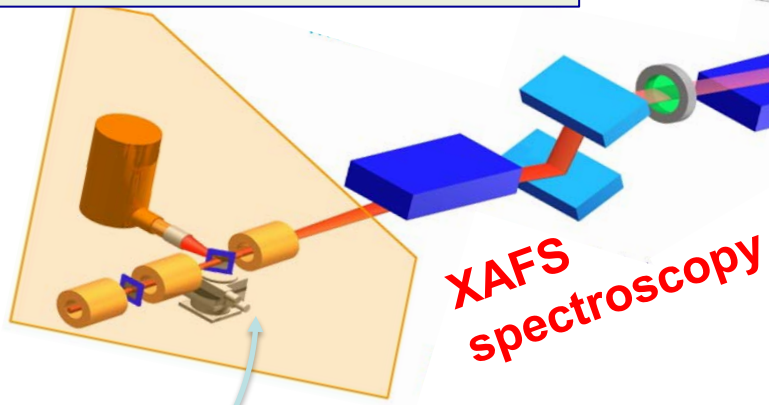


He/DMMP
He/DMCP
He/H_2O
CO_2
H_2, …



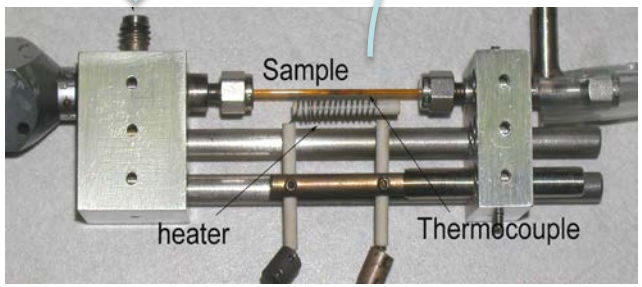
To RGA

Correlative Multi-Technique *Operando* Characterization



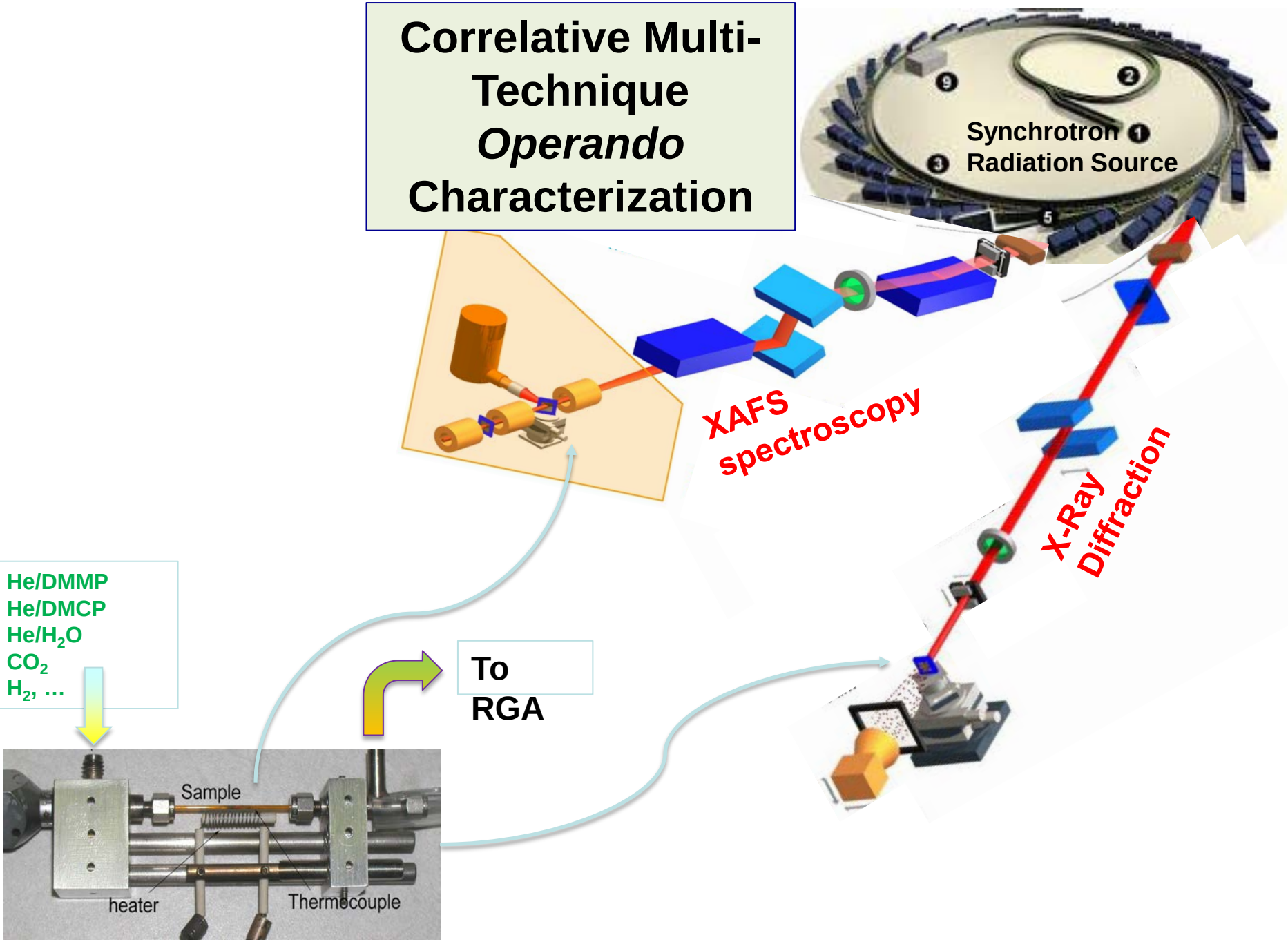
