

Workshop on Catalysis Research at the Advanced Photon Source Report

**Workshop held at the Advanced Photon Source,
Argonne National Laboratory on September 12-13, 2005**

Organizers

Simon Bare UOP LCC
Steve Heald PNNL
Chris Marshall ANL
Peter Stair Northwestern University
Hoydoo You ANL
Randall Winans ANL

Sponsored by: BP, Innovene and the APS

Workshop on Catalysis Research at the APS

Executive Summary

Catalysis is an essential technology for economic prosperity, energy security and environmental preservation in the 21st Century. The importance of catalysis research to meeting the energy needs of the nation and the central role of DOE facilities in advancing catalysis science have been specifically identified in the Energy Policy Act of 2005. A workshop titled “Catalysis Research at the APS” was held on September 12-13, 2005 in order to assess the requirements and opportunities for supporting catalysis research that makes use of the Advanced Photon Source at Argonne National Laboratory. The workshop included lectures and a poster session presented by experts in both catalysis science and the capabilities and development of x-ray characterization methods at the APS. A particular focus of the workshop was to identify specific needs of the catalysis research community for measurements under reaction conditions that are uniquely available APS. A set of recommendations to the APS management were developed following a Panel Discussion and Breakout Sessions.

Recommendations for the support of catalysis research at the APS

- **Beamline for Concurrent XAS and XRD Measurements**

Concurrent in-situ x-ray absorption spectroscopy and in situ x-ray diffraction measurements of catalysts are urgently needed. APS should establish one bending magnet beamline, designed to perform concurrent XAS/XRD measurements (Section 1).

- **Infrastructure for In-situ Experiments on Specialized Beamlines**

Catalytic reactions are normally performed under conditions of elevated temperature and pressure, using a wide variety of reagents. Consequently, the atomic level structure of the working catalyst is often profoundly different than the same material under ambient measurement conditions. The high brightness and wide energy range available at APS enable in-situ measurements that are essential for understanding the working catalyst and cannot be performed elsewhere in the US. These include: small angle scattering, surface scattering, advanced spectroscopy and high energy scattering with PDF analysis. The APS should provide the facilities infrastructure needed to allow measurements under the wide range of reaction conditions employed in catalysis. This infrastructure should preferably be available on both catalysis-specific and dedicated-technique beamlines (Section 2).

- **X-ray Scientist for Catalysis Research**

Enabling catalysis science experiments on the XAS/XRD beamline and coordinating studies on other, dedicated beamlines will require associated staff with catalysis research expertise. APS should provide appropriate, beamline-science staff, specializing in catalysis research (Section 3).

- **Communication between Catalysis Scientists and APS**

Better communication between APS management and the catalysis science community will achieve the goal of expanded access to APS experiments for both basic and applied catalysis research. APS should consult with the “Catalysis Interest Group” about planning and operations that effect catalysis science. Working together will be a win-win solution for both communities (Section 4).

I. Introduction

Catalysis research is currently being conducted at a number of beamlines at the APS using a wide array of techniques. The purpose of this workshop was to evaluate current catalysis research, and discuss future directions. A major objective was to produce this report with recommendations aimed at promoting catalysis research at the APS. A small number of speakers who represent the diverse spectrum of hard x-ray science aimed at solving critical problems in catalysis were invited to present oral talks. All participants, who included representatives from university, industry and National labs, were encouraged to present posters. Another objective was to introduce the catalysis community at-large to some of the unique capabilities of the APS. We believe that this workshop serves as the first step in attracting additional high impact catalysis research to the APS. Catalysis has a significant presence in DOE Basic Energy Sciences, but these programs have not fully utilized the capabilities of 3rd generation light sources. Additionally, resources that would enhance catalysis research at the APS have been identified. Finally, the catalysis community was exposed to techniques which in many cases are unique to the APS. The workshop was attended by 82 participants.

