Chemical and Energy Sciences at the NSLS-II

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1. Introduction

In this document we identify different themes that are in the focus of the synchrotron-based Chemical and Energy Sciences (CES) community. We outline the science drivers behind the need in using advanced synchrotron capabilities and propose how these needs can be matched to the technical capabilities of the NSLS-II beamlines. We point out demands for future developments and novel experimental methods which need a new source like the NSLS-II and a well planned, dedicated infrastructure. We propose the routes for transitioning the CES programs from NSLS to NSLS-II and outline concrete steps that will minimize the disruptions of research programs for CES researchers. This document is also a first coordinated effort of scientists working in multiple CES sub-fields to join forces and create a multidisciplinary research environment, including both the new infrastructure and a new atmosphere of collaboration.

The synchrotron CES community consists of scientists who use synchrotron radiation in the areas of chemical transformations, catalysis, electrochemistry, energy conversion/storage, and hydrogen storage research. Direct impact of synchrotron research on the advancement of these sciences has been pointed out in many reports and reviews.[1] Many industrial applications directly benefit from synchrotron CES research.[2] For example, analysis and optimization of catalytic converters has recently become possible at European synchrotron radiation sources (DESY and ESRF) by performing fast in situ XAFS experiments which are essential to replicate fast (< 1 s) cycling between reducing and oxidizing environments relevant to practical applications. Synchrotron studies have helped to improve the mechanical and temperature resistance of fuel cell membranes, to control the degree of hydration, and to design optimum fuel cell electrodes. The need to advance chemical and energy industries drives advancement in synchrotron innovations as well. For example, the development of new experimental techniques at DESY, e.g., Quick Scanning EXAFS (QEXAFS) and combined XAFS/XRD methods were motivated by, and had significant impact on industrial research and led to the expansion of industrial research there and also at the ESRF, spearheaded by one of the leading catalyst companies (Haldor Topsøe A/S, Denmark). The strong groups (R. Prins, A. Baiker) working on catalysis at the ETH in Zurich were driving forces to implement a dedicated fast QEXAFS monochromator at the SLS, which was just commissioned.

As stated in the report of the 2002 BESAC workshop "Opportunities for Catalysis in the 21st century: "The Grand Challenge for catalysis science in the 21st century is to understand how to design catalyst structures to control catalytic activity and selectivity." Much is known from synchrotron studies about the structure and properties of many model systems at specific conditions. Real systems and processes, however, are extremely complex and require techniques for the characterization of such systems in-situ, as they evolve in time with a changing environment. At the February 20-21, 2008 workshop at the National Institute of Standards (Gaithersburg, MD) "*Measurement Needs for Local Structure Determination in Inorganic Materials*" most participants emphasized that such goals require a highly specialized suite of dedicated instruments to study real systems and processes under conditions relevant to their practical use by the combined use of several complementary techniques. Due to its uniquely high brightness and flux, NSLS II can offer such new tools and solutions for the CES communities. We will outline these new tools in greater detail below.

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[1] M. Boudart, et al, "*Study by synchrotron radiation of the structure of a working catalyst at high temperatures and pressures*", Science, **228**, 717 (1985); A. Bell, et al, "*The impact of nanoscience on heterogeneous catalysis*", Science **299**, 1688 (2003), G. Beaucage, et al, "*Probing the dynamics of nanoparticle growth in a flame using synchrotron radiation*", Nature Materials, **3**, 370 (2004).

[2] B.Clausen, H.Topsøe, R. Frahm. "*Application of combined x-ray diffraction and absorption techniques for in situ catalyst characterization*." Adv. Catalysis **42**, 315 (1998).

The key scientific drivers for chemical transformations, e.g., catalysis and electrochemistry fields, identified at the first strategic planning workshop for Catalysis and Electrochemistry community held at Brookhaven in July 2007 are the atomistic real-time understanding of the mechanism of chemical reactions and of catalyst deactivation, the design of new or more efficient chemical processes, and the more efficient design of high-activity, high-selectivity, and low-cost catalysts.

One of the important missions of energy research is to develop methods for exploiting, converting and optimizing existing and recently developed energy sources. Among the many scientific drivers in energy research, several of them have demonstrated the need for methods of analysis based on synchrotron radiation: development of renewable energy conversion technologies, storage of energy products, portable devices for energy delivery, and engineered nanocomposite materials for various energy applications.

Catalysis serves as a cross-cutting enabling science in each of these disciplines, and thus many technical capabilities required in designing their synchrotron-based lines of research (as well as many challenges toward their realization) are expected to be similar. What further bridges these themes together is the recently emerged approach of space-resolved and time-resolved monitoring and identifying short-lived reaction intermediates.

For both communities, the approaches that need to be undertaken at the synchrotrons are:

-Nanometer-scale understanding of reactivity, selectivity, stability, and degradation mechanisms of catalysts;
-Design of model catalysts that provide indirect but essential and reliable information on more complex commercial catalysts;
-Development of combined multi-technique methodologies and instrumentation for real time, *in situ* catalysis and battery discharge studies;
-Development of instrumentation that simulates laboratory and industrial conditions for energy release, storage, and generation where the catalytic process can be followed in a time-resolved manner.

The challenges are primarily due to the lack of knowledge about:

-Structure of metal and metal compound objects are in sub-nanometer or nanometer length scales
-Interactions of oxide and metal clusters with support;
-Changes of the structure as a function of adsorption of reactants and products;
-Dynamics of elementary steps on surfaces in the millisecond-to-second time scales.

