

Techniques & Instrumentation

Catalytic Carbon K Edge X-ray Absorption Spectroscopy: Multilayer Mirror Detection System

D.A. Fischer¹, S. Sambasivan¹, A. Kuperman², Y. Platonov³ and J.L. Wood³

¹National Institute of Standards and Technology, Gaithersburg, Maryland

²The Dow Chemical Company, Midland, Michigan

³Osmic Inc., Troy, Michigan

Fluorescence yield x-ray absorption spectroscopy of the low Z elements C, N, O, and F is a powerful tool for understanding the local structure and chemistry of diverse materials, even in the presence of reactive atmospheres^{1,2,3,4,5}. This technique uses tunable monochromatic synchrotron radiation in the soft x-ray region to excite inner shell electrons to unoccupied molecular orbitals, providing both elemental tunability and chemical state sensitivity in complex systems (also called Near Edge X-ray Absorption Fine Structure, NEXAFS)⁶. By monitoring carbon fluorescence yield during soft x-ray absorption, a photon-in photon-out spectroscopy has been developed for in-situ single crystal surface science experiments involving chemisorption, displacement, and dehydrogenation^{3,7,8,9,10}.

Fluorescence yield carbon K edge soft x-ray absorption measurements of mixed element ("real") samples are subject to background scattered x-rays and fluorescence from non-carbon atoms within the sample induced by the incident x-ray beam (first and higher orders). Additionally, because the fluorescence yield of carbon is very low in the soft x-ray range (~0.0012), detection efficiency is very important in order to achieve adequate counting statistics, especially in dilute samples. Simply by increasing the incident intensity of the tunable excitation, soft x-rays from the synchrotron beamline can, and often does, induce sample damage. Therefore, enhancing detection efficiency is crucial for overall success. Initially, we developed a high efficiency differentially pumped ultra-high vacuum compatible proportional counter optimized for carbon fluorescence detection¹¹. This detector has an overall detection efficiency of about 40% and collects about 5% of the available solid angle from the sample. The two entrance windows of the detector are 1 μm polypropylene film and provide an effective low pass

soft x-ray filter at the carbon K edge (284 eV) reducing (but not eliminating) the sensitivity to higher-order induced excitation of nitrogen and oxygen background fluorescence from mixed element samples. However, the window's low pass property produces a background carbon edge step in absorption due to the scattered soft x-rays from the sample. A spectral subtraction method can be employed (difference between, spectrum with adsorbate less spectrum without) to extract the carbon K edge spectrum of the carbonaceous adsorbate. In practice, this method can lack sensitivity and relies heavily on the reproducibility of the experimental system.

One approach to eliminating the proportional counter backgrounds in fluorescence yield carbon K edge absorption measurements is to employ a focusing multilayer mirror (MLM) collector in a wavelength dispersive detection system. The multilayer mirror should intercept a large fraction of the solid angle from the sample (operating at near normal incidence), provide adequate reflectivity and bandpass, and focus the collected carbon fluorescence signal to the detector. The bandpass of the multilayer must be centered about the carbon fluorescence line (277 eV) and narrow enough to exclude the scattered soft x-rays above the carbon edge (284 eV), a difference of about 7 eV. This suggests an acceptable bandpass of 1 to 2 eV. Furthermore, higher-order induced excitation of oxygen fluorescence backgrounds from the sample are completely eliminated because of the narrow energy bandpass of the multilayer mirror. Scattered x-rays from the sample are present as a single elastic peak whose peak position is tuned to the carbon K fluorescence line and whose width is representative of the bandpass of the multilayer mirror. The resulting measured carbon fluorescence NEXAFS spectrum would be direct

(no processing needed) and have a very high signal to background. In fact, the background could be nearly zero.

