In situ/operando SCC Capabilities and Catalysis Examples

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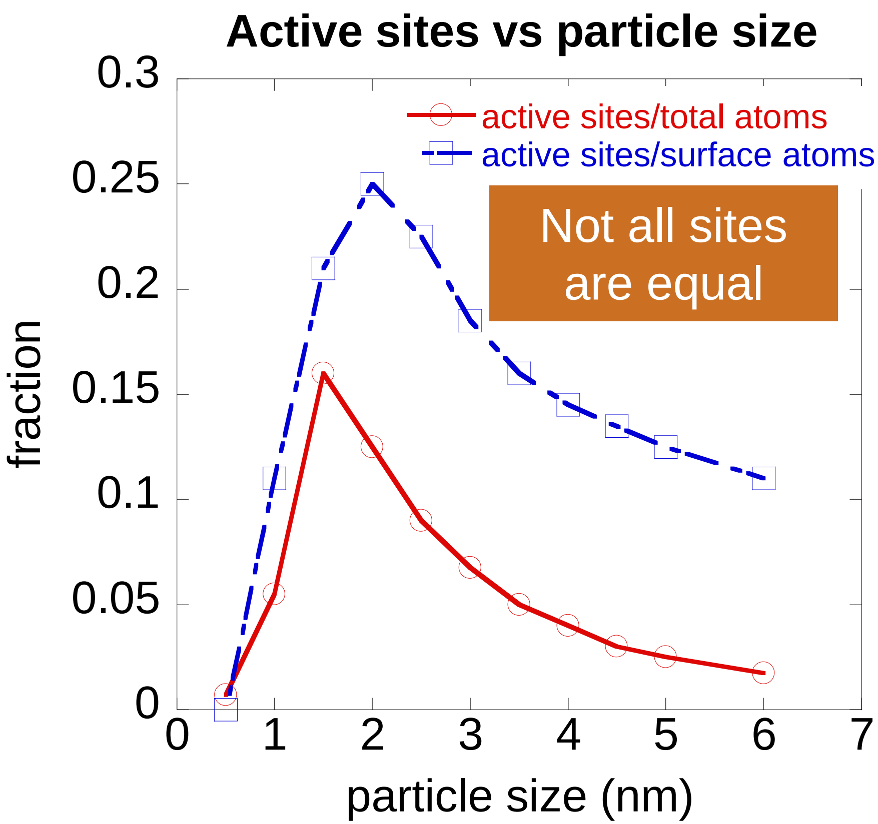
Invent the Future

YESHIVA UNIVERSITY synchrotron^3 catalysis CONSORTIUM UNIVERSITY OF DELAWARE

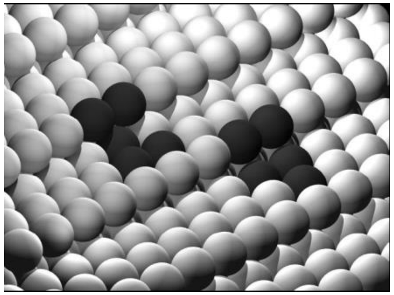
Methods and Applications of X-Ray Absorption Fine Structure Spectroscopy, BNL, November 14, 2014.

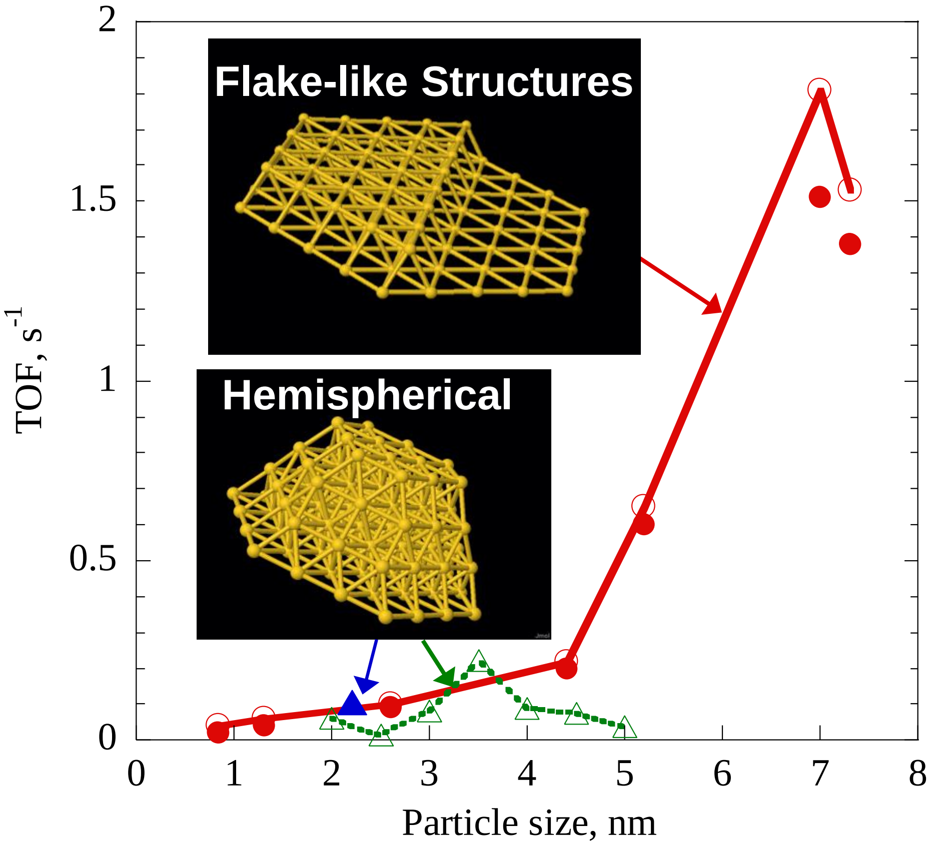
Catalysis: Surface Phenomenon



B_5 step sites on Ru hemispherical particles

B_5 step sites on Ru (0001)

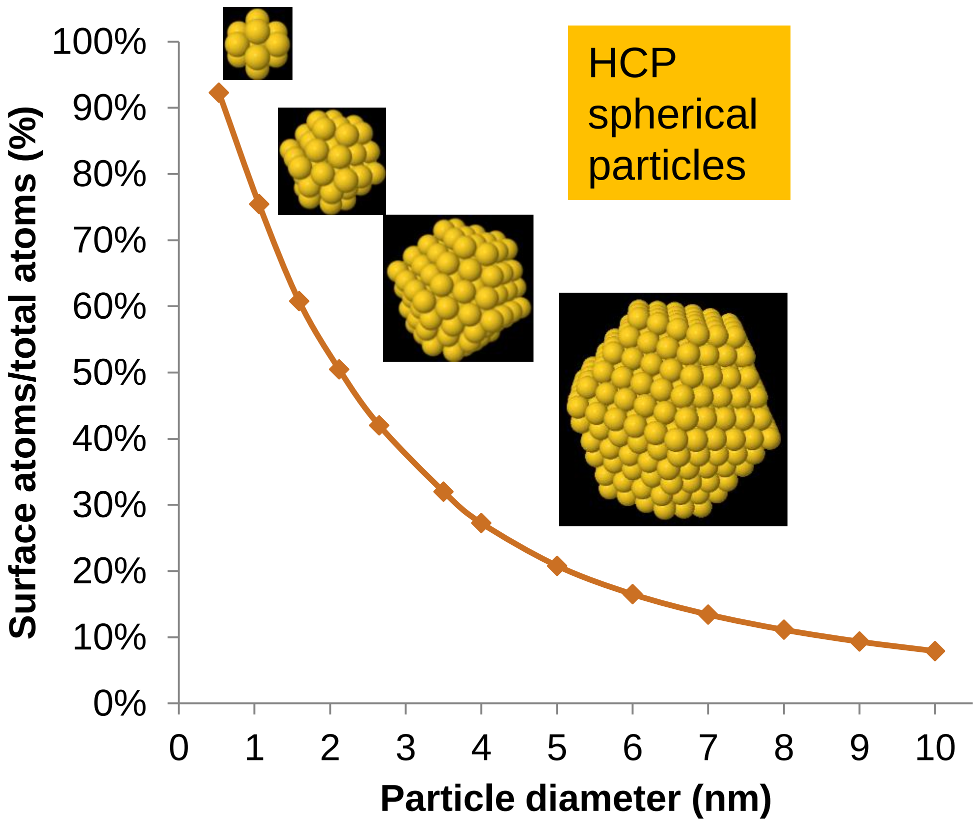


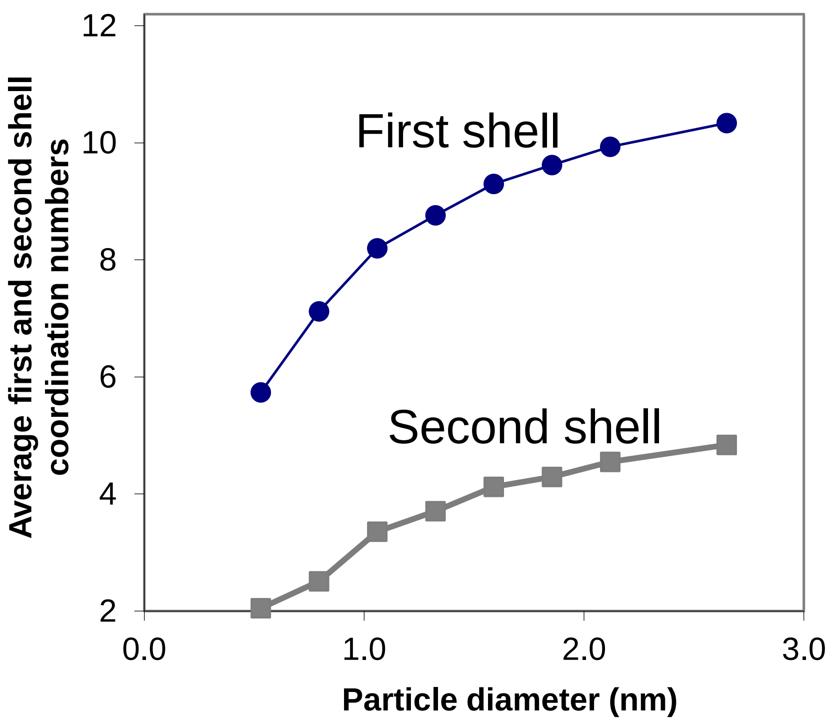


Jacobsen *et al.*, *J. Mol. Cat., A: Chem.* **163** (2000)
Gavnholt *et al., Phys. Rev. B* **77** (2008)
Raróg-Pilecka *et al*., J. Catal., **231** (2005)
Karim *et al.*, *JACS,* **2009,** *131,* 12230

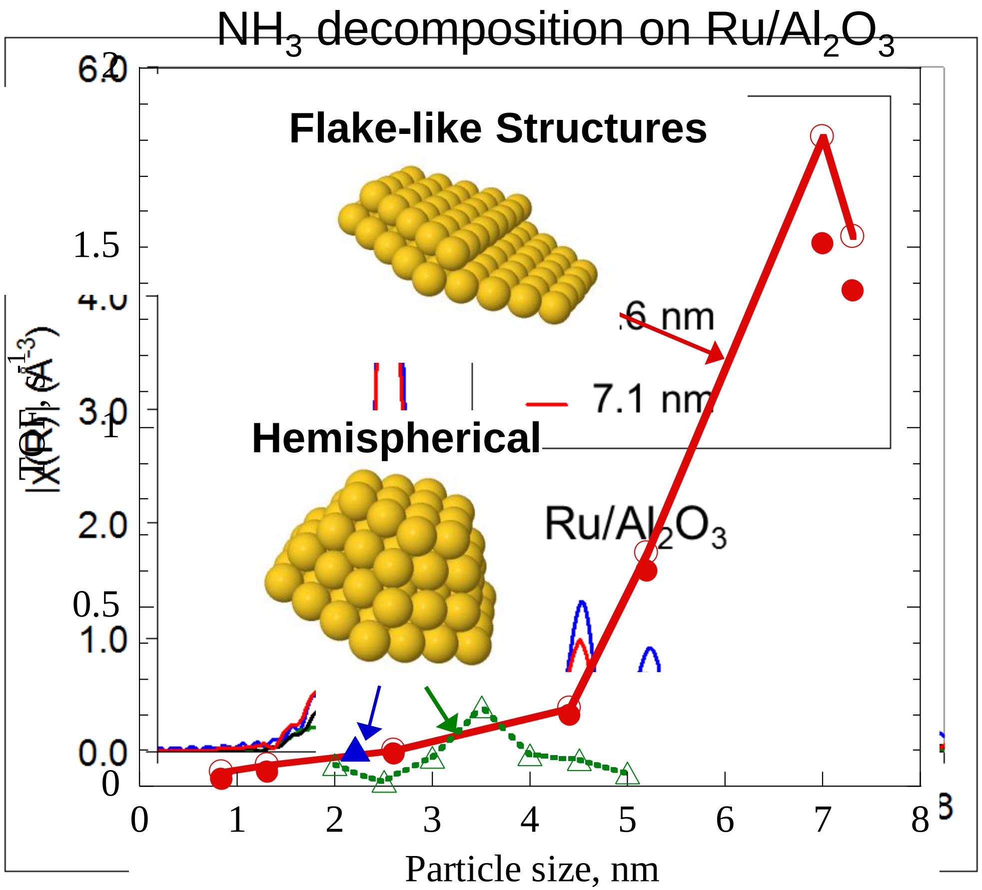
XAFS: Bulk technique for Catalysis?

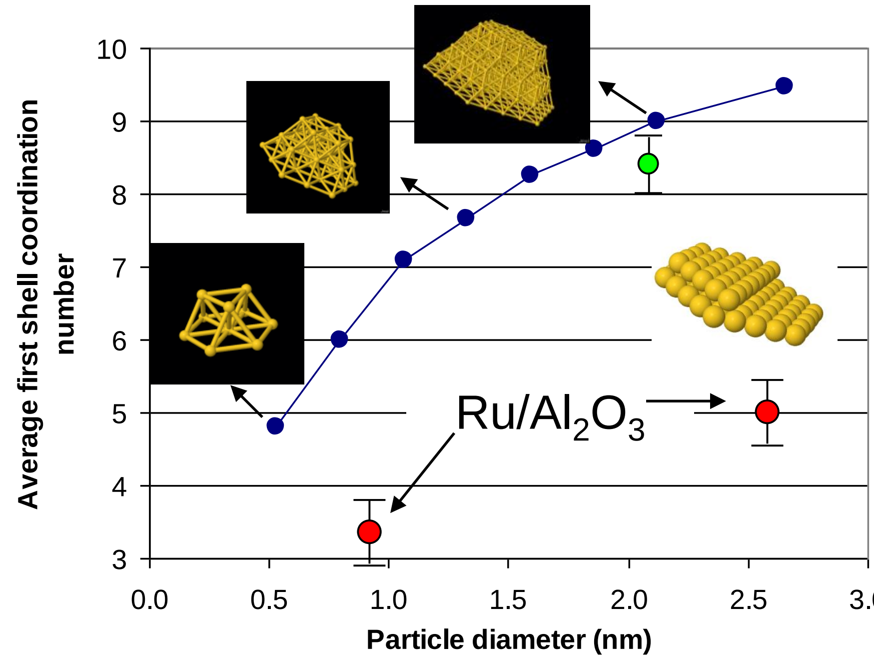
- XAS is a bulk technique while catalysis is a surface phenomenon.
- For small particles, a large fraction of the atoms are on the surface.





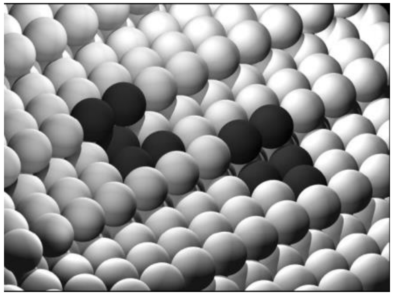
XAFS for Catalysis: Extremely Valuable *in situ/operando* Technique





Average first shell coordination number for hemispherical particles

- Particle size, shape and composition
- Surface structure can be extracted for small particles.



