"Rational design of catalysts remains a pipe dream, because the experimental tools available for monitoring catalysts in action are still, by and large, too rudimentary."

B.M.Weckhuysen, *Nature* 439 (2006) 548

Chemical and Energy Sciences at the NSLS-II

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In this document we identify different themes that are in the focus of the 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 suggest the routes for transitioning the CES programs from NSLS to NSLS-II and propose concrete steps that will minimize the downtime 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 the new atmosphere of collaboration.

1. Introduction

Chemical and Energy Sciences (CES) is a name for the community of scientists using synchrotron radiation in the areas of catalysis, electrochemistry, energy conversion and storage and hydrogen storage research. 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."** To meet this challenge, a fundamental, atomic-scale understanding of the physical and chemical properties of catalytic materials is required. Since real catalysts and catalytic processes are extremely complex, the development of techniques for the characterization of catalytic systems in-situ, as they evolve in time with a changing chemical environment is a high priority. As outlined in the executive summary of the 2003 NSF "Future Directions in Catalysis: Structures that Function on the Nanoscale", **"…although exemplary cases of in situ characterization methodologies have been reported, the consensus is that advancements that extend the limits of temperature, pressure and resolution both in space and time of current spectroscopies will be necessary to meet the grand challenge."**

While these will remain grand challenges, synchrotron x-ray sources are proving to be one invaluable link in these efforts due to their unique capabilities for in situ structural and chemical probing. Due to its uniquely high brightness and flux, there are key areas where NSLS II can offer new solutions for the both communities (chemistry and energy) merging into CES.

The key scientific driver for catalysis and electrochemistry fields, identified at the first strategic planning workshop for Catalysis and Electrochemistry community, held at Brookhaven in July 2007, is the rational design of high-activity, high-selectivity, low-cost catalysts.

The mission of energy research can be generally formulated as developing reliable, economical, and plentiful sources without impairing the natural environment. Quoting Yildirim and Ciraci (*Phys. Rev. Lett.*, **94** 175501 (2005): **"Developing safe, cost-effective, and practical means of storing hydrogen is crucial for the advancement of hydrogen and fuel-cell technologies. The current state of the art is at an impasse in providing any material that meets a storage capacity of 6 wt % or more required for practical applications."**

Among the many scientific drivers in energy research, several of them have demonstrated the need in synchrotron radiation:

-development of renewable energy sources (biofuels and hydrogen energy sources), storage of energy products (hydrogen and CO_2 sequestration),

-portable energy sources (high power density fuel cells and batteries),

-nanocomposite materials for energy applications (membranes, nanoparticles and conducting and flame retardant plastics)

Catalysis serves as a cross cutting feature 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.

The size of the CES community is:

95 (70/25) groups from academia, 20 groups from national laboratories, 35 (10/25) groups from industry: the total of 150 (100/50) groups and estimated 750 (500/250) synchrotron users. The first number in parentheses refers to chemistry, and the second number – to energy researchers.

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

-Atomistic understanding of activity, selectivity, stability, performance and degradation mechanisms of catalysts;

-Development of combined, multi-technique methodologies and instrumentation for real time, *in situ* catalysis 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.

Present challenges, and our proposed implementations of these approaches at the NSLS-II are summarized in the Table I.

Table I. Challenges, science drivers and their proposed implementation

Present challenges and the need for high x-ray brightness	Potential impact	Proposed implementation
Complexity 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)	High energy XRD/PDF at the XAS project beamline on a damping wiggler source; Hard x-rays (XAFS/XRD/DAFS) + soft x-rays (XPS/NEXAFS) experiments at dedicated and shared beamlines

Complexity of catalyst properties: cluster-support/adsorbate interactions, structural relaxation effects is 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 including valence distribution; Resolving the heterogeneity problem by a combination of XAFS and DAFS	Hard x-ray nanoprobe project beamline on an undulator source; XAS Project beamline on a damping wiggler source
Fast kinetics, low concentrations of many operational 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	3-pole wiggler XAFS beamline; XAS Project beamline on a damping wiggler 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 beamline for carrying out in situ surface reactivity studies

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

Research in the areas of catalysis and electrochemistry has a long history at the NSLS and other synchrotrons. Since the Synchrotron Catalysis Consortium (http://www.yu.edu/scc) started its operations in 2006, this user group evolved in a well established NSLS user community, with its user support, user access and user exchange coordinated, in part, by the SCC. Synchrotron-based energy science researchers, the emerging group of users, have not yet organized into such a cohesive synchrotron community as the SCC group. We hope this effort will help the both groups to coordinate and advance their science programs and more effectively use synchrotron facilities, at the NSLS and NSLS-II.