The meeting began with a warm welcome to the participants by Associate Laboratory Director Dr. J. Murray Gibson, followed by an overview of the current capabilities of the APS for catalysis research by Associate Division Director Dr. Gabrielle Long. The morning continued with hour long invited talks on different aspects of X-ray absorption spectroscopy as applied to catalysis research. The first talk, by Prof. Bruce Gates (UC Davis), showed how in situ XAFS is a critical technique for studying the preparation of metal nanoclusters prepared from metal carbonyls, and that these nanoclusters on supports are not simply zero valent metals. He also showed how the structure of the catalyst depends on the reaction environment and therefore giving evidence that in situ characterization is critical for a full understanding of the catalyst. Dr. Jeff Miller (BP Corporation) presented EXAFS data on the structure of supported gold clusters – a hot topic in the catalysis community. He presented data that showed that hydrogen reduction leads to smaller clusters than simple calcination and that the presence of chloride causes sintering. The small Au particles are electron deficient with very short metallic bond distances. A small fraction of the metallic Au oxidizes in small particles, but not large particles. Dr. Thorsten Ressler (Fritz-Haber-Institute, Berlin) presented a talk focused on the time-resolved XAFS and its applicability to studying dynamic systems in catalysis. He showed examples from sulfated zirconia for the isomerization of butane, Cu/ZnO catalysts for methanol steam reforming and molybdenum oxide catalysts for selective oxidation of propene. He concluded that the “real” (defect) structure of catalysts deviates from the ideal structure and dynamically changes under reaction conditions. He was able to derive structure-activity correlations from in situ studies under dynamic conditions.

The invited talks continued in the afternoon beginning with a talk by Prof. Raul Lobo (Univ. Delaware) on how pair distribution functions can be used to better understand the structure of zeolites. He presented data on three different types of structural disorder in zeolites: static, dynamic (local correlated and uncorrelated atomic vibrations) and the structure of an adsorbed phase in the zeolite pores. He also highlighted the strengths and limitations of the method. Prof. Gregory Beaucage (Univ. Cincinnati) described structural studies of heterogeneous catalysts using SAXS. He described the requirements of the technique, some of the unique capabilities of the APS, and that SAXS offers access to an extremely wide range of sample environments from atmospheric conditions to high pressure corrosive gas environments. He concluded by noting that SAXS/WAXS studies at APS offer a unique window for the understanding of structural effects on the activity and activation of heterogeneous catalysts. Opportunities in catalysis research using high resolution interfacial X-ray scattering was the subject matter of the talk by Dr. Paul Fenter (ANL). The techniques using interfacial scattering provide a robust “tool box” for the study of

complex interfaces. Clearly these techniques are only applicable to model catalyst systems, but the demonstrated capabilities, e.g. in situ, real time, element specific, chemically sensitive, and interface specific, provide information on these systems that cannot be obtained by any other method. Spatial resolution was the focus of the talk by Dr. John Budai (ORNL). He described some of the 2D and 3D scanning X-ray techniques being developed at Sector 34 at the APS. The potential for using these scanning X-ray techniques in catalysis research was also discussed.

On Monday evening there was ample time for discussion on these talks and on the many posters presented during a poster session and reception. The second day saw two more invited talks. The first by Dr. Nenad Markovic (ANL) on the characterization of model (single crystal) fuel cell catalysts, and the second by Dr. Uwe Bergmann (SLAC) on advanced spectroscopies using hard X-rays. Bergmann's forward thinking talk provided the audience with a glimpse of the future of X-ray based spectroscopic techniques. These techniques include: X-ray Raman spectroscopy, X-ray emission spectroscopy, selective X-ray absorption spectroscopy, and resonant inelastic X-ray scattering. Bergmann discussed each of these techniques, and gave examples of potential catalytic implications.

The real work began after the morning break with a lively panel discussion on the present and future needs for catalysis research at the APS. After lunch the meeting participants broke up into small groups with each group responsible for discussing and summarizing a different aspect of these needs. The results of these discussions are recommendations which are discussed at the end of this report.