B_5 step sites on Ru (0001)

Jacobsen *et al.*, *J. Mol. Cat., A: Chem.* **163** (2000)

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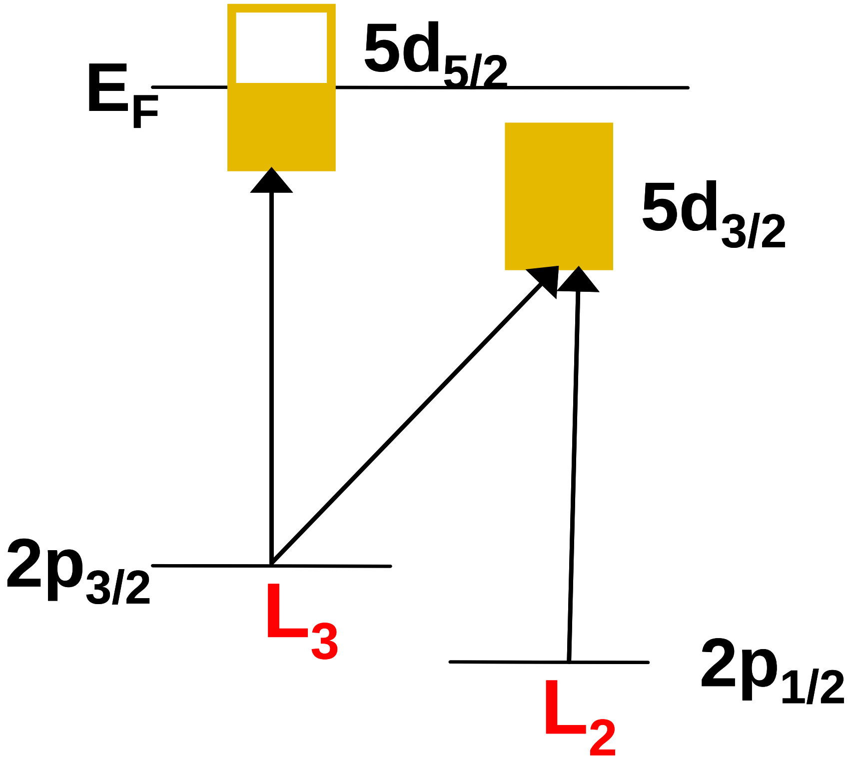
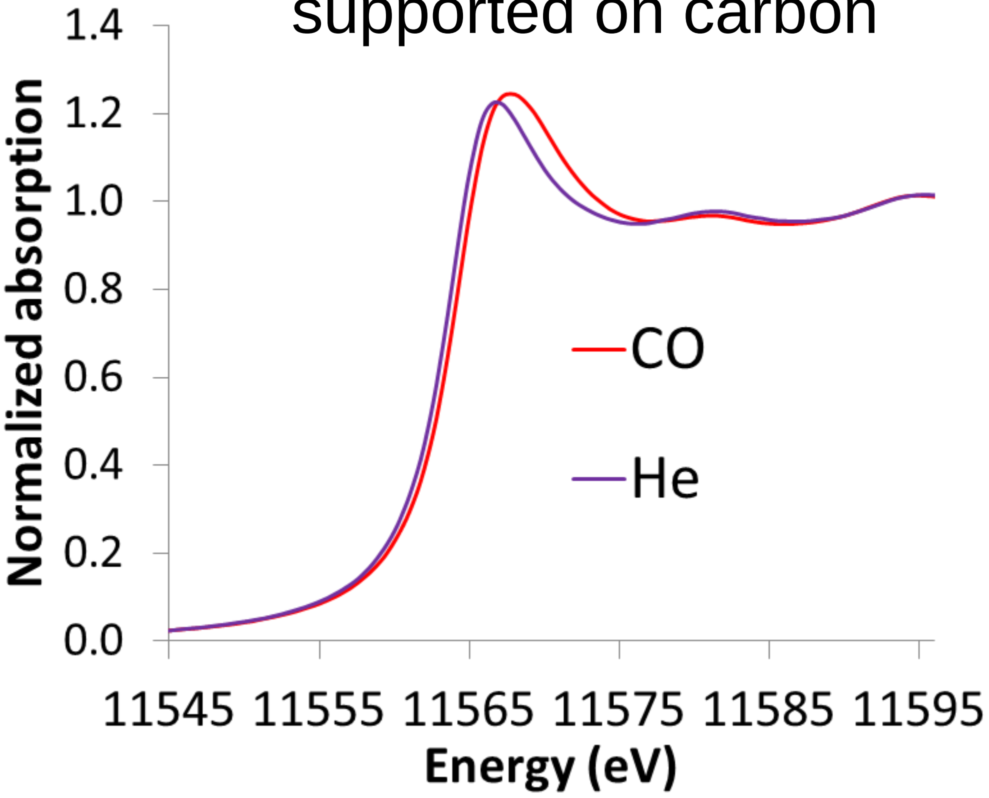
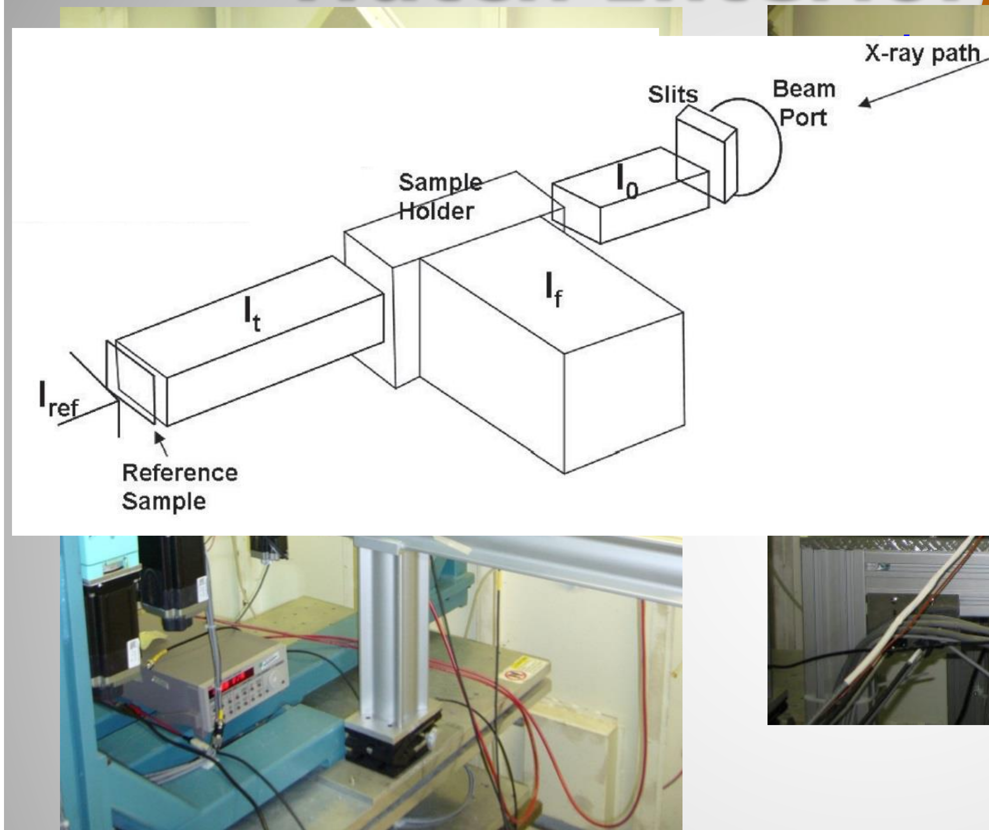
Identification of Adsorbates

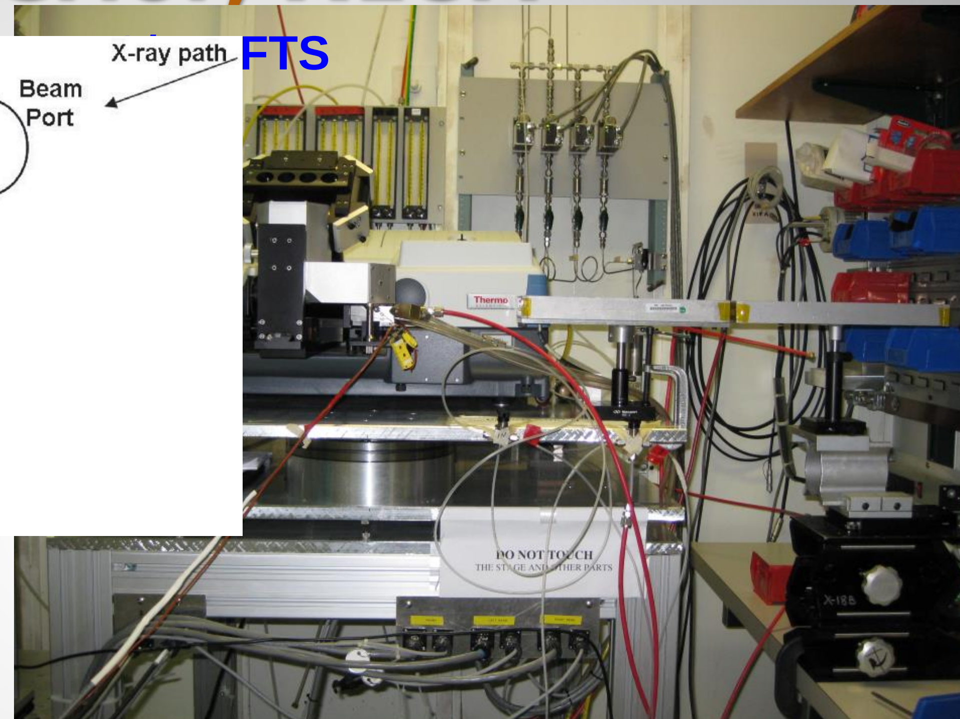


2nm Pt nanoparticles supported on carbon



Hutch Interior, X18A

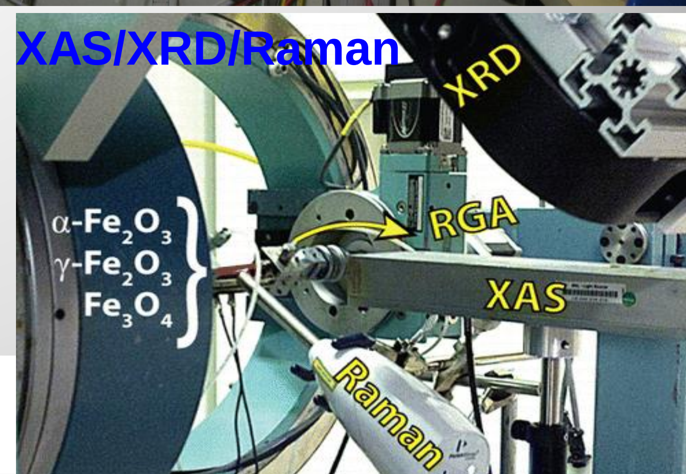




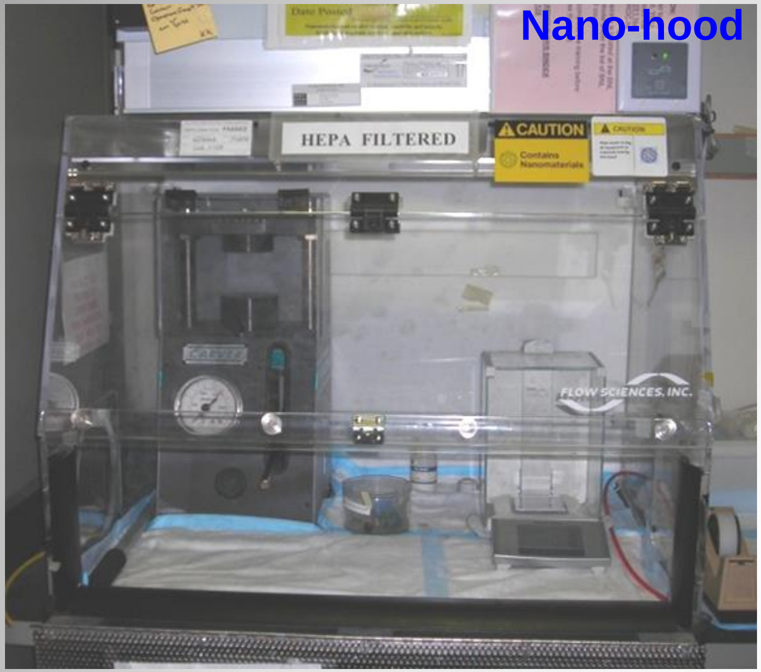
Hutch equipped for XAS, XRD and mass spectrometer (RGA).

5.7-24keV
Bending magnet
Channel cut Si(111) monochromator
Quick-XAS capable

Raman or DRIFTS instruments are moved into the hutch when needed. They can be also used as stand-alone techniques.



Supporting Equipment: Nanomaterial handling stations



Preparation of nanomaterials are done in Nano-hood and Nano-glove box.

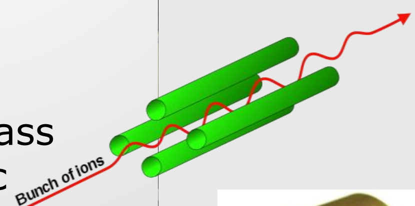
Equipment for heterogeneous catalysis: MFC/RGA

Mass Flow Controllers and Residual Gas Analyzer may be used with DRIFTS and Raman instruments for synchrotron ex-situ trials.

Gas reaction inlet: MFCs

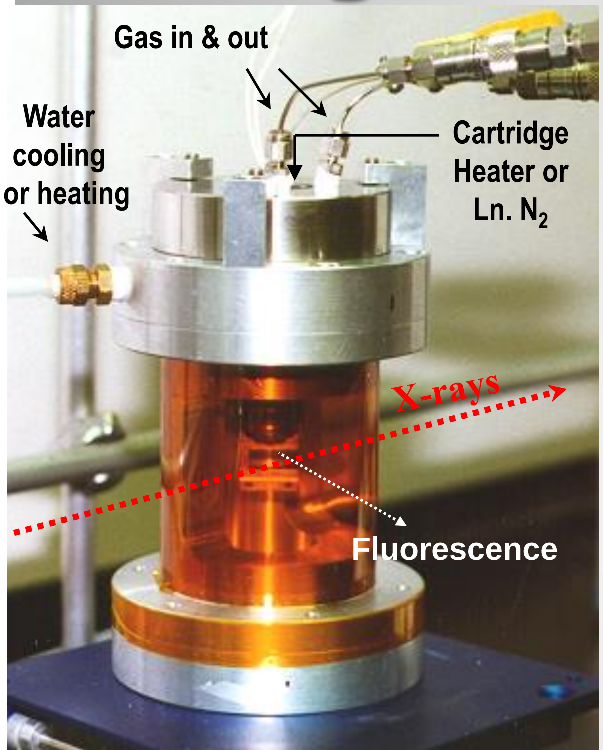
MFC:
He-calibrated
5 – 50 mL /min
4 inputs, 1 output

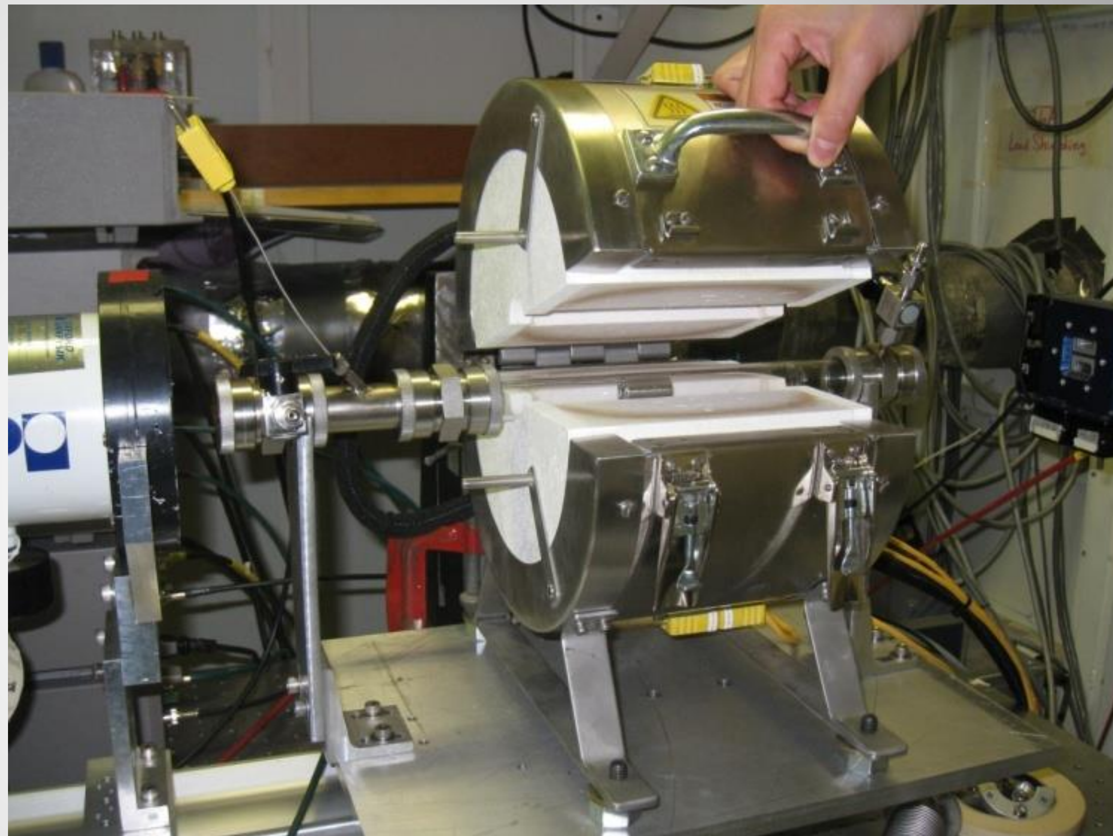
RGA:
1-200 amu
Quadruple mass spectrometric detection by Faraday cup;
50 μm ID capillary;
Chamber pressure ~1 x 10^{-6} torr (He);
Sensitivity to ~10^{-10} torr.