To best serve the needs of CES users, we propose to combine several dedicated and shared facilities at the NSLS-II as summarized in the Table below. More details about each type of beamline are presented in the following sections.

Table II. A suite of beamlines that will utilize CES plans at NSLS-II

Facility	No.	Mode	Purpose	Technique
Beamline on a 3-pole wiggler source	1	Dedicated	In situ studies of chemical transformations	quick, combined XAFS/XRD
Undulator soft x-ray beamline	1	Dedicated	Time-resolved (ms- range) high pressure (< 10 torr) studies of surfaces and adsorbates at near reaction conditions	XPS/NEXAFS
Nanoprobe ("Project")	1	Shared	Single nanoparticle studies	XAFS, imaging, high resolution

				fluorescence
beamline on an undulator source				
XAFS ("project") beamline on a damping wiggler source	1	Shared	Kinetics: in situ, Quick (sub-second time scale) studies of structure and reactivity of catalysts and hydrogen storage materials; Study of dilute catalysis at realistic metal loadings	XAFS, XAFS/XRD, DAFS, HRF
"Soft bend" (0.4 T bending magnet) beamline	???	Shared	-in situ studies of structure, dynamics and reactivity of catalysts in the tender (1-3 keV) x-ray energy region.	XAFS
Beamline on a 3-pole wiggler source	???	Shared	-in situ, time-resolved studies of structure, dynamics and reactivity of catalysts in hard x-ray energy region. Ex situ characterization of catalysis and energy related materials.Time resolution: minutes to hours.	XAFS

3. Detailed description of the dedicated beamlines

3.1 A dedicated CES beamline on a 3-pole wiggler source for quick, combined 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, quick (from ms to minutes) combined, XAFS/XRD studies of structure, dynamics and reactivity of 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 applied in situ as well, either in combination with XAFS/XRD or separately.

Catalytic reactions are normally performed under conditions of elevated temperature and pressure, using a wide variety of reagents and real time product analysis by mass spectrometry or gas chromatography. Homogeneous catalysts (e.g., in a liquid state) require special cells for handling fluid flow studied by the focused beams. Thus, to enable in situ experiments, gas and liquid flow reactors, high temperature and high pressure cells, supplied with the necessary gaseous and/or liquid reactants are required. Gases, chemicals and supplies delivery system requires a permanent, reliable infrastructure. Poisonous gases, like CO, need a safe permanent installation. End station (hutch) instrumentation will include: combined XAFS/XRD instrument, area detector, optimized Quick XAFS detectors, specialized software for synchronized XAFS/DAFS/XRD measurements. Such collection of specialized equipment for cutting edge catalysis research will be most efficiently used at the dedicated catalysis beamline.There already exists a prototype of such a dedicated facility: Synchrotron Catalysis Consortium beamlines X18B/X19A.

XAFS and XRD techniques give 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 information about the electronic properties of the catalysts. Finally, Diffraction Anomalous Fine Structure (DAFS) technique allows to study local structure in ordered species of the heterogeneous samples, i.e., in those systems where the ensemble-average XAFS data analysis would be complicated by mixing different species of a 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 is needed, namely, the simultaneous collection of the XRD and XAFS data under *in situ* conditions together with online product analysis.[1] At present, XAFS and XRD measurements can be performed at the NSLS only at different beamlines, with acquisition times of $1-10^3$ for XAFS and $10-10^2$ sec for XRD. DAFS has been performed only a few times in the last 10 years, and is grossly underutilized in catalysis and hydrogen storage applications where such technique would be a unique tool, due to their inherent heterogeneity.

The SCC and NSLS teams are currently building the first in the US instrument for combined time-resolved XRD/XAFS experiments at beamline X18A which will be a 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 activity of heterogeneous catalysts simultaneously. This will be coupled with online gas analysis, dedicated for studying *in situ* chemical transformations.