To address these needs at the NSLS-II we propose to implement the following strategy:

Present challenges	Impact on science	Proposed implementation
Multiple scales of spatial and temporal metrics: Space: Atomic bonds: 0.1 nm, Clusters: sub-nm to nm, Supports: nm-μm. Time: Charge transfer: fs to ns, Vibrations: ps, Atomic relaxation: ps, Reaction rates: 0.1ms to s	- in situ, quick (<1s) studies of medium range nanoparticles (>nm) and support structure; Complementary in situ studies of reactants, products and catalysts during chemical transformations, by hard x-rays (XAFS, XRD, DAFS) and soft x-rays (XPS, NEXAFS)	Hard x-rays, combined, Quick **XAFS/XRD+DAFS** + soft x-rays (**XPS/NEXAFS**) experiments at dedicated and shared beamlines Combined **high resolution diffraction** and high Q studies by **PDF** method at the project PING beamline.
Complexity of catalyst properties: cluster-support/adsorbate interactions, dynamic structure, structural relaxation effects are difficult if not impossible to resolve at present sources	XAS studies of individual nanoparticles; in situ, quick (< 1s) studies of catalytic activity, deconvolution of heterogeneous species and reaction intermediates	**XAS** at the hard x-ray nanoprobe beamline on a (tapered) undulator source; **High resolution fluorescence** using secondary emission at the XAS project beamline on a damping wiggler source
Catalyst heterogeneity, polydispersity hinder structural and reactivity studies	nm-scale imaging of 3D structure of catalysts and valence distribution; Resolving the heterogeneity problem by a combination of XAFS and DAFS	Hard x-ray nanoprobe project beamline on an undulator source; **XAFS** and **DAFS** studies on a damping wiggler source

| Fast kinetics, low concentrations of operational catalysts or 2D monolayers of model catalysts are not accessible due to low flux	Kinetics: in situ, Quick (sub-second time scale) XAFS/XRD Dilute catalysis: Using a high flux beamline	-Combined, Quick **XAFS/XRD**; -**XAFS** on a damping wiggler beamline - -**XPS/NEXAFS** at an undulator source
Lack of high pressure sample chambers to reproduce reactive environments with pressures up to 10 torr for carrying out in situ measurements	Fast (< 1s) monitoring of the evolution of surface intermediates, mechanistic studies.	Fast high-resolution moderate pressure (up to 10 Torr) **XPS** at an undulator **XPS/NEXAFS** (TEY) beamline for carrying out in situ surface reactivity studies; **NEXAFS** (Fluorescence) measurements of real catalysts
Studies of catalysts within reactors is not available due to ppm concentrations and x-ray absorption by reactor walls	Tomography, fast (10 ms) scan repetition times, μm focusing, high energy diffraction (to penetrate reactor walls)	High energy **XRD** at the project PING beamline; **QEXAFS** at the damping wiggler beamline

Table I. Challenges, science drivers and their proposed implementation

The studies of real time processes in chemistry and energy research are particularly important. For example, the dynamic, time dependent studies are essential for the development for e.g. lithium-ion batteries. To increase the capacity, high current capability and long time operability one has to use fast (in the sub-s range) discharge/charge cycles in the investigations. It is well known that reducing the speed of such processes to make them accessible for current experimental facilities also can change the reactions and intermediate stages. Thus, to get meaningful results, the need is to measure such processes under real dynamic conditions and not to slow them down to match the need of the experiment. The same is especially true for catalysts.

The size of the CES community is: ~100 (75 - chemistry/25-energy sciences) groups from academia, 20 - national laboratories, 35 (10/25) - industry: the total of 150 (100/50) groups and estimated 750 (500/250) synchrotron users. These groups have always had prominent presence at NSLS: CES users publish 10% of all NSLS science highlights (5 in 2007, 8 – in 2006, out of annual of 56)

2. The Growth, Expansion, and Transition of NSLS Scientific Programs

Since the Synchrotron Catalysis Consortium (SCC) started its operations in 2005, this user group has evolved into a well established NSLS user community, with its user support coordinated, in part, by the SCC. Synchrotron-based energy science researchers have not yet organized into a synchrotron community as cohesive as the SCC group. We hope NSLS-II will help the both groups to advance their science programs and more effectively use synchrotron facilities, at the NSLS and NSLS-II. Members of SCC, and its future successor SCC-II (at NSLS-II), will continue active planning role in supporting CES programs.
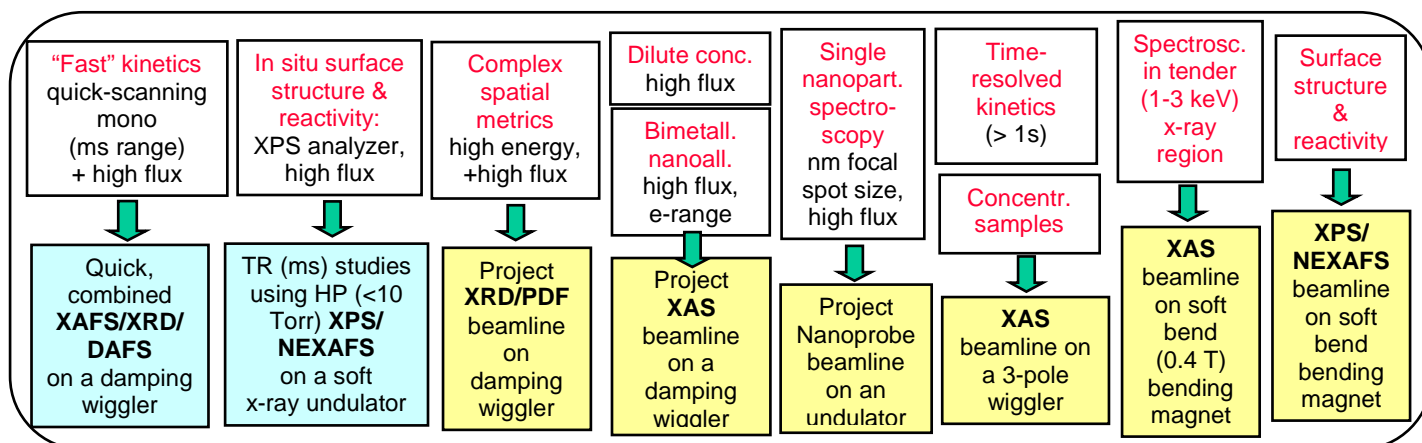
Table II. A proposed infrastructure for CES research at NSLS-II. The two facilities in the bottom left (blue) will be dedicated for CES users, the others (yellow) –shared with other communities.