We have developed a MLM prototype, which has a spherical optic of 100 mm diameter and a radius of 70.6 mm, as shown in figure 1. Tunable soft x-rays are focused to a 1 mm spot on the sample through a 19 mm hole in the mirror. The sample is located on the optical axis of the mirror at a distance 27 mm towards the optic from the center of curvature (R in figure 1). The MLM prototype has an acceptance of nearly 60% of the available solid angle and features a graded d spacing of the multilayer coating. Scattered and fluorescent soft x-rays impinge upon the mirror surface with an angle α varying from 4.3° near the hole to 20.1° near the mirror edge. The graded d spacing permits the

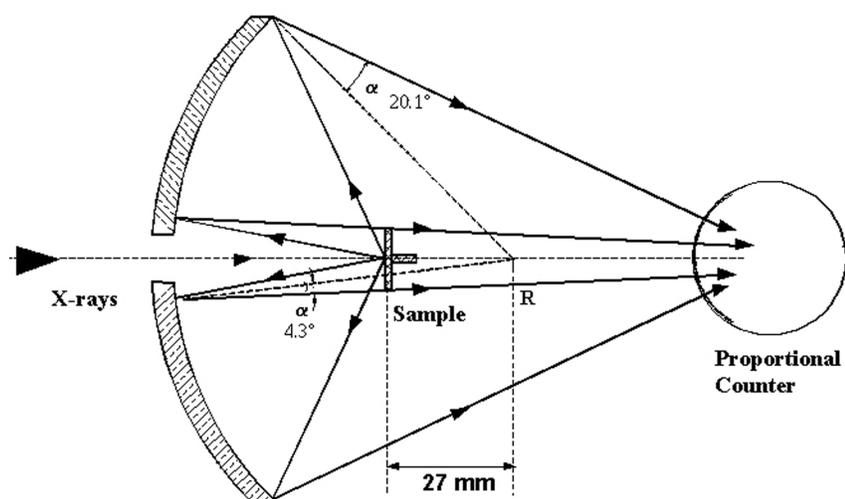


Figure 1. Optical layout of MLM prototype which utilizes a graded d spacing and consists of a spherical optic 100 mm in diameter with a radius of curvature of 70.6 mm.

Bragg condition for reflection of carbon K fluorescence (44.7 Å) to be satisfied at every point on the surface of the MLM. The multilayer coating consists of 120 alternate layer pairs of chromium and carbon, where each pair of layers has a thickness d which varies continuously from 22.4 Å near the entrance hole to about 24.5 Å at the mirror edge. The average near normal reflectivity of this MLM over its surface was measured to be nearly 5% with an average band pass of about 2%.

Fluorescence yield carbon K edge soft x-ray absorption experiments were performed on a variety of test samples utilizing the novel focusing wavelength dispersive detection system described above. Figure 2 shows the graded MLM detection system mounted in the Dow / NIST soft x-ray materials characterization

facility at the U7A beam line of the National Synchrotron Light Source¹². The beamline incident photon energy resolution and intensity were 0.1 eV and 5×10^{10} photon/sec respectively at a photon energy of 300 eV and a typical storage ring current of 500 mA. A sub-millimeter spot is produced at the sample position utilizing a refocusing mirror, which de-magnifies the exit slit image 5:1. Various powder catalyst samples (TSZ-20 and TSZ-390) were pressed into wafers 1 cm in diameter and 0.1 cm in thickness (figure 1) using a hydraulic press, aluminum sample holders, and a die. The catalyst samples could be calcined utilizing a resistive heater to 500 °C under vacuum for 30 minutes prior to high pressure gas dosing in a special cell.

TSZ-20 zeolite is relatively inactive for the absorption of benzene, while TSZ-390 is relatively active. A

study of the carbon K edge absorption spectra of this material facilitates a direct comparison of the amount of benzene absorbed in each zeolite and identifies chemical changes that may occur in the benzene molecule upon absorption. The use of near edge x-ray absorption fine structure (NEXAFS) for identifying the chemical and conformational changes in chemisorbed carbonaceous molecules has been well established as a surface science tool for UHV studies⁶. The graded MLM prototype was used to record I_0 -normalized carbon K edge NEXAFS spectra for benzene-dosed zeolites TSZ-20 and a TSZ-390, shown in the left panel of figure 3. Both spectra were recorded in 25 minutes and exhibit good signal to noise and a very small flat background, both key features of the