The choice of a three-pole wiggler source for this proposed beamline is justified as follows. First, its flux through the $1 \times 10 mm^2$ aperture (Fig. 1) is by an orders of magnitude better than in the 6.88m-radius NSLS bending magnet source (not shown). The useful energy range allows to measure most catalytically important materials, from Ti and V at the lower energies, to Pd, Ag, In at the higher energies. Second, designers of the quick XAFS monochromator at the three-pole wiggler beamline will not face as severe the heat load and monochromator weight problems, as the ones prohibiting the fast energy scanning at a damping wiggler source which is otherwise 2 orders of magnitude better in flux (Fig. 1). Since undulator sources are not suitable for fast energy scans either, the three-pole wiggler is the best available source for quick XAFS studies that we propose.
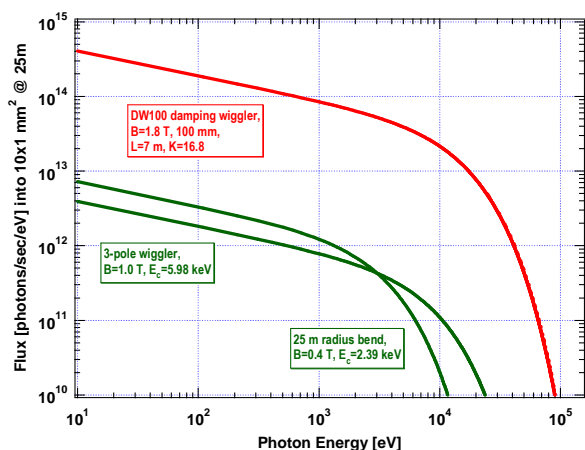

Fig. 1. Flux/per eV for three NSLS-II sources (damping wiggler, a three-pole wiggler and a bending magnet), at the sample position, ca. 25 m from the source and through a $1 \times 10 mm^2$ aperture.

The fast XAFS instrument will be similar to its prototype currently installed at beamline X18B of the NSLS. The current data acquisition method collects 60 K points/minute using a Keithley current amplifier, a 16- channel VME analog-digital converter, and custom written Linux based software. 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 popular EXAFS analysis packages.

A group of these PIs, led by Hanson has run fast TR-XRD experiments at beamline X7B, has recently tested the new QXAFS instrument at beamline X18B. Their experiment focused 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 ^oC.

Data analysis performed by Principal Component Analysis allowed to detect the intermediate phase and study reaction kinetics (Fig. 3). Our team members have the know-how of designing, performing and analyzing the fast XAFS and fast XRD measurements – and we are well positioned to develop their integration at the same beamline.
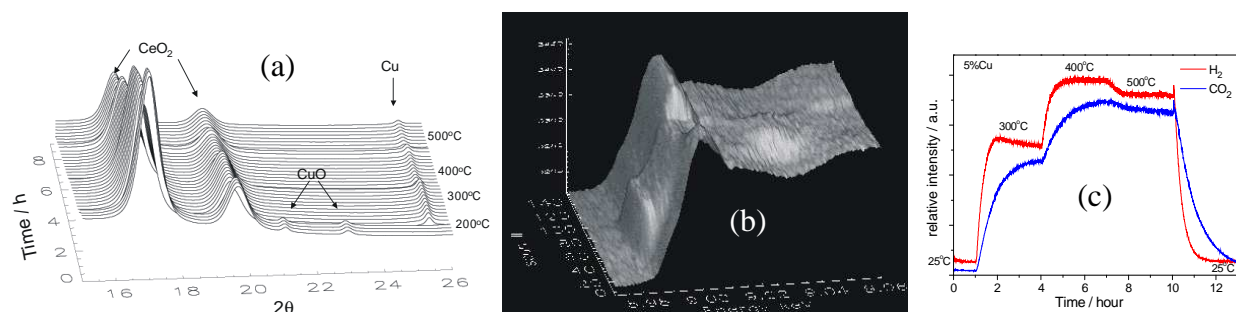

Fig. 2. (a) Time-resolved X-ray diffraction (TR-XRD) patterns collected during the water gas shift (WGS) reaction for the 5%Cu/CeO2 nanocatalysts. (b)TR XANES: reduction/re-oxidation of Cu doped ceria at 200°C.(c) A typical figure for H_2 and CO_2 products from the WGS reaction is shown in the middle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