To best serve the needs of CES users, we propose to combine several dedicated and shared facilities at the NSLS-II as summarized in Table II above and in the more detailed description below.

3. Detailed description of the dedicated beamlines

3.1 A dedicated CES beamline on a damping wiggler source for fast x-ray spectroscopy/diffraction measurements to study in situ chemical transformations

The main purpose of this beamline will be twofold. First, it will enable in situ fast (from few ms to minutes) XAFS/XRD combined studies of structure, dynamics and reactivity for real catalysts. Second, it will be a primary investigation tool for in situ studies of energy-related materials. While the main analytical techniques will be XAFS and XRD, other complementary techniques (DAFS and IR) can be also used in situ, either in combination with XAFS/XRD or indepedently.

Catalytic reactions typically require high temperatures and pressures and use a wide range of molecules requiring real-time assessments by mass spectrometry or gas chromatography. Homogeneous catalysts (e.g., in a liquid state) require special cells. Thus, to enable in situ experiments, gas and liquid flow reactors, high temperature and high pressure cells, supplied with required gaseous and/or liquid reactants are required. Gases, chemicals, and supplies delivery systems require a permanent, reliable infrastructure. Toxic or flammable reagents (e.g. CO, NO_x, H_2, hydrocarbons) require safe permanent installations and robust monitoring infrastructure.
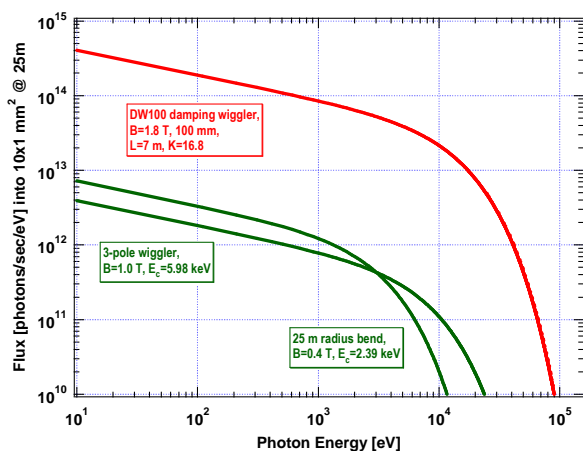

Fig. 1. Flux/per eV for three NSLS-II sources (damping wiggler, a three-pole wiggler and a bending magnet), at the sample position, ca. 25 m from the source and through a 1x10mm² aperture.

XAFS and XRD techniques provide complementary information about the structure of catalytic materials: XRD is effective in pure or mixed crystalline materials while XAFS provides short range order structural features in less ordered or amorphous materials. In addition, XAFS also gives element specific information about the electronic properties of the element being probed at its absorption energy. Finally, Diffraction Anomalous Fine Structure (DAFS) technique allows the assessment of the local structure in ordered species within heterogeneous samples, for those systems in which ensemble-averaged XAFS data analysis would be complicated by different forms of the resonant element. These three methods have been developed and advanced *independently* from each other at synchrotron sources in the US and abroad. To analyze catalysts under their operating conditions, a new approach that allows the simultaneous collection of the XRD and XAFS data under *in situ* conditions together with online product analysis is required. At present, XAFS and XRD measurements can be performed at the NSLS only at separate beamlines, with acquisition times of $1-10^3$ s for XAFS and $10-10^2$ s for XRD. DAFS has been performed only a few times in the last 10 years, and has been used rarely in catalysis and hydrogen storage applications, for which it would provide essential details of their ubiquitous heterogeneity.

The SCC and NSLS teams are currently developing the first US facility for combined time-resolved XRD/XAFS experiments at beamline X18A; this facility is the prototype instrument for our proposed NSLS-II beamline. Such a combination will allow the measurement of changes in the actual structure (in the short, medium and long range order), electronic properties, and chemical reactivity of heterogeneous catalysts simultaneously. This will be coupled with online gas analysis, required for the concurrent assessment of the dynamics of the relevant chemical transformations.

The choice of a damping wiggler source for this proposed beamline is justified as follows. First, its flux through the 1x10mm² aperture (Fig. 1) is 500 times better than in the 6.88m-radius NSLS bending magnet source (not shown). Such increase in flux will allow us to reach even less than 0.1% metal loadings of Pt on γ-Al_2O_3 used

in commercial catalysts and still be able to investigate the time dependence of the underlying processes. <u>Such capability will exceed those available at present synchrotons.</u> The useful energy range allows to measure most catalytically important materials, from Ti and V at the lower energies, to Pd, Ag, and In at the higher energies. Second, the NSLS-II staff (A. Broadbent and P. Northrup) is working with us to optimize the source parameters for addressing the monochromator heat load and weight problems, in order to enable fast energy scanning. There are several possible solutions currently being considered (including a possibility of using a tapered undulator source) which we will address in much greater detail in the Letter of Interest which is currently in preparation.

The fast XAFS instrument will be similar to the prototype currently installed at beamline X18B in NSLS. It is inspired by the designs of several specialized QEXAFS monochromators developed in Germany in the group of R. Frahm who is the leading inventor of these instruments and provides guidance for our organizing committee. The angle of a Si(111) double crystal monochromator is controlled via an assembly containing a micro-stepping motor, a rotating cam, and a small brass lever arm directly attached to the monochromator tangent arm. This setup provides high resolution fast-XAFS energy data that varies as a sinusoidal function of time with a frequency that is inversely proportional to the time resolution of the fast-XAFS scan. These data are then processed with our custom-developed software to provide users with individual and time resolved EXAFS or XANES scans that can be analyzed by widely accessible data analysis packages.