II. Recommendations

1. Beamline for Concurrent XAS and XRD Measurements

Concurrent, in-situ x-ray absorption spectroscopy and x-ray diffraction measurements of catalysts are urgently needed. APS should establish one bending magnet beamline, designed to perform concurrent XAS/XRD measurements

X-ray absorption fine structure, XAFS, spectroscopy (X-ray absorption near edge fine structure, XANES, and extended X-ray absorption fine structure, EXAFS) has become a workhorse technique for catalyst characterization over the last 30 years. The popularity of the technique is primarily the result of the power of the technique to provide *in situ* element-specific atomic-level chemical and geometric information on the structure of real working catalysts (both heterogeneous and homogeneous). From 1997-2004 the number of papers published in peer reviewed journals with the search terms “XANES or EXAFS and catalysis” totals over 2700, with an average of 330 papers per year, and the number published with the search terms “in situ XANES or EXAFS and Catalysis” numbers over 380. Moreover, in the last few years there has been a significant resurgence in the technique due to the development of *ab initio* multiple scattering codes, e.g. FEFF, to aid in the modeling and analysis of the XAFS data, coupled with more user-friendly data analysis packages, e.g. WinXAS, SixPack, and Athena & Artemis.

Similarly synchrotron X-ray powder diffraction (SXRPD) is a core-competency for structural analysis of catalytic materials. The major application of SXRPD is structural analysis of new catalytic materials using Rietveld refinement (e.g. zeolites and mixed oxides). However, similar to XAFS, there has been significant recent emphasis on *in situ* structural studies. Examples include the effect of molecules adsorbed in zeolites and the reduction of crystalline catalytically-relevant metal oxides.

We believe that the vast majority of catalysis-related XAFS and diffraction studies could be accomplished on an APS BM line; provided that the beam line has the infrastructure to handle the demands of catalysis research (see Section 4, below). However, the new capability that we propose that the APS develop is a beamline that allows concurrent XAFS and XRD data to be collected – combined with *in situ* capabilities. Such a combination does not exist at any of the four BES/DOE synchrotron facilities in the US. We believe that there is a significant unmet need in the catalysis community for such a facility, and that the demand will be heavy once such a facility is available to the catalysis community.

The specifications for such a beamline include: XAFS data to be collected in quick-scan mode, so-called QEXAFS, (e.g. 1keV scan in a ~1 minute) and step-scan mode; an energy range of 4-40keV; energy resolution below the lifetime-broadened core hole width of the nearest inner shell state – achieved using a collimating mirror; harmonic rejection and vertical focusing using Pd-coated mirrors (vertical focusing is critical for use of capillary-style *in situ* cells); and possibly a sagittally focusing second crystal in the monochromator that can be dynamically bent.

2. Infrastructure for In-situ Experiments on Specialized Beamlines

The high brightness and wide energy range available at APS enable in-situ measurements that are essential for understanding the working catalyst and cannot be performed elsewhere in the US. In addition to the techniques described in section 1 small angle scattering, surface scattering, advanced spectroscopy and high energy scattering with PDF analysis also provide critical

structural information. Further detail on these methods is provided at the end of this section. Studies using these techniques are currently conducted at beamlines that have been optimized for the technique, but not for the catalysis experiment that often requires an infrastructure typically not found on these beamlines.

The most relevant catalysis research at APS will involve characterization of catalysts under reaction conditions (i.e. catalytically relevant temperatures and pressures and appropriate reagent compositions). This will allow detailed structural information to be determined including hopefully, the catalytically active species. Sample cells for in situ experiments will require flow reactors, supplied with the necessary gaseous and/or liquid reactants, as well as products, poisons, and inhibitors of the catalytic reactions.

The committee cited several important issues that need to be addressed:

1. The safe handling of continuous gas delivery to, and removal from, the hutch is crucially important. Many of the feed gases and catalytic products are hazardous and/or toxic and pre-established protocols should be established to ensure their safe handling.
2. Many catalysts are air or water sensitive and proper handling is crucial to ensuring that meaningful data are collected. Therefore, facilities should be established at the APS for the handling air and water sensitive materials.
3. Catalysts are active under a wide variety of conditions. Feed and activators for one catalyst system can be poisons for other systems. Therefore, systems need to be established to minimize contamination of samples from reaction cells and lines.
4. Many samples need to be prepared fresh and examined at the beamlines immediately after preparation. A catalyst preparation laboratory should be established at the APS.