Gas reaction outlet technique: RGA

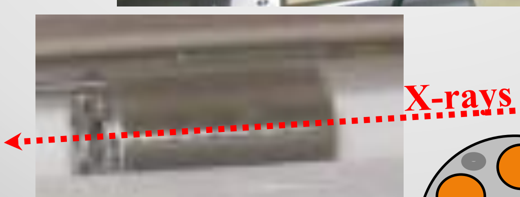
Large-volume Reactor Cells

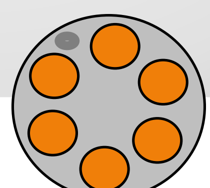




Large reactor cell

- In-situ XAS transmission or fluorescence
- Temp. range -200 – 500 ^{o}C with Ln. N_2
- Pellet catalyst sample
- Products analysis (RGA)
- Large reaction vessel

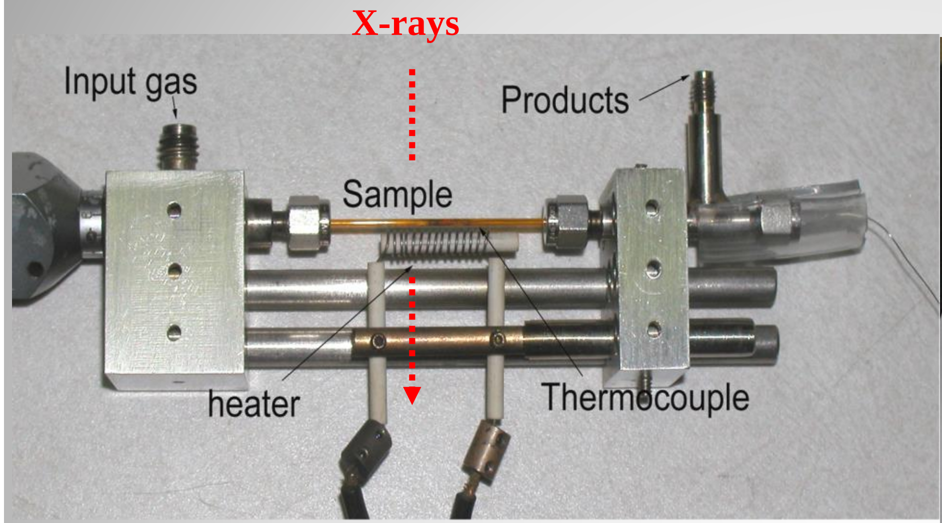


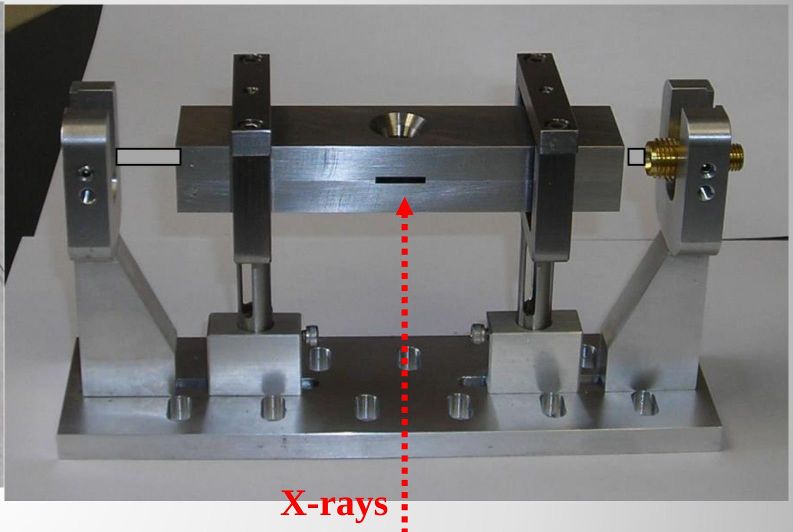


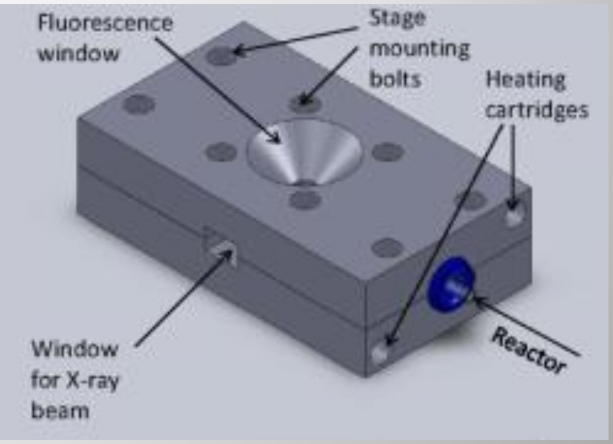
HT multi-sample XAS tube reactor

- In-situ XAS transmission
- Simultaneous gas treatment of up to 6 samples
- Temperature range: RT- 950 ^{o}C
- Pellet sample
- Product analysis (RGA)

Small-volume Reactor Cells







Claussen flow cell

- In-situ XAS, XRD, Raman
- Powder sample
- P < 120 atm.
- Temp. range: -190 - 975°C.
- Product Analysis (RGA)

Modifications

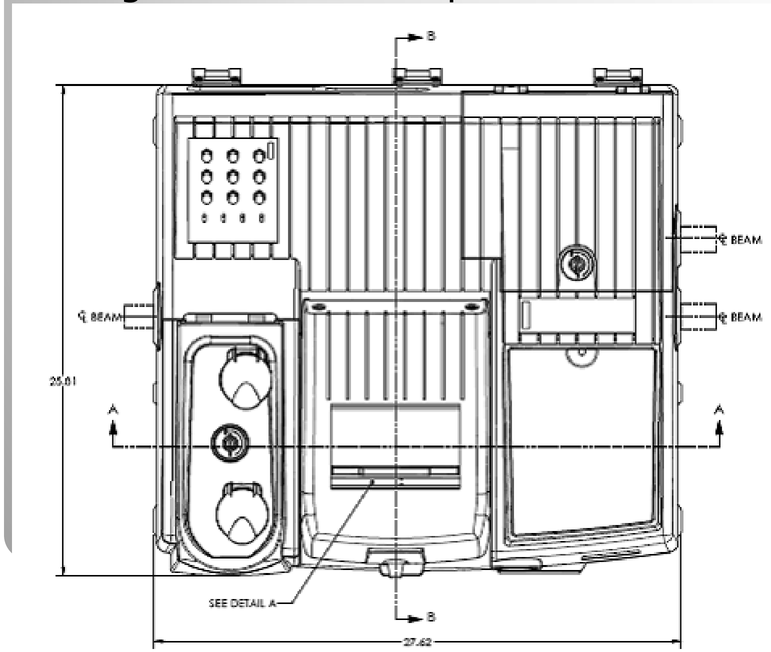
- Uniform temperature

Tubings

- Kapton / polyimide (< 400 °C, >4 keV)
- quartz (< 1000 °C, > 10 keV)
- glassy carbon (<600 °C, > 6 keV)

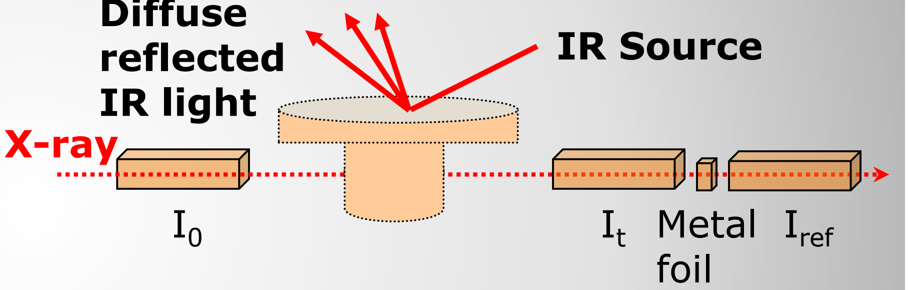
Nicolet 6700 FTIR Spectrometer

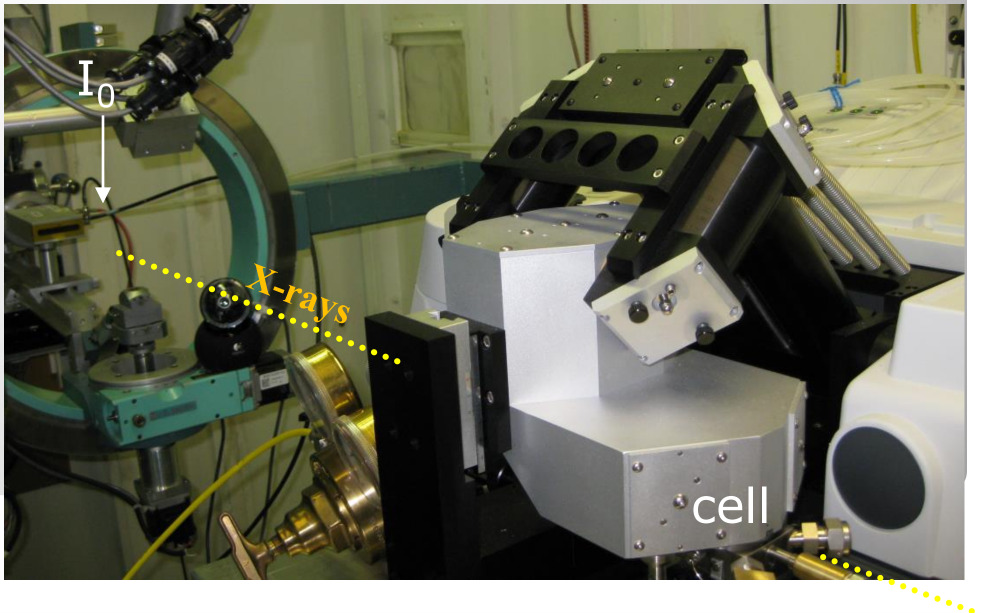
- Compact design;
- Two independent detectors can be placed in the system;
- X-ray penetrates < 0.4 mm below the catalyst surface.
- IR spectrum is a consequence of the molecular change in permanent <u>dipole moment</u>
- Regular scan and rapid scan



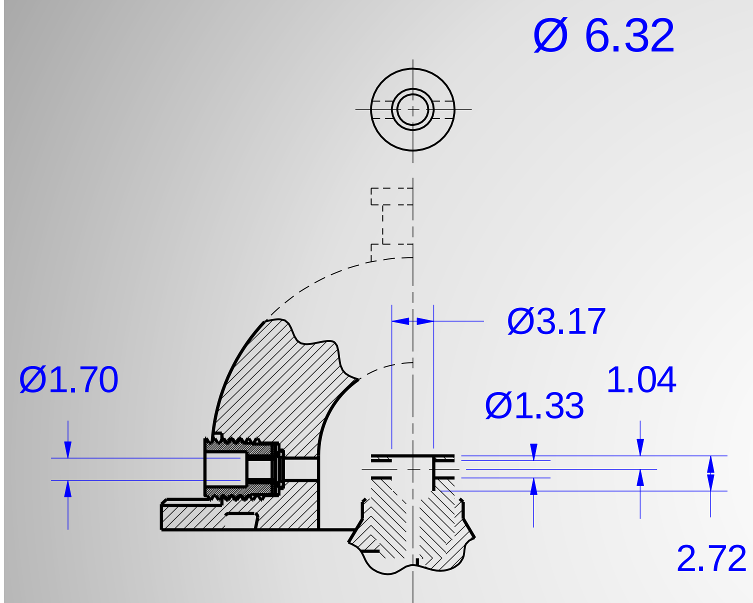
XAS / DRIFTS Setup

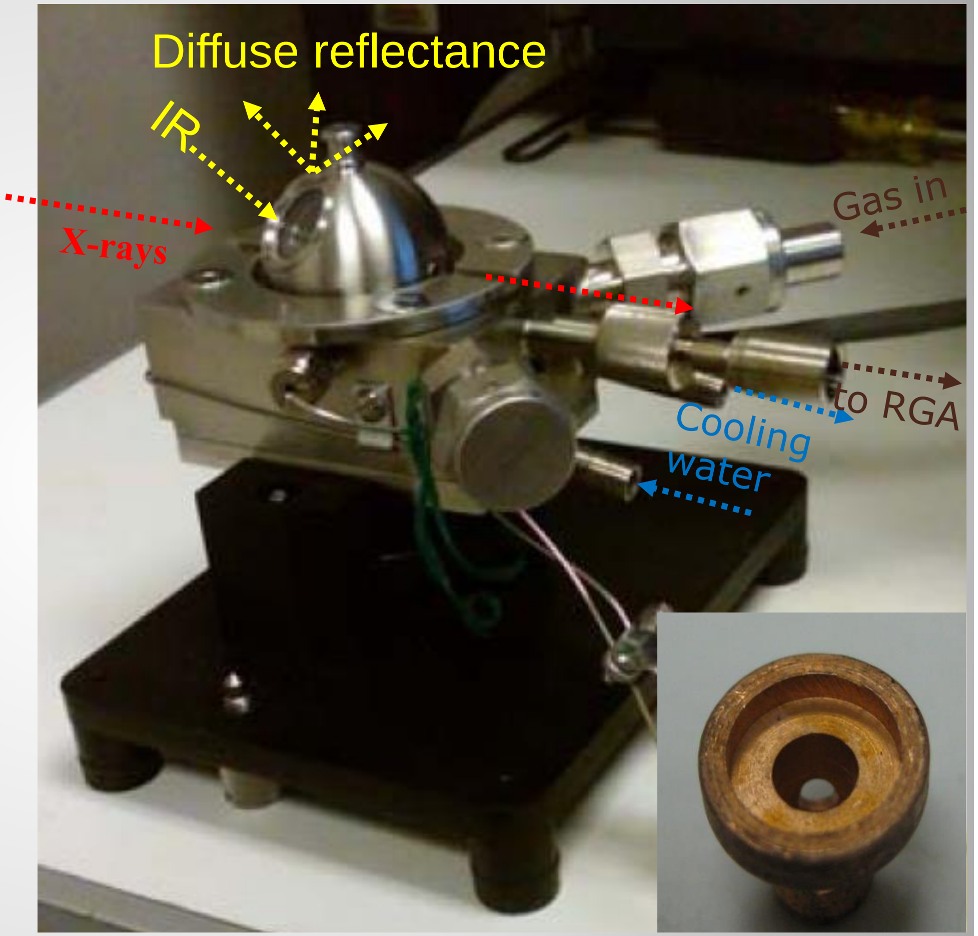
Simultaneous detection of XAS and DRIFTS:
Top of sample surface in sample cup irradiated by IR (Harrick Scientific)
DRIFTS penetration depth reaches 3 mm
X-ray passes ~1 mm below the top of cup





XAS / DRIFTS Cell and schematics





- 3.17 mm dia. DRIFTS cup;
- Glassy carbon windows;
- X-ray beam penetrates <0.4 mm below the catalyst surface;
- Large penetration depth with low IR-absorbing substrates.

- Powder sample;
- Purged / vacuumed cell;
- Temp. range: RT – 450 °C (purged);
- Cell inserts for correct XAS absorption;

- Tilted focusing and collimating mirrors
- minimize specular reflectance;
- Spectra converted into Kubelka-Munk units to correct for scattering efficiency.

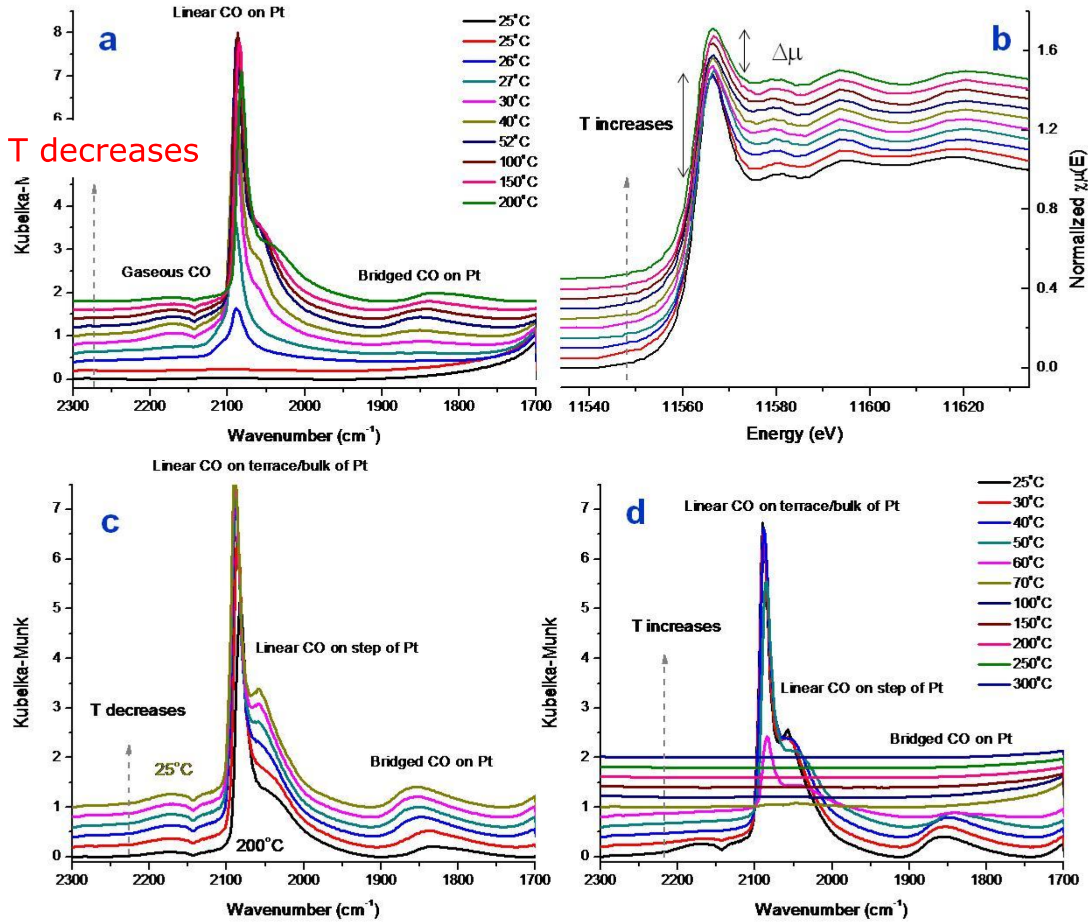
N.S. Marinkovic et al., *Nucl.Instrum.Methods* A **649** (2011) 204.

XAS/DRIFTS examples: CO adsorption on γ-alumina-supported Pt nanocatalysts

(a) CO adsorbed on Pt shows CO_L and CO_B. The CO adsorption is affected by its coverage, nature and oxidation state of the metal and the pretreatment process.

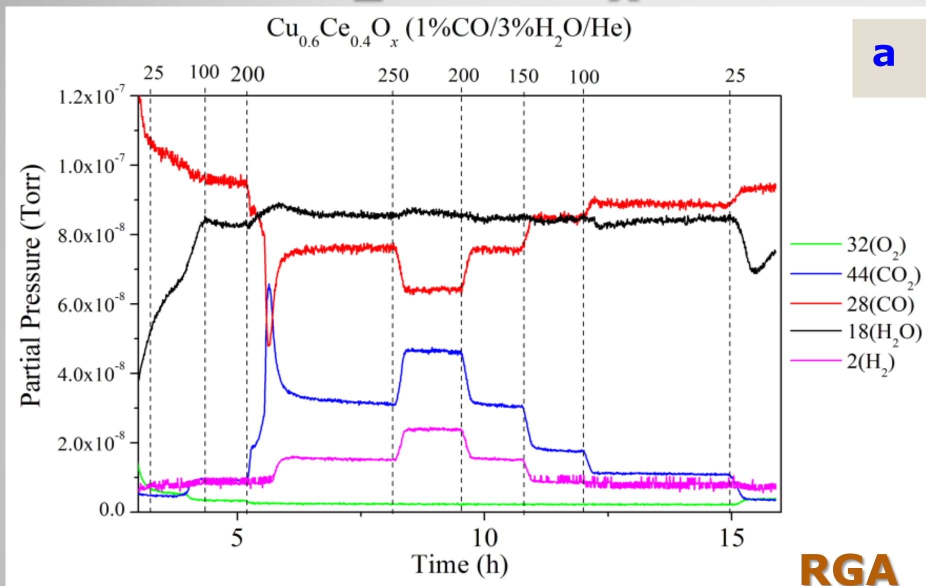
(b) Complementary XAFS allows to follow the electronic and geometrical structure evolution of metal species during *in-situ* pretreatment.

