Catalyst Center at 9-BM

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Introduction

Catalysis is an essential technology for economic prosperity, energy security and environmental preservation in the 21st Century. The importance of catalysis research to meet both the energy needs of the nation and the central role of DOE facilities in advancing catalysis science has been specifically identified in the Energy Policy Act of 2005. One of the recent DOE reports on research needs is entitled: "Basic Research Needs: Catalysis for Energy". In addition, catalysis can be expected to play a major role in a number of other research needs identified in this series of reports. These include Solar Energy Utilization, Clean and Efficient Combustion of 21st Century Fuels, and Research Needs for the Hydrogen Economy. As part of the reports on specific research needs, the DOE also identified five Grand Challenges for Science and the Imagination. Mastery of catalysis and catalytic systems will require advancement in all five of these challenges.

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. This proposal is in response to the major recommendations of this report.

Science

X-ray absorption fine structure (XAFS) and X-ray absorption near-edge fine structure (XANES) have become the workhorse techniques for catalyst characterization over the last 30 years. The popularity of these techniques is primarily the result of their power 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. In addition, the number of published papers found 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.

In recent years, there has also been much interest in *in-situ* catalyst research. Having a beamline with capabilities for both techniques *in-situ* would be highly advantageous to the catalysis community.

Moreover, having a beamline where both techniques can be performed simultaneously with *in-situ* capabilities is the most desirable scenario and any facility that could provide this would be unique among the U.S. DOE synchrotron facilities. The Catalysis Workshop Organizers felt that there was a significant unmet need in the catalysis field for such a facility.

Some specific examples of potential experiments were also given in this report. EXAFS has long been a mainstay of catalysis characterization. For example, work by Prof. Bruce Gates (UC Davis), has shown 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 has also shown how the structure of the catalyst depends on the reaction environment and, therefore, gives evidence that *in situ* characterization is critical for a full understanding of the catalyst. Another example of EXAFS research on catalysts, carried out by Dr. Jeff Miller (BP Corporation), is the study of the structure of supported gold clusters. His data shows that hydrogen reduction leads to smaller clusters than simple calcinations 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 metallic Au oxidizes in small particles, but not in large particles.

Time-resolved EXAFS, or Q-EXAFS, allowing up to 1 keV scans taken in less than a minute, enables researchers to study dynamic systems in catalysis. At the APS Catalysis Workshop, Dr. Thorsten Ressler (Fritz-Haber-Institute, Berlin) presented 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 from his data that the "real" (defect) structure of catalysts deviates from the ideal structure and dynamically changes under reaction conditions. He was also able to derive structure-activity correlations from *in-situ* studies under dynamic conditions.

Added Value of the Mid-term Upgrade

A beamline with enhanced capabilities for catalyst research would serve two needs. It would address the recommendations of the workshop report by providing dedicated capabilities for *in-situ* XAFS and powder diffraction. This would be the first such facility in the US. The beamline and its staff would also serve as a focal point for expanding catalyst research at other APS beamlines using advanced techniques not routinely applied to catalyst systems. It is expected that new users interested in some of these other methods could first contact the 9-BM center for guidance on whom to contact, and that the 9-BM program would have the appropriate support equipment to facilitate the use of other beamlines.

This project would make use of existing beamline equipment and hutches. 9-BM already has much of the gas ventilation capability needed to allow the use of hazardous gases. Almost the entire budget would be directly devoted to the needs of catalyst research by providing the necessary laboratory infrastructure, detectors and sample-related equipment. The only major beamline enhancement would be the addition of a quick-scanning monochromator capable of obtaining a spectrum in one second or less. Much of the support infrastructure and sample-related equipment would be designed to be compatible with the needs of other APS beamlines. Thus, this project should greatly enhance catalyst research at 9-BM and other APS beamlines with a relatively modest investment.

Expected user communities

The catalysis users are distributed around various beamlines. This would help to focus the efforts. The laboratory is in the process of hiring a senior catalysis scientist with extensive XAFS experience and whose goal is to grow the community at APS. It should be noted that many of our current and potential users are from industry such as UOP, BP and ExxonMobil.

Enabling technology and infrastructure

Currently 9-BM is optimized for low-energy applications although it has the capability of reaching energies up to 22 keV. This low-energy station occupies 9-BM-B, and would be substantially unchanged except for an upgrade in detection capabilities. 9-BM-C is currently unoccupied and would be optimized for higher energies (6-7 kev and higher). This would include a motorized optical table, motorized sample stages and detectors. Detectors would include a multi-element Ge detector for fluorescence detection (shared with 9-BM-B) and an area detector to support diffraction studies. Also planned is a moveable beam stop to allow setup to occur in 9-BM-C while 9-BM-B is in use.

An important capability requested by users is a quick-scanning monochromator and the associated electronics for fast readout of the detectors. This capability has proven popular at the NSLS catalyst beamline x-18, even though fluorescence detection is not available. Many catalysts will require fluorescence detection when operating in quick-scanning mode, and this capability will also be provided using digital electronics.

To support the *in-situ* studies we will provide a hazardous gas storage and supply cabinet, as well as an automated gas handling and mixing capability. It is important to monitor the reaction products in real time, and a mass spectrometer system will be provided for this purpose. The associated laboratories will be equipped with necessary sample preparation equipment. Foremost among these is a glove box that includes a balance and sample press such that samples can be made in a dry and oxygen-free environment. Many experimenters are reluctant to rely on beamline-supplied sample cells due to the fear of cross contamination. Therefore, we plan to develop a set of optimized sample cell designs that users can construct or purchase for their own use, and to maintain only a limited supply of standardized holders at the beamline. The beamline infrastructure will include support for high temperature (1000C) and high-pressure (50 bar) work using these standardized designs.

The pretreatment, activation and operation of heterogeneous catalysts spans a wide range of temperatures (298-1200 K), pressures (1-1000 atm), and chemical environments (gas, liquid, oxidizing, reducing). A single catalyst system may be exposed to remarkably diverse environments, all having an important influence on catalyst performance. As a consequence most catalytic studies involving synchrotron radiation involve extensive, preliminary investigations in a conventional laboratory to identify a few interesting and relevant environmental conditions that can be studied at the light source. A much more efficient and productive approach to the discovery of important catalytic materials transformations would be to combine synchrotron radiation measurements and variations in the environmental conditions in the same experiment. This requires in-situ reaction and treatment chambers and rapid data acquisition.

Industry and technology transfer

No technology transfer is anticipated, however this area has a large industrial presence and many of our users are from industry.

Partnerships and user interest

A catalysis SIG meets monthly and has partnered with other SIGs for very successful joint meetings. An Advisory Committee for the Catalysis at APS is being proposed.

Estimated Budget

The total cost for this project is estimated to be $1,145K with the following breakdown:

1. Detectors –	365K
2. Beamline equipment -	105K
3. New fast scan monochromator -	250K
4. Laboratory on the floor –	200K
5. Ancillary equipment for catalysis –	225K
Total	$11450K

To operate the beamline we will need at least 1.5 additional staff members. It is projected that 2.0 FTEs of engineering and technician help will be required.