Scattering and Advanced Spectroscopy Approaches

Wide and small angle scattering

Small angle X-ray scattering (SAXS) has been used to characterize catalysts, following synthesis of catalysts and for in situ studies of catalytic function, resulting in over 400 publications. The approach provides size, shape, and surface morphology of particles and of voids. SAXS has been used for the characterization of catalysts, including an exploration of the properties of metal supported catalysts. Brumberger has found good agreement between SAXS and BET in terms of surface area determinations. SAXS has already been used to study the synthesis of zeolites. The growth of small ZnO clusters in ZSM-5 has been followed *in situ* by SAXS. The sintering in air of Pt-Al₂O₃ with high Pt loadings was followed by SAXS, where a rapid response in sintering was observed with heating. In a study of the preparation of Pt-NaY, it was found that the Pt(0) is highly dispersed when calcined at 250 °C but that sintering begins at 300 °C.

Anomalous SAXS (ASAXS) to extensions of standard SAXS experiments in which the energy of the probing X-rays are tuned near the absorption edge of an element in the sample. By performing SAXS experiments near the characteristic absorption edge of any given atom, it is possible to vary the contrast for scattering of that particular element. This method overcomes the problem of separating the scattering of the sample from that of the support. Established analysis techniques such as Guinier analysis, Gaussian fit of peaks, and modeling will be used for the analysis of

SAXS data as well as the partial structure factors from the ASAXS data. This approach has been used to characterize supported metal catalysts. Microstructural studies have been done on catalyst systems with very low loadings of metals such as 0.2% Au using this approach. Information on particles in the size range of 1 – 2 nm have been obtained which is important considering the activity of metal particles in this size range.

The catalytic particles on surfaces can be characterized by grazing incidence small angle X-ray scattering (GISAXS) both *ex situ* and *in situ* to study their thermal transformations and reactivity. GISAXS can provide the same type of information as regular SAXS such as cluster size, shape and distance between clusters, and in addition, it can give depth profile information. Also, the aspect ratio (height/diameter) of a metal cluster can be calculated from the GISAXS data and using the Wulff-Kaishew construction, the interfacial energy can be obtained. It is ideal for *in situ* studies since it is very sensitive to surface species and there is less parasitic scattering resulting from the substrate compared to a direct transmission scattering experiment. GISAXS was first demonstrated using a lab X-ray source for studying gold films². More recently the technique has become popular for studying quantum dots and clusters on and imbedded into surfaces. Recent work of Renaud et al. demonstrated the high sensitivity of the GISAXS technique to monitor in real time the growth of Pd clusters on MgO(100) and of Co on Au(111) during metal vapor deposition and this work has been extended to a quantitative study of the growth of Pd particles on MgO. GISAXS has been used to study Pt nanoparticles and unexpectedly high thermal stability was observed where their original size was preserved up to about 320 °C. Cylindrical particle shapes were observed at lower levels of surface coverage and more spherical forms at higher levels of coverage. The kinetics data indicate a two-step agglomeration process with final particle size determined by the level of surface coverage. In the case of the supported Au nanoparticles, the onset of aggregation takes place at approximately 180 °C and the particle shape evolves from spherical to oblate. These experiments demonstrate the powerful combination of cluster deposition, atomic layer deposition and synchrotron techniques, which can aid in characterization and design of new nanoparticle-support combinations with potential use, for example, in catalysis. Currently the approach is being used to study these platinum nanoclusters as they are exposed to reactive gases at elevated temperatures. By combining GISAXS with ASAXS (AGISAXS), the sensitivity for small changes on the metal particles on surfaces is greatly enhanced. The first results that have demonstrate the feasibility of this approach.