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.[2] The Ce L_3 edge XANES spectra show the appearance of Ce^{3+} cations as

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

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 me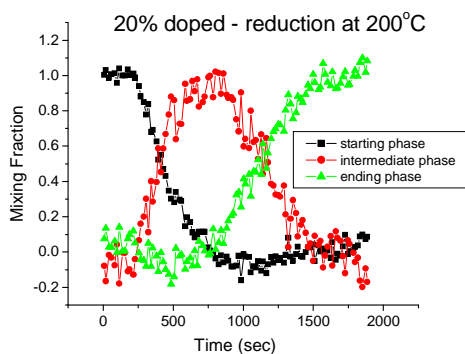asurements of the short range structure and the long range structure of a nanocatalyst will be measured *in situ*, during chemical reaction.

Fig. 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 readout time. Our proposed setup will have both fast XRD (3ms time resolution) and fast XAFS (1s), which will be the best combination in the world. The ultimate performance of these facilities will be achieved when they are moved to the NSLS-II to take full advantage of the high intensity and brightness of this new synchrotron light source. 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.
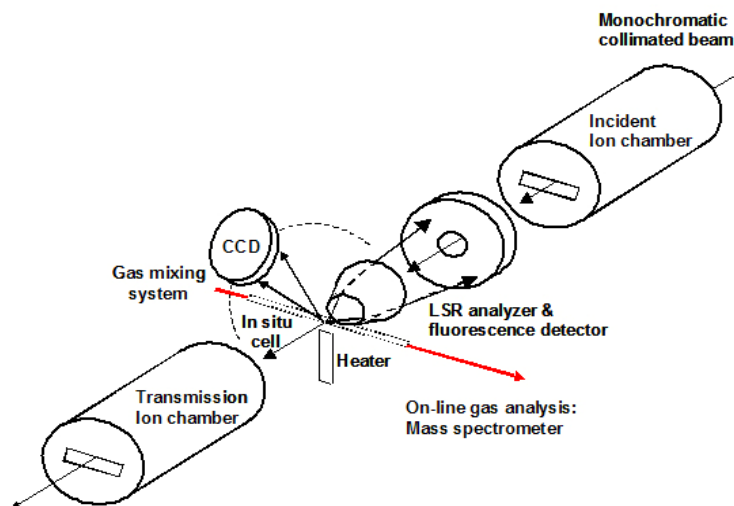

Fig.4.   Schematic of the proposed Fast-XRD/Fast-XAFS instrument

As shown in Fig. 4, the XAFS instrumentation will include sealed Oxford ionization chambers for transmission detectors, a PIPS detector and the Log Spiral of Revolution (LSR) systems for fluorescence measurements. The R&D for the LSR detectors has been performed during the last 5 years by D. Pease and A. Frenkel.[3] These detectors have been built and successfully applied for Ti and Cr detection for ex situ measurements. Pease and Frenkel have the knowledge and the infrastructure necessary to manufacture these detectors. A series of the LSR analyzers, customized for in situ experiments with catalytically active metals, will enable significant improvement in fluorescence data quality. XRD patterns will be collected using a 165mm MarCCD two dimensional detector. This CCD detector can fulfill all the requirements for this project, but a new detector developed by Siddons of the NSLS detector group is also considered because of additional capabilities such as continuous readout and energy discrimination. A 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 stuff.
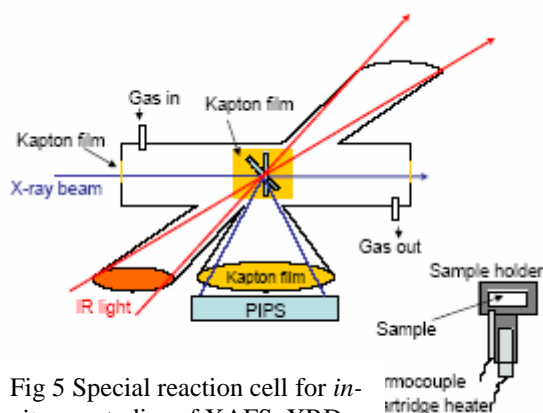

