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Synchrotron Catalysis Consortium (SCC) at NSLS-II: Dedicated Beamline Facilities for In Situ and Operando Characterization of Catalysts

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Introduction

The Synchrotron Catalysis Consortium (SCC) was funded and established in September 2005 at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). For more than a decade, the SCC was the first of its kind in the United States, with a mission to promote the utilization of synchrotron techniques for cutting-edge catalysis research under in-situ conditions [1]. The consortium consists of three Principal Investigators (Jingguang Chen, Columbia University, Anatoly Frenkel, Stony Brook University/BNL, and Jose Rodriguez, BNL) and scientific staff member Nebojsa Marinkovic. The initial team also included Radoslav Adzic, BNL, and collaborators from academic, national, and industrial laboratories. During the first decade of its operations at three NSLS beamlines (X18A, X18B, and X19A) until the closing of NSLS on September 30, 2014, the primary goal of the SCC team was to provide assistance and to develop new sciences/techniques to the catalysis community through the following concerted efforts:

- Dedicated beamtime for catalysis research on three beamlines for in-situ X-ray Absorption Fine Structure (XAFS) measurements. The SCC and NSLS entered into a Contributing User agreement that allocated a portion of beamtime to the SCC for methods development at the three beamlines. An important development was the collaboration with beamline staff on testing of Quick EXAFS (QEXAFS) monochromators for catalysis applications, developing software packages for data analysis and performing several exemplary studies to educate and train the catalysis community [2, 3].
- Dedicated facilities, including state-of-the-art in-situ reaction cells and gas-handling systems (mass flow controllers for reaction gas delivery into the cells and residual gas analyzers).
- A dedicated research staff with expertise in the application of synchrotron methods to in-situ catalysis science to assist with experimental setup and safety training.
- Training courses for graduate students and postdoctoral fellows on XAFS techniques and data analysis.

- Assistance with idea development and proposal writing for potential XAFS users from the catalysis community.
- Development of new hardware for catalytic and electrocatalytic research. Important new (at the time) capabilities for catalysis research using combined techniques (XAFS-XRD [4, 5], XAFS-DRIFTS [6, 7], and XAFS-Raman spectroscopy [8, 9]) were designed and developed at the three beamlines.
- Design and implementation of plans for the transition of SCC operations from NSLS to NSLS-II.

In 2014–2016, during the transition from NSLS to NSLS-II, the SCC collaborated with SSRL (SLAC Laboratory) to enable dedicated catalysis operations and support at Beamline BL 2-2. Working with staff at SSRL, the consortium continued to provide in-situ XAFS capabilities to the catalysis community. At the same time, the SCC engaged with NSLS-II in the design and implementation of the Quick X-ray Absorption and Scattering (QAS) beamline 7-BM. Due to complementary X-ray energy ranges and capabilities of the QAS and Tender Energy X-ray Spectroscopy (TES) beamline 8-BM, the SCC reached a Partner User (PU) agreement with NSLS-II to provide dedicated support to catalysis and electrocatalysis communities at these two beamlines. In the remainder of this article, we will outline the specifications of the QAS and TES beamlines and describe dedicated hardware and end-station instruments that are designed and built with SCC support. We will then briefly summarize the training and outreach activities of SCC at NSLS-II and beyond.

Technical specifications of QAS and TES beamlines and dedicated catalysis-related equipment

The QAS beamline at NSLS-II port 7-BM was designed and constructed to enable in-situ studies of chemical and physical transformations by both conventional and quick X-ray absorption and by powder diffraction. QAS covers the energy range of 4.7–31 keV, from the Ti K-edge to the Sn K-edge. It uses a three-pole wiggler source. The beamline provides high photon flux ($\sim 7 \times 10^{11}$ ph/sec at 10 keV; ring

current = 400 mA) along with an adjustable beam size. The beamline can run in unfocused mode with a maximum spot size of ~ 1.5 mm (V) \times 10 mm (H) and in focused mode with a spot size of ~ 300 μ m.

The main technique at QAS is transmission and fluorescence X-ray absorption spectroscopy (XAS). The beamline's quick scanning capability allows time-resolved measurements of chemical reactions and structural transformations under operando and realistic conditions. QAS offers powder diffraction using an area detector. These two techniques can be used separately or in combination to measure different characteristics of the same samples.