X-ray reflectivity and surface scattering

Heterogeneous catalysis takes place at the interfaces of the high-pressure gas and catalysts and heterogeneous electrocatalysis at the interfaces of electrolyte and catalysts. The catalysts are typically in nano-scales and their activities occur in molecular length scales. The surface-interface x-ray scattering (SIXS) techniques are powerful for the nanoscale to molecular-scale structure and chemistry, especially when they are applied to well-defined and well-controlled interfaces. The penetrating hard x-rays available at the Advanced photon source allows us to perform such molecular-level studies *in situ*, therefore, to close the pressure gap, more generally environmental gap, between the experimental conditions and the real catalytic conditions. Although it is much more difficult to overcome the materials gap, the gap existing between the well-defined interfaces and the real nanoparticle interfaces, careful fabrication of model systems can also lead to the investigation of realistic catalytic materials under realistic environments. It is important to emphasize that x-ray techniques are true unique microscopic probes which can yield both structural and chemical information simultaneously.

A more recent development in the SIXS techniques is the utilization of anomalous resonant phenomena. Like XANES and EXFAS, the anomalous resonant component of the scattering factors carries information about the chemical and local structure information of the resonant atom. However, unlike XANES and EXFAS, the anomalous resonant SIXS can provide momentum-transfer (q) dependence and polarization (p) dependence with respect to the surface/interface specific to catalytic reactions of our interest. The q - and p - dependences enable us to study the chemical and local information but in an interface-sensitive manner. This interfacial sensitivity is unique and only available when we use the advanced resonant SIXS techniques with the most powerful x-rays available at the Advanced photon source. We must fully exploit the capabilities of the q - and p - dependent SIXS techniques for studies of heterogeneous catalysis and electrocatalysis.

Advanced x-ray spectroscopic techniques (XRS, XES, RIXS)

Advanced spectroscopic techniques require a high resolution (~ 1 eV) fluorescence spectrometer in addition to a standard XAS setup. These advanced methods include x-ray Raman spectroscopy, selective x-ray absorption, x-ray emission spectroscopy, and resonant inelastic x-ray spectroscopy (RIXS). They can extend the power of XAS by providing more detailed information or by allowing new types of measurements. All of these techniques benefit greatly from a third generation source since the signals are often weak, and the detector efficiency is low. For example, in the x-ray Raman process the cross section is typically several orders of magnitude less than for elastic scattering. X-ray Raman measurements, however, allow the measurements of low-Z edges while maintaining the advantages of hard x-rays. These advantages include a true bulk measurement with no need for vacuum environments, and easy access to samples in a variety of *in-situ* conditions. The Raman signal also allows the probing of non-dipole transition information by going to high q .

The other advanced techniques can also offer significant advantages in specialized cases. Selective x-ray absorption uses the energy dependence of the fluorescence to selectively measure the species of interest. In the simplest case the fluorescence of interest can be separated from the nearby fluorescence of interfering elements to extend the range of the EXAFS measurements. A more elegant application uses the energy dependence of the fluorescence with valence to make valence specific XAS measurements. For example, Fe(II) and Fe(III) sites can be separately probed by tuning to the appropriate fluorescence energy. The related method of x-ray emission spectroscopy uses a detailed study of the differences in fluorescence spectra to deduce information about oxidation state, spin state, and ligand type and geometry. The most complete study of the fluorescence is RIXS, where the fluorescence emission spectrum is probed as the incident energy is scanned through the absorption edge. This gives a two dimensional plot of the fluorescence intensity versus excitation and emission energies. By taking various cuts through this 2-d data it is possible to get L or M edge information with hard x-rays, mitigate lifetime broadening of edges, and isolate LUMO resonances.

Pair Distribution Function Method

With the increased availability of large fluxes of high energy X-rays (>60 keV, $\lambda < 0.2$ Å) at third generation synchrotrons such as the Advanced Photon Source at Argonne, the Pair Distribution Function (PDF) method has re-emerged as a powerful technique for structural characterization in catalysis. The PDF method is a total scattering method, and measures the probability of finding two atoms at a distance r (*i.e.* atom-atom correlations), including those that may deviate from the *average* long range structure both statically and dynamically. High resolution PDFs, *i.e.* $G(r)$ s, necessitate the measurement of $S(Q)$ to high values of momentum transfer, Q , often $30-40$ Å⁻¹,

and require the use of high energy X-ray sources. The information obtained relates largely to the local structure $<5 \text{ \AA}$ and extends to intermediate ranges, 1-5 nanometers. The PDF technique has been applied with great success to bulk systems in catalysis, including both ceria and RuO_2 .

