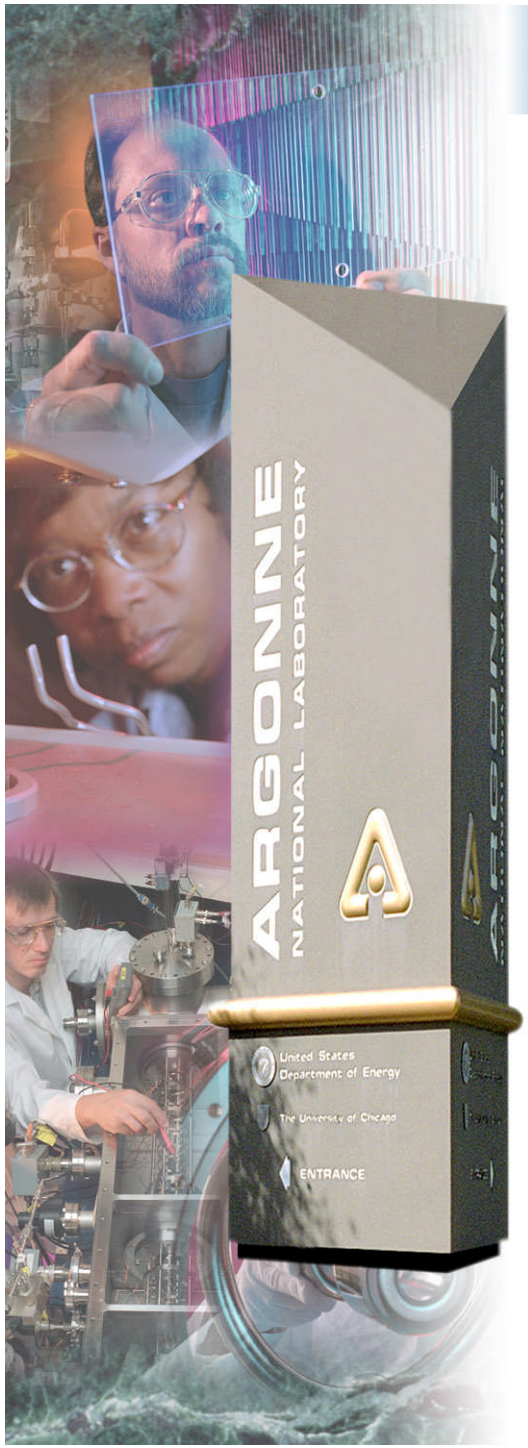

ARGONNE NATIONAL LABORATORY

Workshop on Catalysis Research at the APS

Advanced Photon Source

Argonne National Laboratory

September 12-13, 2005

Organizing Committee

Simon Bare, UOP LLC
Steve Heald, PNNL
Chris Marshall, ANL
Peter Stair, Northwestern U.
Randall Winans, ANL
Hoydoo You, ANL

Support from BP, Innovene and the APS is gratefully acknowledged.

THE UNIVERSITY OF CHICAGO

Office of Science
U.S. DEPARTMENT OF ENERGY

Argonne National Laboratory is managed by
The University of Chicago for the U.S. Department of Energy

Purpose

- Catalysis research is being done at a number of beam lines at the APS using several techniques. The purpose of this workshop is to evaluate current catalysis research and future directions.

- One objective will be to introduce the catalysis community to some of the unique capabilities of the APS.

- A second objective will be to produce a report with recommendations to promote catalysis research at the APS.

Program September 12

8:00	Registration and continental breakfast
8:20 - 8:35	Murray Gibson, Associate Laboratory Director APS, Welcome
8:35 - 9:00	Gabrielle Long, APS, Introduction to the APS
9:00 - 9:50	Bruce Gates, U. of California at Davis "Supported Metal Catalysts with Virtually Molecular Structures: Characterization by Spectroscopic Methods with Emphasis on X-ray Absorption Spectroscopy"
9:50 - 10:00	Break
10:10 -11:00	Jeff Miller, BP, "XAFS Spectroscopy in Catalysis Research: Application to Au Catalysts"
11:00 - 11:50	Thorsten Ressler, Fritz-Haber-Institute "Time-resolved X-ray Absorption Spectroscopy in Catalysis"
11:50 - 12:00	Charge to working groups
12:00 - 1:00	Lunch (not hosted)
1:00 - 1:50	Raul Lobo, U. of Delaware "The Pair Distribution Function Method and its Application to Zeolite Catalysts"
1:50 - 2:40	Gregory Beaucage U.of Cincinnati, "Structural and Surface Studies of Heterogeneous Catalysts using Small-Angle X-ray Scattering"
2:40 - 3:00	Break
3:00 - 3:50	Paul Fenter, ANL, "Opportunities in Catalysis Research using High Resolution Interfacial X-ray Scattering"
3:50 - 4:40	John Budai, ORNL, "How polychromatic microbeams can provide new tools for spatially-resolved materials studies"
5:30	Poster Session/Reception – Gallery