XAFS spectroscopy

He/DMMP
He/DMCP
He/H_2O
CO_2
H_2, …

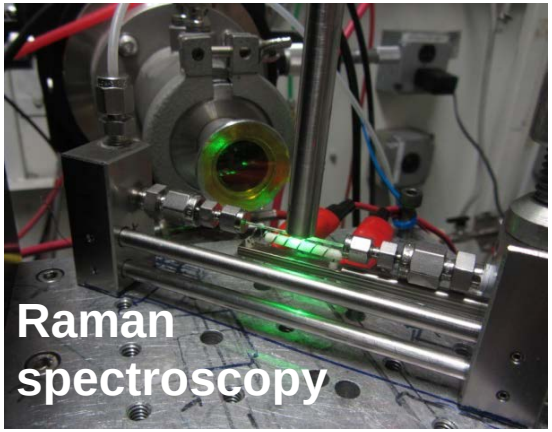


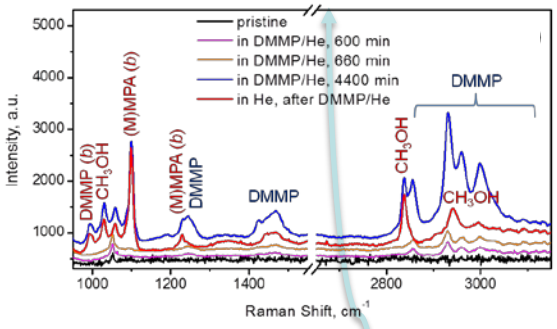
To RGA

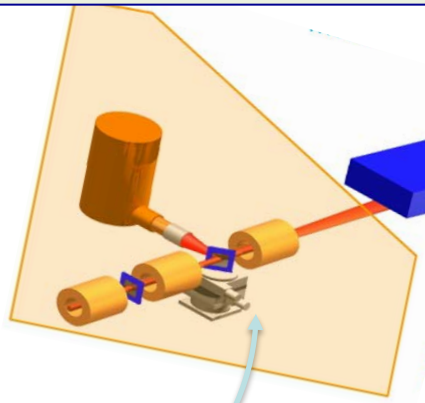
Correlative Multi-Technique *Operando* Characterization