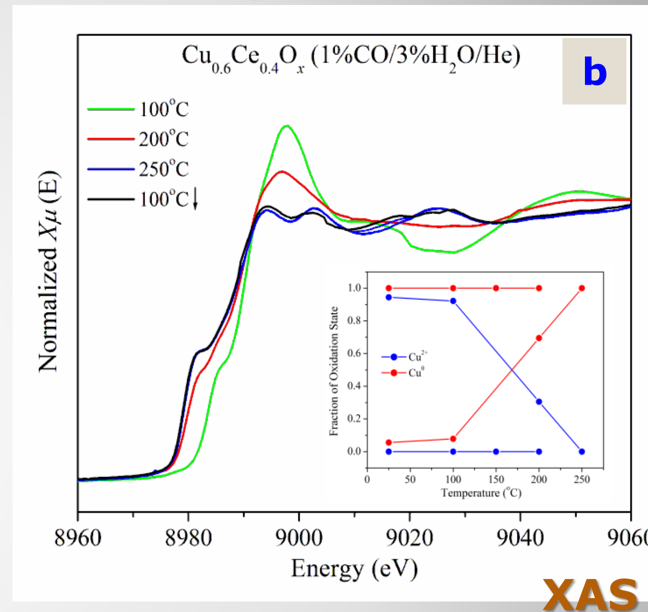
(c), (d) The effects of temperature and coverage on the CO adsorption were followed by DRIFTS in both adsorption (c), and desorption process (d).



N.S. Marinkovic et al., *J.Synchrotron Rad*. **18** (2011) 447.

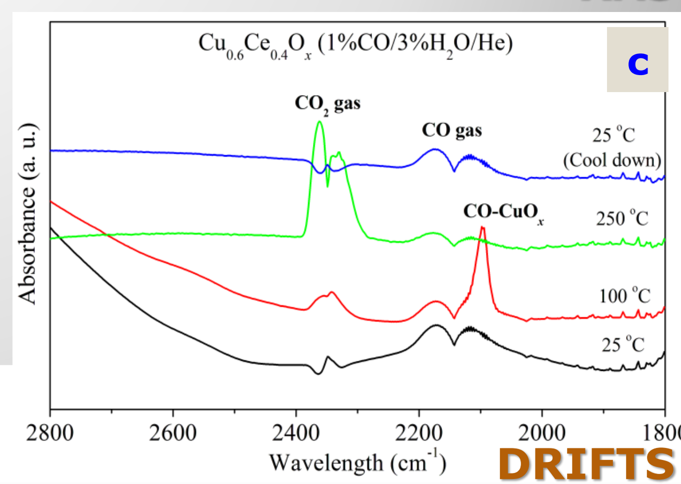
XAS/DRIFTS examples: WGS on CeO_2/CuO_x Inverse Catalyst





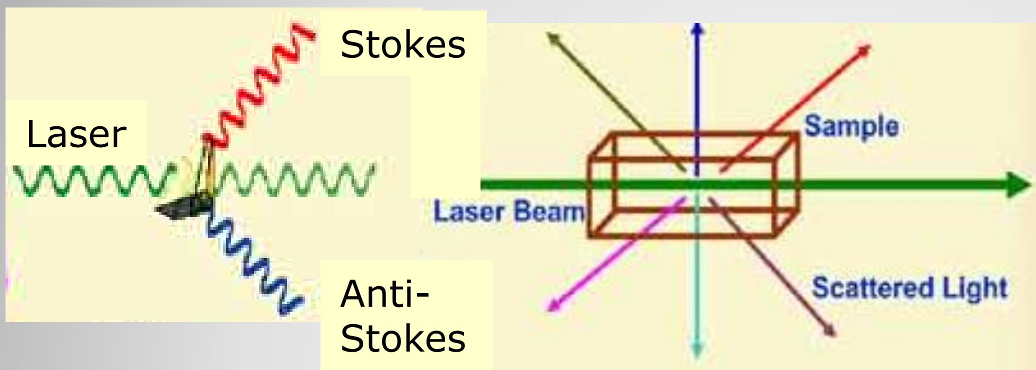
(a) Inverse CeO_2/CuO ($Cu_{0.6}Ce_{0.4}O_x$) catalyst was prepared by reverse micro-emulsion method shows high activity for the low-temperature (WGS) reaction.

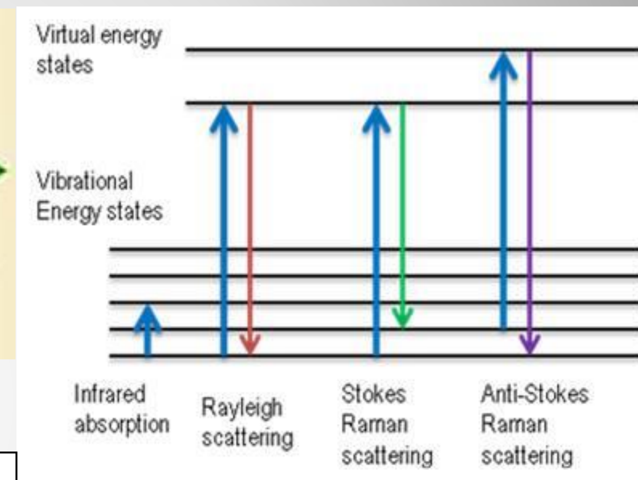
(b) Transmission XAFS shows reduction of Cu; Linear combination (insert) determines Cu oxidation states during the reaction at different temperatures.

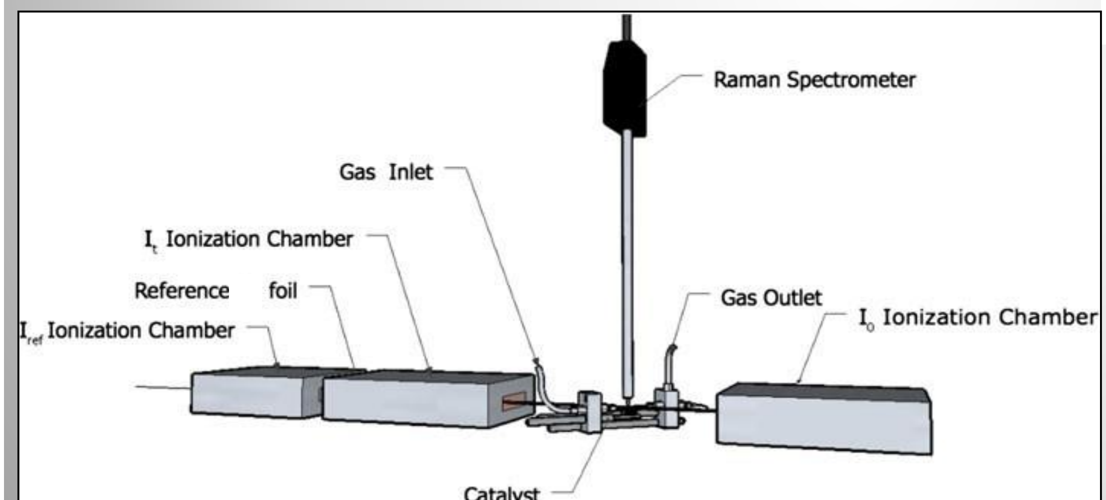


(c) DRIFTS identifies species on CeO_2/CuO_x surface: adsorbed CO on CuO_x and carbonate-like species, as well as gaseous CO and CO_2.

Raman Principle, XAS/Raman Schematics





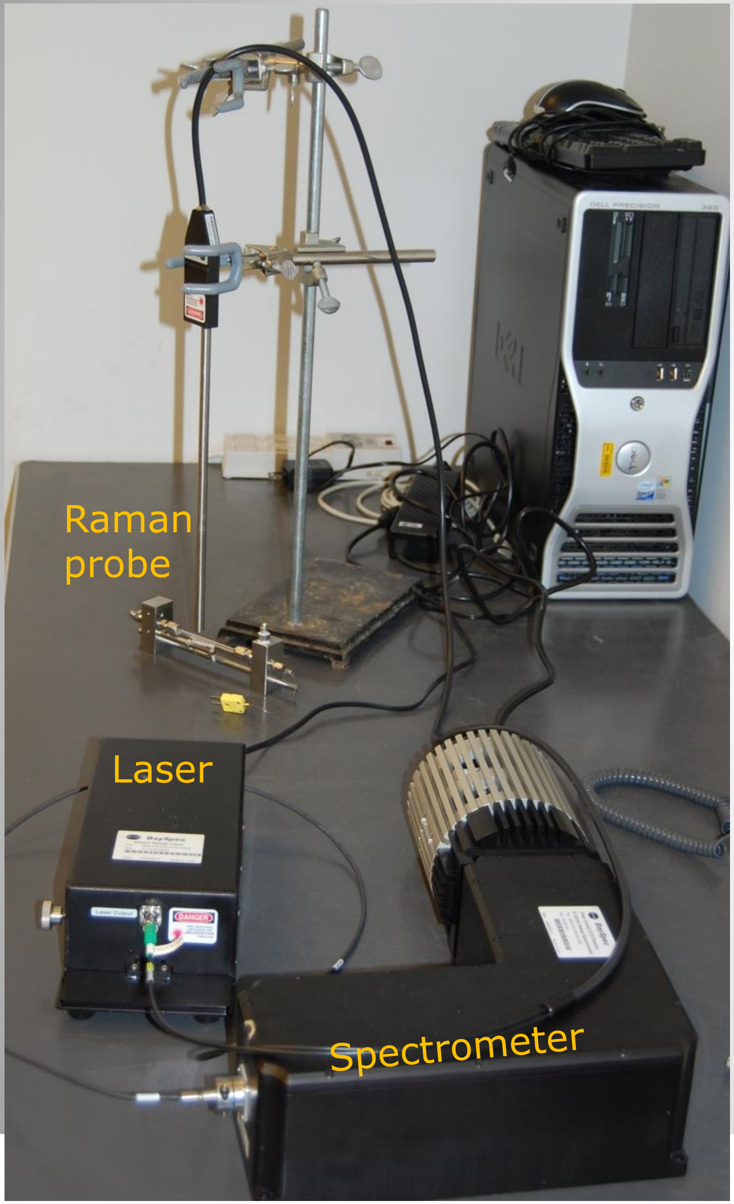


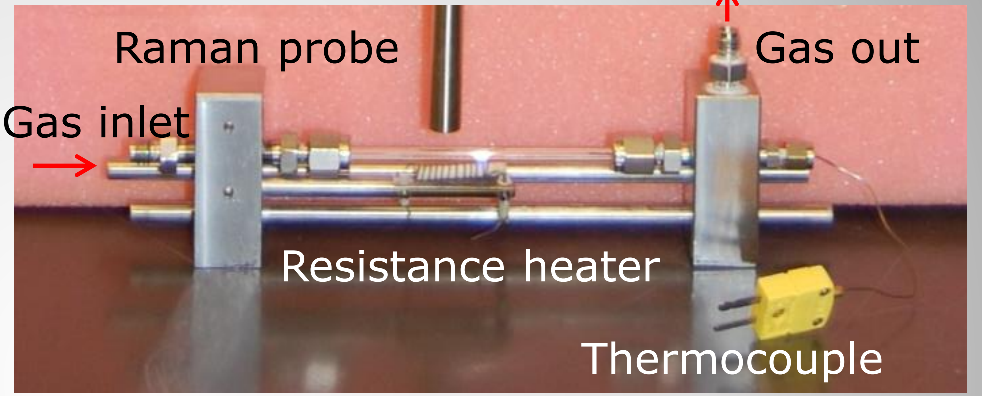
Spectrum arises as a consequence of the change in the polarizability of the molecule.

Raman active vibrations are often silent in IR, and *vice versa*. Thus, IR and Raman are complementary techniques.

- 23 mW, 532 nm Laser excitation
- Non-contact Raman probe provides both excitation and signal through fiber optics

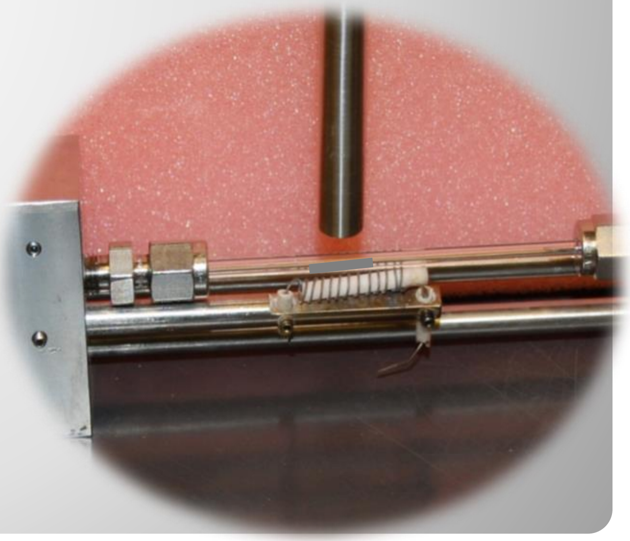
XAS/Raman Setup



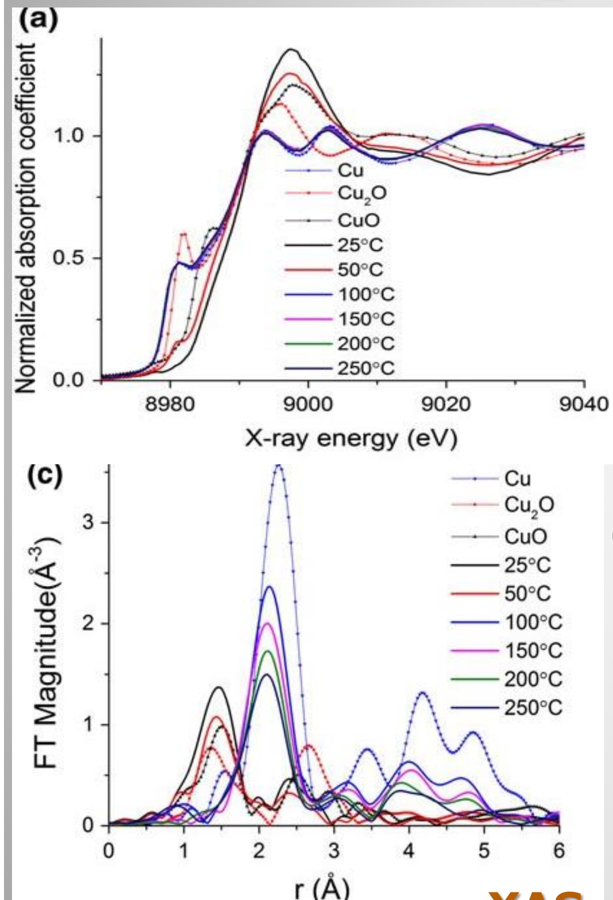


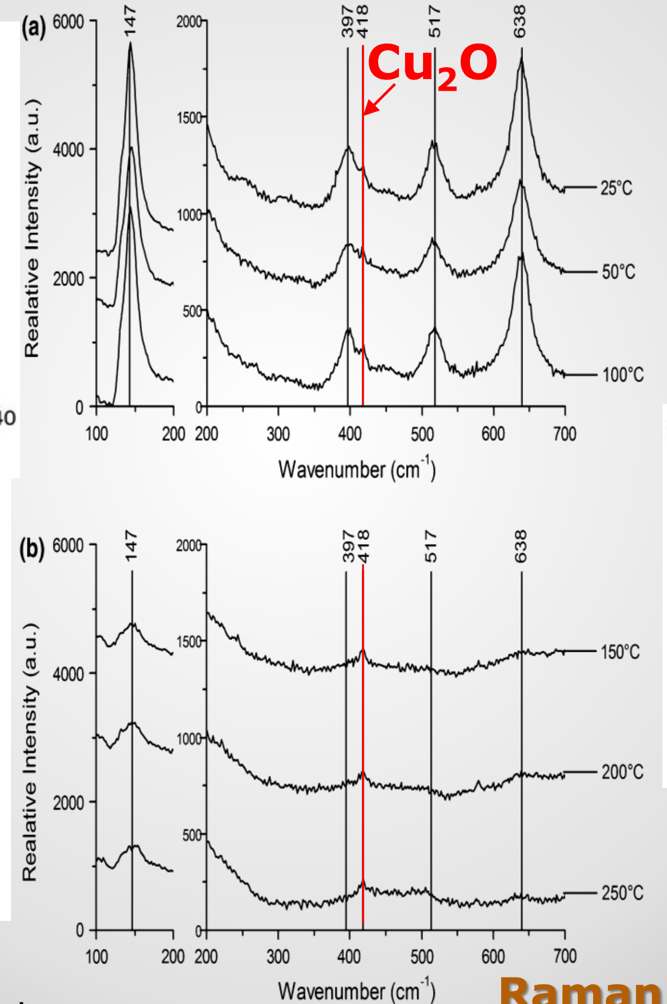
Claussen flow cell tubing:

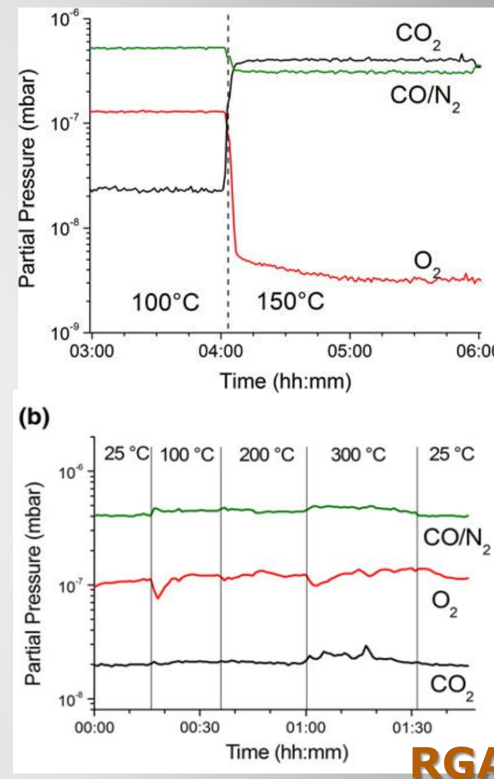
- 1 mm OD, 0.9 mm ID quartz tube, XAS > 7 keV
- 3.2 mm OD, 3 mm ID quartz tube, XAS / 10 keV
- Product Analysis Techniques (RGA)



XAS/Raman/RGA examples: $CO \rightarrow CO_2$ conversion on CuO_x/TiO_2







CuO_x / TiO_2 (anatase) is active for $CO \rightarrow CO_2$ conversion, whereas pure TiO_2 is not.

