Studying Real Catalysts at Work: From Macro to Micro to Nano

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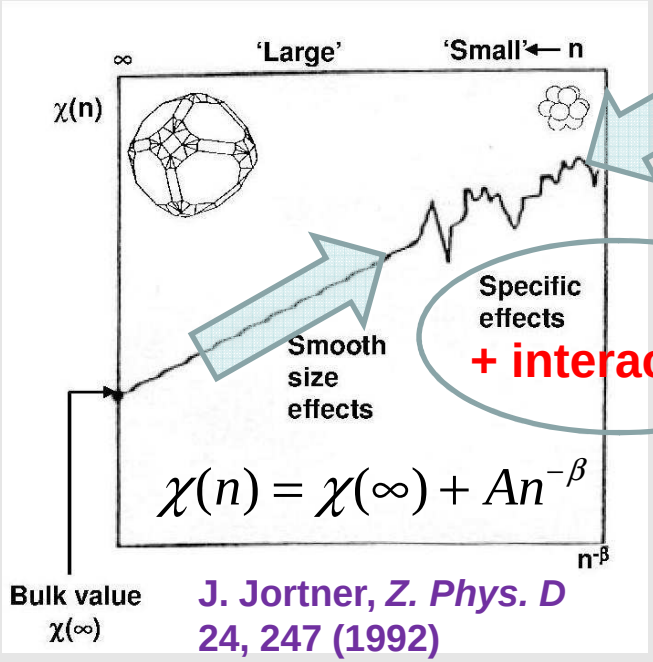
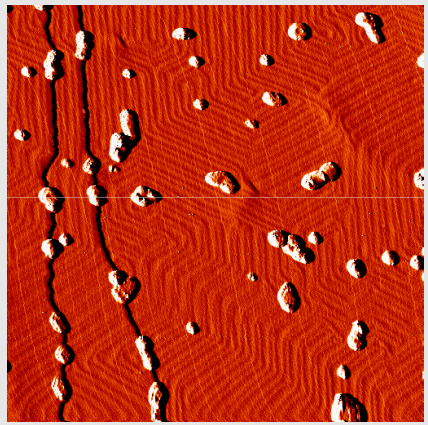
Synchrotron Catalysis Consortium, Brookhaven National Laboratory

macro-powder



J. Jortner, *Z. Phys. D* 24, 247 (1992)



200 nm x 200 nm

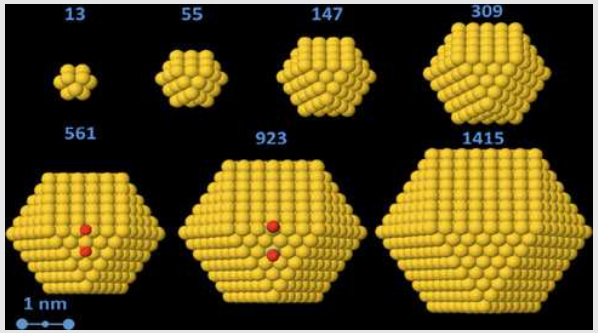
model single crystal

"The temptation for those used to macroscopic theory is to believe nanoscience is miniaturised macroscience; for those used to the atomic scale, the temptation is to believe that it suffices to extend familiar atomistic ideas."

A. M. Stoneham, J. L. Gavartin, Mat.Sci. and Eng., 2007

Descriptors of catalytic activity:

- ❖Geometry and surface binding sites
- ❖Surface free energy
- ❖Chemisorption energy
- ❖d-band center
- ❖Strain



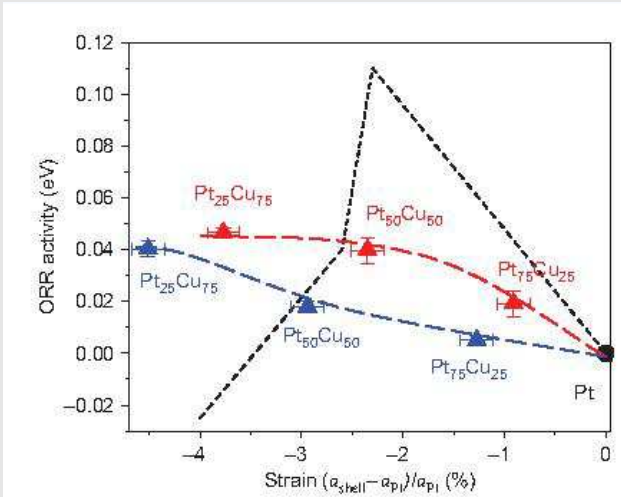
J. Kleis, et al,
***Cat. Letters* 141, 1067 (2011)**

Y. Xu et al,
***PhysChemChemPhys* 10, 6009 (2008)**

Hammer and Nørskov,
***Nature* 376, 238 (1995)**

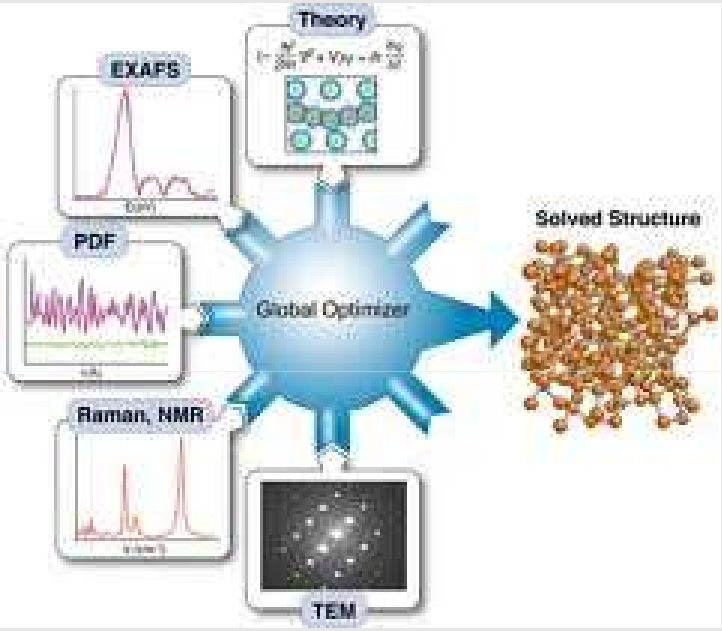
Limitations:

- ❖Regular geometric shapes (e.g., 111, 110, etc.)
- ❖Bulk/slabs for lattice dynamics calculations
- ❖Single crystal supports
- ❖<u>Intrinsically impossible to vary one factor at a time!</u>



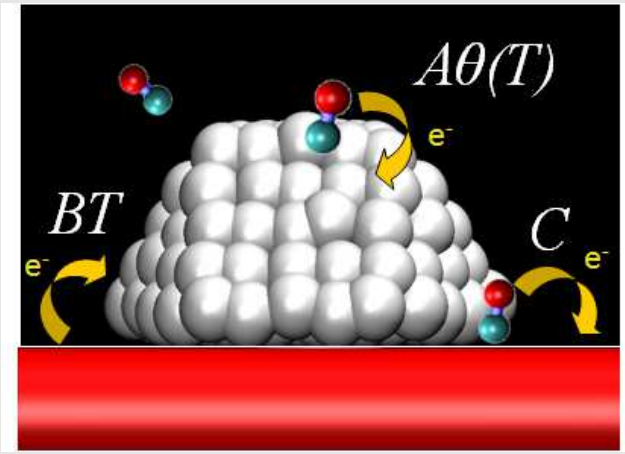
P. Strasser, et al,
***Nature Chem.* 2, 454, 2010**

How to solve a nanostructure problem



S. J. L. Billinge and I. Levin,
Science 316, 561 (2007).

Unsolved problem:
How to resolve competing influences in the same system:
Size, shape, support, strain, coverage



M. Small, S. Sanchez, N. Marinkovic, A. I. Frenkel, R. G. Nuzzo, *ACS Nano* **6**, 5583 (2010)

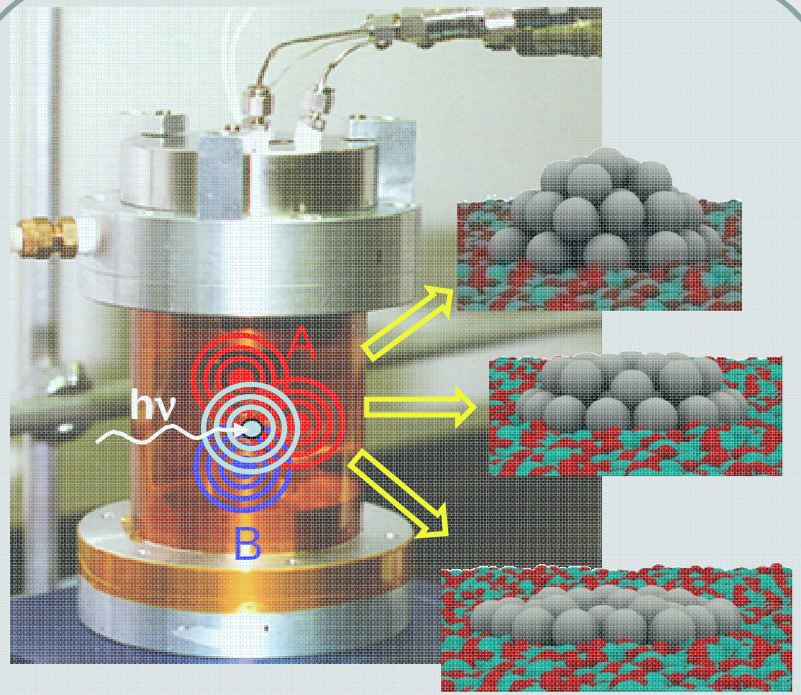
Our approach:

Identify and evaluate relevant catalytic descriptors of a working catalyst in *operando* conditions:

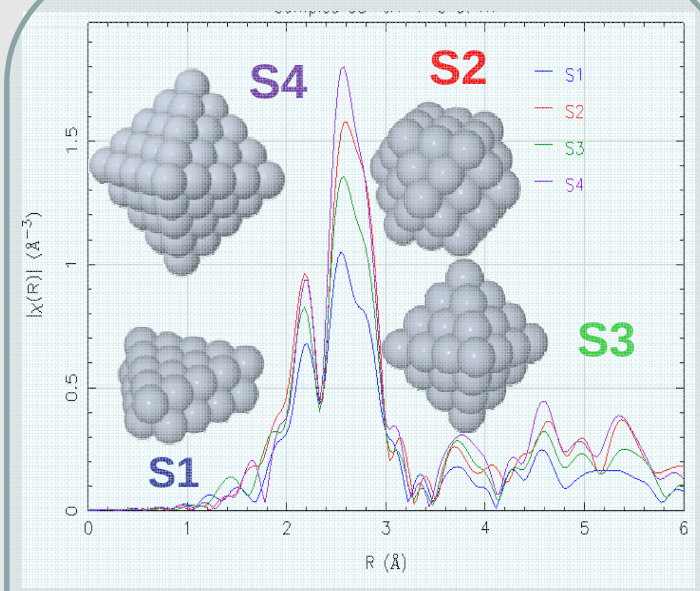
- ❖Geometry
- ❖Shape change
- ❖Adsorbate coverage
- ❖Heat of adsorption
- ❖Surface free energy
- ❖Charge transfer
- ❖d-band center
- ❖Strain

Characterization of chemical and structural order:

- ❖XRD
- ❖TEM (HAADF-STEM, EDX)
- ❖XPS
- ❖UV-Vis/FTIR/Raman
- ❖XANES and EXAFS



M. Small, S. Sanchez, N. Marinkovic, A. I. Frenkel, R. G. Nuzzo
ACS Nano **6**, 5583 (2010)



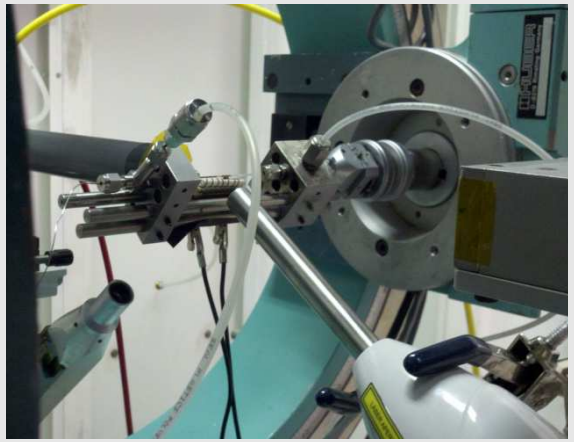
B. Roldan Cuenya, A. I. Frenkel, et al, *Phys. Rev. B*. **82**, 155450 (2010)

A good match!