Bruce Gates

SOME CHALLENGES IN CATALYSIS RESEARCH

FIND STRUCTURES THAT DO THE CATALYSIS
(**ELIMINATE RED HERRINGS**)

STRUCTURES CHANGE DEPENDING ON CONDITIONS
SUCH AS TEMPERATURE & REACTIVE ATMOSPHERE

DETERMINE **RELATIONSHIPS** BETWEEN **STRUCTURE & CATALYTIC PROPERTIES**

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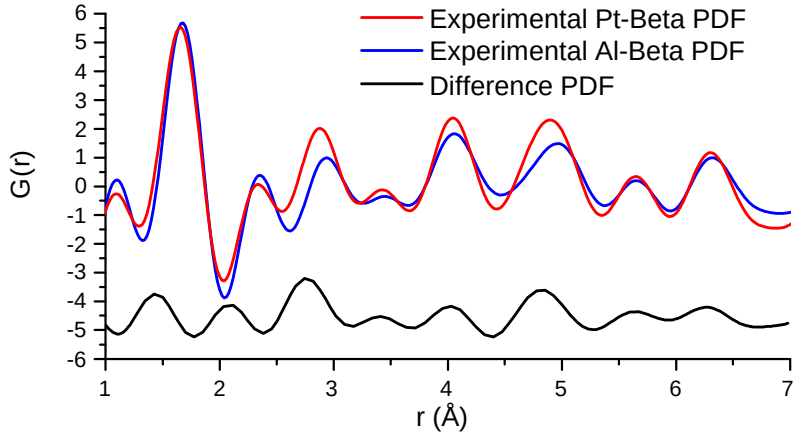
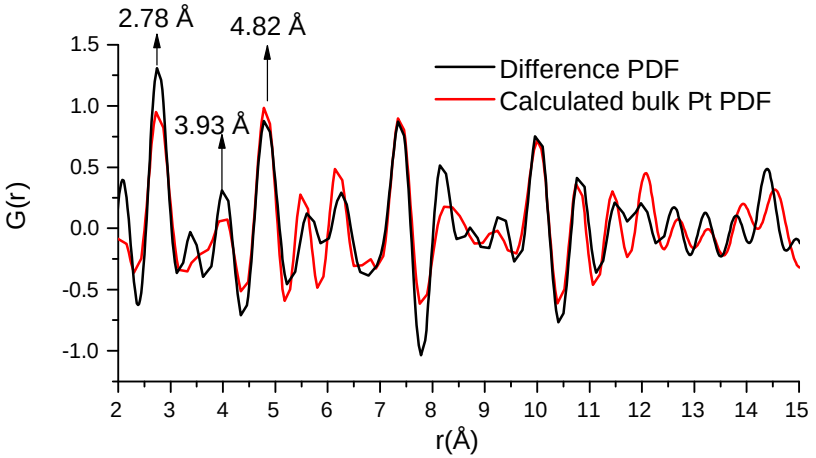
Raul Lobo

Pt Cluster Experimental PDF

- By substracting the zeolite PDF from Pt-zeolite PDF12
- Structure observed up to 15 Å
- Same peaks as bulk Pt
  - Same symmetry
- Different peak intensity
  - Different possible causes
    - *Limited cluster size*
    - *Interactions with zeolite included in PDF*





