Biomass Catalysis X-Ray Characterization

In-situ X-ray Absorption Facilities X-ray absorption spectroscopy is an essential method for determination of the local structure (number and type of neighboring atoms and bond distances) up to about 5 Å from the selected atomic species. In addition, to fluorescence and transmission environmental reactors, a fixed-bed, plug-flow operando reactor has been developed by our research team, Figure 1. The borosilicate glass, or polyimide tubular reactor allows high quality X-ray absorbance and kinetic data to be measured simultaneously, which is important since the structure and electronic properties often change with the reaction conditions. Because of the penetration depth of the high energy X-rays, catalysts can also be analyzed under reaction conditions up to about 400C and 50 atm in transmission, or fluorescence for most transition metal catalysts and reactions. With fast data acquisition times of 1 minute for full scans, data can be obtained under steady-state or temperature dependent transient mode, e.g., TPD.

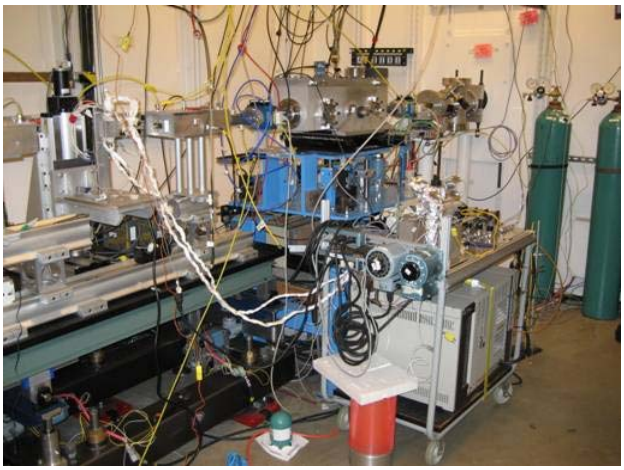

Figure 1. Plug-flow, Operando EXAFS reactor at the insertion device beamline at the APS

X-ray Absorption Near Edge Spectroscopy (XANES) is often used to determine the metal oxidation state, fraction of metallic and oxidized metal, formation of alloys. However, the intensity and position of the XANES spectrum also changes upon chemisorption of adsorbates. Since the changes in XANES depend only on metal-adsorbate bond formation, this analysis can been used to identify surface adsorbates that cannot be determined by spectroscopic methods, for example H_2 by IR. From the XANES analysis, the identity and surface coverage of reactants and products under reaction conditions and the importance of adsorption on the observed reaction kinetics can be determined.

X-ray Scattering Facilities. This program takes advantage of a close association with the Chemistry, Environmental and Polymer Sciences (formerly BESSRC/XOR) group at the Advanced Photon Source (APS), Sectors 11 and 12. R. E. Winans is the Group Leader of this facility. At 12-ID, the SAXS facility is equipped for doing a number of *in situ* experiments with furnaces, burners, low temperature capabilities, electrochemistry equipment, TGA, flow systems, and reactive gases. On 11-ID, high energy scattering is available, which provides atom-atom correlation out to ~ 15 Å. Time-resolved spectroscopy is available of 11-ID and regular spectroscopy on BM-12. Spectroscopy experiments can be done at high temperatures and with reactive gases. A Prisma Quadrupole Mass Spectrometer Model QMS 200 M2 with a mass range 1 - 200 amu using a SEM/Faraday detector is dedicated to the SAXS facility.

In the SAXS beamline, X-rays produced in an undulator (5.0 – 30.0 keV) pass through initially a high heat load mirror followed by a double-crystal monochromator ($\Delta E/E \sim 10^{-4}$) and a second focusing mirror (see Figure 4, below). Pink beam operation is possible by moving the monochromator. The scattered X-rays are detected by a nine-element mosaic CCD detector (150 x 150 mm) with a maximum resolution of 3000 x 3000 pixels.