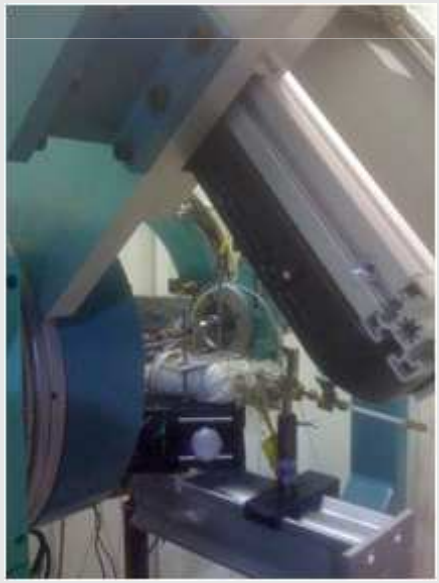
- ❑ structure,
- ❑ electronic properties,
- ❑ thermodynamics (P,T)
- ❑ kinetics

Synchrotron Catalysis Consortium
NSLS Beamlines X18B, X19A and X18A

In situ and operando reaction cells



Combined XAFS/XRD/Raman



Combined XAFS/XRD/DAFS

Combined XAFS/DRIFTS

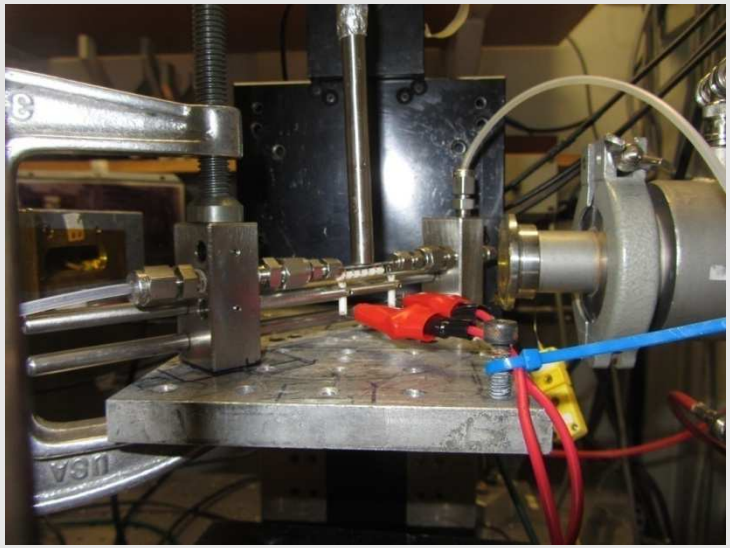
QEXAFS

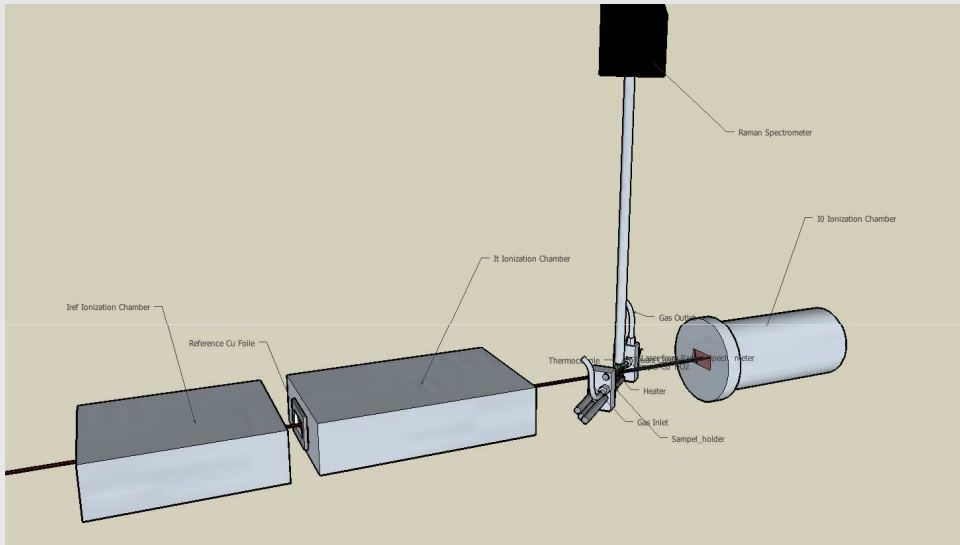
http://www.yu.edu/scc

Model catalyst:

Measuring catalytic activity at *multiple length scales* in the same experiment

Determination of catalytically active phase of Cu/TiO_2 catalyst in CO oxidation reaction by *operando* XAFS/XRD/Raman/MS





Raman spectrometer:

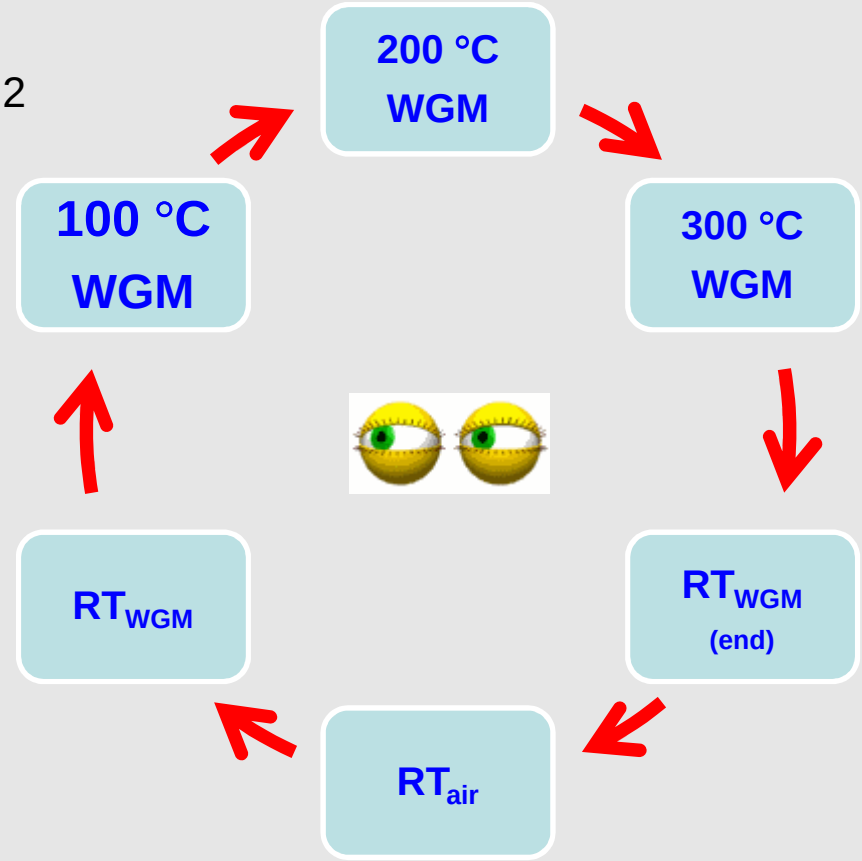
Portable fiber optic system (Bay Spec), HT probe
532 nm laser, 50-3200 cm^{-1} CCD detector
Compatible with capillary cell (quartz) and absorption/scattering geometry

Monitoring catalytic activity and selectivity by combined XAFS/Raman/RGA

$CO + H_2O \rightarrow CO_2 + H_2$

$2CO + O_2 \rightarrow 2CO_2$

5%CO/He
10 mL/min

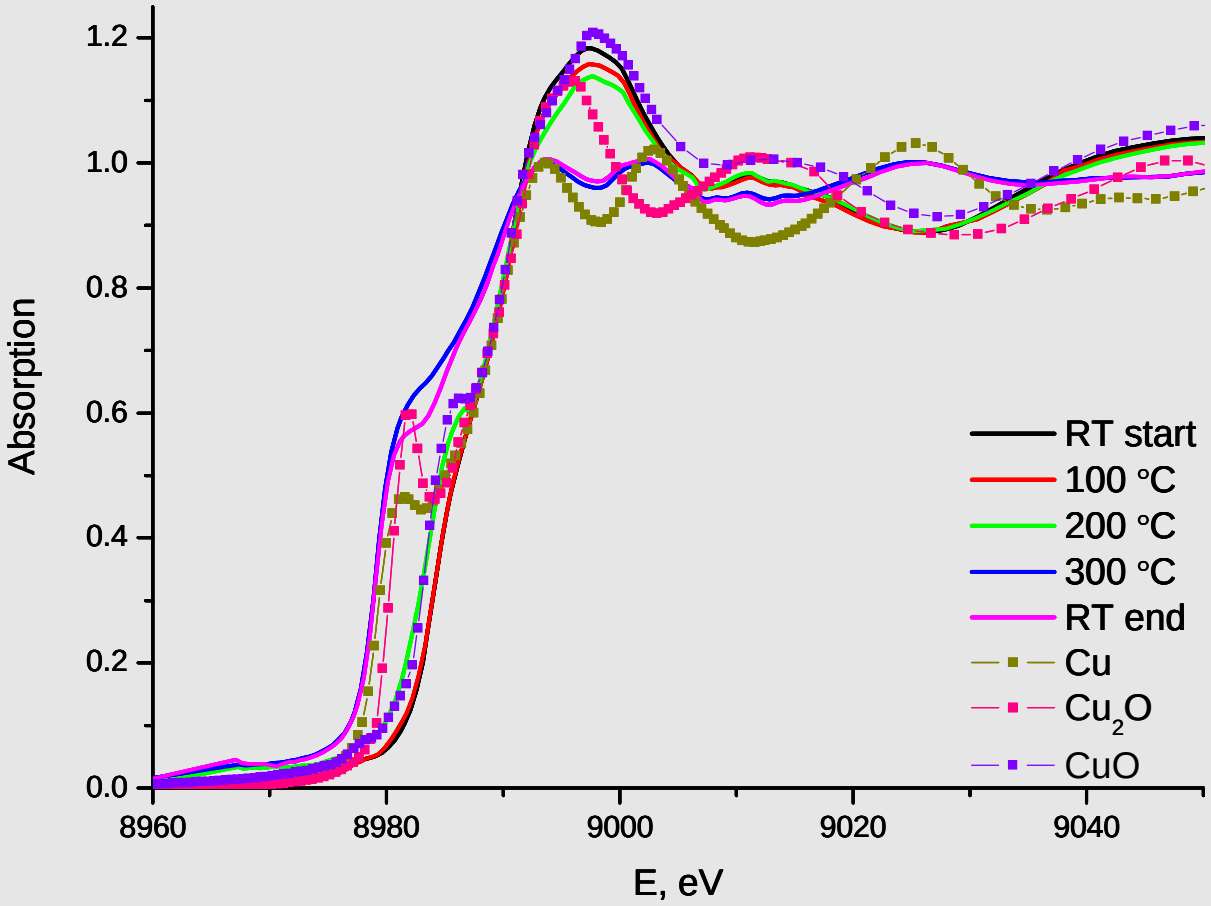


XAFS/ Raman/ RGA

Cu/TiO_2 catalyst
(courtesy:
S. Senanayake,
L. Barrio, R. Si)

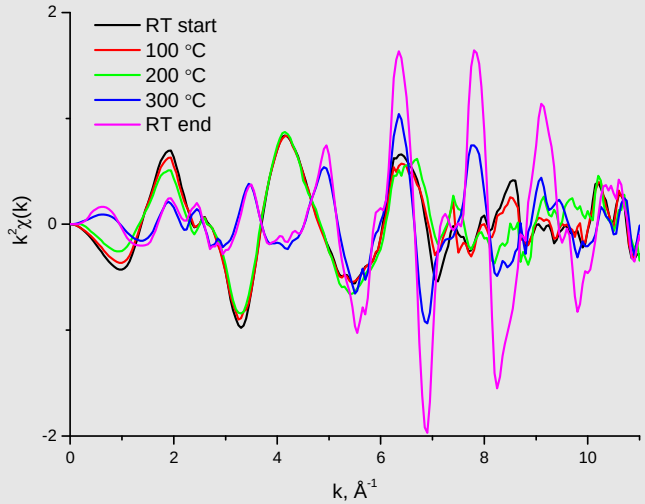
X19A beamline
NSLS

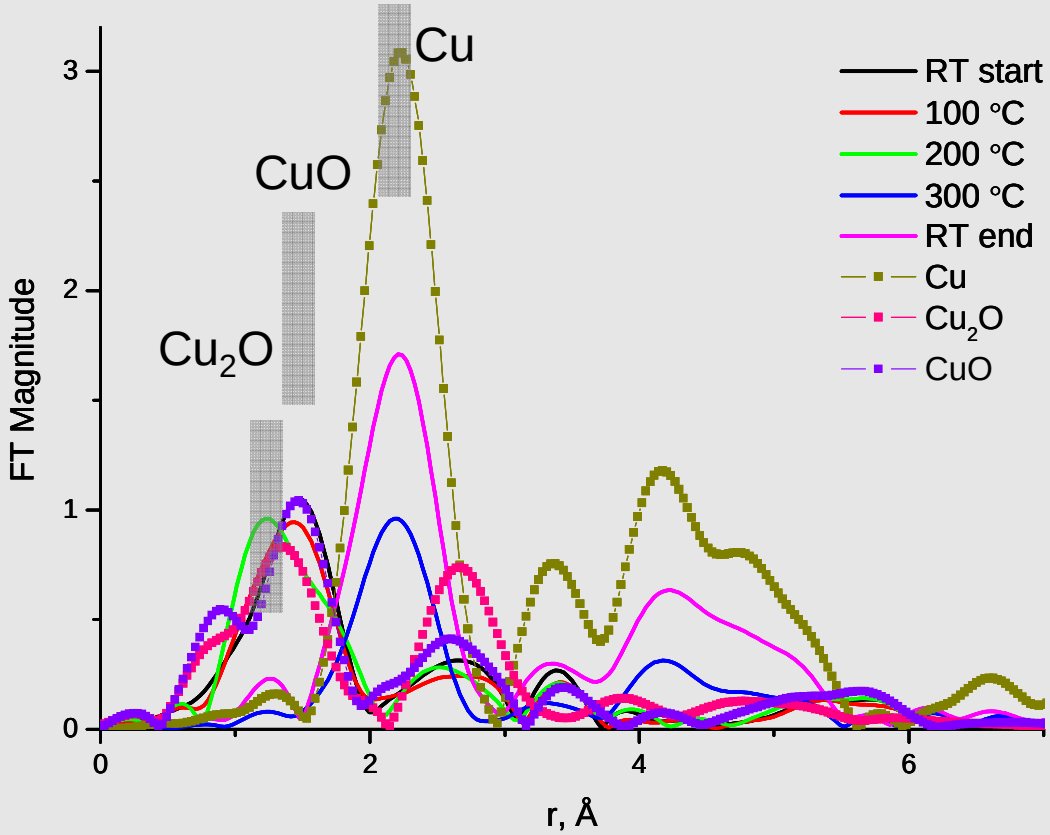
1. XANES



RT, 100 °C :	**CuO***
200 °C:	**CuO**
300 °C:	**Cu+Cu_2O**
RT (end):	**Cu+Cu_2O**