Additional QEXAFS monochromators are - besides the one recently installed at the SLS - under construction at, e.g., SOLEIL, and the SSRF (Shanghai Synchrotron Radiation Facility). The fact that such a monochromator system is now available commercially now points out the importance in the future which is given to such hardware by the community. The monochromator design for NSLS II will follow those developments and include the best of the most recent hard- and software.

J. Hanson and other SCC members run fast TR-XRD experiments at beamline X7B and QEXAFS measurements beamline X18B. Their recent QEXAFS experiments focus on the Cu K-edge XANES of the $Ce_{1-x}Cu_xO_2$ system under reducing (reaction with H_2) and oxidizing environments (reaction with O_2). The *in-situ* data (Fig. 2) point to the chemical transformation of copper oxide to zerovalent copper under reducing conditions and back to $Ce_{1-x}Cu_xO_2$ for oxidizing conditions at 275, 300, and 325 ^{o}C.
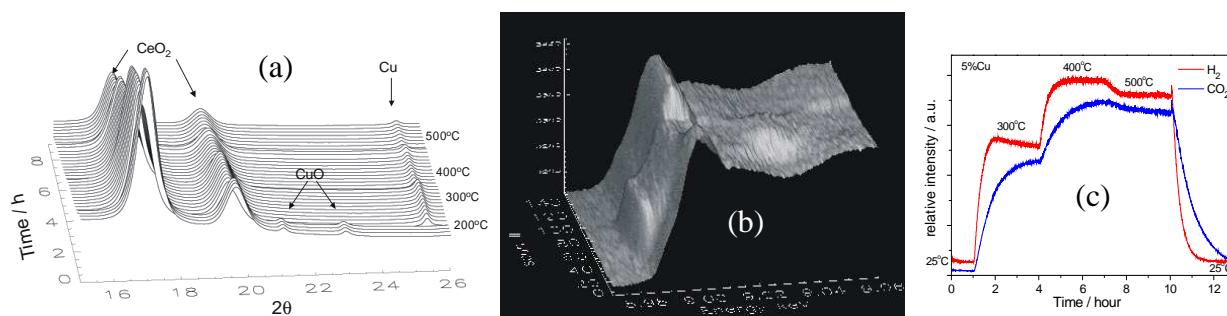

Fig. 2. (a) Time-resolved X-ray diffraction (TR-XRD) patterns collected during the water gas shift (WGS) reaction for the 5%Cu/CeO2 nanocatalysts. (b)TR XANES: reduction/re-oxidation of Cu doped ceria at 200°C.(c) A typical figure for H_2 and CO_2 products from the WGS reaction is shown in the middle pane. The products were analyzed with mass spectrometer (MS).

Data analysis performed by Principal Component Analysis allowed to detect the intermediate phase and study the dynamics of structural transformations accompanying reduction processes (Fig. 3). Our team members have the know-how to design and perform experiments and to analyze data for fast XAFS and XRD approaches and are well positioned to develop their integration at the same beamline.

The XAFS and XRD data displayed in Fig 2 clearly illustrate why the integration of fast XAFS and fast XRD is necessary. These data, obtained in separate beamlines, is for a $Ce_{0.8}Cu_{0.2}O_2$ catalyst during the water-gas shift reaction. The Ce L_3 edge XANES spectra show the appearance of Ce^{3+} cations as a consequence of the formation of O vacancies. The lattice of the oxide is sensitive to the concentration of Ce^{3+}, and expands (or

contracts) when the concentration of this cation increases (or decreases). The XRD data indicate in an indirect way that the amount of Ce^{3+} in the catalyst varies with the CO/H_2O ratio. *Both sets of data are consistent, but there is important information missing.* To get a complete picture of the behavior of the catalyst, one needs the combination of fast XAFS and fast XRD to get information about the composition, oxidation state and structure of the system simultaneously. The proposed integration of experimental setups will guarantee that XRD and XAFS techniques study the same intermediate states – and thus can be used to complement each other. For the first time, the simultaneous measurements of the short range structure and the long range structure of a nanocatalyst will be measured *in situ*, during chemical reaction.
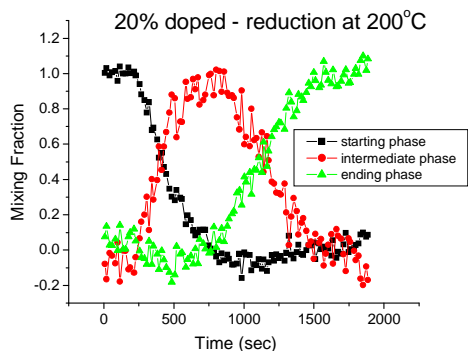

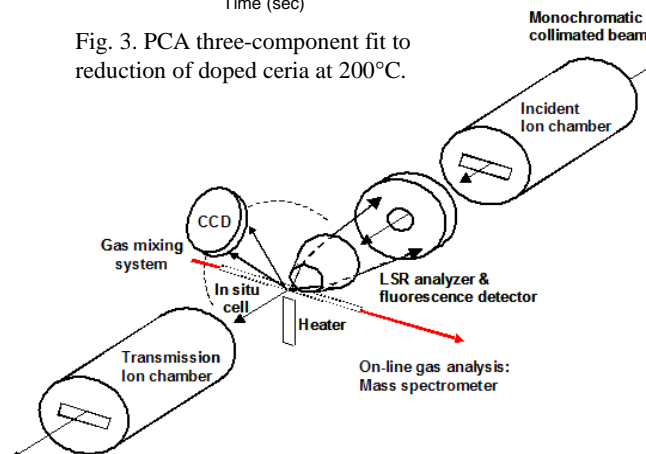Fig. 3. PCA three-component fit to reduction of doped ceria at 200°C.