Only with the combination of Raman and XAS it was possible to detect both Cu metallic phase and Cu_2O: Metallic Cu insensitive in Raman, detectable by XAS; Cu_2O identified with Raman, XAS may overlook it due to the dominating Cu metal lines.

A. Patlolla et al., *Topics Catal*. **56** (2013) 896.

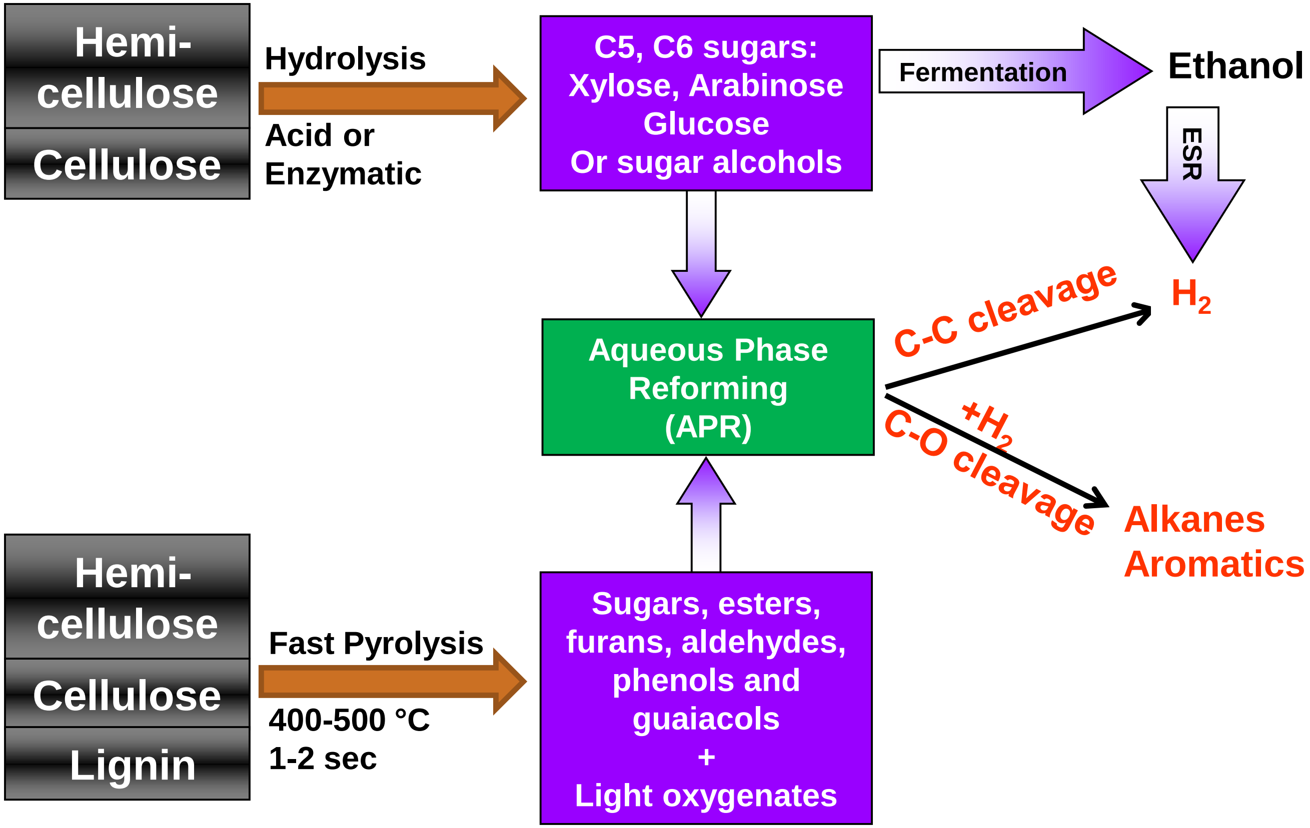
Biomass Conversion: High P/T Catalysis

Agriculture

- Rotational crops
- Energy crops
  (switch grass, poplar, etc)
- Oil crops
- Rotational crop residue
(stover, wheat & rice straws, etc)

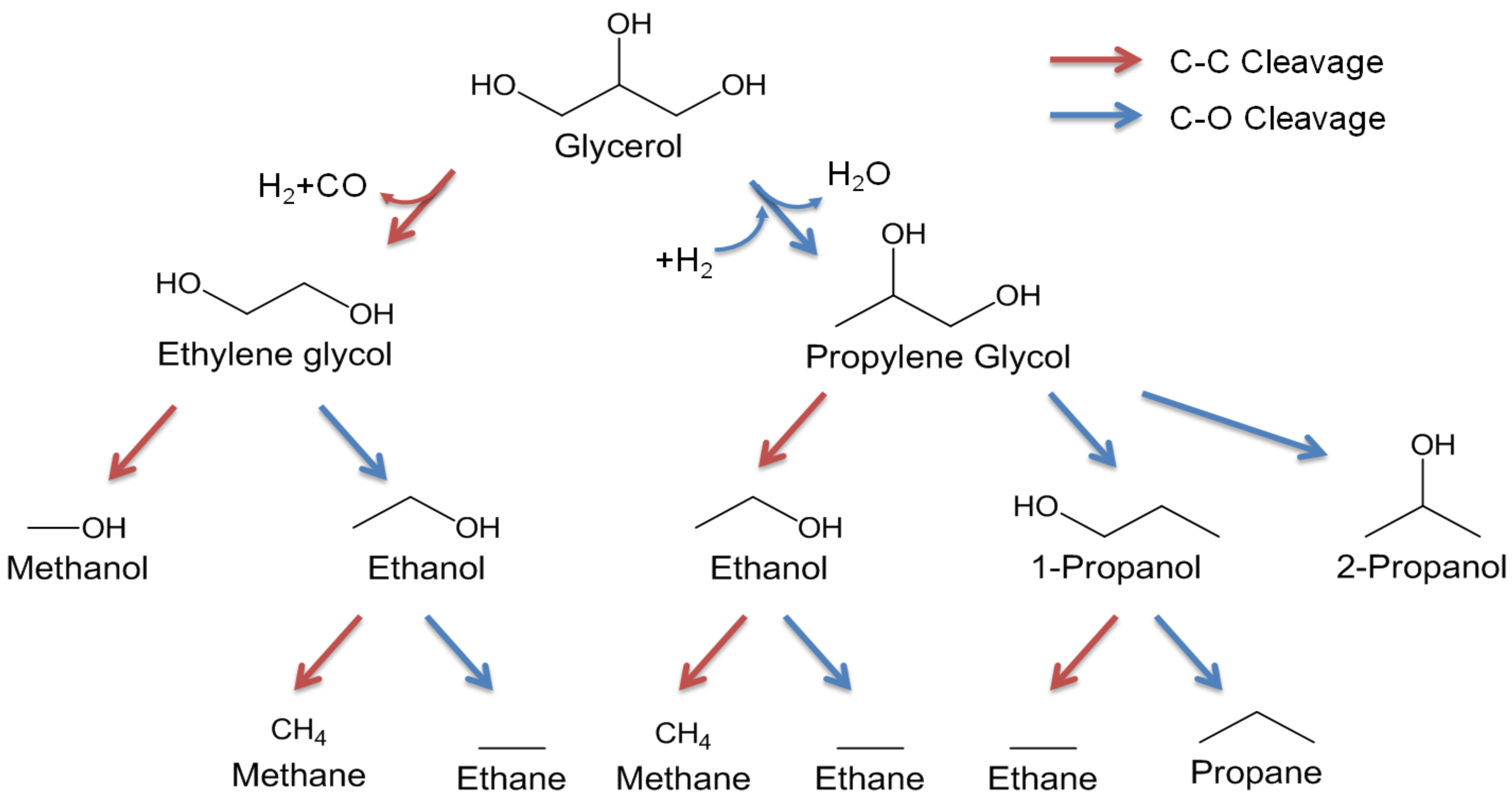
Forest residue

MSW **Animal waste**



- APR catalyst exposed to harsh environment
  - High P, T
  - High water content, low pH
- Catalyst structure and oxidation state unknown under APR conditions.

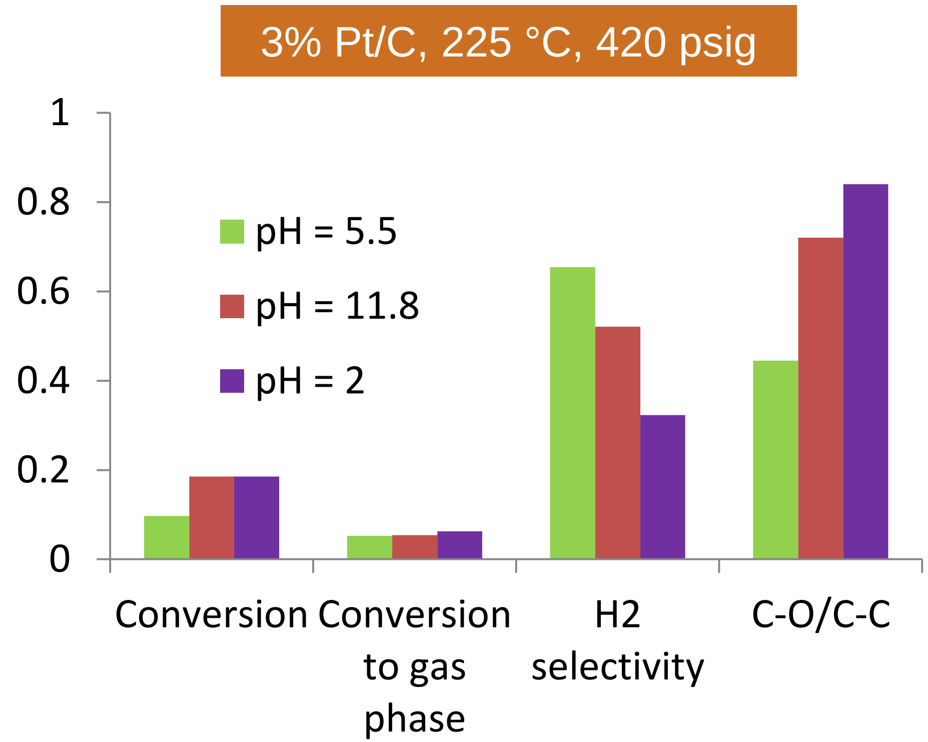
Reactions Pathway for Glycerol APR



$$\frac{C-O}{C-C} = \frac{\sum_i \text{moles dehydrated product}_i \times \text{dehydration steps to reach product}_i}{\text{Moles of } CO_2}$$

Zhang, Karim et al. *J. Catal.* 287, **2012**, 37-43

Catalyst Activity and Selectivity Affected by pH



- Catalyst activity and selectivity is affected by pH.
- Particle size similar under different pH
  - *ex situ* STEM d_{avg} = 2.1-2.3 nm
- No measurable reaction in an empty reactor

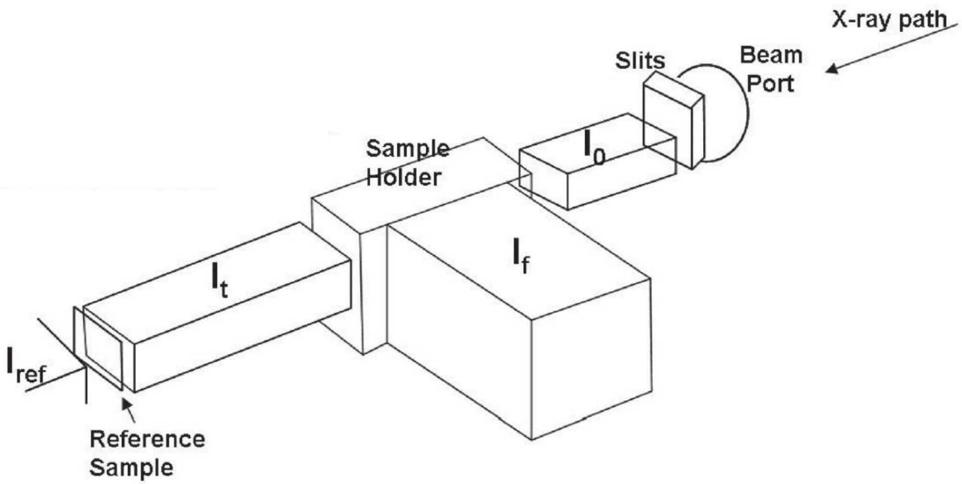
Karim et al. *ACS Catalysis,* **2012,** 2, 2387

Questions

- Why does pH affect the activity and selectivity
  - Change in nanoparticles size/shape?
  - Homogeneous catalysis?
  - Effect of pH on adsorbates?

→ *in operando* XAFS

Experimental Setup



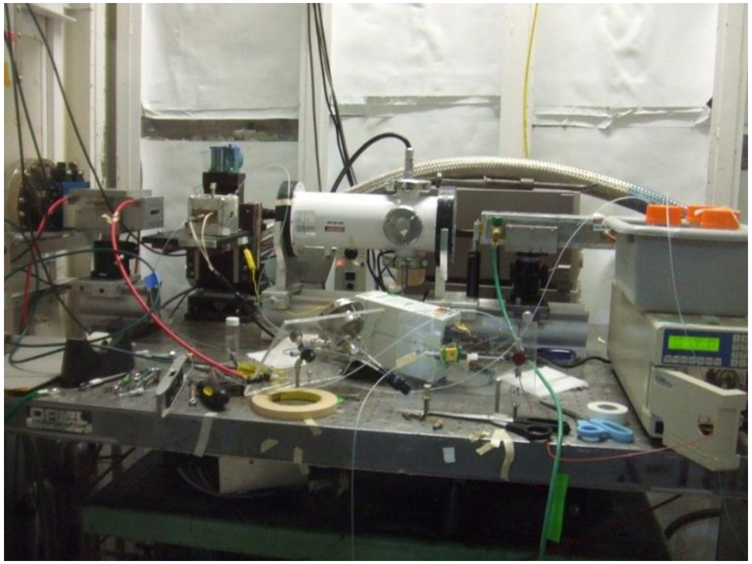
Transmission

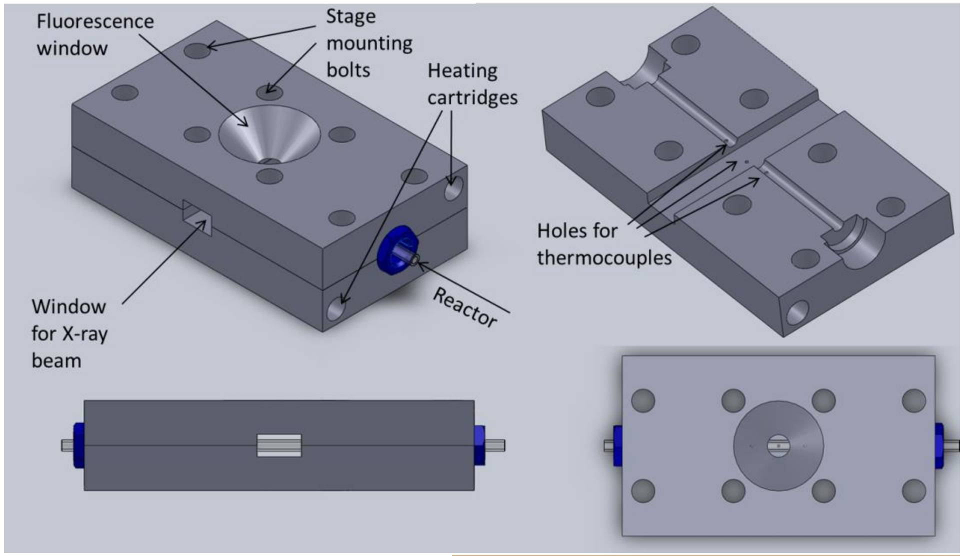
$$I = I_0 e^{-\mu(E)t}$$

$$\mu(E)t = -\ln(I/I_0)$$

Fluorescence

$$\mu(E) \propto I_f / I_0$$

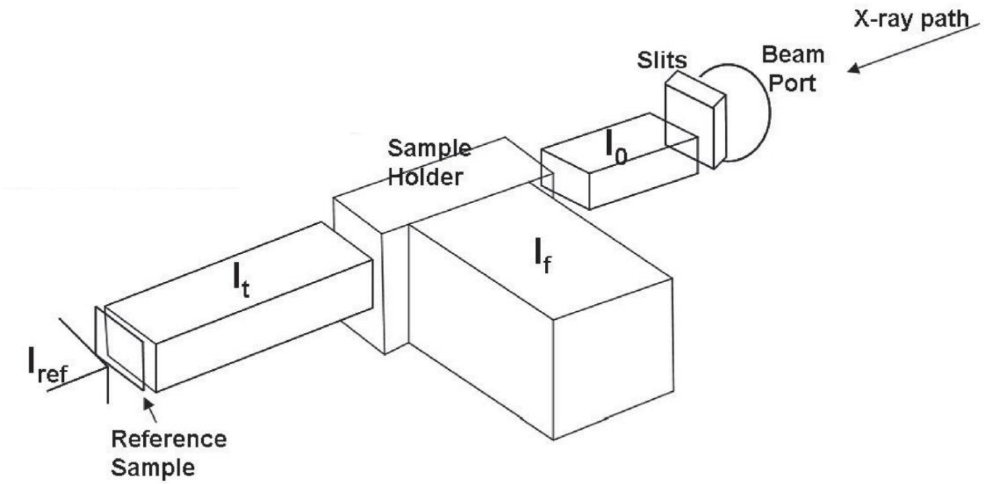




T and P
- 700 °C
- 1200 psig (83 bar)