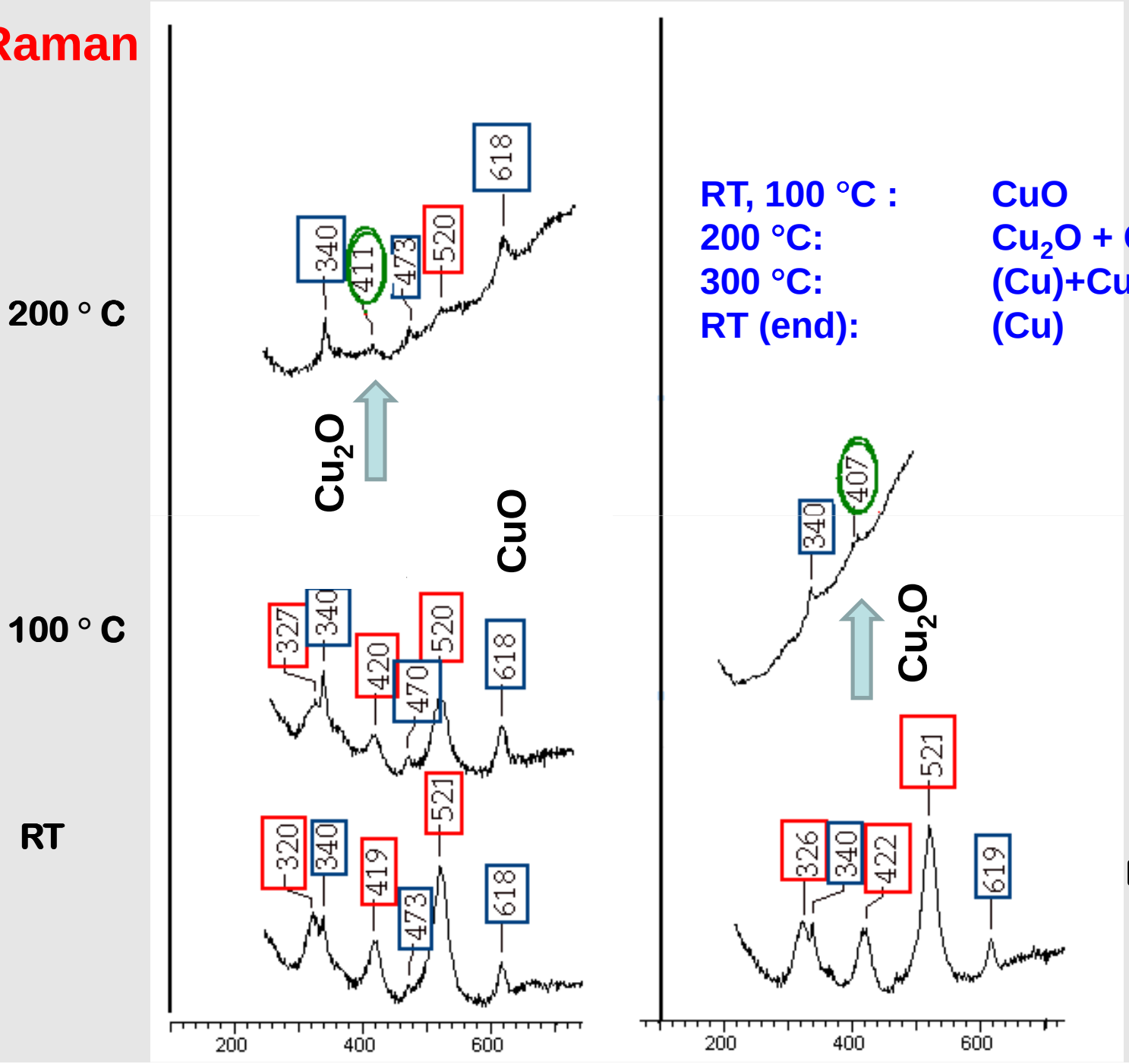
2. EXAFS





RT, 100 °C :	**CuO**
200 °C:	**Cu_2O + CuO**
300 °C:	**Cu**
RT (end):	**Cu**

3. Raman



RT, 100 °C : CuO
200 °C: Cu_2O + CuO
300 °C: (Cu)+Cu_2O
RT (end): (Cu)

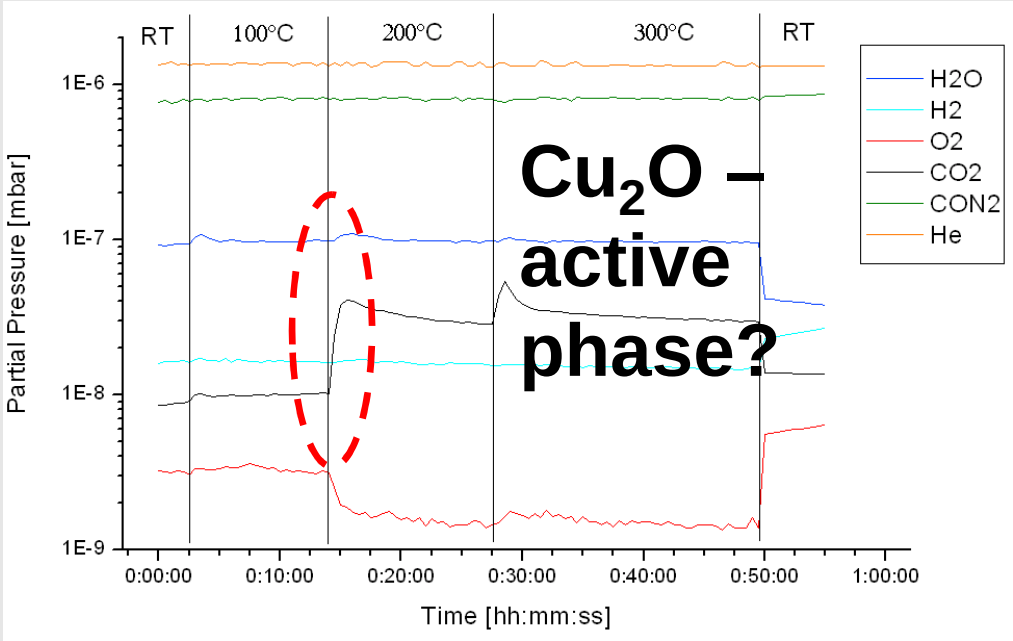
4. RGA

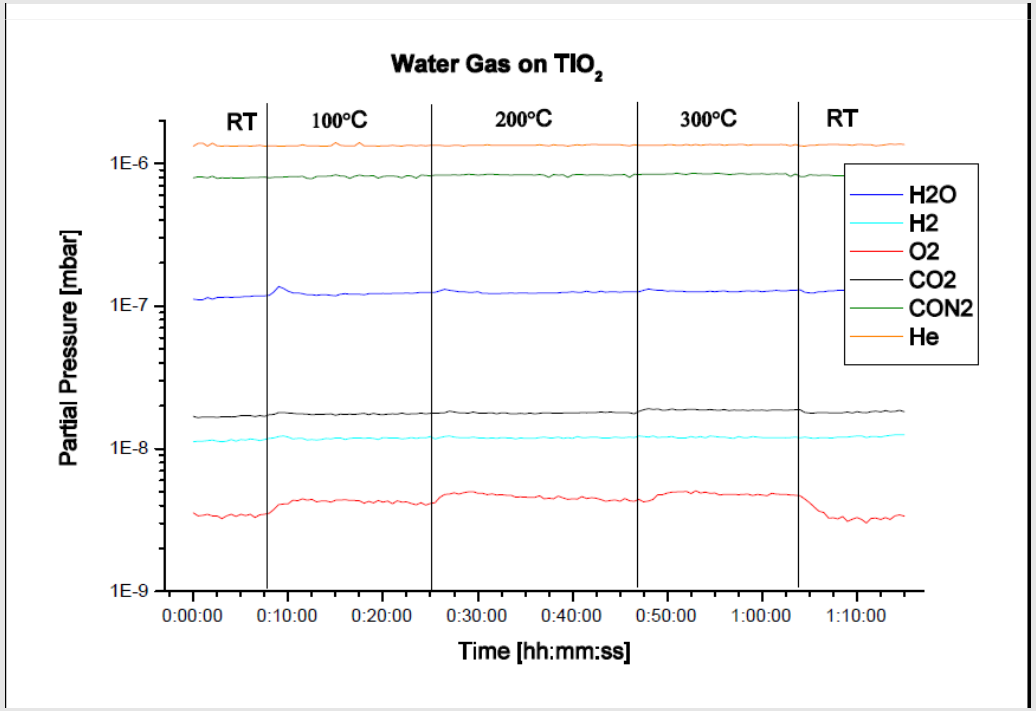
Cu/TiO_2

$CO + H_2O \rightarrow CO_2 + H_2$

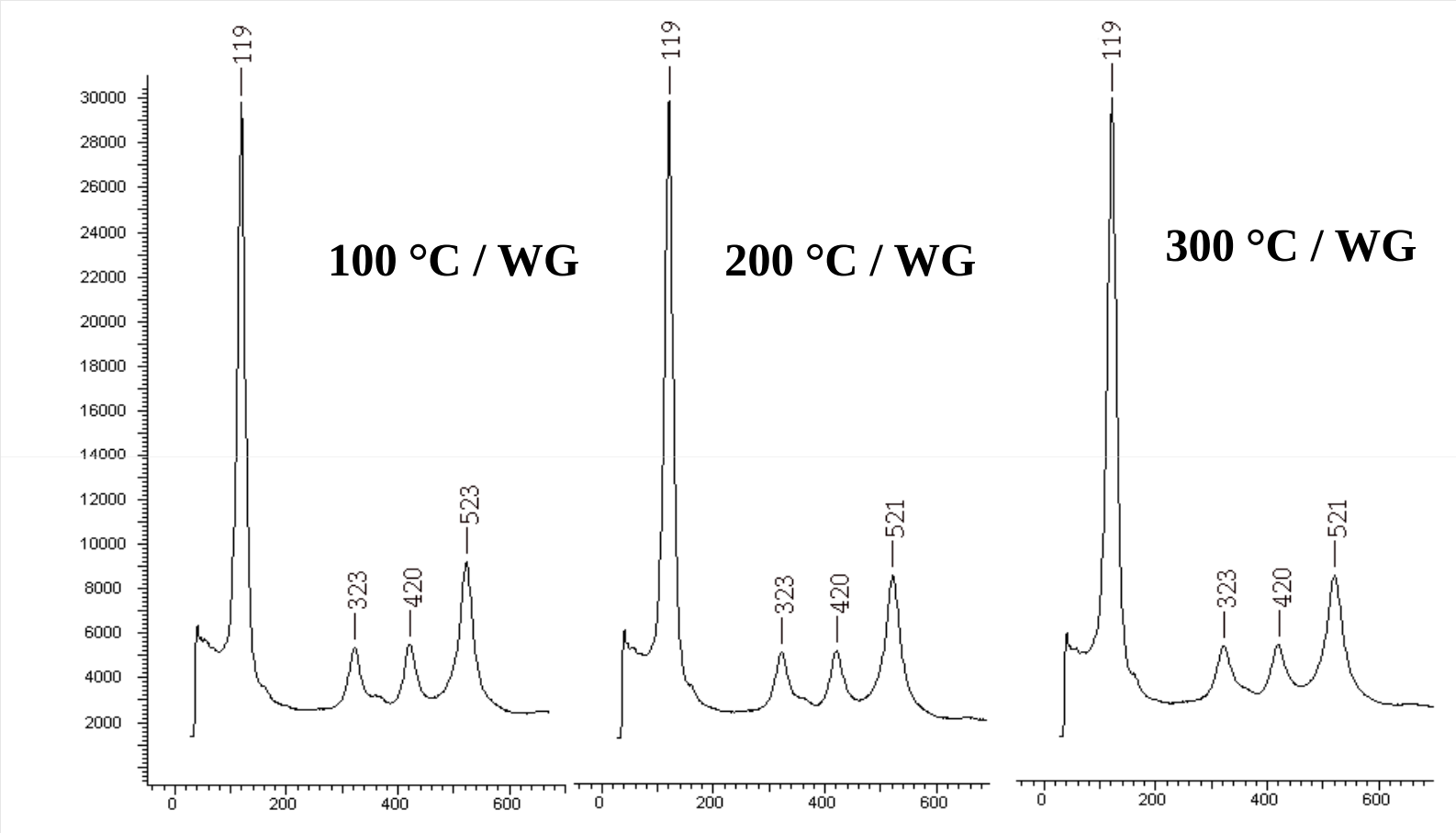
$2CO + O_2 \rightarrow 2CO_2$

TiO_2
(control)





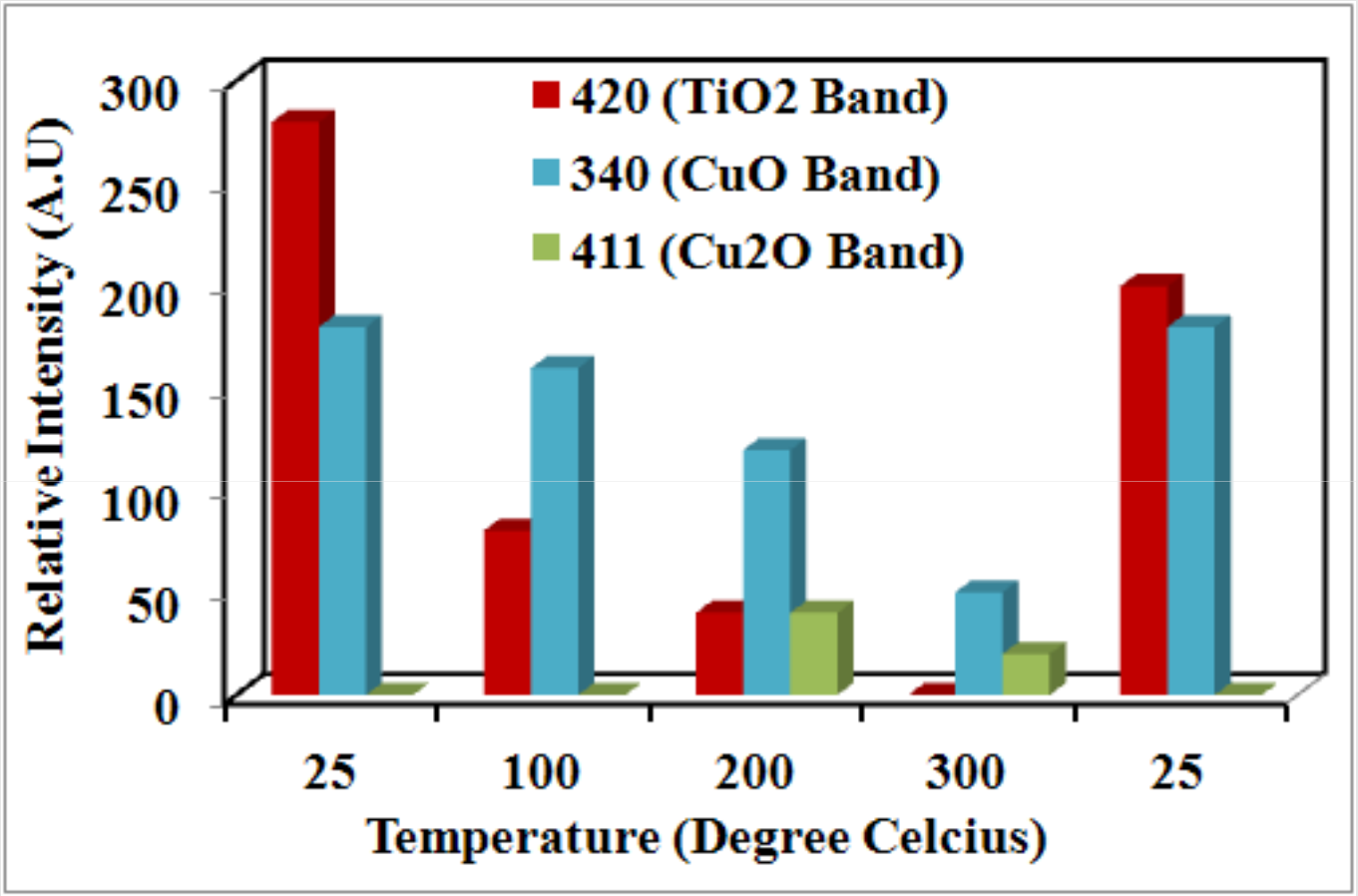
Where is oxygen coming from?