Fig.4. Schematic of the proposed Fast-XRD/Fast-XAFS instrument

Figure 4 shows a schematic for our proposed Fast-XRD/XAFS/gas analysis setup. Although combined XRD/Fast XAFS facilities are at various stages of advancement at HASYLAB/DESY (Hamburg) and at the SRS (Daresbury), most have one-dimensional position sensitive detectors and thus have long characteristic time. Our proposed setup will have both fast XRD (3ms time resolution) and fast XAFS (10 ms), which will represent the state-of-the-art worldwide. For example, we will gain the ability to study metal loadings as diluted as 0.1% by fast XAFS with the same data quality presently achievable at the NSLS-I for much higher concentrations.

As shown in Figure 4, the XAFS instrumentation will include sealed ionization chambers for transmission detectors, and the Log Spiral of Revolution (LSR) analyzed coupled with an annular ion chamber for fluorescence measurements, designed by D. Pease and A. Frenkel. XRD patterns will be collected using a CCD detector. A final decision on optimum design will be made during the early LOI preparation period.

The research team will design synchrotron end-stations with an optimal spatial configuration for the coupling of the detectors. The integration of a gas mixing system and a product analysis system (mass spectrometer) will be performed using the prototype setup being built at the beamline X18A at the NSLS by SCC members and NSLS staff.
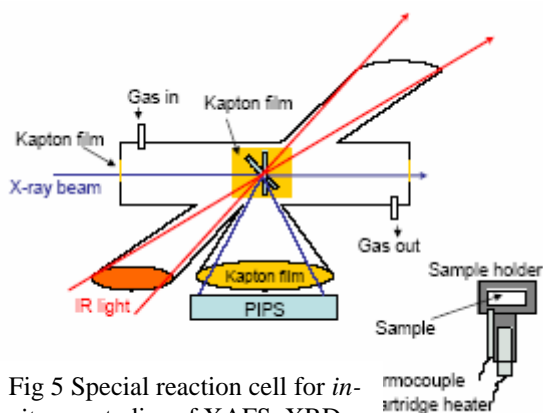

Fig 5 Special reaction cell for *in-situ* studies of XAFS, XRD and IR

The utilization of the instrumentation described above for fast XRD and XAFS will expand our knowledge significantly about the state of the catalyst material (crystalline phases, oxidation states, composition, etc.) and particularly its real time dynamic changes under working conditions. It will have, however, a limited utility to follow at the same time the surface chemistry of the catalytic process. The addition of a vibrational spectroscopy tool (in particular FTIR) to the combined XRD/XAFS would greatly expand the capabilities of this characterization system, giving insight into the surface chemistry, and the changes in that chemistry as the attributes of the catalyst change. We therefore propose to fabricate a special in situ cell that will enable IR absorption spectra

simultaneously with XAFS and XRD, and to implement IR spectroscopic capability with the addition of an FTIR spectrometer at X18A. Fig. 5 shows a special cell proposed for acquiring XAFS, XRD and IR data from the same sample at a given set of conditions. The sample can be mounted at 90° towards the beam for transmission studies, or at 45° for fluorescence. The tube for IR light is sealed with a IR-transparent window. An opening, covered with Kapton, can be also done for XRD measurements. The IR beam is focused at the sample by means of a 90° off-axis parabolic mirror.

- *End station instrumentation:*

   Setup for in situ studies will include: combined XAFS/XRD instrument, specialized software for synchronized XAFS/DAFS/XRD measurements, gas mixing and purification system, on line analytical capabilities including gas analysis systems (multi-detector GC and GC/MS); high temperature, high pressure, and electrochemical reactors which must be designed not only for effective spectroscopy/diffraction measurements but also for quantitative representation of chemical reactions that take place in them. For example, quantitative studies reaction kinetics, mass and heat transfer should be made possible. Some analytical methods should be developed for analyzing biomass conversion. Analysis should be made possible in solution and liquid flow cells. Such collection of specialized equipment for cutting edge catalysis research will be most efficiently used at the dedicated catalysis beamline, as it is presently done at SCC beamlines X18B/X19A.

- *Software and computing infrastructure requirements for this beamline:*

   -Integration of data collection, gas input/output and other external parameters into the same software;
   -Data acquisition software for synchronizing combined techniques (XAFS/DAFS/XRD);
   -Integration of rapid throughput data processing software with data display and analysis software, to handle data storage and data access requirements and to make fast decision about the quality of the experiment (R&D required). High speed or combined measurements and data storage need an individual solution without much computing/networking overhead;
   -Software for on line reactivity analysis.

- *Detector requirements for this beamline:*

   Fast readout XRD detectors, fluorescence analyzers (LSR's, and others), HRF analyzers..