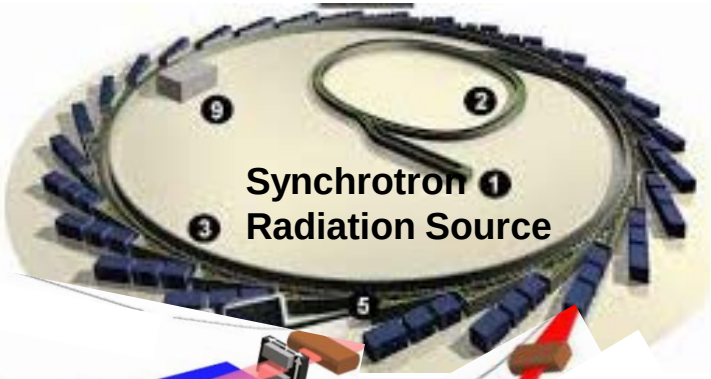


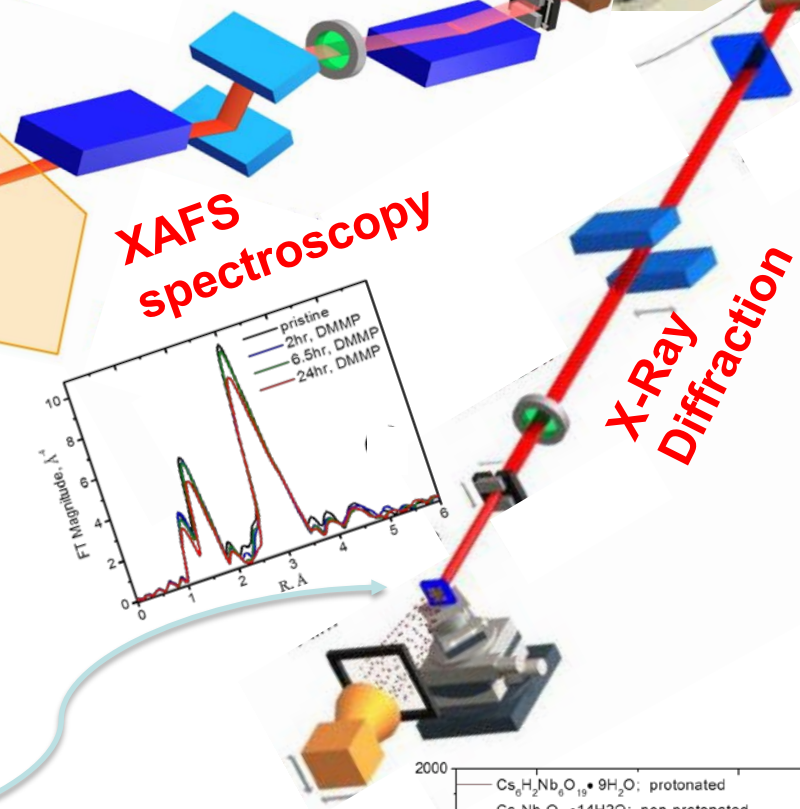
Correlative Multi-Technique *Operando* Characterization