Control experiment:

No change in TiO_2 peak intensity with temperature

Hypothesis: TiO_2 is a oxygen reservoir

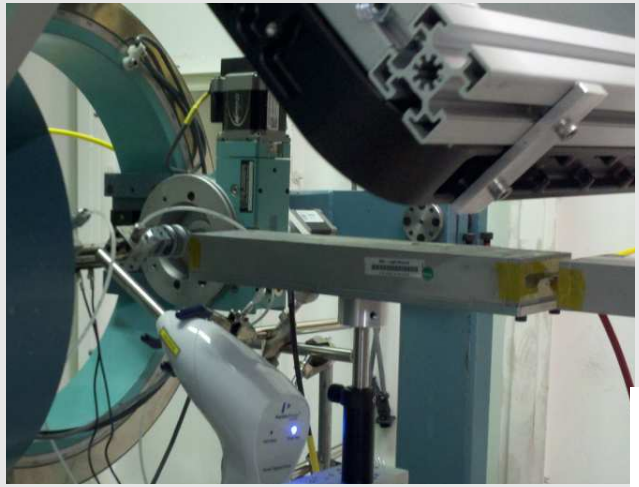


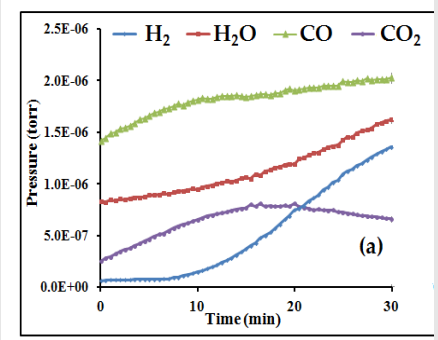
TiO_2 peak intensity decreases faster than CuO

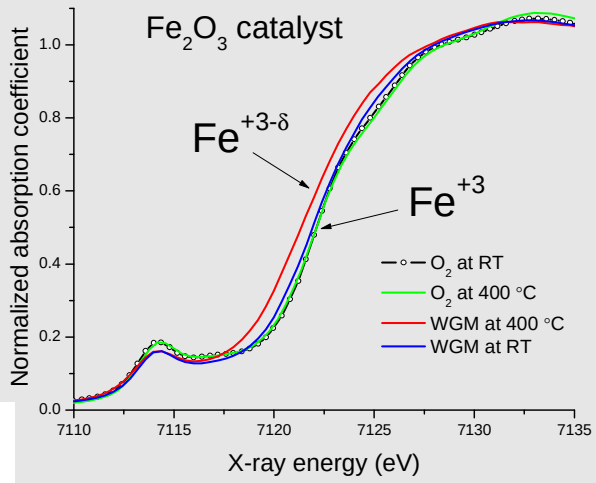
Real catalysts:

Heterogeneity of phases at the length scale of the order of *>10s of nm*.

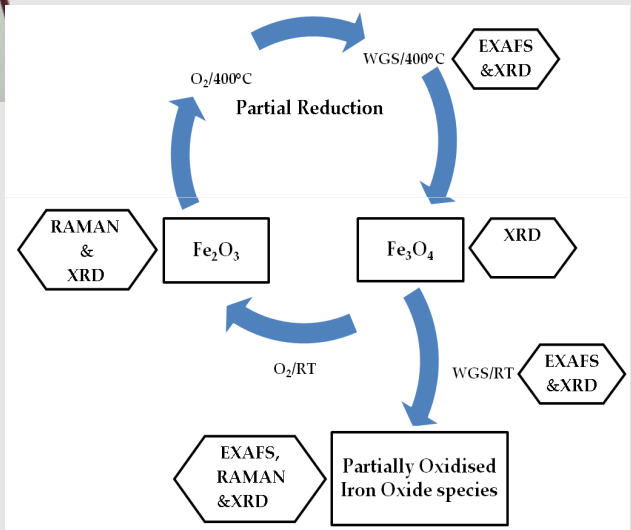
Phase Heterogeneity

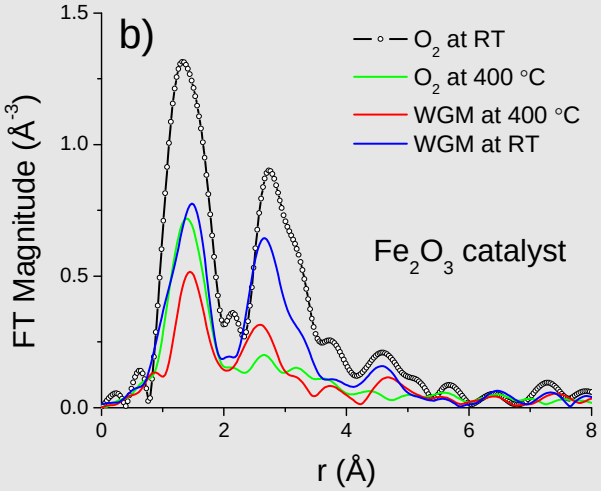


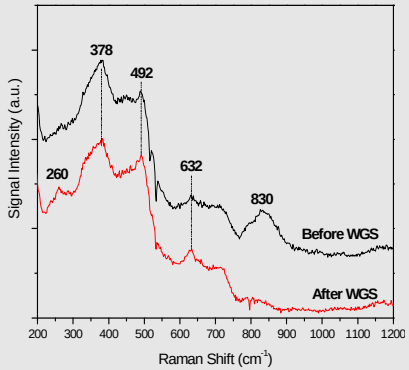


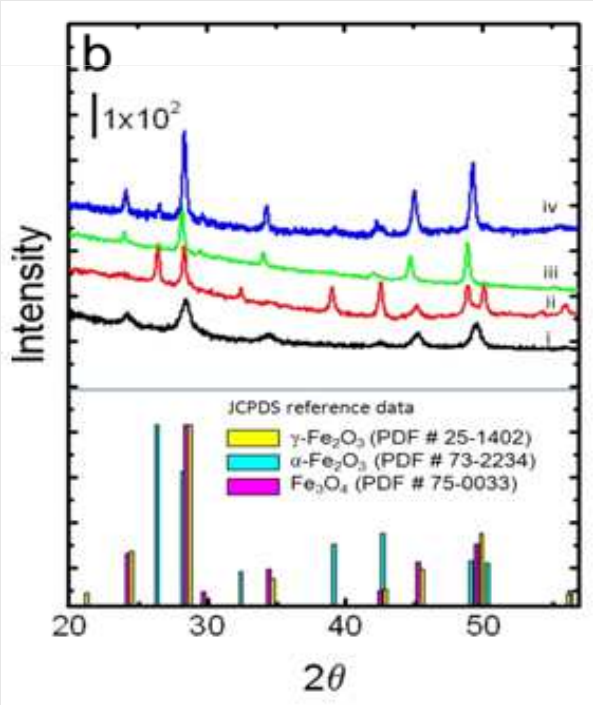


A. Patlolla, et al
(ACS Catalysis, in press)

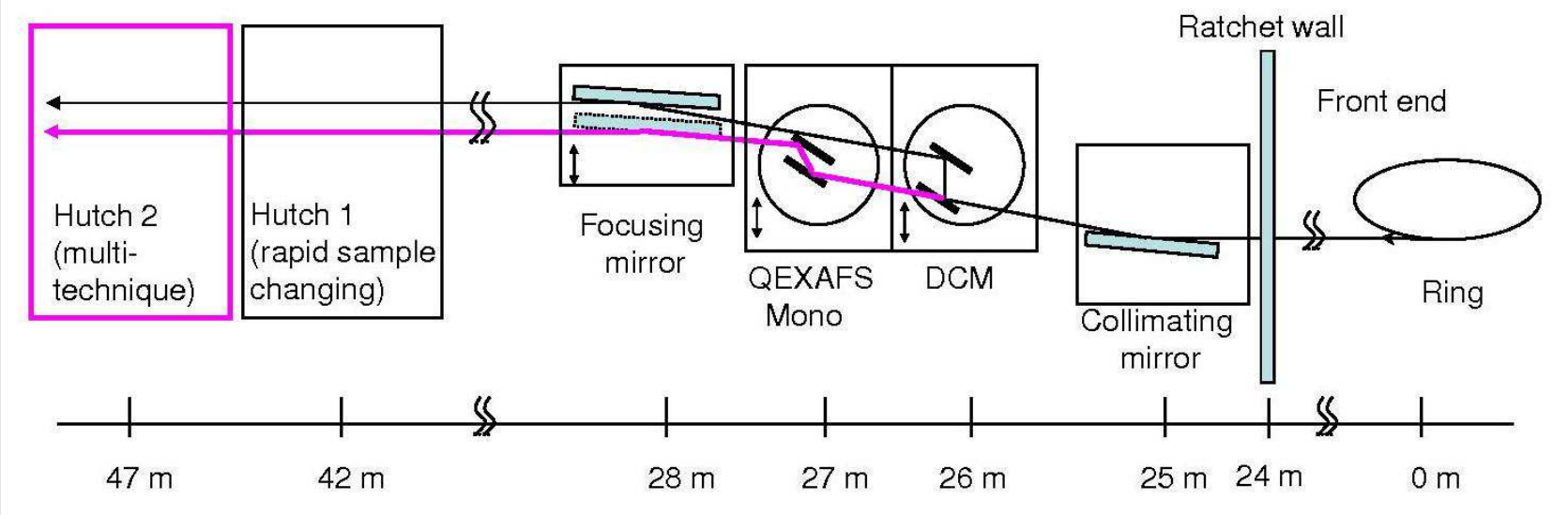


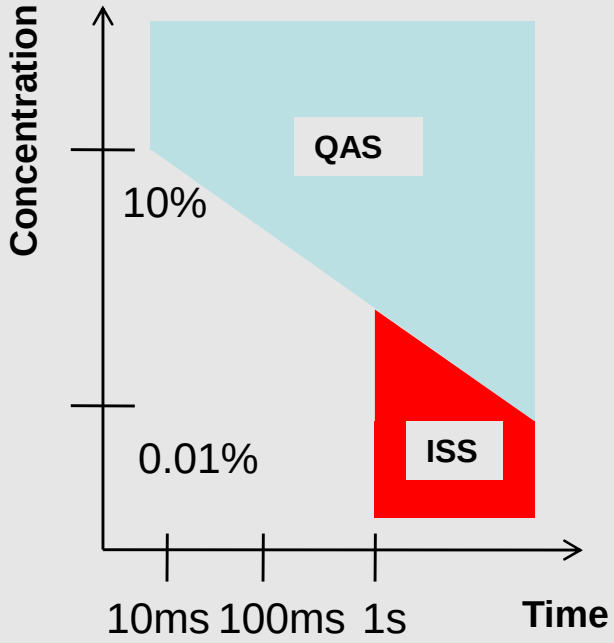






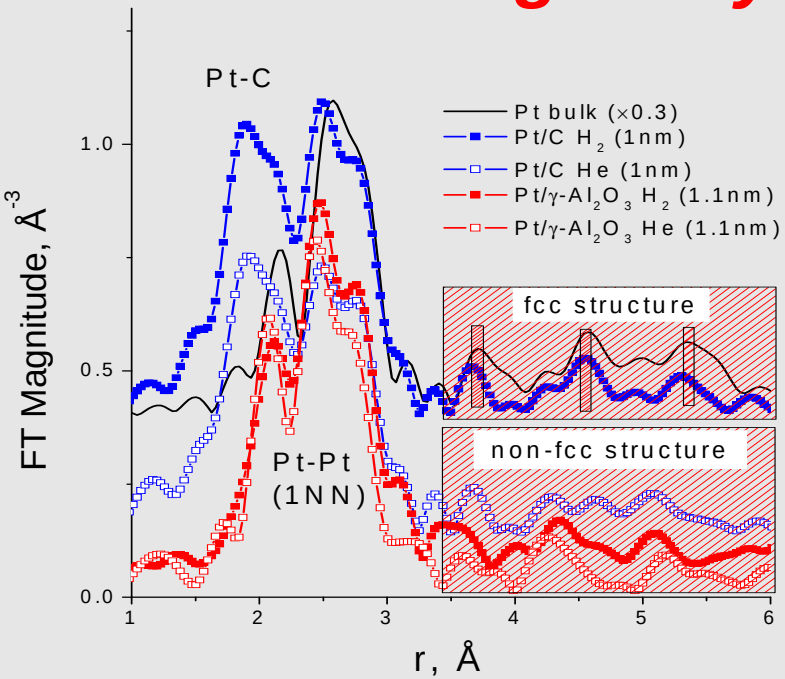
NxtGenQuick Absorption and Scattering (QAS) beamline