3.2. A dedicated CES undulator beamline for millisecond time-resolved high pressure XPS and fluorescence yield NEXAFS measurements of surfaces, adsorbates and reaction intermediates at pressures up to 10 Torr

A necessary requirement for a catalyst's function is its ability to undergo dynamic and reversible chemical and/or structural transformations. For example, in the NO_x storage catalyst used for emissions control in lean-burn gasoline engines, a BaO containing catalyst traps NO_x species during fuel-lean conditions and is converted into $Ba(NO_3)_2$. Subsequently, this is transformed back into BaO during brief fuel-rich transients when the trapped NO_x species are released and reduced to N_2. The necessity for such dynamic, non-equilibrium, structural and chemical properties are not limited to NO_x storage catalysts, but are essential to the operation of catalysts in general. Experimental techniques that directly probe such dynamic chemical transformations of a catalyst are, however, rare. This is because such a measurement requires the combined capabilities of providing quantitative, chemically specific information on the millisecond timescale or less under catalytic operating conditions, presenting great experimental challenges. We plan to take advantage of the properties of a Soft X-ray EPU beamline in order to construct two complementary experiments with these capabilities. By combining the high brightness of the undulator beamline with stroboscopic Elevated Pressure Photoemission Spectroscopy (EP-PES), we will perform kinetic photoemission spectroscopy experiments at pressures of at least 10 torr with time resolution on the sub 10 ms timescale. This will provide unprecedented chemical detail of the dynamic nature of catalytic function. In addition, we will, in collaboration with NIST, construct a photon-in, photon-out Near Edge X-ray Absorption Fine Structure (NEXAFS) endstation optimized for the catalytically important Carbon K-edge, and which allows also measurements at the Oxygen and Nitrogen K-edges. This instrument will facilitate the chemical identification and concentrations of adsorbed hydrocarbons and reaction intermediates which is crucial for understanding

hydrocarbon chemistry. Further developments could allow the application of these experimental techniques to systems of environmental and more general chemical interest as well, therefore serving a broad user community.

Photoemission spectroscopy is a well-established technique for the chemical identification and quantification of adsorbates on surfaces. Typically these measurements are performed under Ultra-High Vacuum (UHV) which is far removed from catalytically operating conditions. However, the recent development of synchrotron based PES that incorporates a differentially pumped electrostatic lens into the analyzer has allowed PES measurements under elevated pressures, up to approximately 5 -10 torr. This development is beginning to transform our understanding of a variety of surfaces under elevated pressure conditions including the nature of water mineral interfaces under ambient conditions, and ice and liquid surfaces under atmospheric conditions. Similar to these experiments we expect a significant impact of such measurements for the field of catalysis. Further, we plan to extend this technique through the use of a small volume flow cell that rapidly exchanges gas on the millisecond timescale with the simultaneous acquisition of spectra during this dynamic gas exchange. This provides a new type of measurement for users of this technique facilitating specifically the direct interrogation of catalysts under dynamic conditions. As described below, these measurements will only be possible through the use of an x-ray source with high brightness such as that found on the soft x-ray undulator EPU 100 VUV beamline.

Fluorescence yield NEXAFS of low Z materials has become a powerful tool for understanding the local structure and chemistry of diverse materials even in the presence of reactive atmospheres. In particular, C K-edge fluorescence yield NEXAFS has demonstrated the ability to identify the local chemistry and type of carbon bonding (sp^3, sp^2, or sp) of adsorbed hydrocarbon species. The NIST Synchrotron Methods group has developed a high efficiency near normal incidence focusing multilayer mirror detection system for carbon K edge fluorescence yield soft x-ray NEXAFS. This wavelength dispersive detector technology is the culmination of over a decade of research in fluorescence yield soft x-ray absorption spectroscopy and has enabled a whole new class of in situ soft x-ray absorption measurements of carbon chemistry in catalysts to be made under reactive atmospheres. The extraordinary chemical reaction sensitivity demonstrated for metal single crystal experiments can now be effectively applied to metals on supported catalysts at pressures up to 10 Torr. As an example, several practical zeolite catalyst experiments have been accomplished for propylene and benzene absorption chemistry, see Fig. 6.
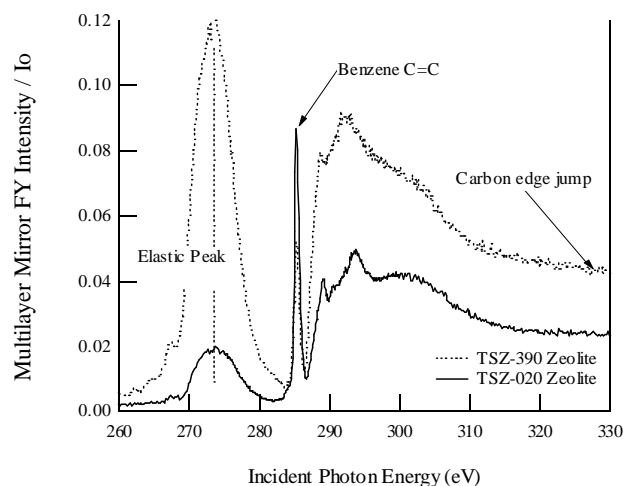

Fig. 6. Fluorescence yield carbon K edge NEXAFS spectra for benzene dosed in zeolites TSZ-20 (solid) and TSZ-390 (dashed).

The spectra show nearly zero background and have sensitivities nearly 1000 times greater than IR spectroscopy. The active TSZ-390 shows a significant reduction in pi states compared to the less active TSZ-20, as well as increased uptake of benzene indicated by the larger carbon edge jump. The TSZ-390 spectrum confirms chemical bonding to the zeolite where as the TSZ-20 spectrum is gas phase like indicating physisorption. As described below we also expect significant benefit for this technique at an undulator source due to its high brightness.

General Considerations for Beamline Characteristics

The soft x-ray region (from approximately 10 eV up to 2000 eV) provides access to the catalytically relevant core levels and K-edges C1s (binding energy ~285 eV), O1s (~530 eV), and N1s (~400 eV) as well as many transition metal L-edges. Also, in this region the maximum K-shell x-ray absorption cross-sections for low Z elements can be found, making it the desired region for C K-edge NEXAFS. Further, for photoemission experiments photoelectron kinetic energies are in the range of highest surface sensitivity, 50 to 200 eV. Photon energies

exceeding ~1000 eV can be used to increase the photoelectron kinetic energy and allow one to probe more deeply below the surface. Such depth-profiling experiments address the depth and extent of chemical composition changes in the surface region. Since photoemission signal intensities are proportional to the photon flux, maintaining a high photon flux at higher photon energies is also vital in performing depth profiling experiments. The EPU 100 VUV Undulator beamline with its high photon flux at over 2000 eV will allow probe depths of approximately 20 Å (up to 10 atomic layers) covering a significant portion of the surface region.