12. Obtained at APS, ANL

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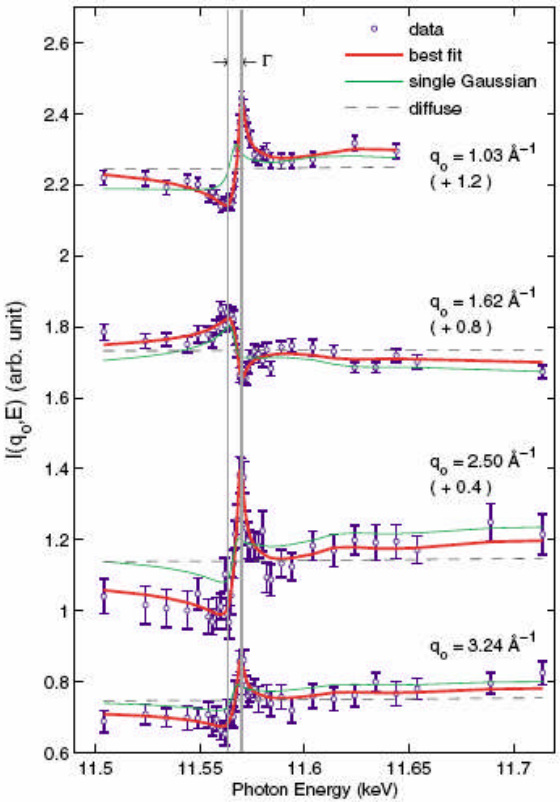
Paul Fenter

Probing catalyst preparation with resonant anomalous X-ray reflectivity

$Pt(NH_3)_4^{2+}$ (platinum tetraammine) Adsorption at the Quartz (100) to Water Interface

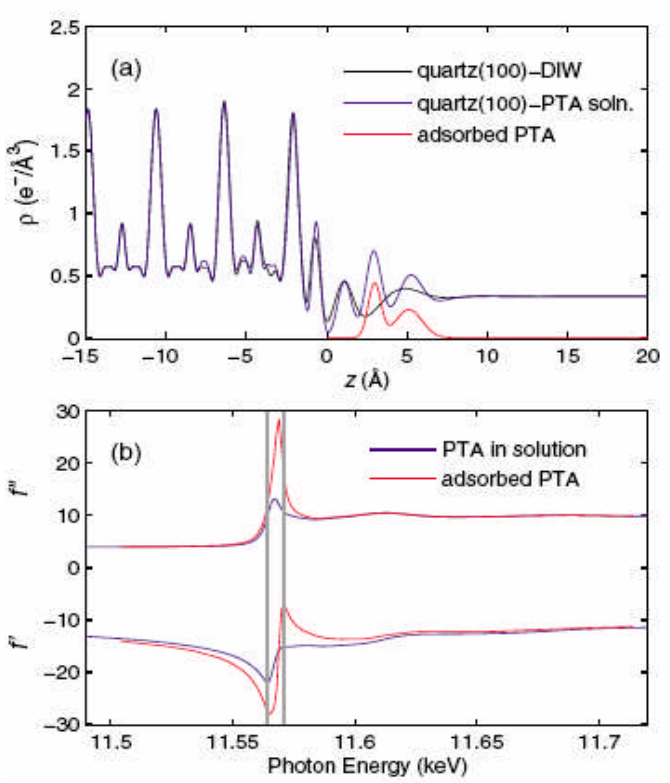


Resonant anomalous x-ray reflectivity near the Pt L_{III} edge

The Pt distribution contains at least two distinct layers

There is a substantial white line in f".

C Park, PA Fenter, NC Sturchio, JR Regalbuto, *Phys. Rev. Lett.* **94**, 076104 (2005)



- ***Simultaneously* probes the geometric and spectroscopic structures of interfaces**
- **Directly probes interfacial chemistry: ion adsorption, oxidation/reduction reactions**