The optical system of the beamline is shown in Figure 1. It consists of a 700-mm-long flat vertically collimating mirror at 11.7 m from the source that can be switched between two stripes, Rh and Pt, for harmonic rejection. The Rh stripe is typically used from 4.7–23 keV and the Pt stripe is used above 23 keV. The monochromator uses a Si(111) channel-cut crystal and a direct-drive servo-motor and runs in continuous scan mode, with EXAFS scan times ranging from 30 sec to less than 1 sec. Focusing is provided by a 1000-mm-long Rh-coated toroidal focusing mirror, 30 m from the source, providing 2:1 horizontal demagnification. The sample is located 45 m from the source. Detectors include three gridded ion chambers for transmission XAS, passivated implanted planar silicon (PIPS) and silicon drift (SDD) detectors for fluorescence XAS, and a PerkinElmer area detector for diffraction/scattering.

The TES Beamline at 8-BM is optimized for the tender energy range with routine operations at 2.0 to 5.5 keV, for spatially resolved and in-situ XAS and for X-ray fluorescence elemental mapping, both at the micrometers scale. Elements (absorption edges) accessible in that energy range are P through Ti (K edges), Y through Cs (L edges), and Ir through Pu (M edges), including many key catalysts, supports, and acti-

vators/poisons [10, 11]. Utilizing a bend-magnet source, TES provides a focused beam size that can be user-tuned from ~ 25 μ m down to ~ 2 μ m, with flux scaling with spot size. XAS, including XANES and EXAFS, of heterogeneous and structured samples is possible because the beam does not move measurably on the sample during energy scanning and across the full energy range. Scanning is conducted in traditional step-scanning mode or in continuous on-the-fly mode for fast scans (10 to 100 s for XANES, 1 to 3 min EXAFS, with multiple scans to achieve sufficient statistics). The sample environment is a helium atmosphere at room pressure. Because absorption effects at this low energy range require thin windows, short path lengths through gases or solvents, and small sampling depths, our focus for in-situ measurements has been on development and optimization of small cells or microreactors [12]. In these, samples are necessarily small and heterogeneous on the scale of the beam size, so positional stability of beam is critical.

Typical imaging and microspectroscopy analysis is shown in Figure 2. In addition, in some systems, "speciation imaging" is possible; by tuning the incident energy to XANES features specific to different oxidation states or species, the distributions of different species can be mapped.

The optical layout of TES is designed to bring XAFS capabilities down to the microscale. There is a vertically collimating and harmonics rejection mirror pair operating at tunable pitch with fixed offset, a fixed-exit double crystal monochromator utilizing Si(111) crystals, and a toroidal mirror for primary focus to a secondary source; beam diverging from the secondary source is refocused by KB mirrors to the sample (Figure 3). All mirrors are Ni-coated. The sample is oriented at 45 degrees in the classic fluorescence geometry, and transmission intensity can be measured for samples thin enough at low energy.