In modern elevated pressure photoemission spectroscopy experiments the maximum pressure is limited by the attenuation of the photoemitted electrons via gas phase scattering. Gas phase attenuation follows a Beer's law dependence, $I_p \alpha I_{vac} \exp(-z\sigma(E)p)$, where z is the path length of the photoelectrons through the gas, $\sigma(E)$
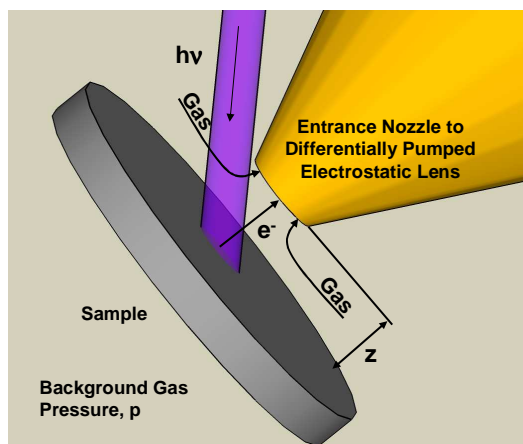

is the energy dependent scattering cross-section of the gas, p is the gas pressure and I_{vac} is the photoelectron intensity under UHV conditions (Fig. 7). From this equation it is apparent that EP-PES experiments require the use of high photon flux (large I_{vac}) and short distances between the sample and entrance aperture to the differentially pumped electrostatic lens of the analyzer (small z). Since gas is pumped through the entrance aperture, which reduces the gas pressure at the sample, minimum values of z are limited to approximately the diameter of the aperture. Therefore a reduction in gas phase attenuation can only be achieved by a reduction in aperture size which allows smaller values of z. Typical aperture sizes currently used range from about 1 mm to 100 microns. Using smaller aperture sizes requires a reduction in the size of the x-ray spot on the sample. Thus the combined necessity of a high photon flux and small x-ray spot sizes for performing photoemission spectroscopy experiments under elevated pressures indicates that a high brightness undulator source is desirable for

Fig. 7. Sample/first aperture geometry for a standard elevated pressure photoemission spectroscopy experiment.

these experiments. Current elevated pressure photoemission spectroscopy experiments can operate at pressures up to approximately 5 - 10 torr. The increased flux of EPU 100 at NSLS-II together with the decrease in photon beam size to approximately 10 x 40 microns (at 500 eV) may allow operating pressures that exceed 100 torr a full order of magnitude greater than current maximum operating pressures. This new pressure regime may be important for revealing the true chemically active phases of a catalyst during its activity.

Similarly, fluorescence yield C, O, N K-edge NEXAFS measurements will benefit from the high flux and brightness of an undulator source. The wavelength dispersive soft X-ray fluorescence NEXAFS method is a low count rate experiment since the intrinsic carbon fluorescence yield is very low (0.0012) and the overall efficiency of the NIST multilayer mirror and X-ray detector although the best to date are also low. Thus the high flux of an undulator source significantly reduces data collection times and makes possible the observation of chemical reactions as they occur on a surface or in a real catalyst on the time scale of minutes by sitting on bond specific resonances and monitoring their time evolution. The second beneficial aspect of the undulator is its brightness. The wavelength dispersive soft X-ray fluorescence NEXAFS method relies on a small bright spot on the sample to well define the optical paths of the multilayer mirror system to optimize the energy resolution which ultimately effects the ability to reduce the signal to background in the NEXAFS measurement.

Special Consideration for Kinetic Measurements Using Stroboscopic Methods

In order to provide unique experimental capabilities, we plan to integrate a gas flow cell into the elevated pressure x-ray photoemission spectroscopy experiment and use a delay-line detector for stroboscopic measurements (Fig. 8). This will allow one to quantitatively measure changes in chemical composition of surfaces at pressures up to at least 10 torr on the sub-10 ms timescale. In this experiment short pulses of gas on the 10's of ms timescale enter the celland spectra are collected using a delay-line detector a specific delay time after the pulse in a single shot covering a specific time-width. The time resolution in such an experiment is not determined by the time required
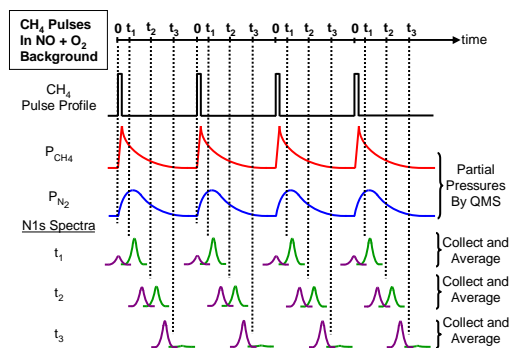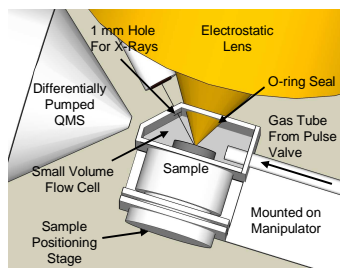
Fig. 8. Close-up view of an elevated pressure photoemission spectroscopy experiment using a small volume flow cell. Gas enters the flow cell from a pulse valve and leaves through the 1 mm hole for the x-rays. Partial pressures of the gas exiting the flow cell are measured with the differentially pumped QMS. The right hand side of the figure shows potential data from such a set-up where spectra are collected at specified delay times following a gas pulse.

to scan a full spectrum, but instead by a balance between the width of the acquisition time window and the time necessary for the surface to return to its initial state following the gas pulse. Using typical dwell times, resolution and number of spectra to average for a current EP-PES experiment at an undulator beamline we estimate that a similar quality spectrum representing a 5 ms time-window at a specific delay time following the gas pulse can be acquired by averaging about 1000 spectra, requiring 1000 gas pulses.