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Program September 13

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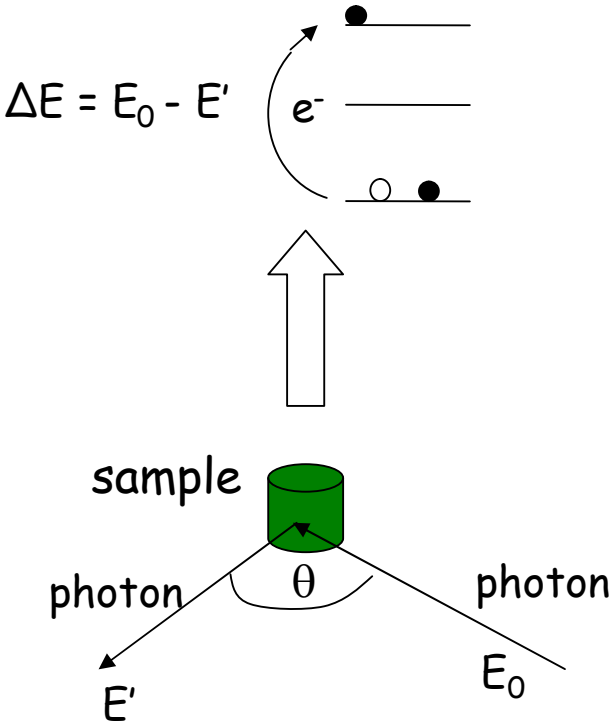
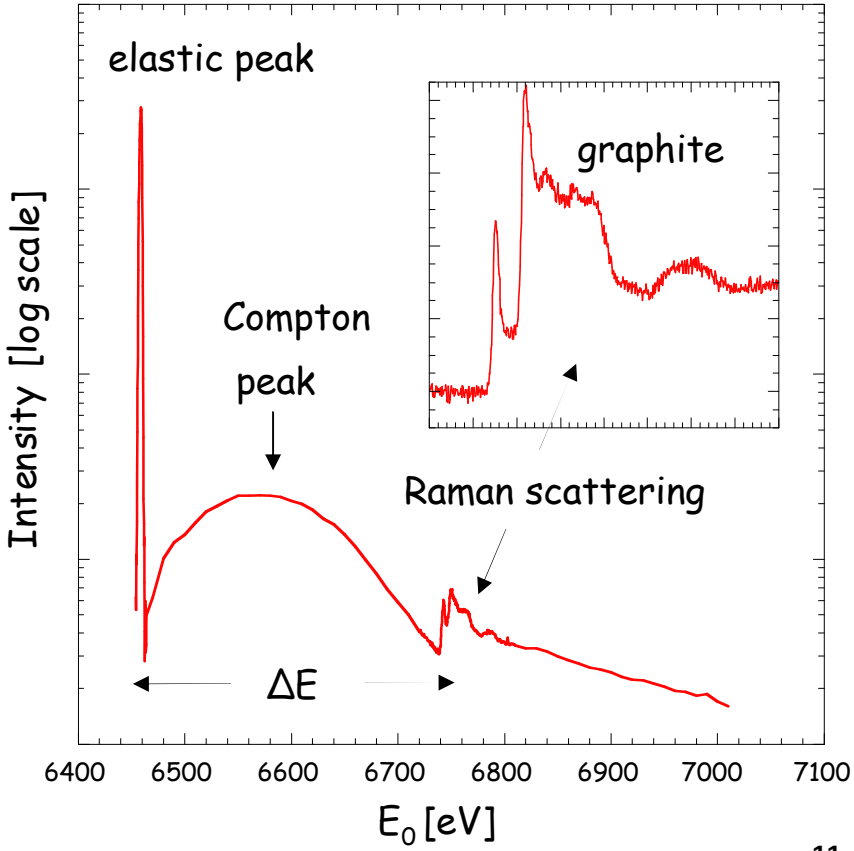
8:30 – 9:20	Nenad Markovic, ANL, "Surface science studies of fuel cell reactions: from model systems to real catalysts"
9:20 – 10:10	Uwe Bergmann, SLAC, “Application of Advanced Hard X-ray Spectroscopy and Inelastic Scattering to Catalysis”
10:10 – 10:30	Break
10:30 – 12:00	Panel Discussion
12:00 – 1:00	Lunch
1:00 – 2:30	Breakout Session
2:30 – 3:00	Summary of Reports

Uwe Bergmann

X-ray Raman Process (Non Resonant)





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- To promote the panel discussion on Tuesday a set of four questions have been generated which are designed to get the participants thinking about possible issues concerning catalysis research at the APS:

1. What are the X-ray techniques that are most important for catalysis research and what are the predicted demands for these techniques?

•**XAFS and powder diffraction** are the core x-ray techniques utilized in catalysis research and will be in the most demand.

•Many other techniques are available at the APS and are potentially critical for specific applications and include:

Wide and small angle scattering
X-ray reflectivity and surface scattering
Advanced x-ray spectroscopic techniques (XRS, XES, RIXS),
Micro-crystal diffraction
PDF

•A major strength of the APS for the catalyst community is the ability to do in situ, real time studies with the above techniques.

•Scattering measurements on an element specific basis (via anomalous techniques) are also an APS strength that will be valued by the catalysis community.

2. Which are more appropriate, beam lines dedicated to a particular field or portable catalysis facilities that are useable on any beam line? What are the advantages and disadvantages of each?