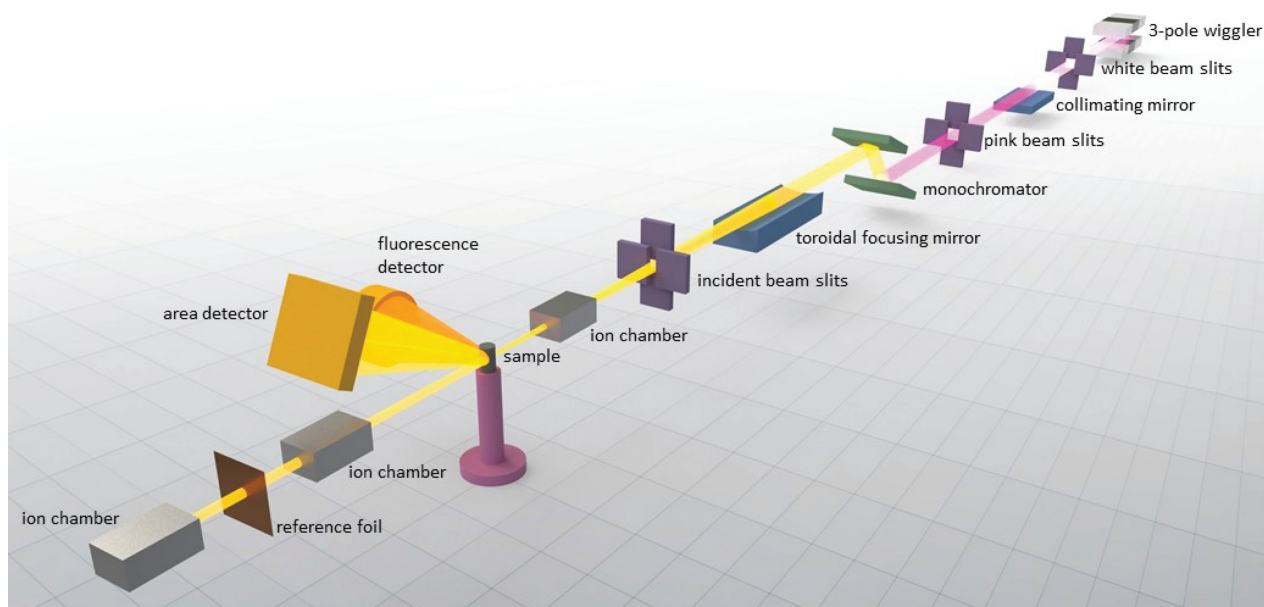


Figure 1: Schematic of the QAS 7-BM beamline at NSLS-II.

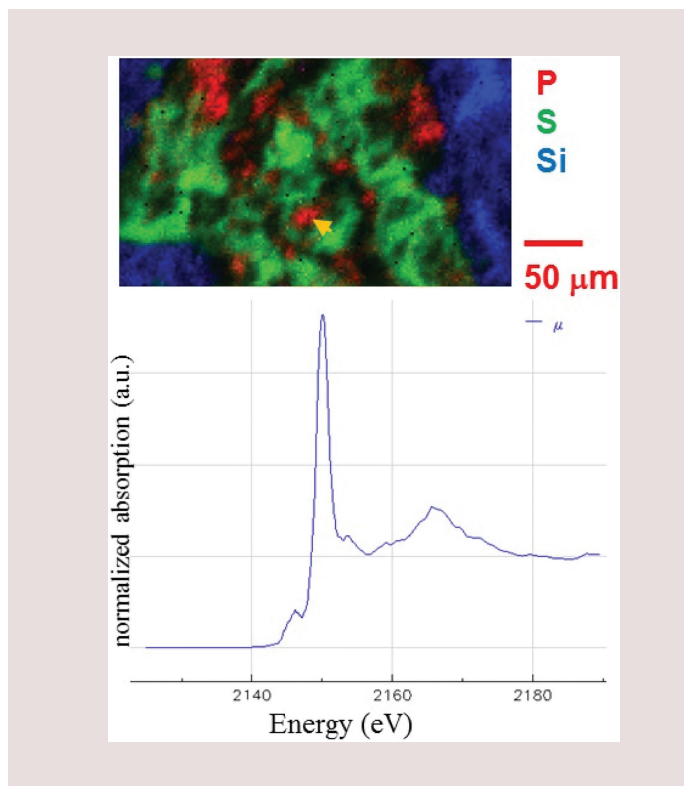


Figure 2: (Top) Heterogeneous sample imaged with $2 \times 2 \mu\text{m}^2$ spot size at 2700 eV, with $1.25 \mu\text{m}$ pixels, showing distributions of P, S, and Si. (Bottom) P micro-XANES measured using $4 \times 8 \mu\text{m}^2$ beam; spectrum is sum of 20 scans, 40 s each. The peak position identifies phosphate, and the strong pre-edge structure identifies an Fe^{3+} phosphate [13].

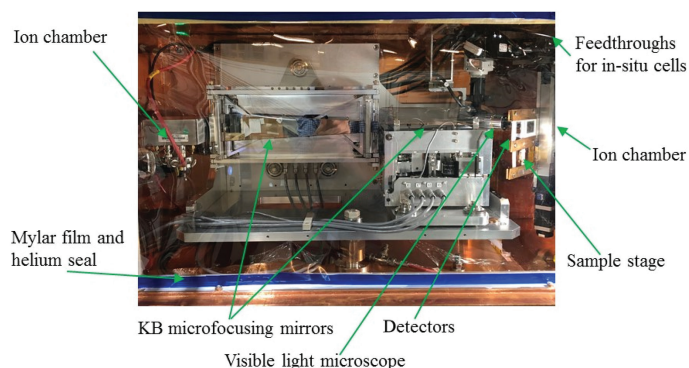


Figure 3: Photograph of the TES endstation sample chamber, with beam entering from the left. A single helium-atmosphere environment contains the KB microfocusing mirrors, sample stage, and detectors. Feedthroughs to the sample position deliver electrical, thermocouple, and gas/fluid connections.

Gas handling and analysis system

The gas handling system consists of gas input (gas cart with lecture bottles), gas analysis system (RGA or gas chromatograph), and exhaust

system (N_2 dilution and environment gas monitoring device is installed at QAS only).