Karim et al. *ACS Catalysis*, **2012**, 2, 2387

Experimental Setup



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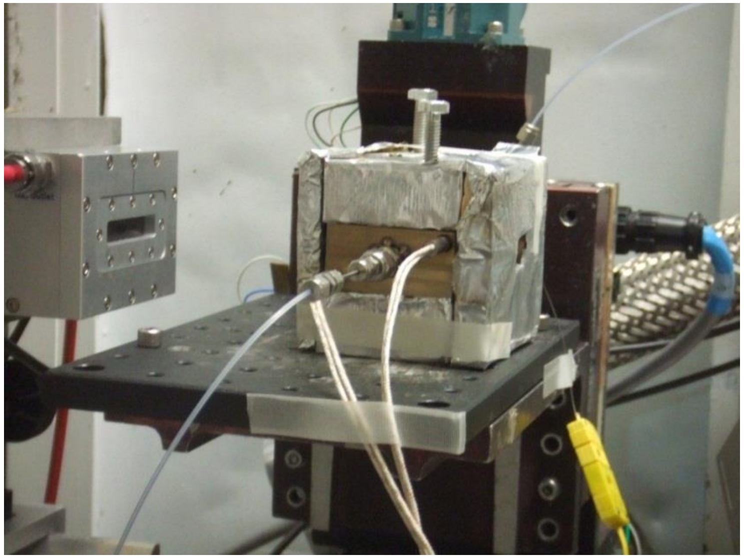
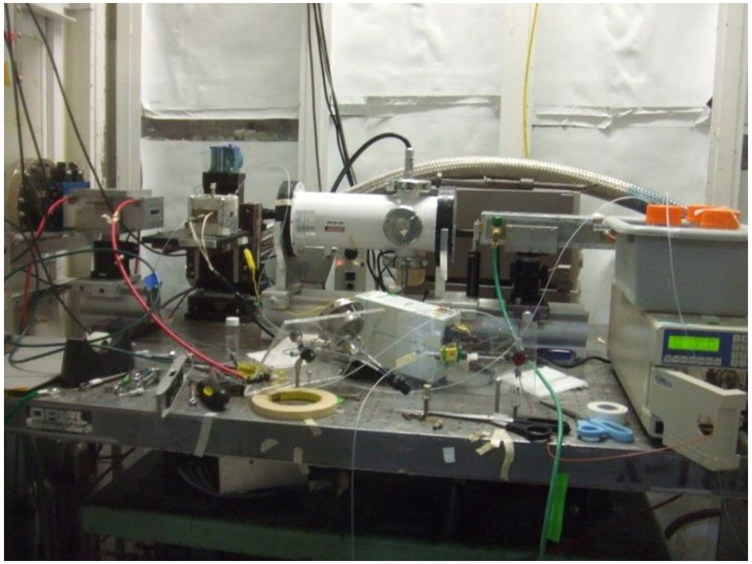
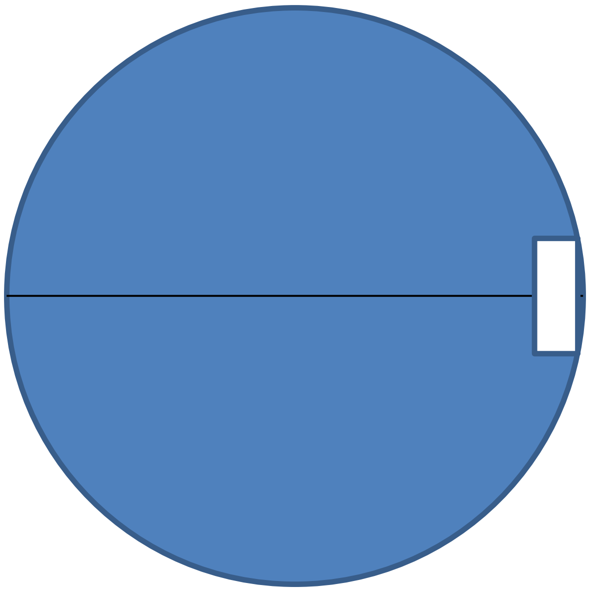




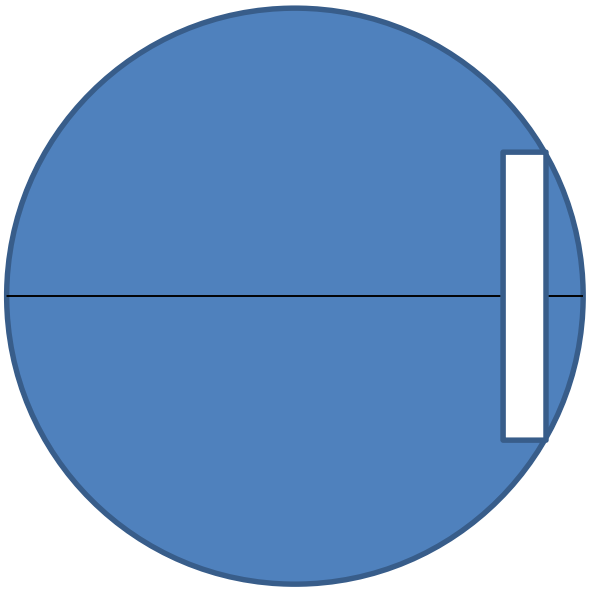
Kelly, Hesterberg, & Ravel, chapter 14
Methods of Soil Analysis. Part 5. Mineralogical Methods. SSSA Book Series, no. 5

Important Practical Details

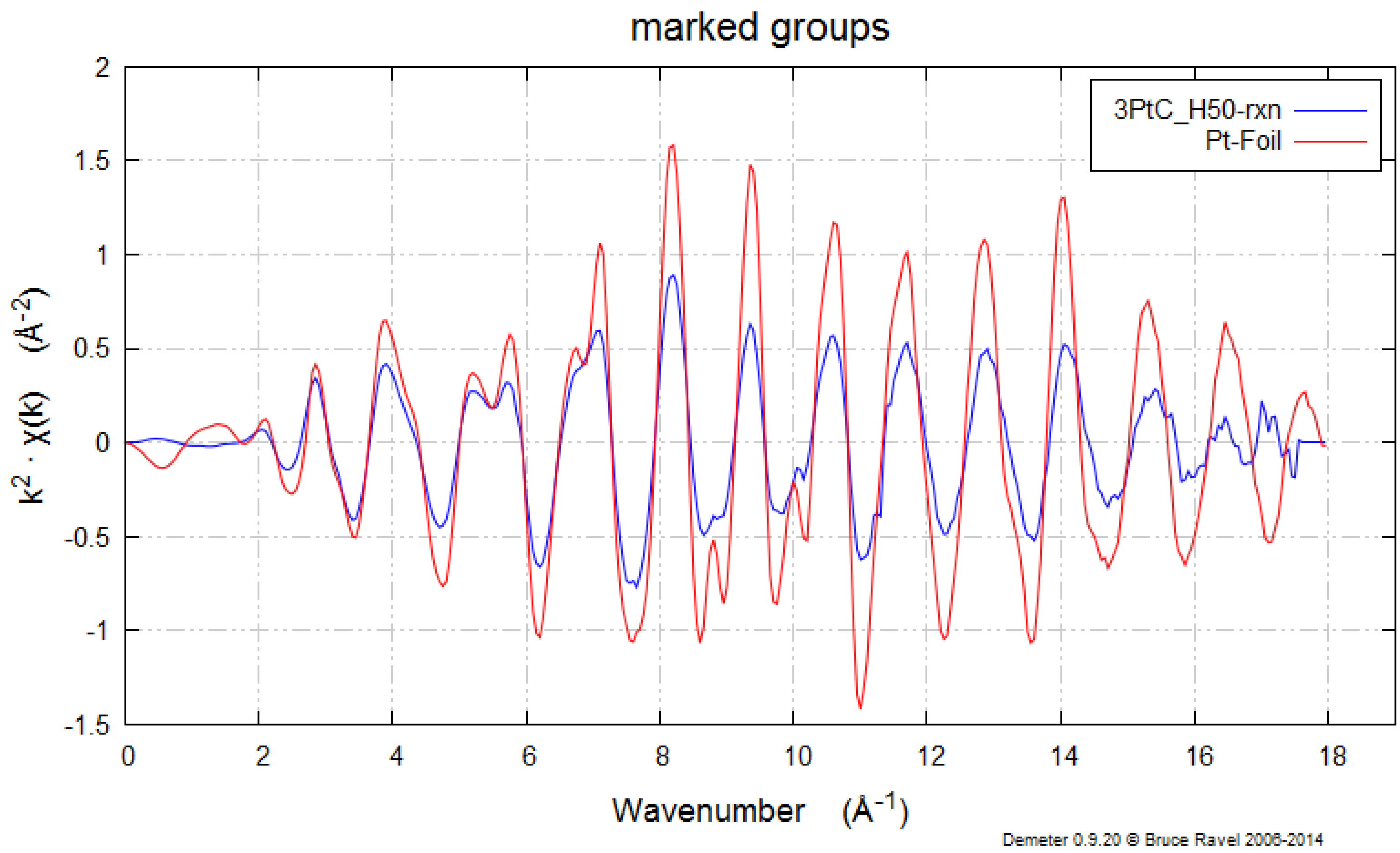
- Catalyst particle size needs to be 10x smaller than reactor i.d.
- Beam size needs to be 3-5x smaller than reactor i.d.

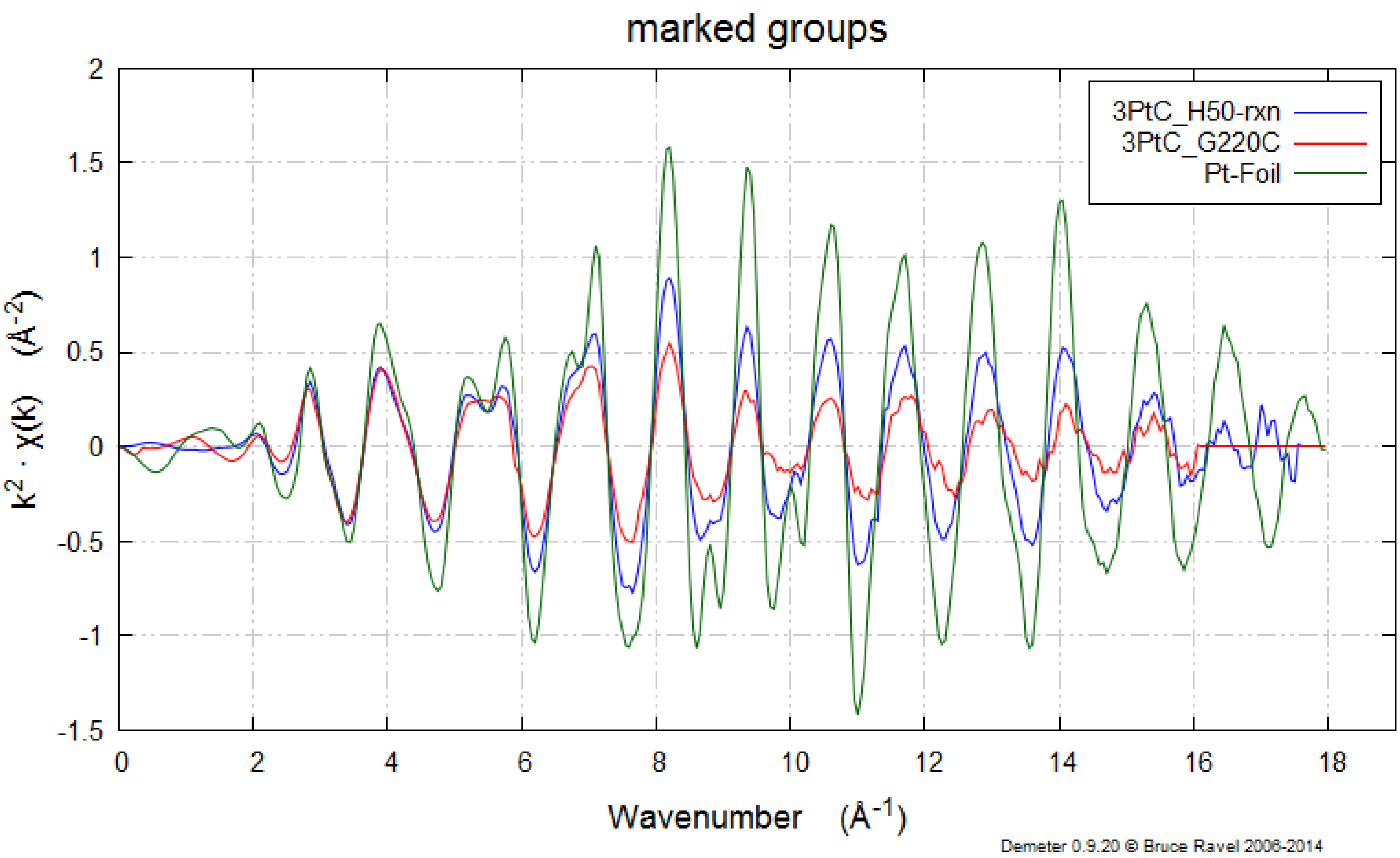


Beam size = 0.3 mm
Tube i.d. = 1.5 mm

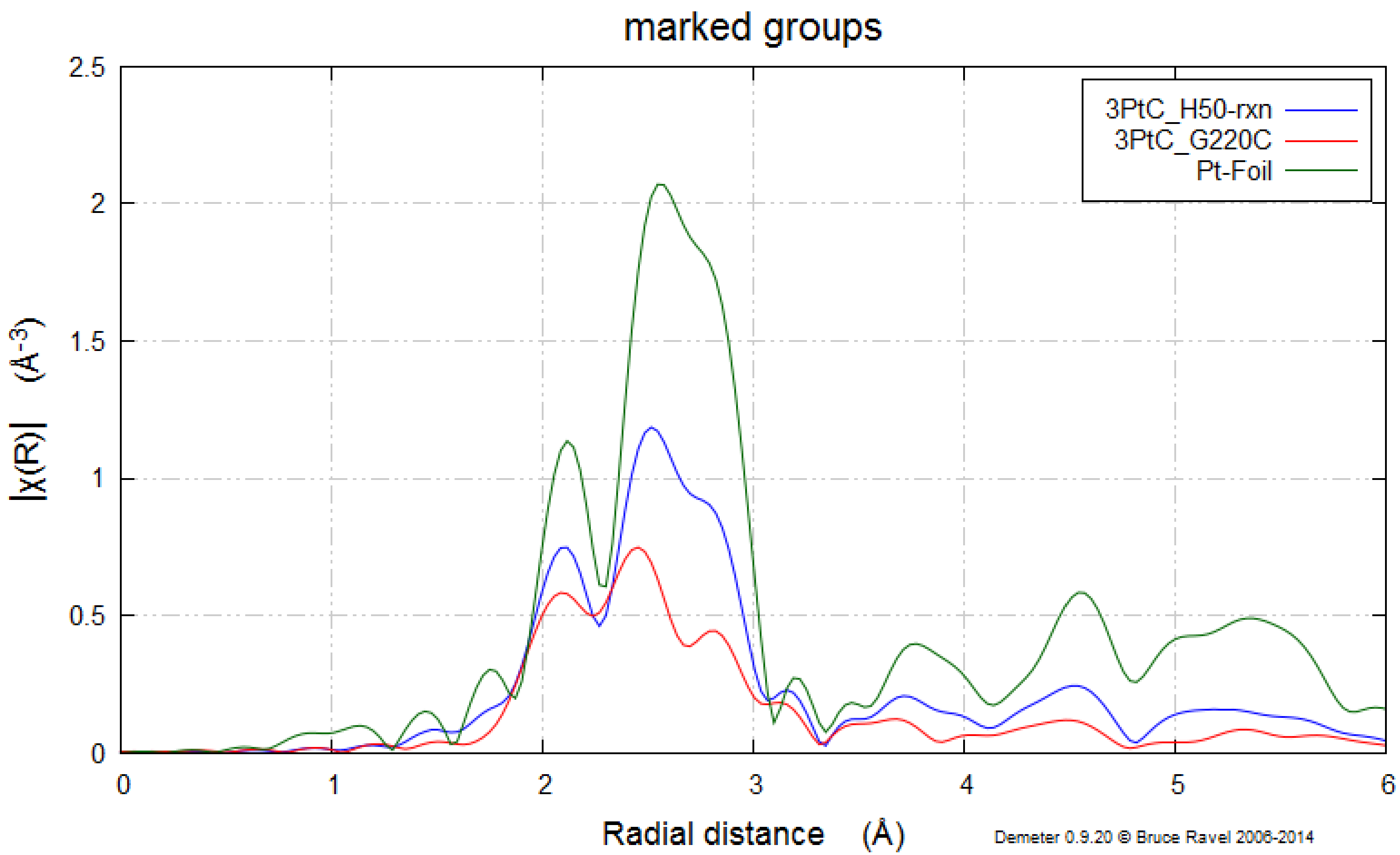


Beam size = 0.75 mm
Tube i.d. = 1.5 mm


marked groups
3PtC_H50-rxn
Pt-Foil
$k^2 \cdot \chi(k)$ $(Å^{-2})$
Wavenumber $(Å^{-1})$
Demeter 0.9.20 © Bruce Ravel 2006-2014