Fig 5 Special reaction cell for *in-situ* studies of XAFS, XRD and IR

The utilization of the above described instrumentation for fast XRD and XAFS will expand our knowledge immensely about the state of the catalyst material (crystalline phases, oxidation states, composition, etc.) under working conditions, but it will have 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 cell has openings for the x-ray beam covered with

Kapton film. The sample can be mounted at 90° towards the beam for transmission studies, or at 45° for fluorescence. Perpendicular to the cell length there is a conical tube for fluorescence X-ray beam. It is covered with Kapton film. Also, two more conical tubes are mounted at 45° towards the X-ray path for IR beam. The tube for IR light is sealed with a IR-transparent window. If required, X-ray diffraction measurements could be done if an opening, perpendicular to the plane of X-rays and IR beam, is made and covered with a X-ray transparent material (e.g. Kapton). The IR beam is focused at the sample by means of a 90° off-axis parabolic mirror.

- *End station instrumentation:*

Setup for in situ catalysis studies will include: gas mixing and purification system, residual gas analysis systems (MS and GC); high temperature, high pressure, and electrochemical reactors.

- *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.

- *Detector requirements for this beamline:*

Fast readout XRD detectors, fluorescence analyzers (Log-spiral of revolution based, and others), HRF analyzers. R&D of QXAFS detectors is required (time constant should be in sub-ms range).

3.2. A dedicated CES undulator beamline for millisecond time-resolved high pressure XPS and NEXAFS measurements of surfaces and adsorbates at near reaction conditions

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.[4] 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, which presents great experimental challenges. We plan to take advantage of the unique properties of the Soft X-ray EPU 100 VUV beamline in order to construct such an instrument. By combining the high brightness of the EPU 100 beamline with stroboscopic Elevated Pressure Photoemission Spectroscopy (EP-PES) using a small volume rapid gas exchange flow-cell, we will perform kinetic photoemission spectroscopy experiments at near reaction conditions with time resolution on at least the 10 ms timescale. This will provide unprecented chemical detail of the dynamic nature of catalytic function. Further developments could facilitate the application of this experimental technique 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.[5] Typically these measurements are performed under Ultra-

High Vacuum (UHV) conditions which are 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 pressure conditions, up to approximately 5 -10 torr.[6,7] Since this pressure range represents ambient conditions for a broad variety of surfaces, this development is beginning to transform our understanding of surfaces under realistic conditions. These include the nature of water mineral interfaces under ambient conditions,[8] ice and liquid surfaces under atmospheric conditions,[9,10,11] as well as catalytically relevant surfaces under near operating conditions.[7,12] To date, these experiments have been carried out by changing the surface temperature at constant gas pressure or flow due to their relatively large reaction cell volumes limiting their use in investigating catalysts under dynamic conditions. Thus, the ability to rapidly exchange gases on the millisecond timescale through the use of a small volume flow cell while recording spectra during this dynamic gas exchange provides a new type of measurement for users 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.

- *General Considerations for Beamline Characteristics*

For catalytic applications, the soft x-ray region (from approximately 10 eV up to 2000 eV) provides the best combination of relevant core levels and surface sensitivity. This region allows measuring the valence band, C1s (binding energy ~285 eV), O1s (~530 eV), and N1s (~400 eV) core-levels, and many transition metal L-edges while keeping photoelectron kinetic energies in the range of highest surface sensitivity, 50 to 200 eV. Using higher photon energies increases the photoelectron kinetic energy allowing one to probe more deeply below the surface. These depth-profiling experiments address the extent and depth of changes in chemical composition in the surface region. Since, in general, the photoemission signal intensity is proportional to the phot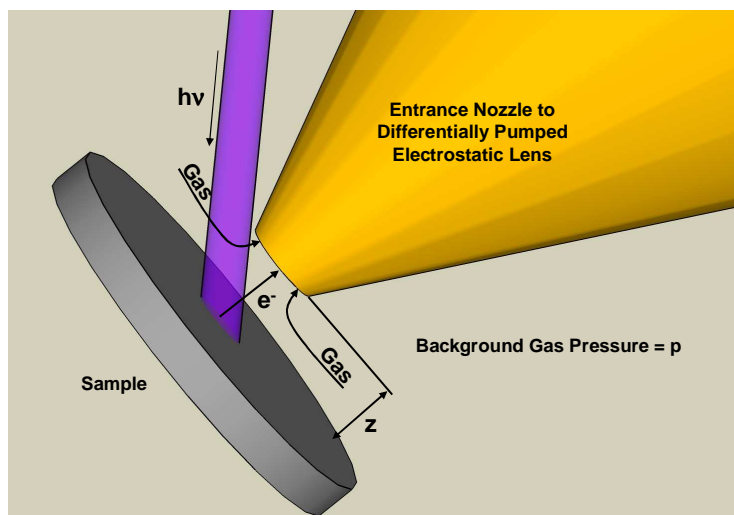on flux, maintaining a high photon flux to higher photon energies is also vital in performing these depth profiling experiments. The EPU 100 VUV Undulator beamline with its high photon flux at over 2000 eV will allow probe depths of approximately 20 Å (up to 10 atomic layers) covering a significant portion of the surface region.