The integrated gas inlet/analysis system and exhaust are shown in Figure 4. The gas cart contains H_2 , O_2 , CO , CO_2 , C_xH_y , and He, and a user-selected gas. A residual gas analyzer (RGA) and gas chromatograph can be connected to the outlet of the reactor to monitor the reactants and products. The exhaust system captures the exhaust gases from the gas cart, reactor, and RGA and dilutes flammable and toxic gases with N_2 to $< 1\%$ before releasing them into the atmosphere. The gas inside the hutch is monitored by a personal environment gas monitoring device.

Dedicated reactors

For research at the QAS beamline, a gas flow reactor (Clausen cell), pellet reactors (six-shooter tube reactor and Nashner-Adler reactor), and electrochemical cells (for regular potentials within the solvent solubility and for extensive gas evolution) are available. High-pressure cells will be available in the future. Of the reactors used in simulation of the catalyst environment in gas-solid heterogeneous catalysis, the most widely used is the Clausen cell (Figure 5a), consisting of an X-ray transparent tube and a catalyst bed in powder form. Different tube materials and thicknesses are available for optimal signal in both transmission and fluorescence modes. Tubes are heated by resistive heating in the temperature range of RT-300°C, RT-600°C, and RT-700°C for Kapton, glassy carbon, and quartz tubes, respectively. The Nashner-Adler reactor (Figure 5b) uses pellets of 10–13 mm in diameter, cartridge heating or liquid nitrogen (LN_2) cooling for a temperature range of -150 to 500°C , and allows for both transmission and fluorescence geometry (Figure 4). The six-shooter reactor allows for simultaneous preparation of up to six pellets of 6 mm diameter and their successive XAS investigation in continuous mode by a batch program in transmission geometry [14]. Two types of electrochemical cells for aqueous electrolytes are available. For in-situ transmission and fluorescence measurements in the potential regime within the stability of the supporting electrolyte (0.0–1.6 V), the sandwich cell with catalyst applied as a paste on carbon cloth is available. For research outside this range (e.g., CO_2 reduction, organic fuel oxidation) where oxygen and/or hydrogen evolution reactions simultaneously occur on the electrodes, the carbon paper cell is used. The cell minimizes the deterioration effects in the signal quality by allowing the gas to escape away from the X-ray path, thus significantly prolonging the potential regime for XAS measurements in fluorescence geometry [15, 16].

Combination of techniques

X-ray absorption spectroscopy can be combined with X-ray diffraction (XAS-XRD) [4], diffuse reflectance infrared Fourier transform spectroscopy (XAS-DRIFTS) [7], and Raman spectroscopy (XAS-Raman) [8] (Figure 6). For the combined XAS-XRD regime, powder diffraction is performed using a PerkinElmer XRD 1621 N ES Series area detector (Figure 6a). It has a 16-inch square amorphous Si sensor with a pixel size of $200 \mu\text{m}$. The area detector can be positioned at different heights with respect to the incoming beam and different distances from the sample. Diffraction can be done alone, with the detector center



Figure 4: Integrated gas inlet and gas analysis system (left) and exhaust system (right) at QAS: (a) gas cart (flammable side); (b) mass flow controllers (MFCs); (c) MFC electronics; (d) residual gas analysis (RGA) turbomolecular pump; (e) RGA head and electronics; (f) turbo pump controller and pressure readout; (g) camera; (h) gas outlet flowmeter; (i) multiple gas environment monitoring device; (k) nitrogen flowmeter.

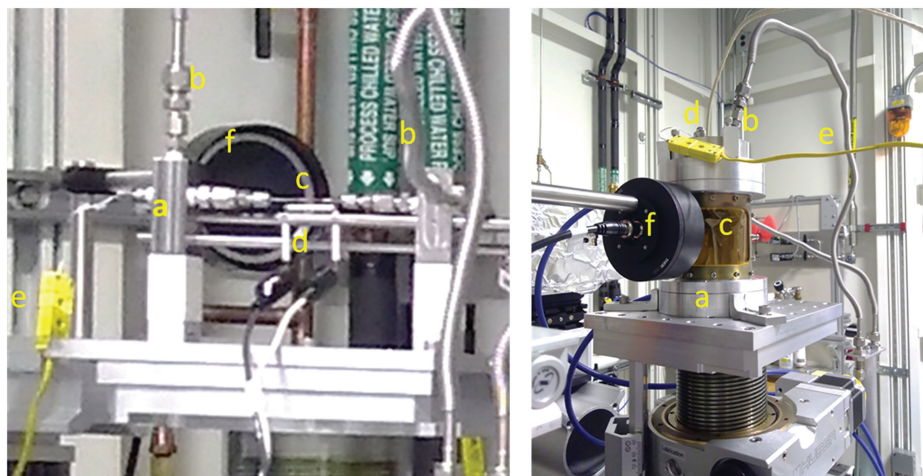


Figure 5: Clausen cell (left) and Nashner-Adler cell (right) on sample stage in the QAS hut: (a) reactor cell; (b) gas inlet and outlets; (c) sample; (d) heating element; (e) thermocouple connection; (f) PIPS fluorescence detector.