The PDF method is particularly advantageous in studying materials that incorporate disorder (e.g. stacking faults) such as zeolites. For example, Lobo and coworkers have used the PDF approach to probe the defect structure of zeolite Beta. The dynamic disorder of structures can also be important in particular physical properties and Martinez-Inesta and Lobo have recently questioned the widely believed vibrational mechanism for negative thermal expansion behavior in a zeolite, Chabazite, using reverse Monte Carlo modeling of the PDF.

Beyond direct analysis of the individual PDF, new approaches are being developed to maximize the available structural information such as fitting the differential PDF. In complex structures it is not always straightforward to assign the individual peaks in the PDF to specific pair correlations. Differential PDFs can directly probe structure around specific atom types or sites, an approach with a large potential impact on the study of supported metal catalysts, which find widespread use in chemical reforming. Using differential methods, the structure of the supported metal particles can be selectively recovered isolating particle-particle and particle-support correlations.

While steady state/ambient measurements are relatively straightforward, the application of the PDF technique to *in-situ* studies has been severely limited due to the typically long measurement times (~ 8 -12 hours). Recently work performed at the APS has demonstrated that the use of area detectors can reduce the time needed to collect data suitable for PDF analysis by *three orders* of magnitude. With time resolution of seconds to minutes, *in-situ* PDF studies of functional materials are now possible.

3. X-ray Scientist for Catalysis Research

We recommend hiring staff that are expert in both x-ray science and catalysis research. While the dedicated EXAFS/Diffraction BM proposed above will be the home base for the scientific staff we expect they will become familiar to many other advanced techniques and specialized beamlines available at the APS. The staff will be a point of contact for the catalysis community, help users at the dedicated facility, and advise them in selecting the appropriate techniques and beamlines for more advanced stage of their research.

4. Communication between Catalysis Scientists and APS

Better communication between APS management and the catalysis science community will achieve the goal of expanded access to APS experiments for both basic and applied catalysis research. A "Catalysis Interest Group" has formed as a result of this workshop and will hold monthly meetings. APS should consult with this group about planning and operations that effect catalysis science.

Specific recommendations include: (a) Formation of a liaison group that would facilitate obtaining beamtime for first time users, provide contacts with potential collaborators, act as a resource for questions related to data analysis, and provide regular training courses. (b) Provide beamtime on a 2-tier basis, one being initial beamtime (several visits during 1st year) to new users and the second peer-reviewed proposals for experienced users and (c) Formation of catalysis group to be part of the review system to evaluate catalysis proposals

III. Appendix

Specific infrastructure (Section 2) recommendations include:

1. Beam lines should be supplied with high-purity gases, including H₂, O₂, N₂, He, and CO. Sensors for detecting the accidental release of these gasses should be included in the hutches. Ventilation systems with flow detectors are needed for removing all gases.
2. For the detection of products for determining conversions and selectivities, at least one mass spectrometer and one gas chromatograph (and preferably two of each) should be available.
3. One (preferably two) preparation laboratory is needed. The preparation laboratory should be equipped with a fume hood, a glove box, cabinets for safe storage of flammable chemicals, gas handling systems, and ovens/furnaces for catalyst calcinations/activation, and drying of catalyst samples.
4. The infrastructure for delivery of gases, chemicals, and supplies must be reliable.
5. Cross contamination is potentially a key problem to the use of shared in situ cells. Users should supply their own reaction cells and gas transfer lines, etc., to avoid possible contamination.
6. Users should share standardized reaction cell designs and design criteria. The sharing should include safety documentation and operating procedures. A standardized set of cells could be established so that new investigators can move through the safety approval process quickly.
7. Beam lines should be set up to make possible various measurements simultaneously such as diffraction and spectroscopy. Again, these experiments need to be done under in situ conditions.
8. Guidelines for safe work with a standard set of gases should be determined and made available to potential users.
9. Uniform data collection software (at least for spectroscopy) should be supplied.