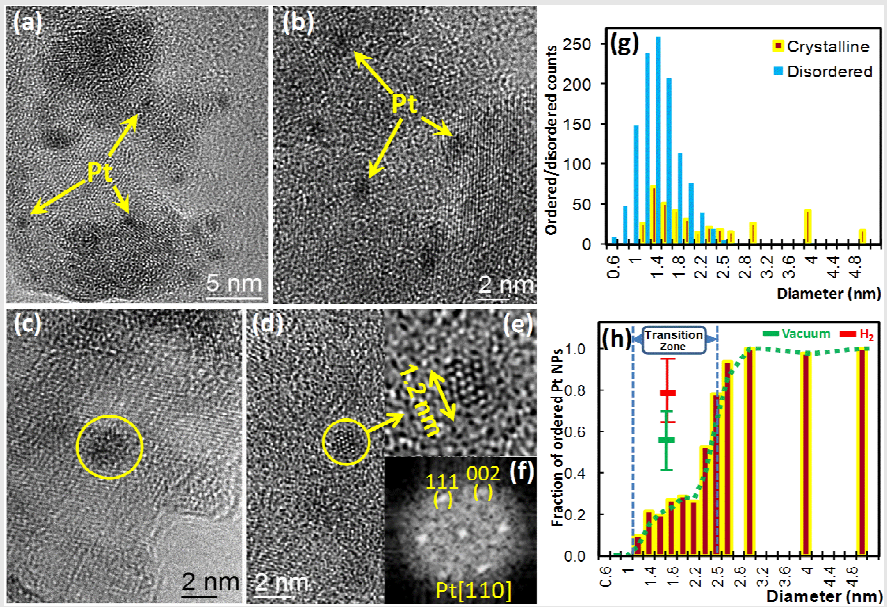


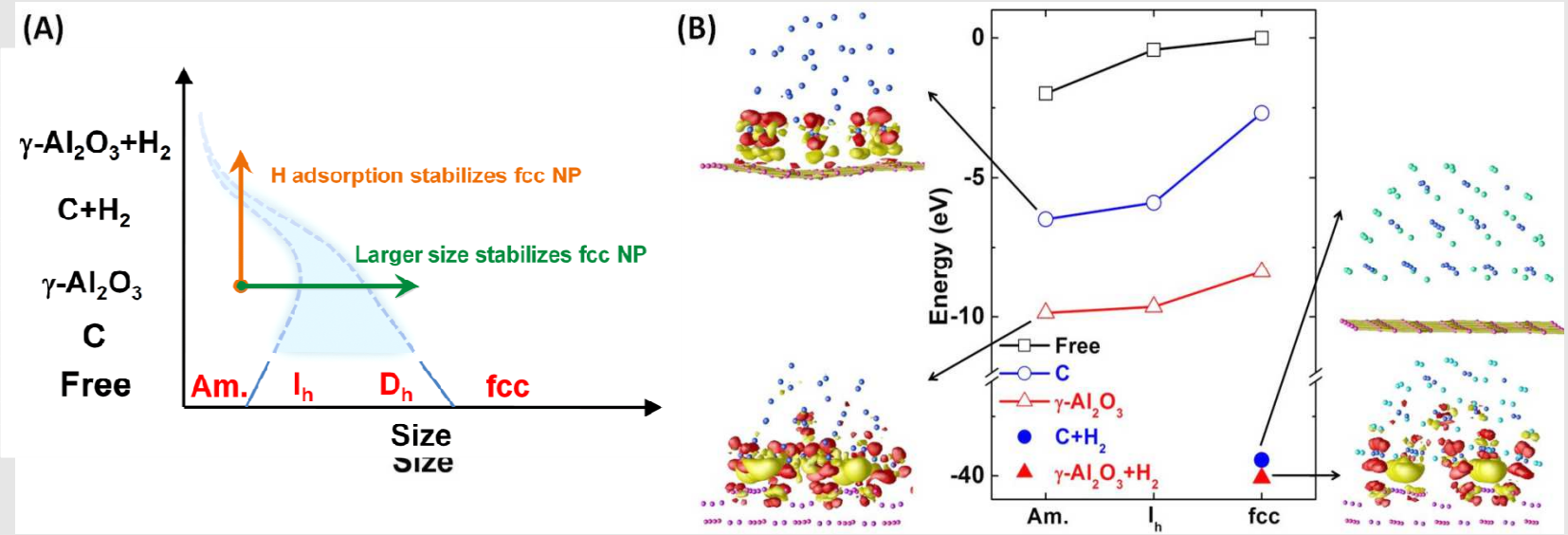


Supported metal catalysts:
Heterogeneity of phases at the length scale of the order of *a few nm*.

Heterogeneity in the short range:



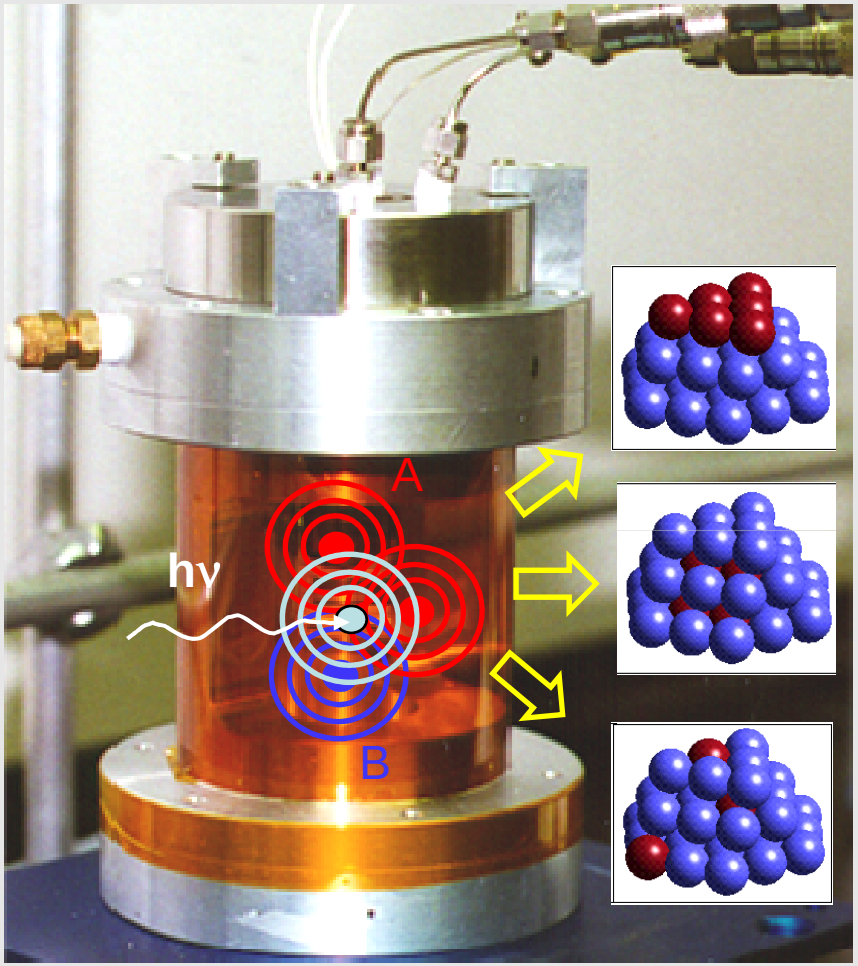




J. C. Yang, D. Johnson, R. G. Nuzzo, A. I. Frenkel, submitted

“Ensemble-average structure”
makes little sense!

Compositional heterogeneity

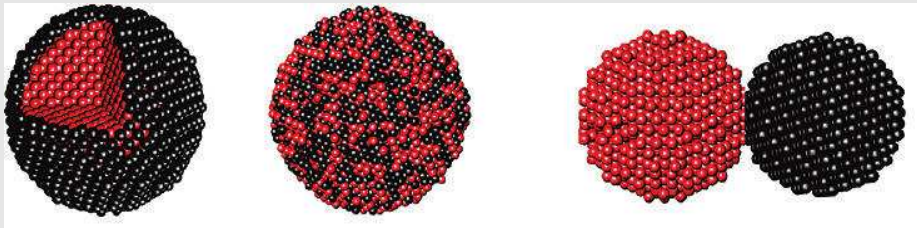


Can bimetallic compositions be analyzed by EXAFS coordination numbers?

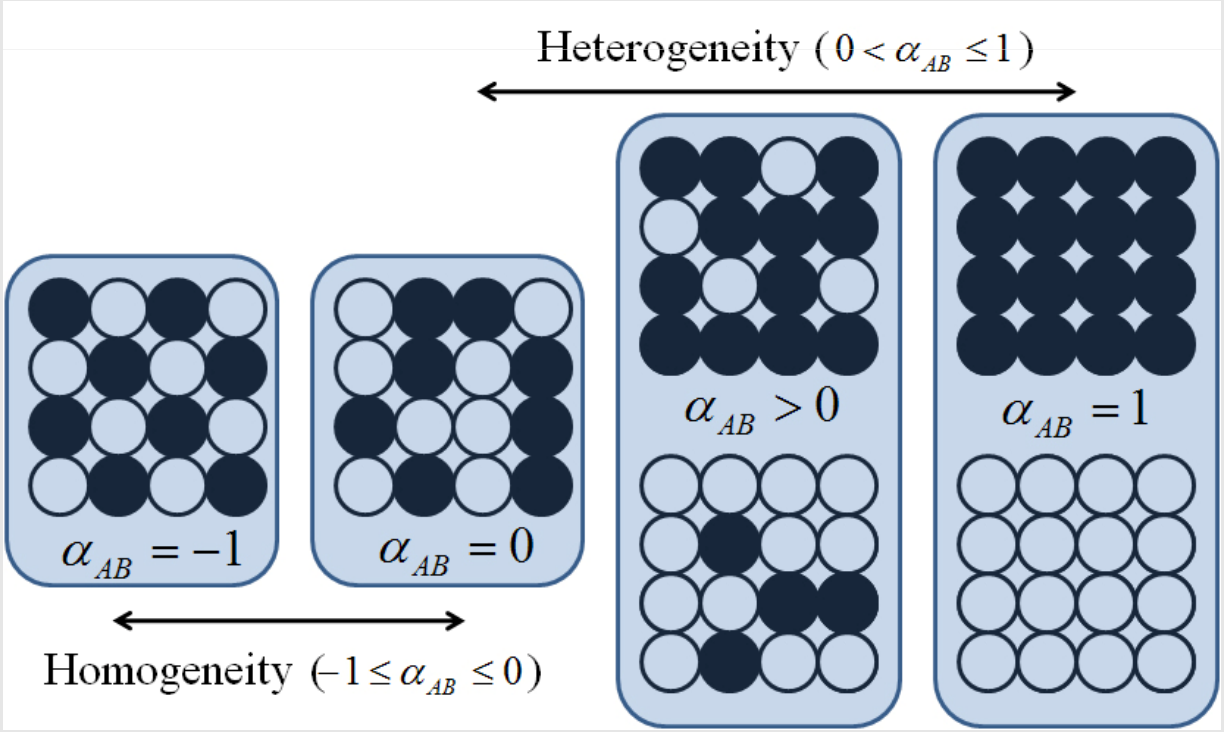
Binary alloys: Homogeneity and SRO in 2D

$$n_{AA} = \frac{2N_{AA}}{N_A} \qquad n_{AB} = \frac{N_{AB}}{N_A} \qquad n_{AM} = n_{AA} + n_{AB}$$

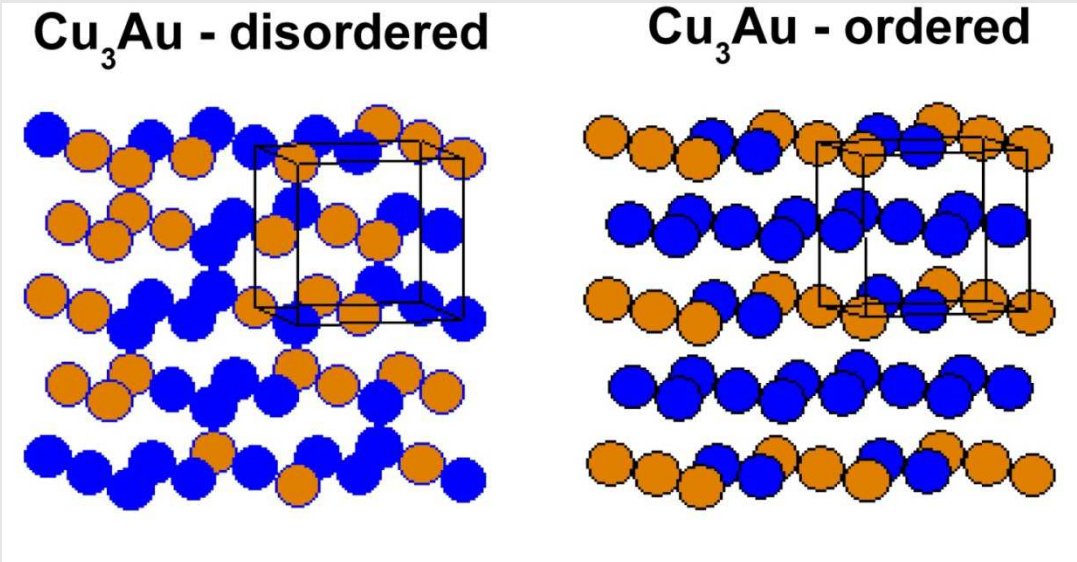
S.R.O. $$\alpha_{AB} = 1 - \frac{n_{AB}/n_{AM}}{x_B}$$