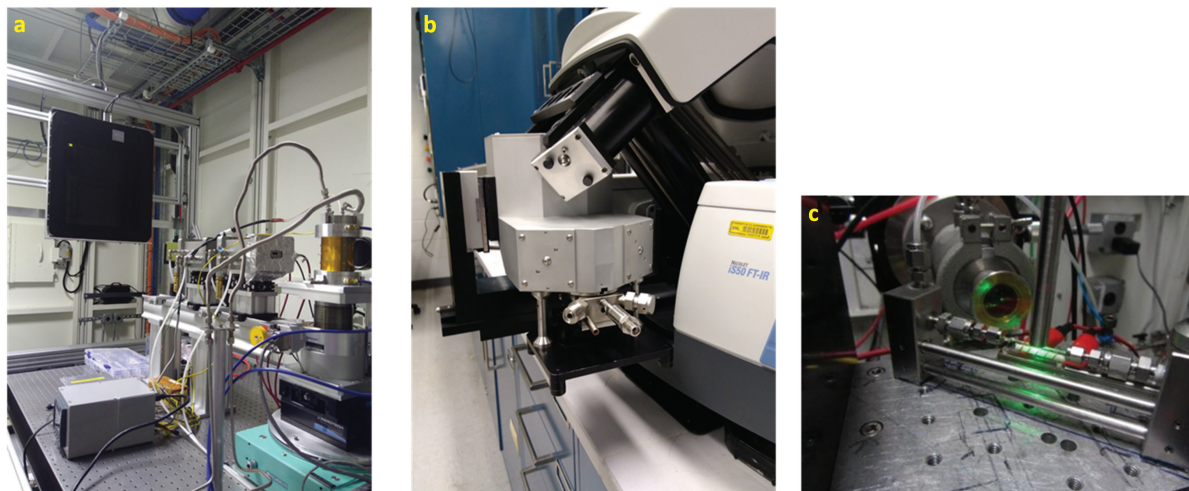


Figure 6: Combined instruments at QAS: (a) XAS-XRD; (b) XAS-DRIFTS; (c) XAS-Raman.



Figure 7: Instructors and participants of the 2018 annual short course on X-ray absorption fine structure at Brookhaven National Laboratory.

normal to the beam, or it can be raised above the I_t and I_{ref} ion chambers, allowing XAS and XRD to be performed on the same sample.

For a combined XAS-DRIFTS regime, the IR beam from the Nicolet iS-50Ft-IR spectrometer is redirected through a Harrick Da Vinci arm firmly attached to a Praying Mantis DRIFTS accessory that focuses the light onto the surface of a powdered sample in the cup of the Harrick high-temperature reaction chamber (Figure 6b). The chamber can be heated to about 500 °C and allows reaction gases to either blanket the sample powder or to flow through it. The X-ray beam passes through two carbon windows and about 1 mm below the surface of the sample, thus allowing simultaneous acquisition of XAS in transmission geometry and DRIFT spectra [17–19].

Combined XAS-Raman spectroscopy uses the custom-made Clausen cell with a thin-wall SiO_2 tube that is sufficiently transparent in the X-ray, visible, and IR regions (Figure 6c). A fiber optic probe is placed a few mm from the top of the tube, shining visible (532 nm) laser light and simultaneously capturing the Raman signal. The X-ray beam passes perpendicular to the Raman probe and allows XAS spectra in both fluorescence and transmission geometry.

In situ/operando capabilities at TES beamline for catalysis and electrocatalysis research include a reaction cell designed for minimized beam path through solvent and insulation to reduce heat transfer to the hutch environment. Other microreactors are under development [20].

Training and outreach

In order to promote the utilization of synchrotron facilities in the catalysis and electrocatalysis communities, SCC PIs and their group members train graduate students, postdoctoral fellows, and young research staff on data collection and data analysis. In the past 15 years, SCC members have organized many training courses and workshops, primarily focused on the applications of X-ray absorption spectroscopy, which is the main technique at the SCC-supported beamlines. These courses, attracting up to 45 registered participants and up to 20 auditors, include lectures, software demonstrations, a practical session at the beamlines, and data analysis sessions (Figure 7).

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