- There are inherent conflicts between beamlines dedicated to techniques and the need for multiple techniques at a single beamline.
  - Dedication to particular techniques is a more efficient use of hardware and manpower. The instrumentation associated with a specific technique are expected to improve as time goes by..
  - At the same time it is critical to provide the capability to perform more than one technique, particularly XAS and powder XRD, on a catalyst during pretreatment and under reaction conditions.
- We recommend the establishment of one bending magnet beamline with associated staff specializing in catalysis.
  - This facility will serve as a focus for the catalysis community, and it provides the necessary home base for the staff specializing in catalysis.
  - The staff can act as the point person to organize measurements on more specialized beamlines when needed.
  - It is also critical for the dedicated beamlines to provide the capability for measurements on catalysts under pretreatment and working reaction conditions.

3. How do you promote accessibility for catalysis research for both basic research and industrial research? What should be the criteria for awarding beam time? What kind of user support is necessary? What kind of assistance in data reduction is required?

- Assumptions:
  - There is justification and demand for a dedicated XAFS-Diffraction beamline at the APS dedicated to catalysis
  - The beamline will be instrumented and staffed for support of catalysis work
- Issues:
  - Increase the availability of the beamline to new users who are most often novice synchrotron users
  - Much of the work be standard characterization, rather than frontline science

3. Recommendations

- Formation of a liaison group to:
  - Facilitate obtaining beamtime for first time users
  - Providing contacts with potential collaborators
  - Resource for questions related to doing experiments and fitting data
  - Provide regular training courses for doing experiments and fitting data
- Provide beamtime on a 2-tier basis
  - Initial beamtime (several visits during 1st year) to new users
  - Peer-reviewed proposals for experienced users
- Formation of catalysis group to review group to evaluate catalysis proposals

4. What are the equipment needs that are unique to catalysis research? How can reactor contamination be avoided?

- Working from the premise that catalysis research at APS should take advantage of uniqueness of the high-intensity beams offered by the synchrotron, we conclude that the most appropriate catalysis research at APS will involve characterization of catalysts in the functioning state (specifically in transient states and also at high temperatures and pressures), so that structural information can be determined about catalyst structures, specifically including the catalytically active species.

- An implication of this premise is that the sample cells will also be flow reactors, fed with gaseous and/or liquid reactants, as well as products, poisons, and inhibitors of the catalytic reactions.

- Important issues are concerned with:
  - Safety in continuous gas delivery to and removal in hutches
  - Equipment is needed for handling air sensitive catalysis.
  - Avoidance of contamination of samples from cells and lines
  - Sample preparation often requires prep labs.

4. Recommendations:

- Beam lines should be supplied with high-purity gases, including H2, O2, N2, He, and CO, and sensors to detect them as well as facilities for removing gases..
- At least one mass spectrometer and one gas chromatograph (and preferably two of each) should be available
- One very good prep lab is needed, or, even better, two appropriately located around the beam. The prep lab(s) should be equipped with fume hoods, glove box(es), cabinets for safe storage of flammable chemicals, ovens/furnaces for calcination, activation, and drying of catalyst samples
- Be sure that infrastructure for delivery of gases, chemicals, and supplies is reliable.
- Users should supply their own cells, lines, etc., to avoid possible contamination
- Users should share standardized cell designs and design criteria. Work is needed to delineate the reaction engineering issues of flow-through cells.
- Beam lines should be set up to make possible various measurements simultaneously, such as diffraction and spectroscopy, for example.
- Guidelines for safe work with gases should be determined realistically and made available to potential users.
- Uniform software should be supplied, at least for EXAFS spectroscopy.

Energy Policy Act of 2005 (Enrolled as Agreed to or Passed by Both House and Senate)

SEC. 973. CATALYSIS RESEARCH PROGRAM.

(a) Establishment- The Secretary, acting through the Office of Science, shall support a program of research and development in catalysis science consistent with the statutory authorities of the Department related to research and development.

(b) Components- The program shall include efforts to--

(1) enable catalyst design using combinations of experimental and mechanistic methodologies coupled with computational modeling of catalytic reactions at the molecular level;

(2) develop techniques for high throughput synthesis, assay, and characterization at nanometer and subnanometer scales in-situ under actual operating conditions;

(3) synthesize catalysts with specific site architectures;

(4) conduct research on the use of precious metals for catalysis ; and

(5) translate molecular understanding to the design of catalytic compounds.