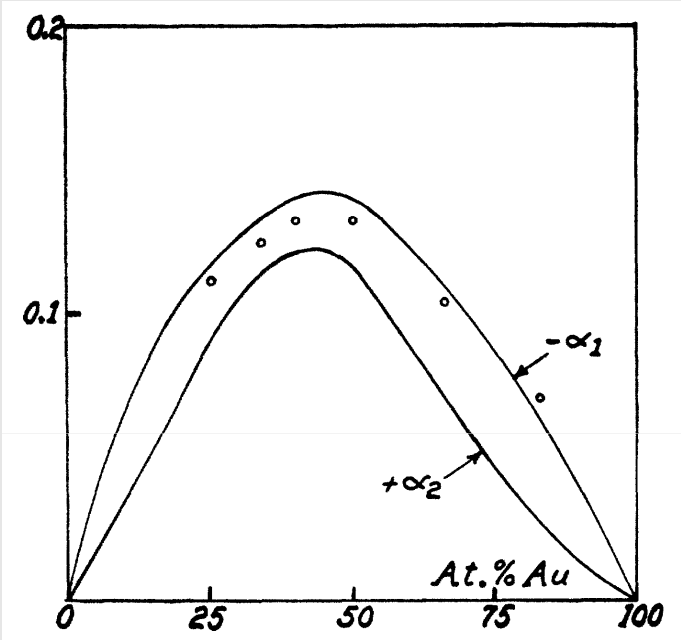


Z. Liu, et al,
J. Am. Chem. Soc., 131, 6924, 2009.



Binary alloys: Homogeneity and SRO in 3D





Homogeneity: $-\frac{1}{3} \leq \alpha_{AB} \leq 0$

J. Cowley,
***Phys. Rev.* 77, 669, 1950**

Effects of compositional heterogeneity on the EXAFS coordination numbers

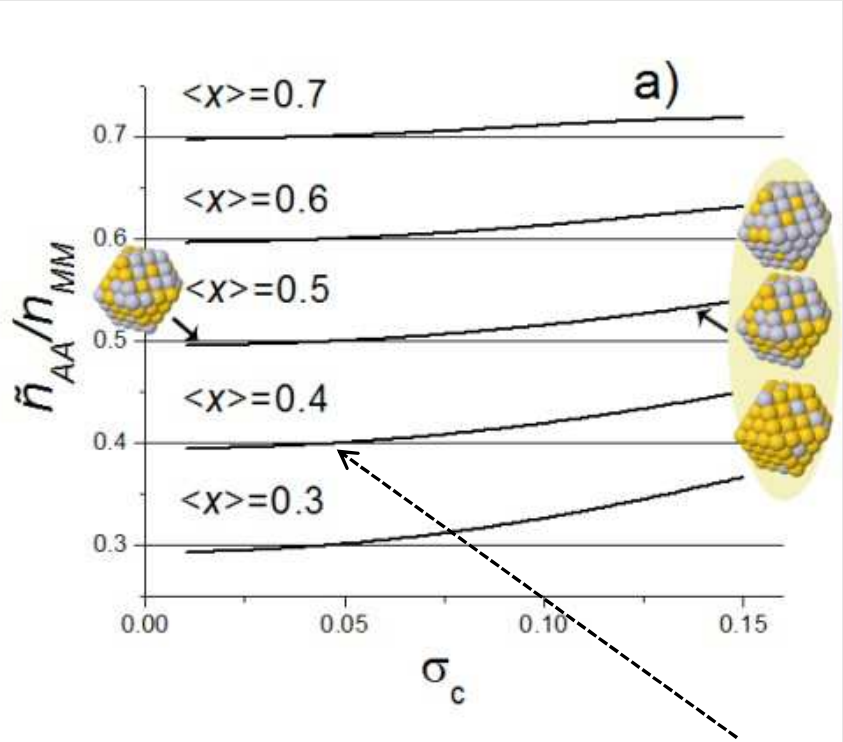
Assume that particles are random alloys (α=0), of the same size (n_{MM}), but have inter-particle compositional disorder:

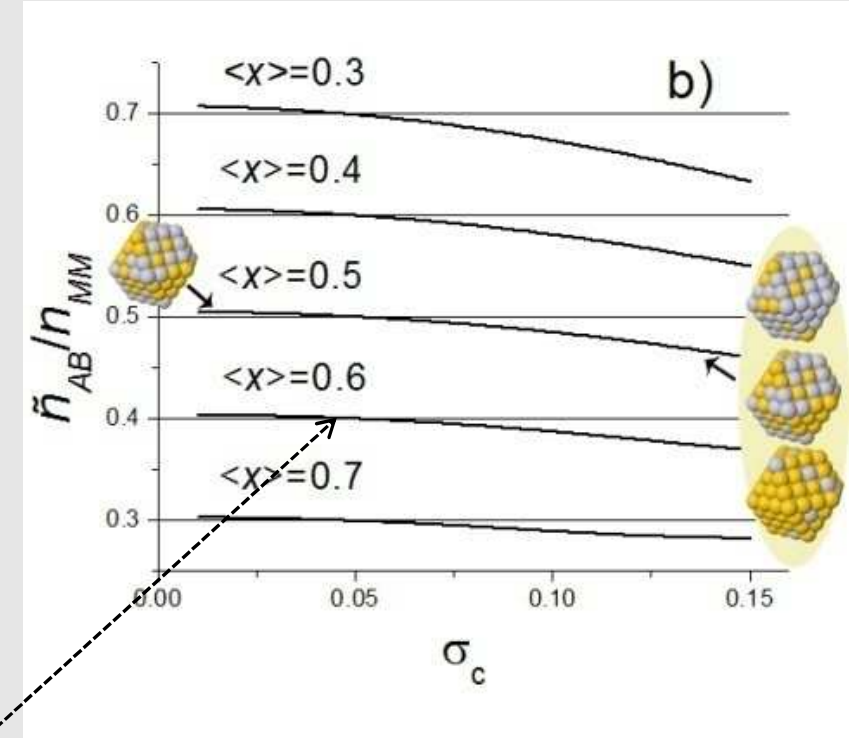
$$\rho(x) \propto \exp\left(-\frac{(x-\bar{x})^2}{2\sigma_c^2}\right)$$

What coordination numbers will be measured in EXAFS experiment?

$$\tilde{n}_{AA} = \frac{\int_0^1 \rho(x)\, x\, n_{AA}(x)\, dx}{\int_0^1 \rho(x)\, x\, dx}$$

Theoretical coordination numbers for clusters of *N* = 100 atoms, calculated assuming Gaussian compositional distribution.





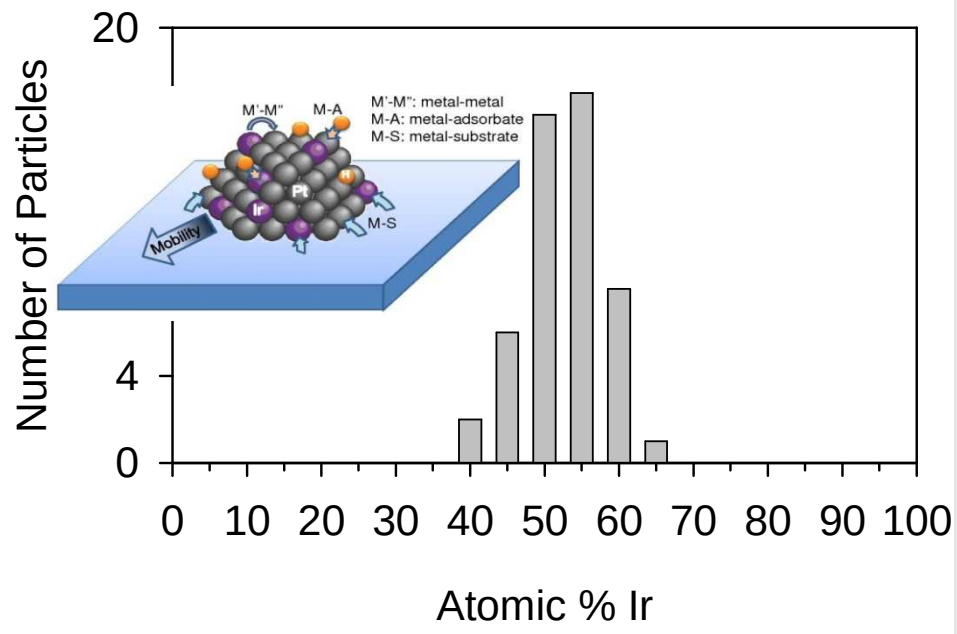
$$\sigma_c = \sqrt{x(1-x)/N}$$

At this value normal distribution coincides with binominal distribution

A. I. Frenkel,
Chem. Soc. Reviews, 2012
DOI: 10.1039/c2cs35174a

How narrow should the cluster composition be for SRO analysis to be reliable?

σ= 0.15 will cause 10-20% error in CN
Well defined clusters have much narrower distributions:



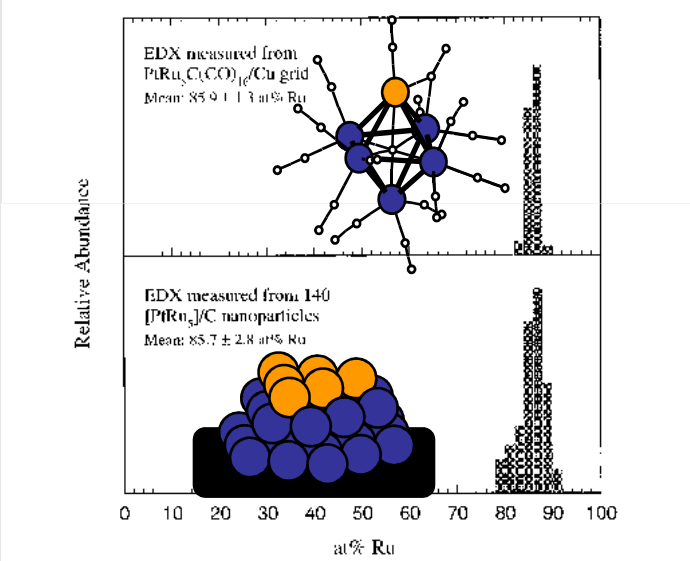
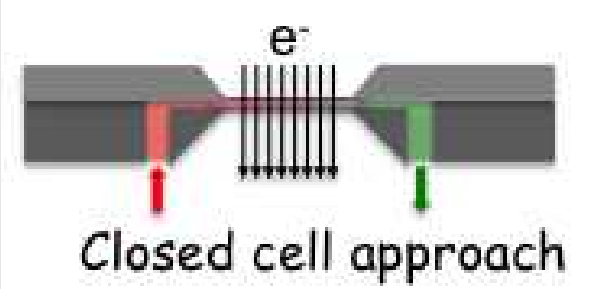


Figure 4. Comparison between the atomic fraction of Pt and Ru determined by quantitatively analyzing the EDX spectra measured from the reference $PtRu_5C(CO)_{16}$ cluster (top) and from 140 $[PtRu_5]/C$ nanoparticles (bottom).

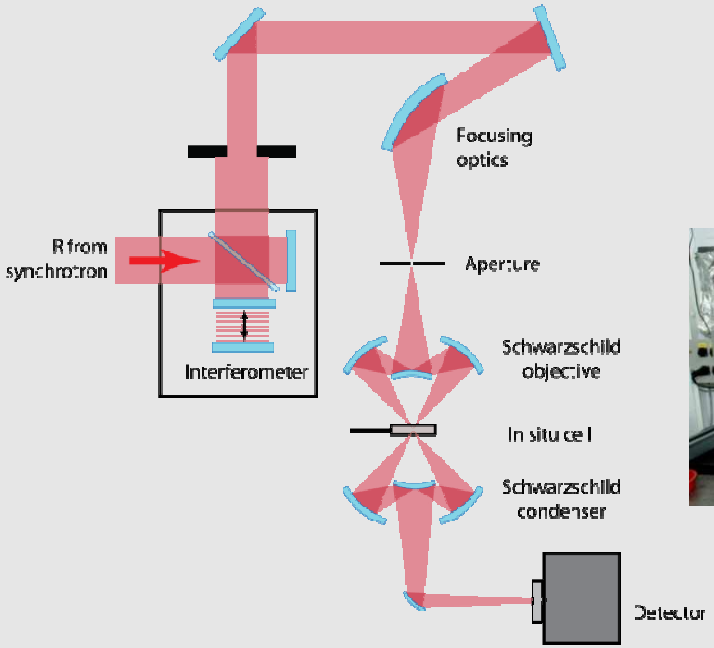
M. W. Small, S. I. Sanchez, L. D. Menard, J. H. Kang, A. I. Frenkel, R. G. Nuzzo
***J. Am. Chem. Soc.* 133, 3582 (2011)**

M. Nashner, A. Frenkel, et al,
***J. Am. Chem. Soc*. 119, 7760 (1997)**

A paradigm shift: a versatile, portable reactor



Electrochemical cell
Gas or liquid cell
Catalytic reactor

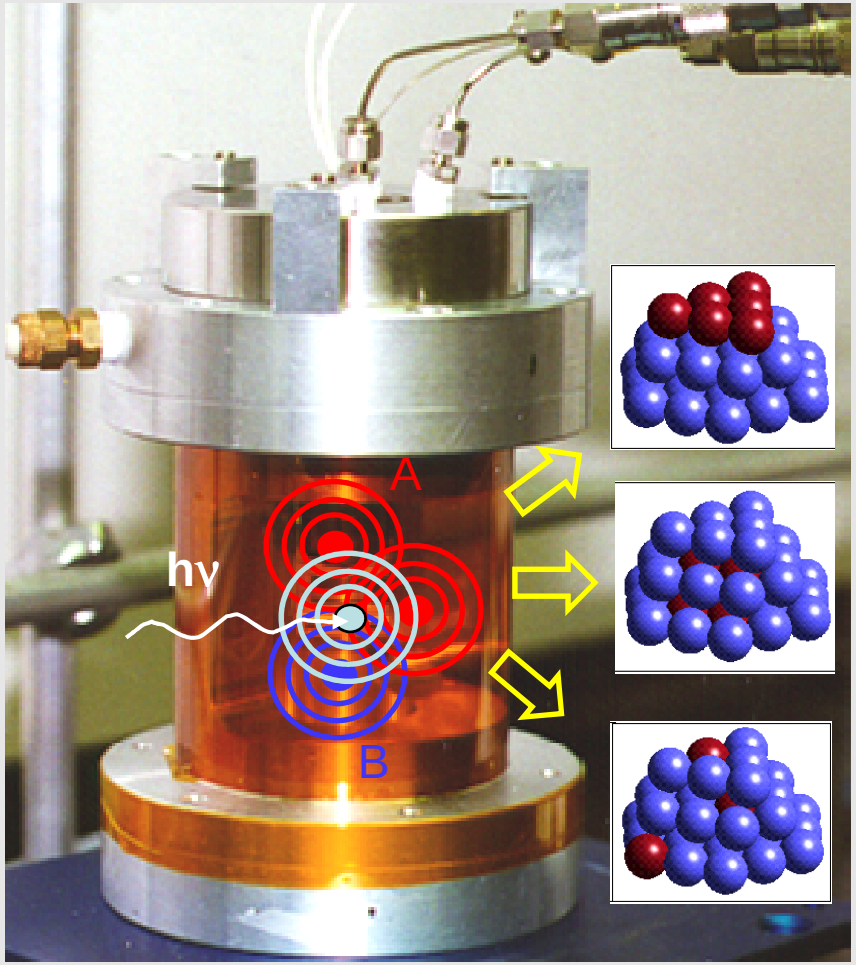


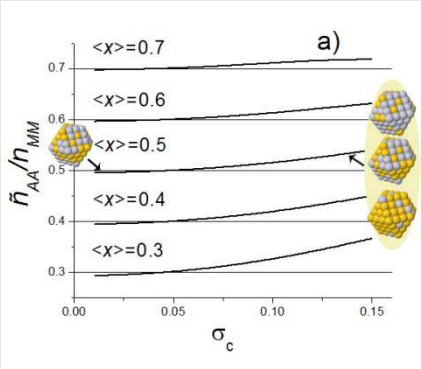
IR Microscope

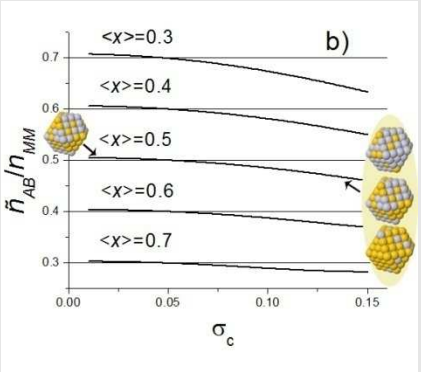
XANES and EXAFS

TEM

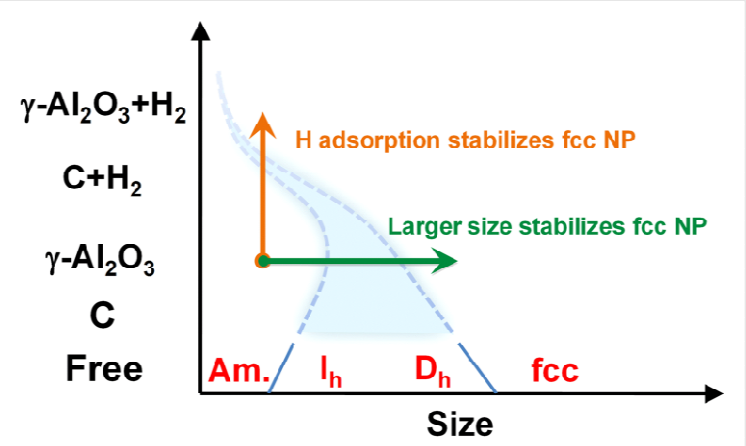
TEM + EXAFS: Local info + ensemble average