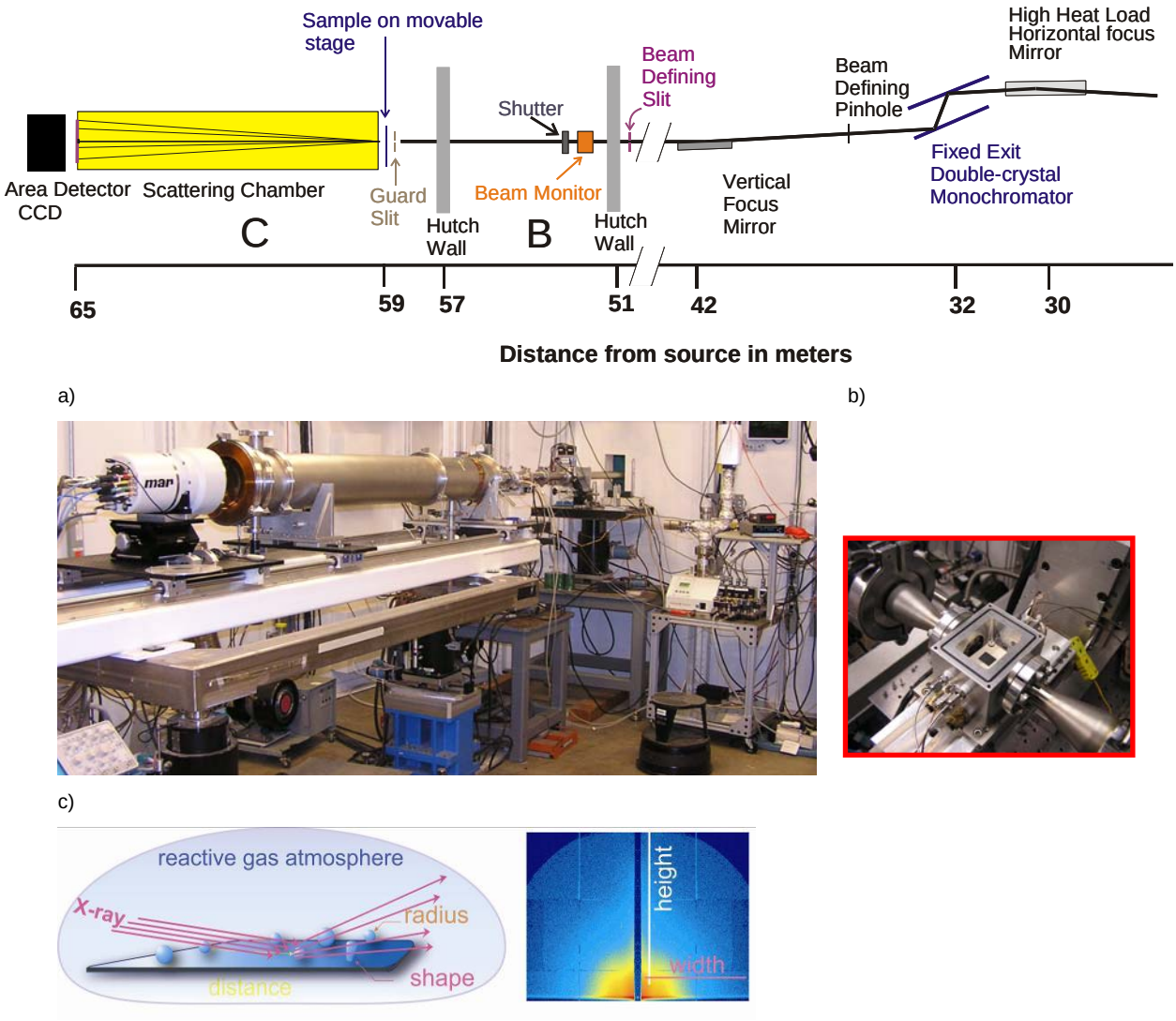

Figure 2. (a) GISAXS-TPRx experimental setup for combined in situ GISAXS and temperature programmed reactivity.(b) Closeout of the reaction cell. (c) Schematic illustration of the *in situ* GISAXS experiment.

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