QEXAFS Project at NSLS


In order to learn about in-situ structural changes of materials at sub-seconds time scale we have developed the techniques of Quick Extended X-ray Absorption Fine Structure (QEXAFS) and Quick X-ray Absorption Near Edge Structure (QXANES) spectroscopy at beamline X18B at the National Synchrotron Light Source (NSLS). The channel cut Si (111) monochromator oscillation is driven through a tangential arm at 5 Hz, using a cam, DC motor, pulley and belt system. The rubber belt between the motor and the cam damps the mechanical noise. EXAFS scan taken in 100 ms is comparable to standard data. The angle and the angular range of the monochromator can be changed to collect a full EXAFS or XANES spectrum in the energy range 4.7 - 40.0 KeV. The data is recorded in ascending and descending order of energy, on the fly, without any loss of beam time. The QEXAFS mechanical system is outside the vacuum system, and therefore changing the mode of operation from conventional to QEXAFS takes only a few minutes. This instrument allows the acquisition of time-resolved data in a variety of systems relevant to electrochemical, photochemical, catalytic, materials and environmental sciences.

The improvement of catalysts requires knowing the structure of the active catalysts. In situ EXAFS and X-ray measurements of Cu doped cerium oxide under water gas reaction conditions shows that the active species is Cu0 supported on cerium oxide. To understand the transformation to the active catalyst we used QEXAFS to look for short lived intermediates under reducing conditions. A series of Cu edge QEXAFS scans taken in fluorescence mode from an in situ flow cell containing Cu doped cerium oxide. Each scan is an average of many scans taken in a 15 second period. The beginning spectra show the oxidized copper in the cerium oxide and the final spectra show the reduced copper on the surface of the cerium oxide. Principle component analysis of similar data collected at 200ºC in 5%H2/He, showed that at 1000 second a reaction intermediate was present. There would not have been enough data to observe this intermediate with normal 15 minute EXAFS scans.

In the environment, chemical reactions at the mineral/water interface occur over a range of temporal scales, ranging from microseconds to years. Many important mineral surface processes (e.g., adsorption, oxidation-reduction, precipitation) are characterized by a rapid initial reaction on time-scales ofmilliseconds to minutes in which the significant portion of the reaction process may occur. Knowledge of these initial reaction rates is critical to determining chemical kinetic rate constants and reaction mechanisms, both of which are required to fully understand environmental chemical processes. For example the group at Department of Plant and Soil Sciences, Delaware Environmental Institute, University of Delaware has measured the kinetics of As (III) oxidation by manganese (IV) with a time-resolution of ~1 s. By using linear combinations to determine the As(III) and As(V) ratios at each time point, it’s possible to determine the oxidation rate during the first 30 s of reaction.