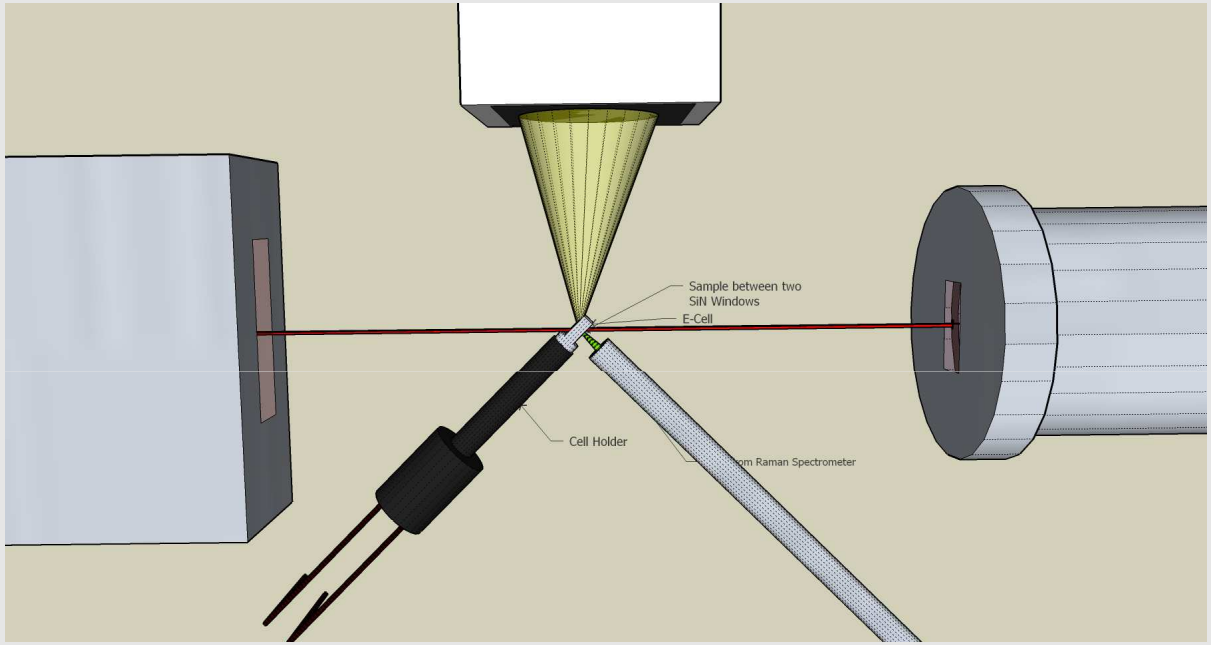




A. Frenkel, A. Yevick, C. Cooper, R. Vasic
Ann. Rev. Anal. Chem. **4**, 23 (2011)

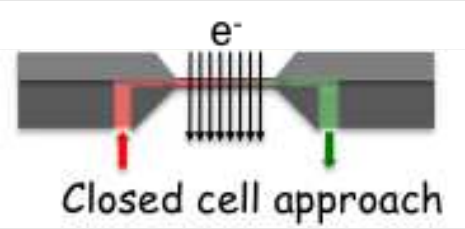


J. C. Yang, D. Johnson, R. G. Nuzzo,
A. I. Frenkel, submitted


Sample between two
SiN Windows
E-Cell
Cell Holder
m Raman Spectrometer

In situ studies of real catalysts by combined XAFS/µ-IR/TEM

-Spectroscopy (XAS, IR), scattering (e-diffraction) and imaging (TEM)
-Short range and long range order (EXAFS & TEM)
-Charge exchange with support (XAS, EELS)
-Core/shell structure (TEM & EXAFS)
-Reactivity studies (IR)

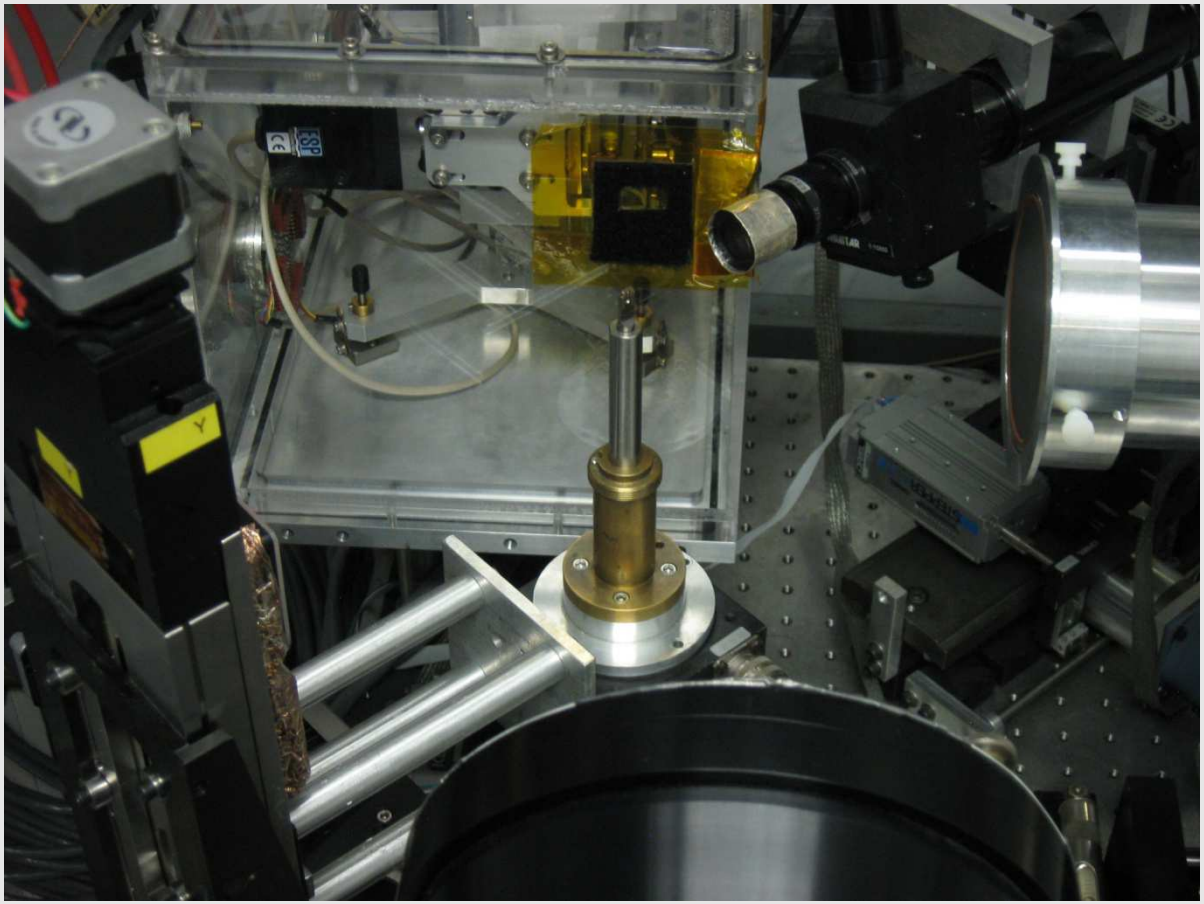


Dimensions:
50µm x 100µm x 1µm
SiN windows:
50nm thick

E. Stach

HUMMINGBIRD SCIENTIFIC

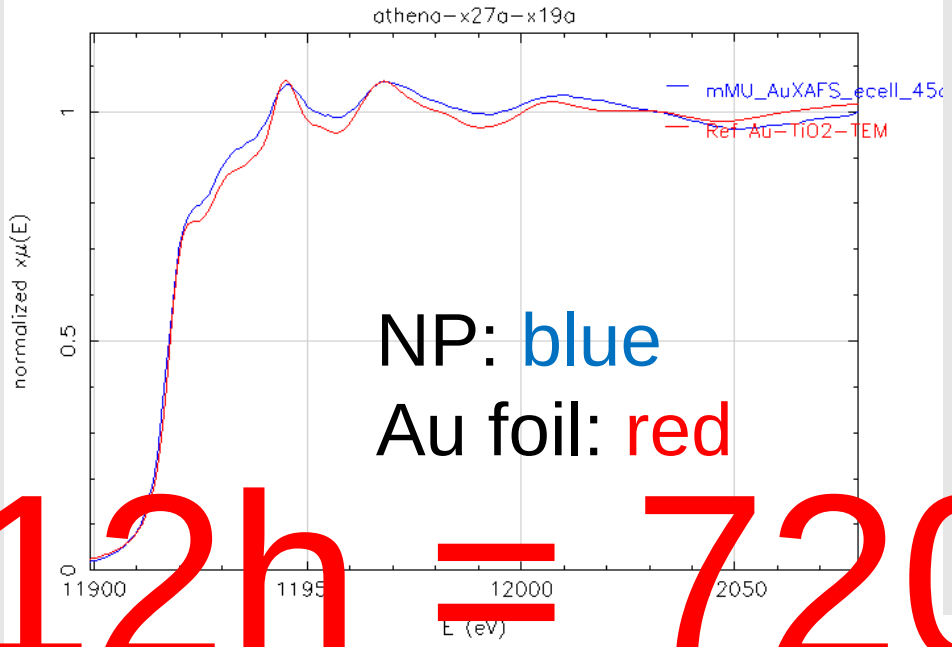
E-cell tested at the microprobe beamline



XAS Experiments at X27A beamline at the NSLS

10μm (KB mirrors) beam

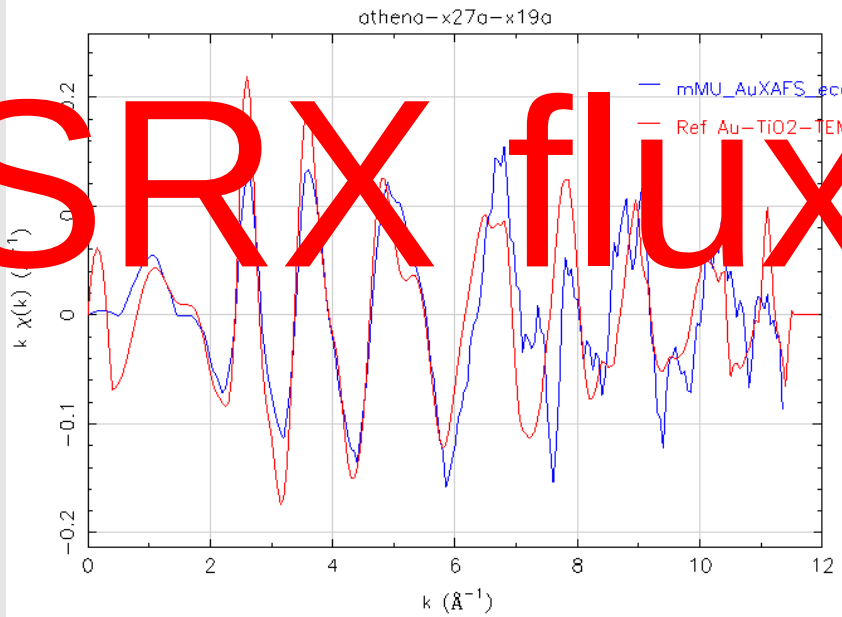
X27A results:

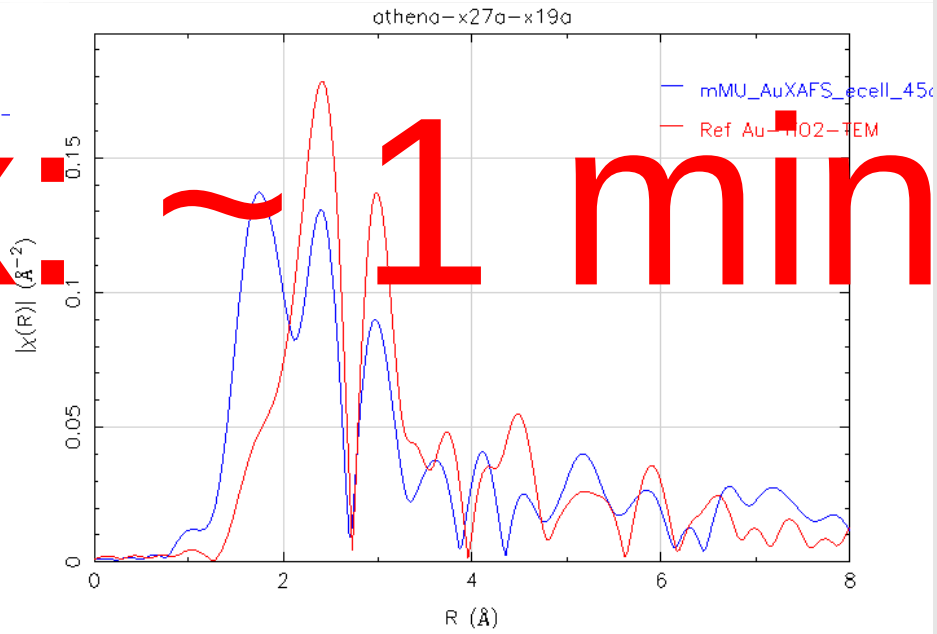


XANES: metallic Au
EXAFS: size effect
Evidence of low Z interaction
(low r peak)
TEM is needed to independently evaluate the size and distribution!

