***Workshop C**: In situ Phenomena in Catalysis*
Workshop held on May 3, 2011
Organizers: Jeff Greeley (CNM), Jeff Miller (CSE), Judy Yang (EMC, Univ. Pittsburgh)

This thematic workshop brought together experts in catalysis to discuss the state of the art in catalyst reactivity and characterization using scientific methods available through Argonne's user facilities (Advanced Photon Source, Electron Microscopy Center, and Center for Nanoscale Materials). Researchers with expertise in the use of x-ray probes, transmission electron microscopy and electronic structure theory highlighted current efforts in the dynamic characterization of heterogeneous catalysts under realistic reaction conditions. The presentations were designed to foster cross-disciplinary interactions between these thematic areas, from which new directions in the rigorous study of *in-situ* catalytic phenomena will emerge.

Anders Nilsson (Stanford Synchrotron Radiation Lightsource), the keynote speaker in the area of synchrotron methods, described how time resolved, x-ray photoelectron spectroscopy (XPS) spectroscopy can be used to address fundamental questions regarding the mechanism of the oxygen reduction reaction (ORR). In addition, he demonstrated how oxide growth occurs at certain potentials on single crystal surfaces using high resolution Pt L-edge XANES spectroscopy under real electrochemical conditions.

Anatoly Frenkel (Yeshiva University) reviewed recent advances in synchrotron characterization of catalytic materials including improved time (QEXAFS) and energy (HERFD) resolution methods, coupling of x-ray absorption and scattering methods to vibrational spectroscopies in a single reactor, and measuring several materials at one time.

Lin Chen (Argonne National Laboratory and Northwestern University) described advances on ultrafast time scale measurements in order to determine transition state structures of photo-excited transition metal complexes. Approaches for studying those catalytic reactions that are not photo-activated and those with low turnover numbers were proposed.

Larry Allard, (Oak Ridge National Laboratory), the keynote speaker in electron microscopy, described recent developments in a new 3rd generation, prototype, environmental cell from Protochips Aduro™, which when used with state of the art aberration-corrected TEM provides sub-Ångström image resolution at elevated temperatures and pressures. Several examples of these capabilities were described.

Chris Kiely, (Lehigh University) presented an in-depth characterization of bimetallic Au-Pd nano-particle catalysts with aberration corrected, analytical electron microscopy. By combining x-ray energy dispersive spectroscopy (XEDS) spectrum imaging with multivariate statistical analysis (MSA) techniques, the structure of the Pd-Au nanoparticles was determined to be 5 nm in size with a core-shell structure and a 0.5 nm active bi-layer surface, which is responsible for high CO oxidation activity.

Eric Stach, (Purdue University and Brookhaven National Lab) described the use of environmental, transmission electron microscopy to characterize catalyst nano-particle structure and composition at atomic resolution. A case study of the growth of carbon nanotubes was presented to demonstrate the capabilities applicable to other catalysts.

Duane Johnson, (Ames Laboratory) demonstrated how by combining ab-initio simulations and advanced characterization methods (i.e., HR-TEM, environmental-TEM, and EXAFS), structure-property relations in catalytic nano-particles can be better understood. Theory predicts and experiment confirms that there is an amorphous-to-crystalline transition for supported nano-particles depending on cluster size, support, and adsorbates. Comparison of the structural properties of Pt NPs on C and gamma-Al2O3 in an inert and reactive atmosphere were compared to experimental results, emphasizing the need for complementary characterization methods.

Felix Studt, (SLAC National Accelerator Laboratory), described the use of scaling relations for adsorption energies and transition-states on transition-metal surfaces for catalytic conversion of syngas (a mixture of CO and H2) to methane and methanol using density functional theory (DFT) calculations. The combination of these scaling relations with a micro-kinetic modeling leads to volcano activity plots for methane and methanol formation as a function of carbon and oxygen binding energies. These two competing reactions determine the selectivity for the different transition metal catalysts.