Assuming that the surface returns to its initial state in approximately 1 second following the gas pulse this requires 1000 seconds allowing the collection of multiple delay times in a single synchrotron shift. This provides unprecedented time resolution for XPS and as a result unprecedented details about the dynamics of the chemical composition of a surface and how this couples to its catalytic function. Combining this type of measurement with depth-profiling experiments will provide information about how changes in surface composition couple to changes in bulk composition. Estimates of the flux of a 0.4 T bending magnet source at NSLS-II are 10^2 lower than that of VUV EPU 100 indicating that it would require 10^2 longer time to acquire a spectrum (or approximately 10^5 seconds) of roughly the same quality. This assumes similar x-ray spot sizes on the sample which may be difficult to achieve at a bending magnet beamline without additional loses in photon beam intensities. Therefore, these experiments are difficult to achieve without the high brightness of an undulator source.

User Instrumentation Permanent Set-up: Elevated Pressure Photoemission Spectroscopy Endstation

The Elevated Pressure Photoemission Spectroscopy Endstation will consist of a surface preparation chamber for the production of single crystal and model catalyst surfaces. To perform standard photoemission at elevated pressures an electron energy analyzer with a differentially pumped electrostatic lens will be used. For the stroboscopic measurements a small volume flow cell along with a delay-line detector is necessary. In addition, a gas manifold with the necessary precautions (storage and gas cabinets) for hazardous gases is required. Gas phase analysis will initially be conducted using a differentially pumped mass spectrometer.

End station for photon-in/photon out NEXAFS of catalytic reaction intermediates under reaction pressures of 10 Torr utilizing unique wavelength dispersive focusing multi-layer mirrors

In collaboration with NIST, we propose to add a second endstation for photon-in photon out in-situ NEXAFS (carbon K edge, 285 eV) of catalytic reaction intermediates under reaction pressures (10 Torr) utilizing unique wavelength dispersive focusing multi-layer mirrors pioneered by NIST. The high pressure NEXAFS endstation would complement the high pressure XPS endstation and provide a complete chemical and structural picture of an operating catalyst.

Software and computing infrastructure requirements for this beamline:

- General beamline control software
- Integrated beamline control and data acquisition software for NEXAFS
- Integrated gas supply (pulse valve control), beamline control (if a shutter is used), and data acquisition software for the stroboscopic experiments

Detector requirements for this beamline:

For moderate-pressure XPS experiments: an advanced, differential- pumped electron-energy analyzer, e.g., Specs Phobios 150 with 2-D delay line detector (all commercial instruments). For fluorescence yield NEXAFS a high efficiency near normal incidence focusing multilayer mirror detection system optimized for the carbon K-edge. This detector technology has been developed by NIST (D. Fischer).

4. Recommended transition/construction sequence

As discussed above, the size of the CES community that will utilize the facilities discussed in this white paper (XAS, XRD XPS, NEXAFS) exceeds 150 groups and over 750 potential users. Therefore, several more beamlines, each having 1-2 end stations, in addition to the dedicated beamlines described in Section 2 will be needed to serve this community. The project beamlines will offer the best-in-class instruments for unique characterizations – ultra-thin or ultra-dilute samples, for examples, can be studied at the XAS project beamline; the medium scale (>5-10 nm in diameter) catalysts on support – at the powder diffraction project beamline, using advanced techniques such as a high energy XRD. PIs of the Synchrotron Catalysis Consortium (Frenkel and Hanson) are active members of the beamline advisory teams (BATs) of these beamlines

Building the shared (non-project) beamlines listed in Tables 1,2 could conceivably be done via maintaining, upgrading and transitioning existing beamlines from the NSLS. As indicated in the Table, several beamlines will be needed to cover a wide energy range and different techniques. Future "state of the art" needs will require small spot size at the sample, rapid scanning for sub-second data acquisition, and sensitive detectors for dilute samples and/or rapid acquisition.

There is a number of beamlines currently in use at the NSLS that already provide some of the capabilities desired. This community will work with the NSLS II transitioning team along with PRTs and Contributing Users to determine what beamlines, or possibly what parts of beamlines, will meet requirements needed for a transition to the NSLS II. This assessment will include an appraisal of the optics, vacuum systems, motors, computer controls and detectors. It may be determined that components of one beamline should be combined with another so that the best possible beamline will become operational after the transition. Planning and resources will be allocated over the remaining operating life of the NSLS so that maintenance and upgrades will not only provide optimal performance in the near term but will position identified beamlines for rapid transition and operation at the NSLS II. Our group is committed to work with the facility to develop an effective plan for this transition.

5. Facility infrastructure at NSLS-II

We anticipate the need of a minimum of 4 laboratories adjacent to the beamlines for performing the experiments of moderate-pressure XPS, XRD and XAFS. The laboratories will be used for the storage and assembly of equipment and for the assembly of samples. They should be equipped with standard fume hoods for the manipulation of chemicals and toxic gases. The laboratories should have access to electricity, water, and pressured air supply, and have lab-approved equipment for safe handling of nanomaterials (e.g., hoods and glove boxes should have HEPA filters). The size of each laboratory should be at a minimum the equivalent of 25x25 sq. feet. Capabilities for preparation, handling and transfer of intrinsically reactive and air- and moisture-sensitive samples to reactor, without contamination should be provided.

A set offices and a multimedia-equipped conference room facility should be available to facilitate data analysis and multi-technique collaboration during the on-going experiments. Some experiments may require access to large-scale computer facilities that could be available at BNL or elsewhere.