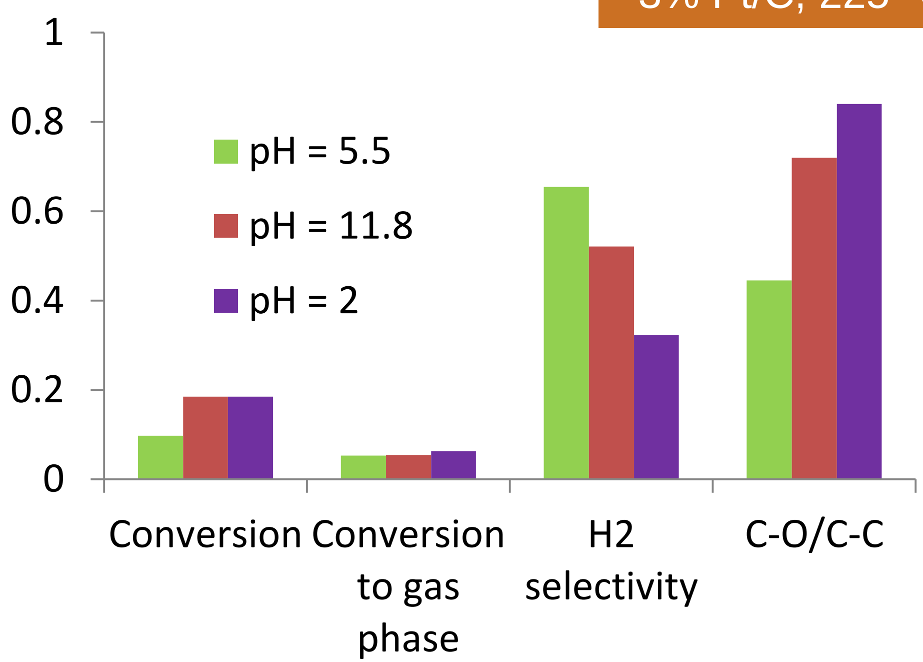
marked groups
3PtC_H50-rxn
3PtC_G220C
Pt-Foil
2
1.5
1
0.5
0
-0.5
-1
-1.5
0
2
4
6
8
10
12
14
16
18
$k^2 \cdot \chi(k)$ $(Å^{-2})$
Wavenumber $(Å^{-1})$
Demeter 0.9.20 © Bruce Ravel 2006-2014

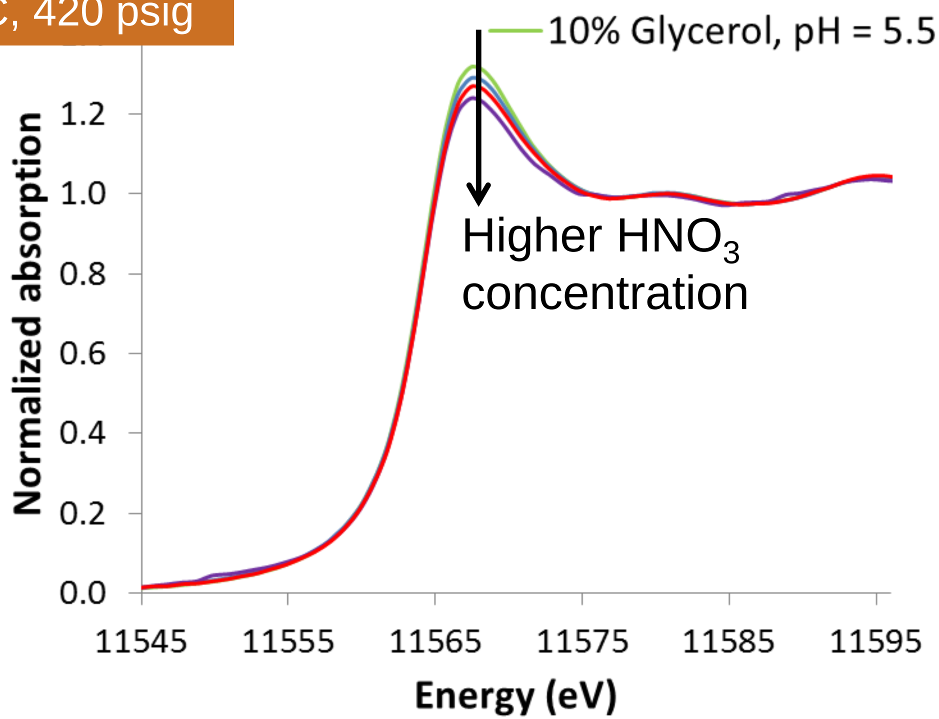


marked groups
2.5
2
1.5
1
0.5
0
|χ(R)| (Å-3)
0
1
2
3
4
5
6
Radial distance (Å)
3PtC_H50-rxn
3PtC_G220C
Pt-Foil
Demeter 0.9.20 © Bruce Ravel 2006-2014

In Operando: What can we learn?

3% Pt/C, 225 °C, 420 psig





- Catalyst activity and selectivity is affected by pH.
- Particle size similar under different pH
  - *In operando* EXAFS $N_{Pt\text{-}Pt}$ = 9.3-9.7
  - *ex situ* STEM d_{avg} = 2.1-2.3 nm
- XANES under reaction conditions reveals changes in Pt electronic structure under different pH (especially acidic).

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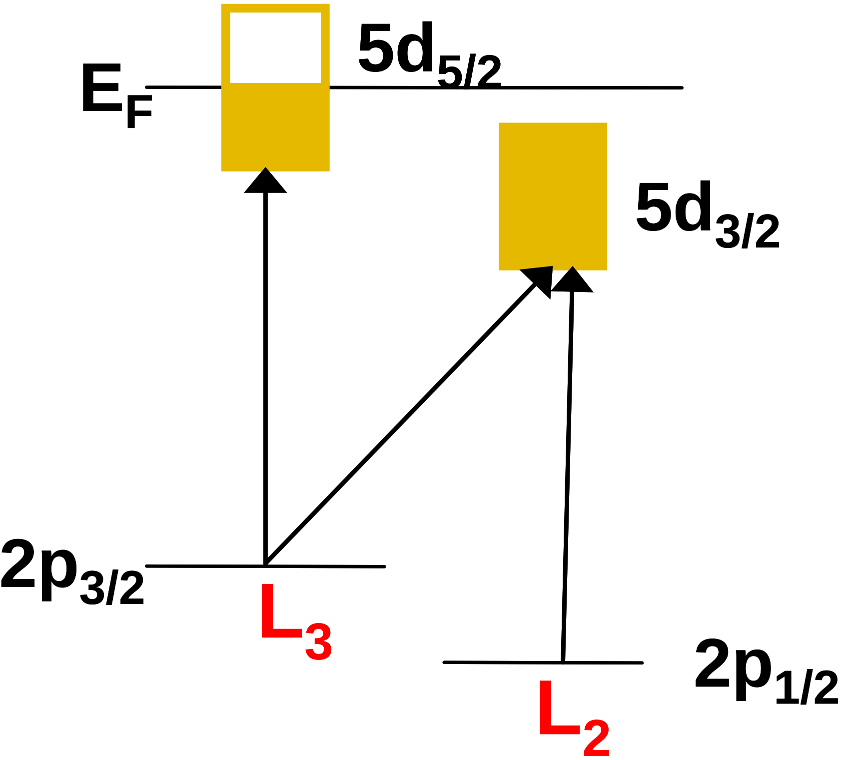
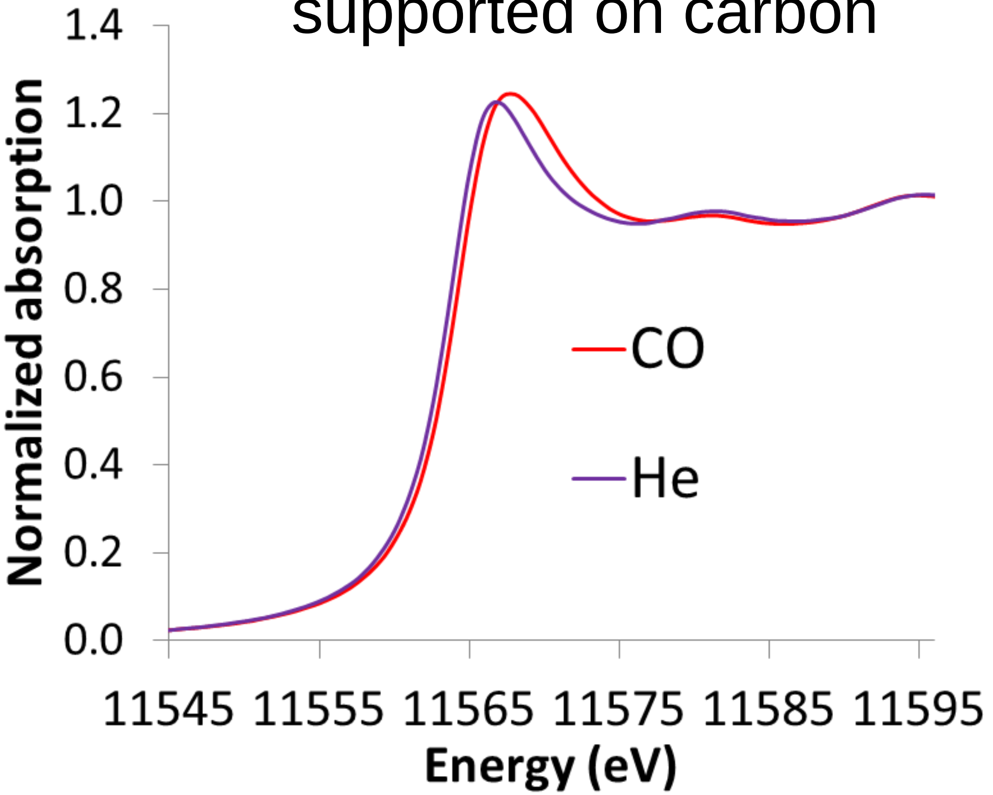
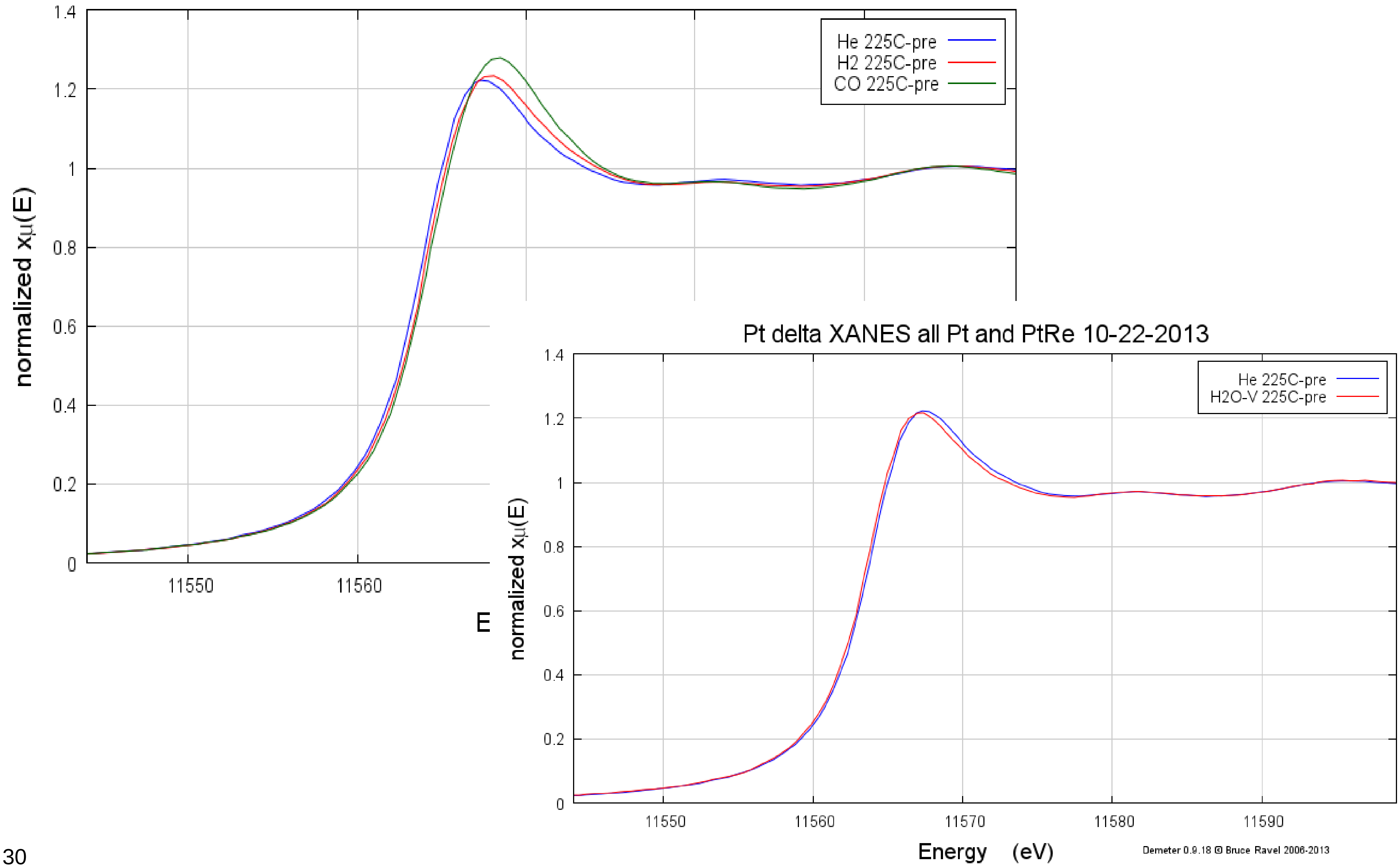
L Edge XANES



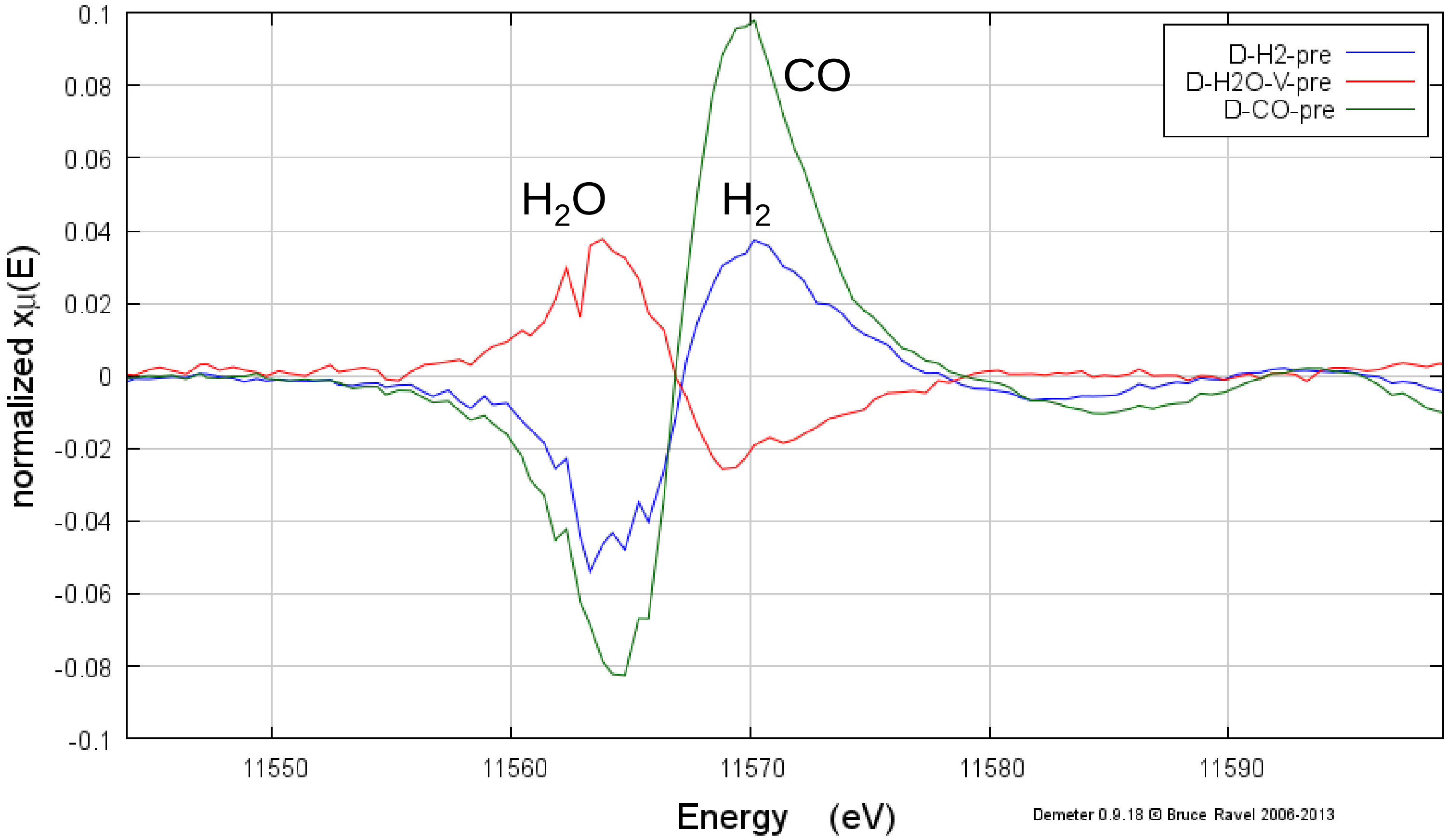
2nm Pt nanoparticles supported on carbon



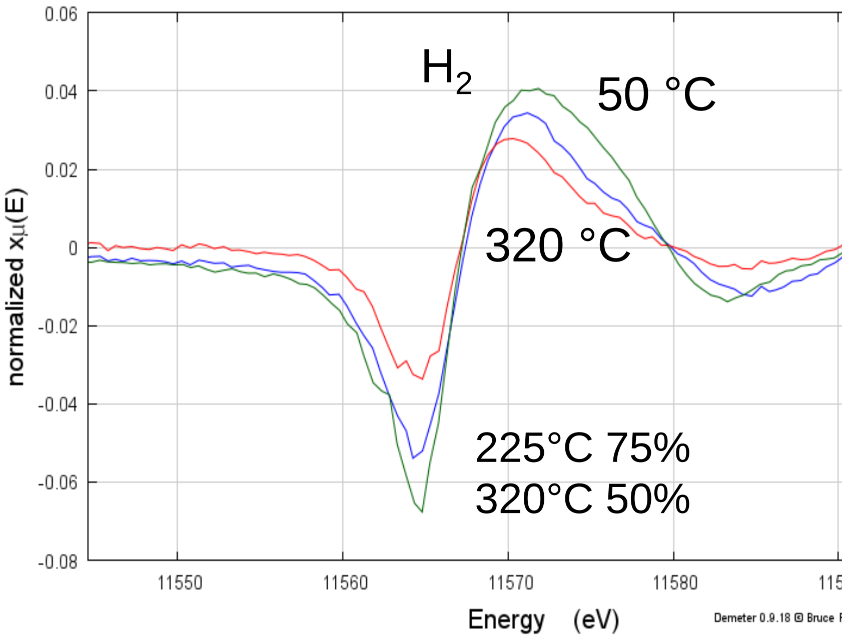
XANES, effect of adsorbates: CO, H_2 and H_2O