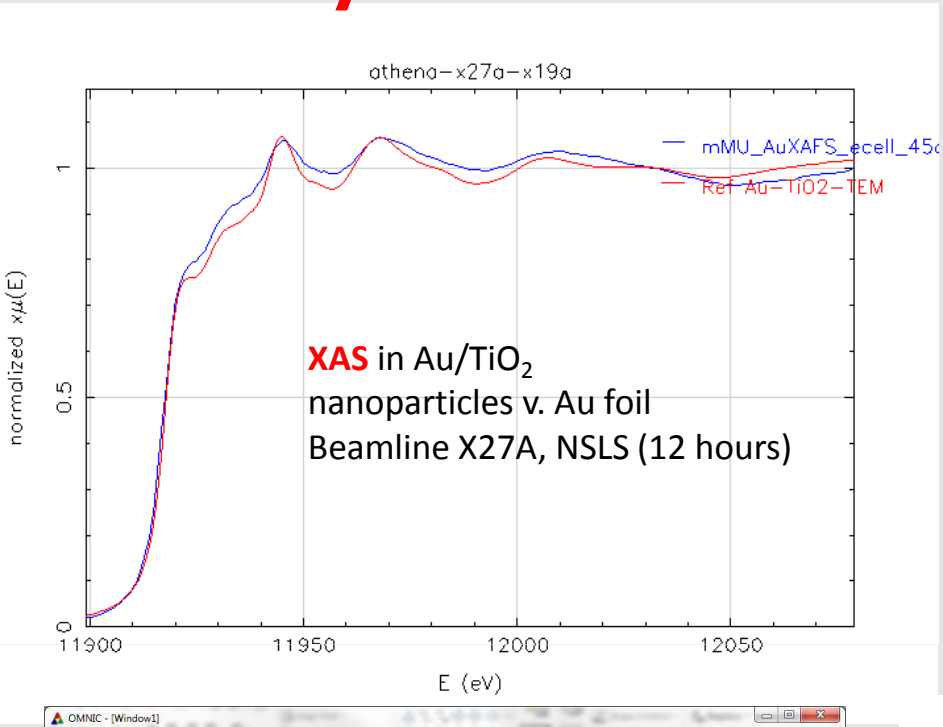
12h = 720 min

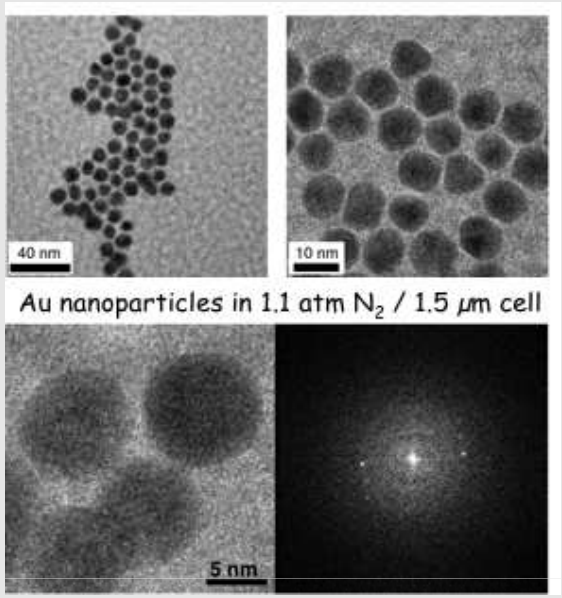
SRX flux: ~1 min



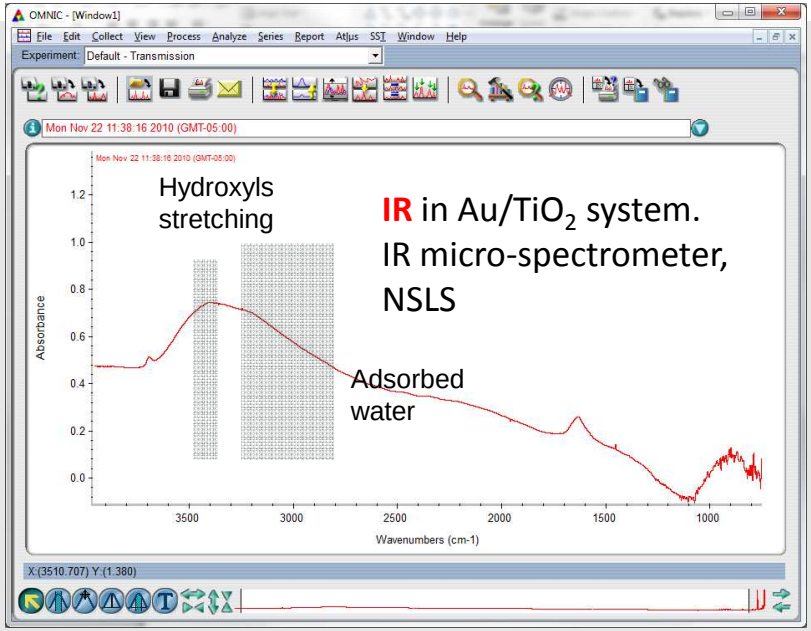


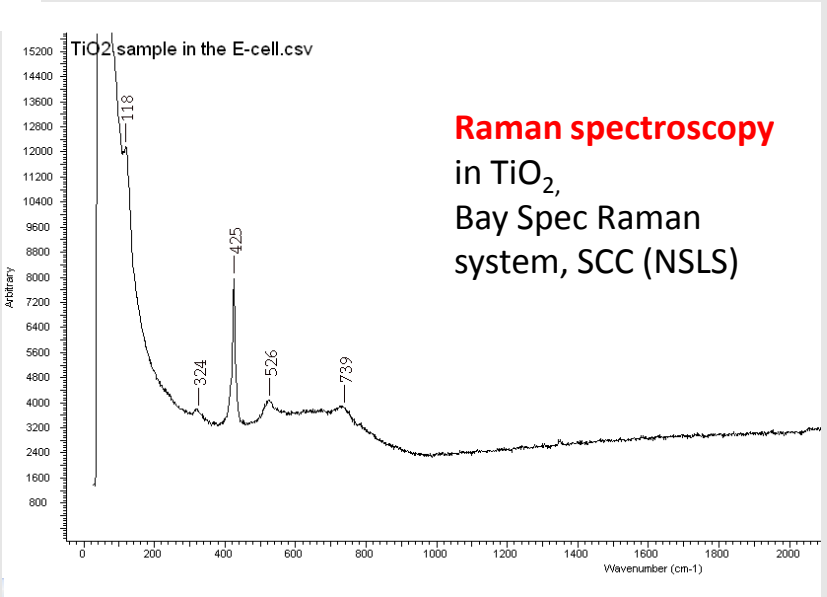
Feasibility tests: XAS+TEM+IR+Raman in the same cell





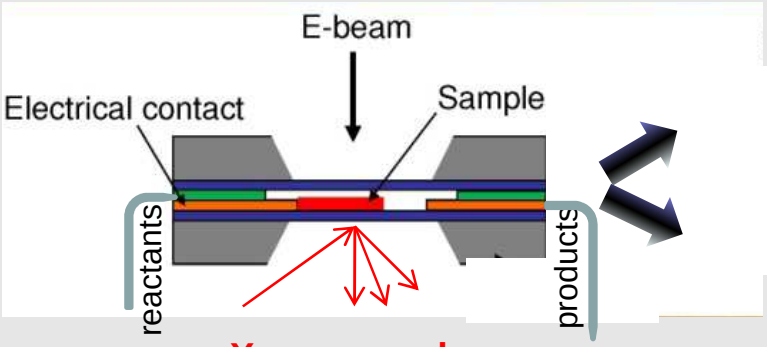
TEM in Au nanoparticles (From Hummingbird Scientific)





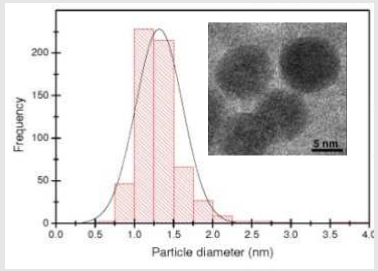
Resolving size and composition heterogeneity effects: In situ studies of real catalysts by combined μ-XAS/TEM

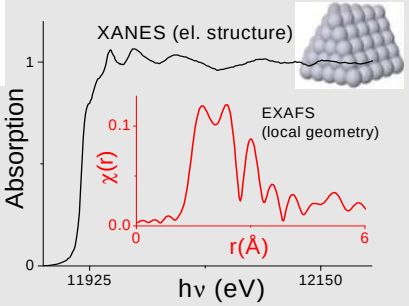
TEM (CFN)



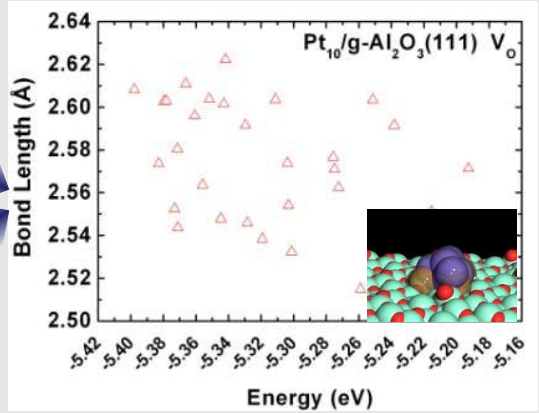
X-ray μ-probe (NSLS-II)

Reaction E-cell





Size (TEM) + Structure (EXAFS)



Theory: MD/DFT/XAS

- ❖Shape-dependent and size-dependent catalysis
- ❖Structure, dynamics and kinetics of real catalysts
- ❖Order-disorder transition in NPs

Chem Soc Rev

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CRITICAL REVIEW

Applications of extended X-ray absorption fine-structure spectroscopy to studies of bimetallic nanoparticle catalysts†

Anatoly I. Frenkel*

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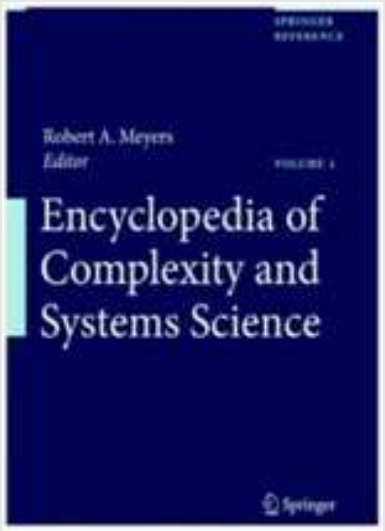
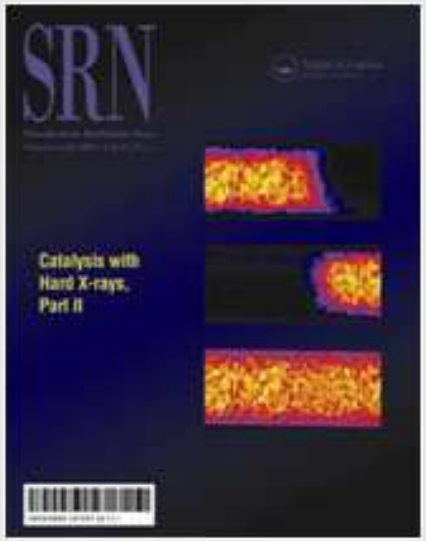
Extended X-ray absorption fine structure (EXAFS) spectroscopy has been used to study short range order in heterometallic alloys for almost four decades. In this *critical review*, experimental, theoretical and data analytical approaches are revisited to examine their power, and limitations, in studies of bimetallic nanocatalysts. This article covers the basics of EXAFS experiments, data analysis, and modelling of nanoscale clusters. It demonstrates that, in the best case scenario, quantitative information about the nanocatalyst's size, shape, details of core–shell architecture, as well as static and dynamic disorder in metal–metal bond lengths can be obtained. The article also emphasizes the main challenge accompanying such insights: the need to account for the statistical nature of the EXAFS technique, and discusses corrective strategies.





AIF, J. Yang, R. Nuzzo, D. Johnson, 2009

Special issues on catalysis with hard X-rays, 2009

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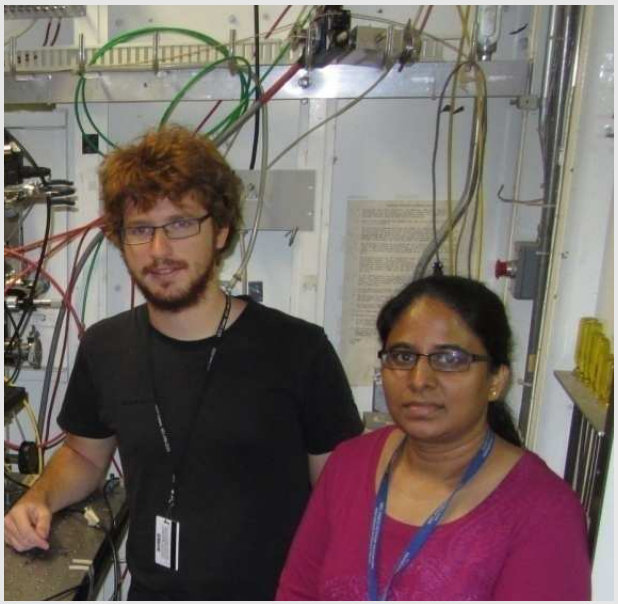

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