Fig. 6: Sample/first aperture geometry for a standard elevated pressure photoemission spectroscopy experiment.

The maximum pressure in modern high pressure photoemission spectroscopy experiments is limited by the attenuation of the photoemitted electrons via gas phase scattering. Gas phase attenuation follows a Beer´s law dependence,

$$I_p \propto I_{vac} \exp(-z\sigma(E)p)$$

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. 6). 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 reducing the gas pressure at the sample, there are limitations on the minimum value of z to values approximately equal to the diameter of the aperture.[13] Therefore a reduction in the aperture size allows the reduction of z and a reduction in gas phase attenuation. 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 these experiments. Current elevated pressure photoemission spectroscopy experiments can operate at pressures up to approximately 5 - 10 torr.[6,7] 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.

- *Special Consideration for Kinetic Measurements Using Stroboscopic Methods*

    Currently, very few experimental techniques allow one to quantitatively measure the chemical composition of a surface under catalytically relevant operating conditions and time-scales. To develop these capabilities, we will integrate a rapid exchange flow cell into the elevated pressure x-ray photoemission spectroscopy experiment using a delay-line detector for stroboscopic measurements (Fig. 7). As an example experiment, consider investigating the formation of $Ba(NO_3)_2$ particles from BaO particles following brief fuel rich transients on a NO_x storage model catalyst. During this experiment a preset mixture of fuel, oxygen and NO (representing fuel-lean conditions) are allowed to flow through a small volume flow cell. For a flow cell of approximately 5 ml volume at room temperature and gas pressures of a few torr that exits the flow cell through a 1 mm hole (Fig. 7), gas exchange in the cell occurs in approximately 50 ms. Through the use of a pulse valve, short pulses of fuel of a specific duration (on the 10's of ms timescale) are allowed to enter the cell, providing brief fuel rich transients. Following the injection of the gas pulse, spectra are collected using a delay-line detector on the electron energy analyzer at a specific delay time after the pulse in a single shot covering a specific time-width. The importance here is that the
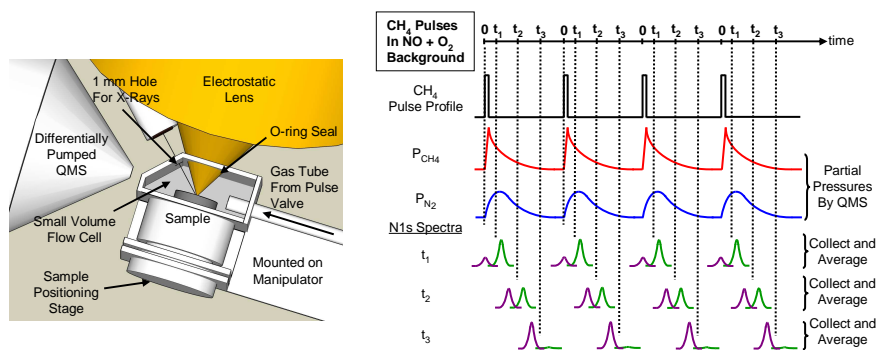

Fig. 7: Close-up view of an elevated pressure photoemission spectroscopy experiment using a small volume flow cell. Gas enters the flow cell from a pulse valve and leaves through the 1 mm hole for the x-rays. Partial pressures of the gas exiting the flow cell are measured with the differentially pumped 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.