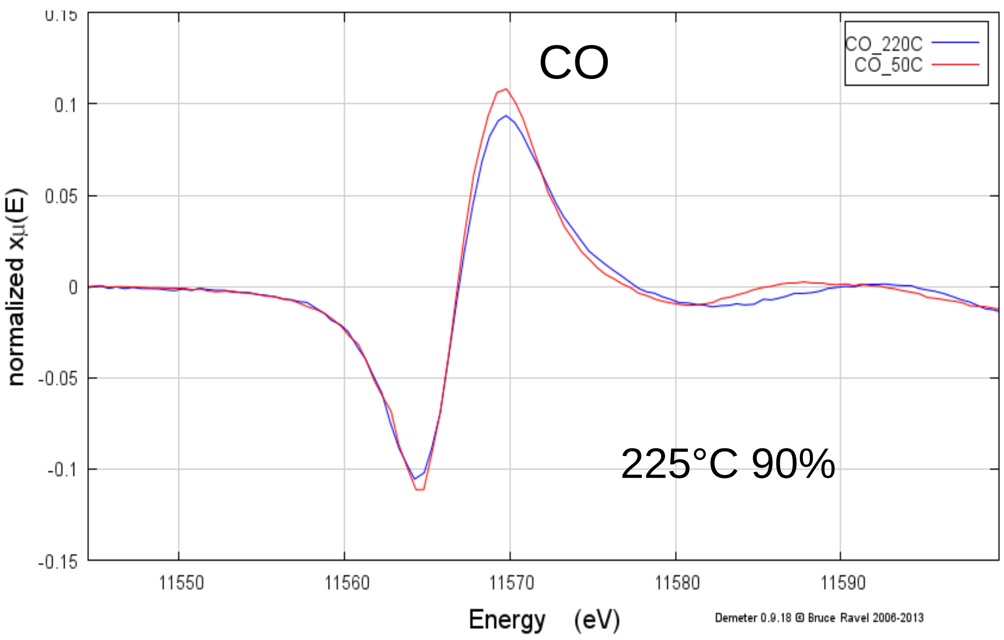


ΔXANES, CO, H_2 and H_2O

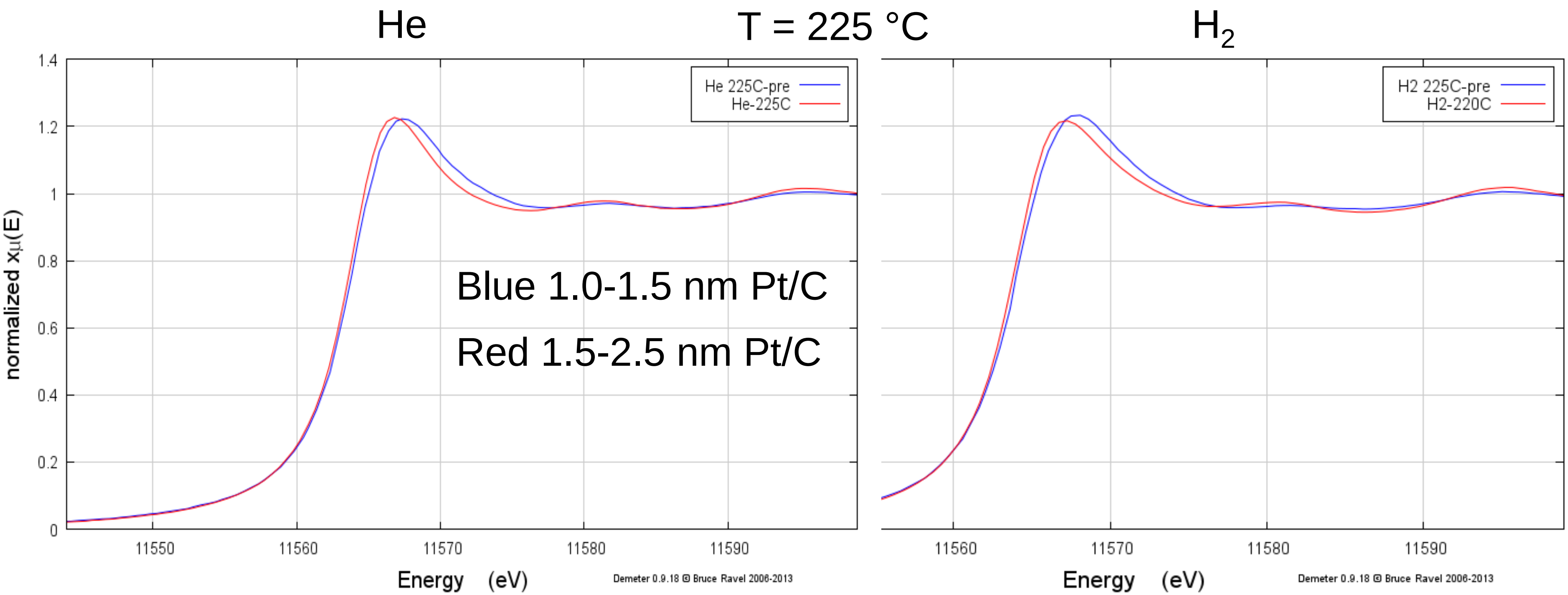


Effect of temperature on H_2 and CO coverage





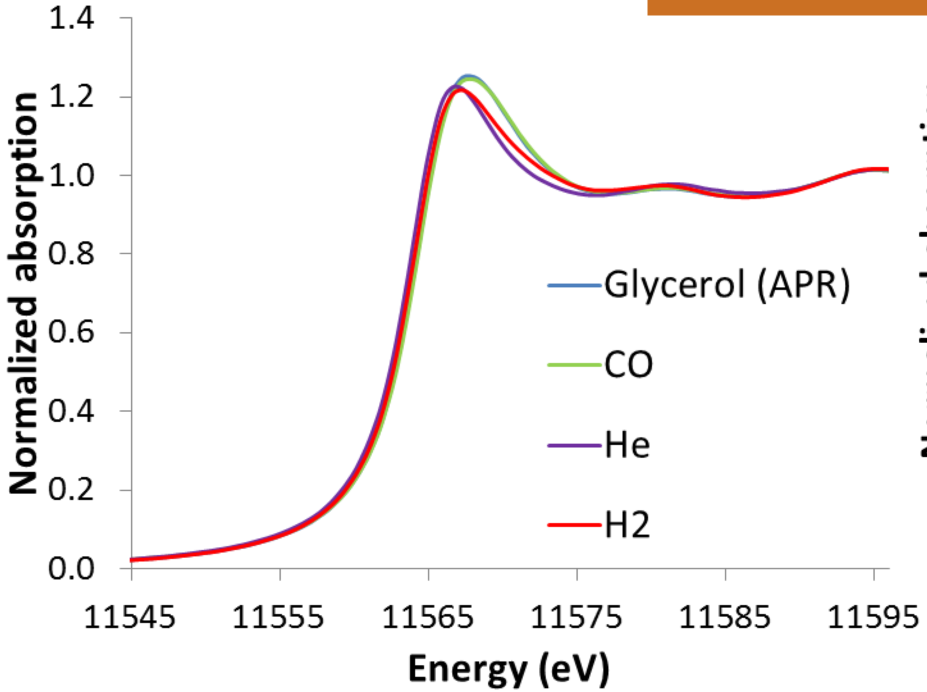
Effect of NP size on XANES

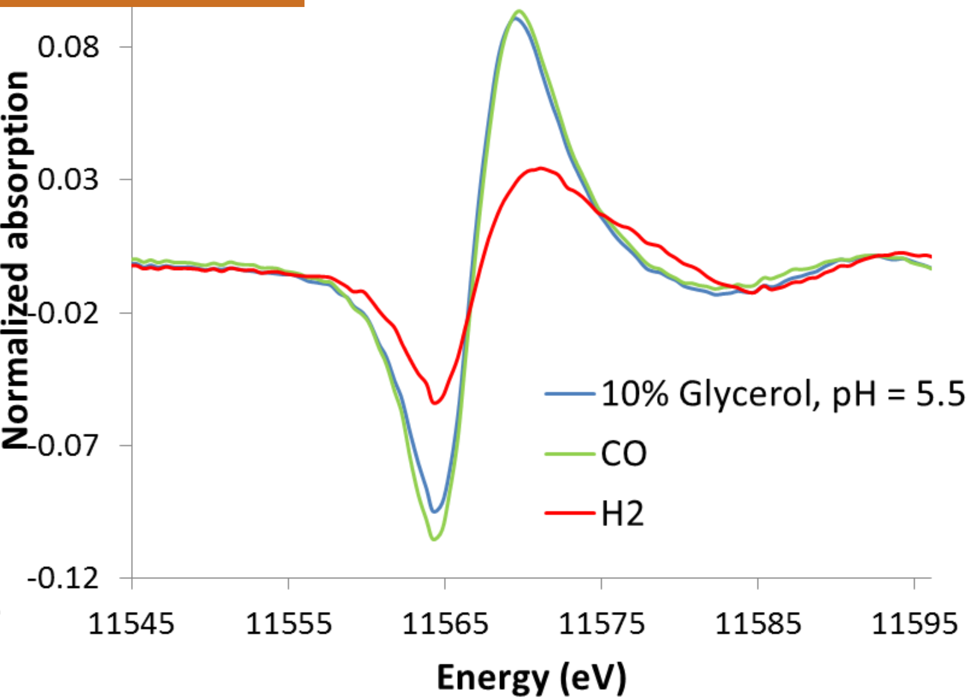


- It is important to determine if the nanoparticles change size under reaction conditions.

Adsorbates during Glycerol APR

3% Pt/C, 225 °C





- ΔXANES shows that Pt surface is mostly covered by CO during glycerol APR.

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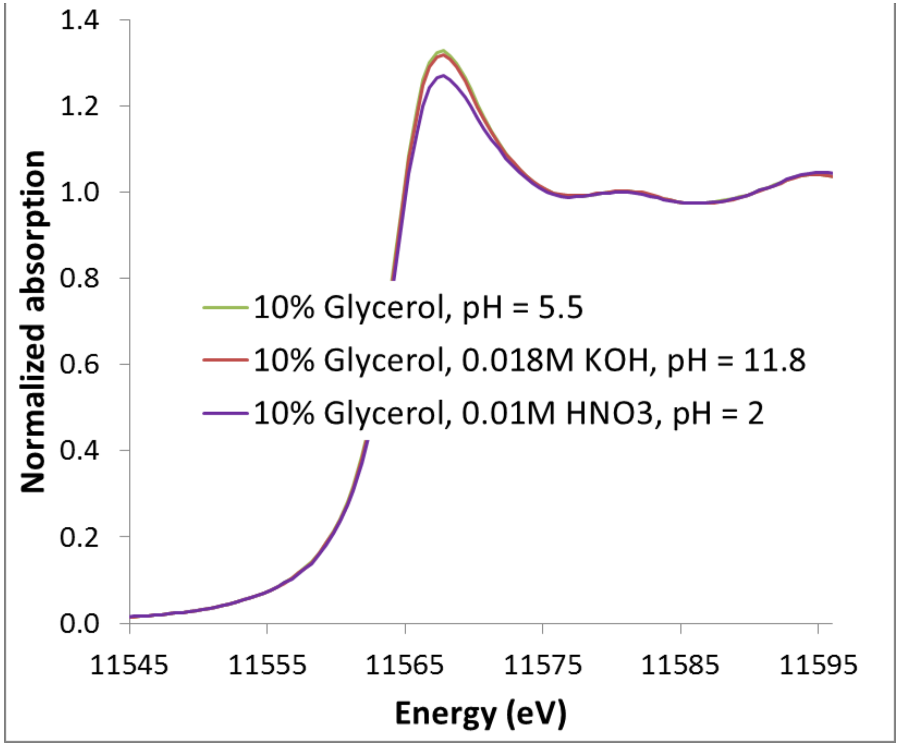
Effect of pH on Pt Electronic Structure and Adsorbates



Coverage relative to pure gas at 225 °C	**pH**		
	5.5	11.8	2
H_2 (%)	2	3	53
CO (%)	95	93	68

- Effect of KOH is due to interaction with reaction intermediates (aldehydes).
- Effect of HNO_3 is due to direct interaction with adsorbed species (i.e. CO and H_2) and/or direct interaction with Pt surface.
  - CO coverage decrease and H_2 coverage increase.
  - Adsorbates other than H_2, CO and H_2O can be present under HNO_3.

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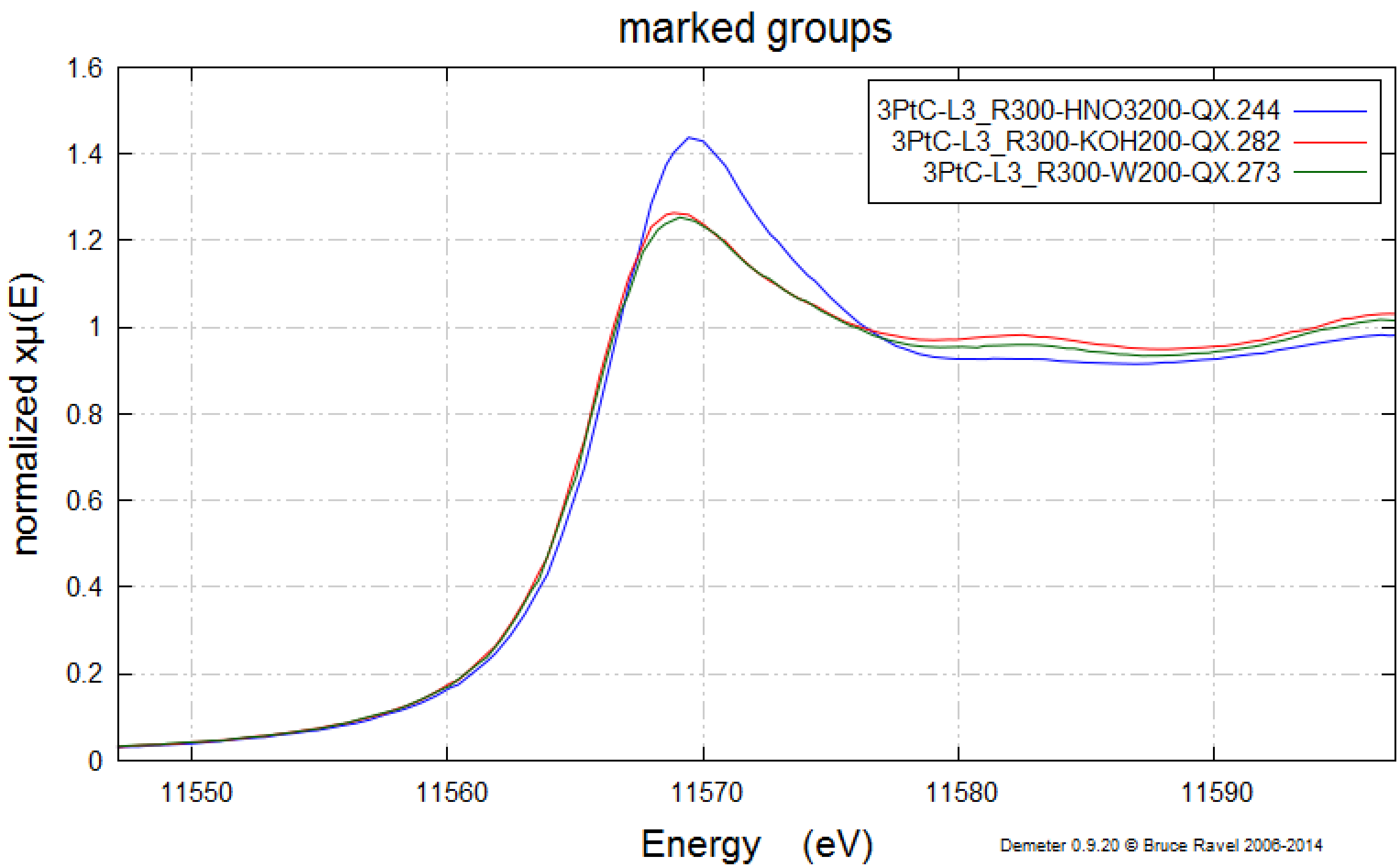
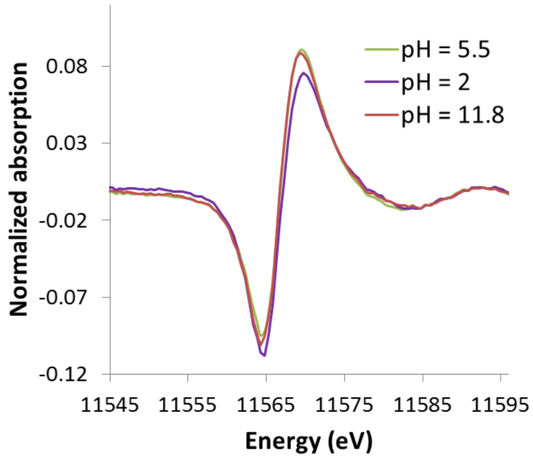
Effect of high and low pH on Pt



Effect of pH

- Acids have an effect on the Pt electronic properties.
- Acid effect:
  - Acid-adsorbate and/or acid-Pt interaction (and possibly homogeneous chemistry).
  - Increased H_2 coverage → higher selectivity to C–O cleavage.
- Selective H_2 production from biomass derived liquids under realistic conditions is challenging.
  - Hydrodeoxygenation is favored under acidic conditions
- Define your question
- Plan your experiment
  - XAFS should not be your first attempt at characterizing the sample



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