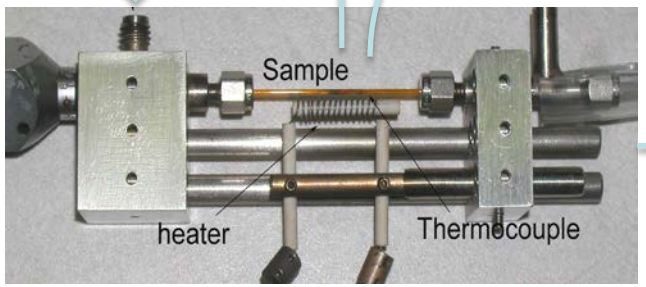




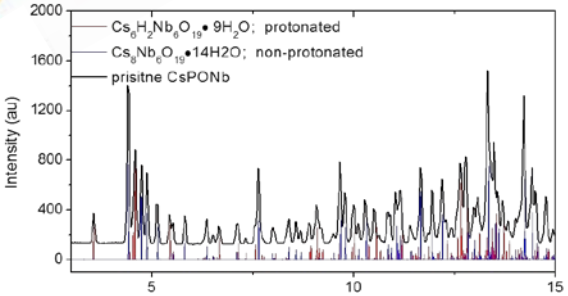




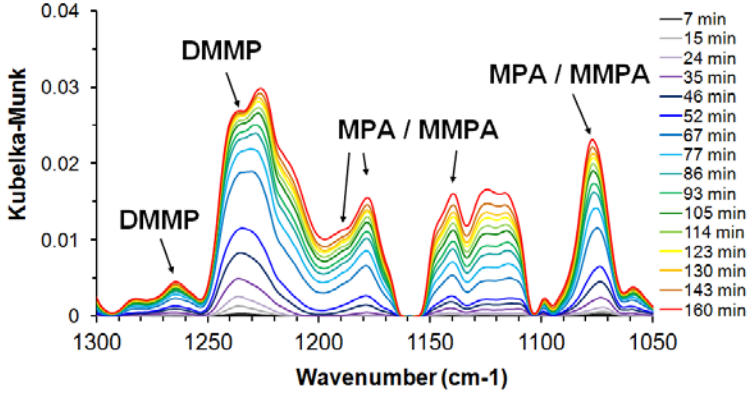
He/DMMP
He/DMCP
He/H_2O
CO_2
H_2, …

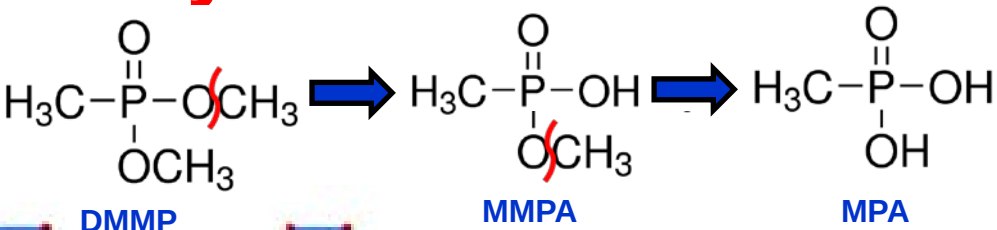


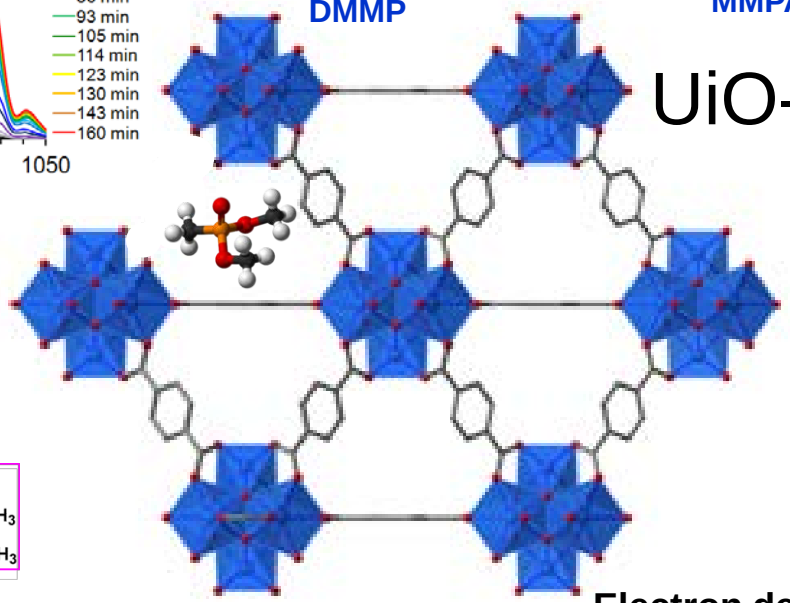
To RGA

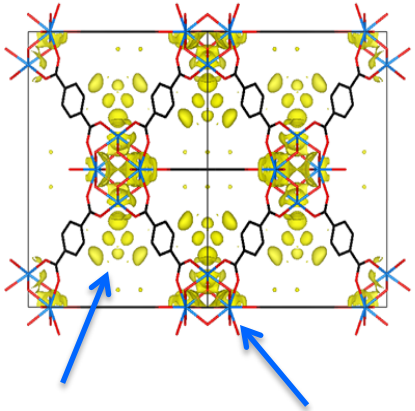


Filtration activity of MOFs

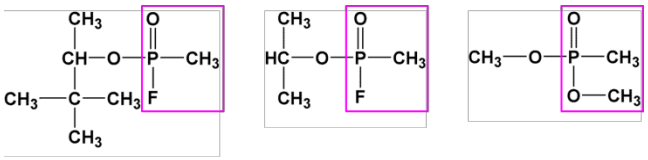


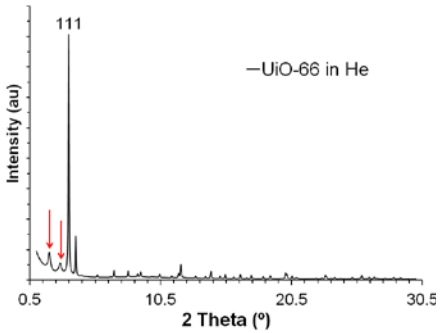


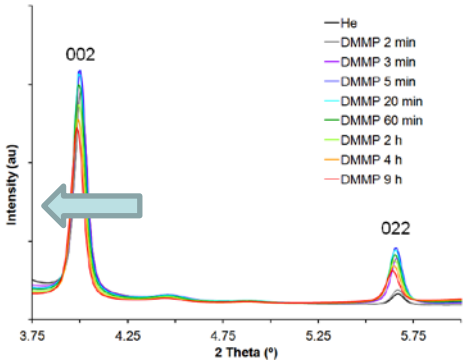


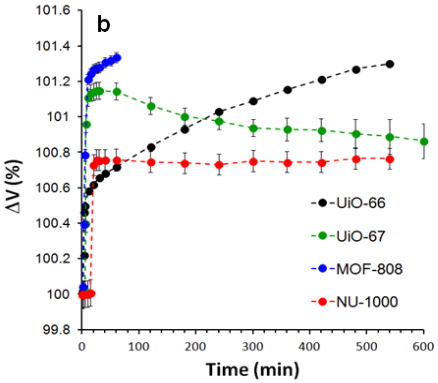


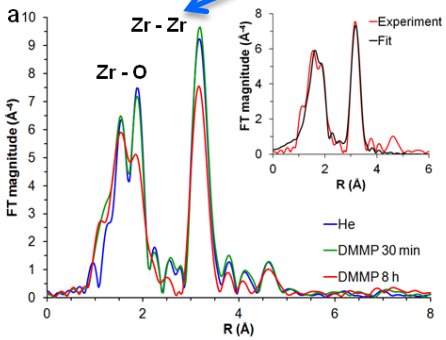
Dimethyl methylphosphonate (DMMP)











UiO-66

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Synchrotron Catalysis Consortium
Structure
Property
Function
Design

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Raman, DRIFTS, Staging lab:
BNL Chem.

XAFS experiments:
BL 2-2 @ SSRL
9BM @APS

XRD experiments:
XPD @ NSLS2
17BM @APS

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XAFS
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Theory

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