time resolution in such an experiment is not determined by the time required to acquire a full spectrum, but instead by a balance between the width of the acquisition window and the time necessary for the surface to return to its initial state following the gas pulse. If we assume that the surface returns to its initial state in approximately 1 second following the gas pulse then a spectrum representative of this specific time delay and width can be acquired every second. Better signal to noise is achieved by averaging such spectra. We estimate using typical dwell times, resolution and number of spectra to average for a current EP-PES experiment at an undulator beamline (which uses a 9 channeltron MCD detector) that we can acquire a similar quality spectrum that represents a 5 ms time-window at a specific

delay time following the gas pulse in about 1000 seconds, or 1000 gas pulses. This is a very reasonable acquisition time and allows collecting multiple delay times following a gas pulse in a single synchrotron shift. Further this provides unprecedented time resolution for XPS and as a result unprecedented details about the dynamics of the chemical composition, such as $Ba(NO_3)_2$ formation from BaO, of a surface and how they couple to its catalytic function. Combining this type of measurement with depth-profiling experiments will provide information relating to how changes in surface composition relate to changes in bulk composition. The time resolution estimate above is high since it is expected that the undulator source at NSLS-II will be approximately 10 times brighter than current undulator sources which implies either less time to acquire a spectrum or 10 times greater time resolution than this estimate. Therefore it may be possible to realize sub-ms time resolution in these experiments. Lastly, these types of measurements are intractable at a bending magnet beamline at NSLS-II due to its lower flux. Estimates of the flux of a 0.4 T bending magnet source are 10^2 lower than that of VUV EPU 100. This means that it would require 10^2 longer time to acquire a spectrum (or approximately 10^5 seconds) of roughly the same quality. Note that this also 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.

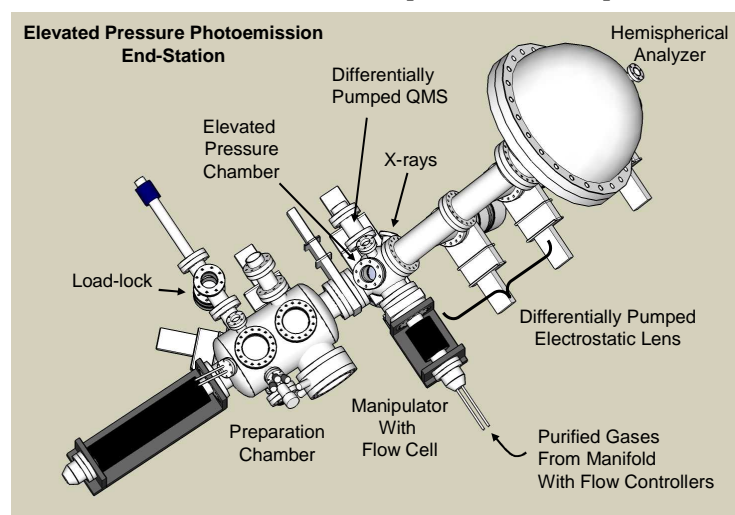- *End station instrumentation (permanent setup):*

Fig. 8 presents an overall conceptual design of an EP-PES endstation.

- Surface Preparation Chamber;
- Elevated Pressure Chamber Incorporating a Small Volume Rapid Gas Exchange Flow-Cell;
- Electron Energy Analyzer with Differentially Pumped Electrostatic Lens (for example a modified Specs Phoibos 150);
- 2D Delay Line Detector for Stroboscopic Measurements;
- Gas Manifold with Cabinets for Hazardous Gas Storage.

- *Software and computing infrastructure requirements for this beamline (David):*

- *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).

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 in addition to the dedicated beamlines described in Section 2 will be needed to serve this community.

Building the last three beamlines listed in Table 1, categorized as shared facilities, could conceivably be done via maintaining, upgrading and transitioning existing beamlines from the NSLS. As indicated

in the Table, three beamlines will be needed to cover a wide energy range. 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. A shared XPS/NEXAFS beamline will require a small spot size, multichannel XPS analyzer, fluorescence and electron NEXAFS detectors and a load lock / rapid sample access system.

There are 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.

5. Facility infrastructure at NSLS-II

We anticipate the need of a minimum of 3-4 laboratories adjacent to the beamlines for performing the experiments of moderate-pressure XPS, XRD and XAFS. The laboratories will be used for the storage 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 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.

A set of 4 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.

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