MLM wavelength dispersive detection method. A difference in the x-ray scattering power of each zeolite is revealed in the strength of the elastic peak. TSZ-390 scatters about six times more x-rays than TSZ-20. This may be accounted for by the difference in sample morphology. Although interesting, scattering power differences produce very different backgrounds for each zeolite when using energy dispersive detectors (proportional counters, SiLi, Ge) with polymer windows. The right panel of figure 3 illustrates proportional counter acquired NEXAFS spectra (I_0 normalized) for TSZ-390 and TSZ-20. The difference in the scattered x-ray background is so extreme that comparisons are difficult or impossible in the resonance part of the spectrum just below and above the carbon K edge. Although attenuated by the polymer window of the proportional counter,

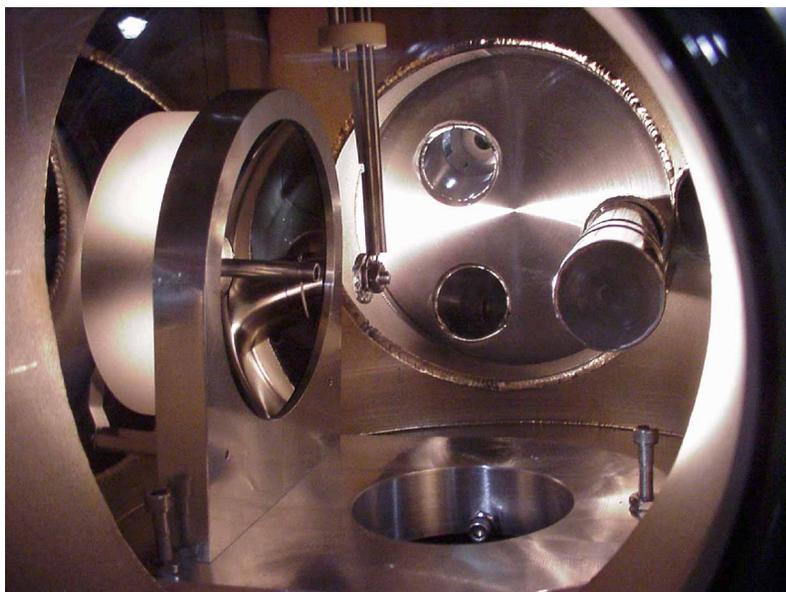


Figure 2. Graded MLM prototype, sample stud and proportional counter soft x-ray detector mounted in the Dow / NIST soft x-ray materials characterization facility.

background oxygen fluorescence from Silica (induced by second order) is present in the spectra, but are completely absent, as would be expected from the MLM spectra. Analysis of the MLM zeolite spectra is straightforward; by comparing the carbon edge jump (320-330 eV), TSZ-390 absorbs about twice as much benzene as TSZ-20. Another easy spectroscopic comparison is the weakening of the benzene π^* resonance (~285eV) for the more active TSZ-390 zeolite. Such observations are very difficult to extract from the proportional counter

spectra directly. They require further normalization by “clean” zeolite spectra in order to extract any useful information. Any variation in the scattering power between samples or measurements will make the analysis impossible. In comparison, the wavelength dispersive MLM system drastically reduces the scattered x-ray and oxygen fluorescence backgrounds from zeolite catalysts. We achieve nearly background-free carbon NEXAFS spectra.

The benzene-dosed TSZ-20 normalized spectrum shown in the left panel of figure 3 is nearly background free and displays the characteristic π^* and σ^* near edge resonance features of benzene⁶. The carbon K edge jump intensity above 320 eV is a direct measure of the carbon sensitivity of the detection system under test. The total number (N) of benzene molecules within the soft x-ray sampling volume of the TSZ-20 can be estimated from the zeolite density ($\rho=1.7 \text{ gm/cm}^3$), unit cell vol. ($V=2.8 \times 10^3 \text{ \AA}^3$), mass absorption coefficient of SiO_2 (at 277 eV, $\mu_m = 2.05 \times 10^4 \text{ cm}^2/\text{gm}$), 1 mm² x-ray beam size, and assuming 2 benzene molecules per unit cell. We estimate the soft x-ray absorption sampling depth is about one linear absorption length, since soft x-rays must both enter the sample and leave after inducing fluorescence from the dosed hydrocarbon. Hence we may estimate $N = (2 \text{ benzene molecules / unit cell})(1 \text{ mm}^2) (\rho \cdot \mu_m^{-1} / V) = 2 \times 10^{14} \text{ benzene molecules}$. The spectra shown in figure 3 were acquired in

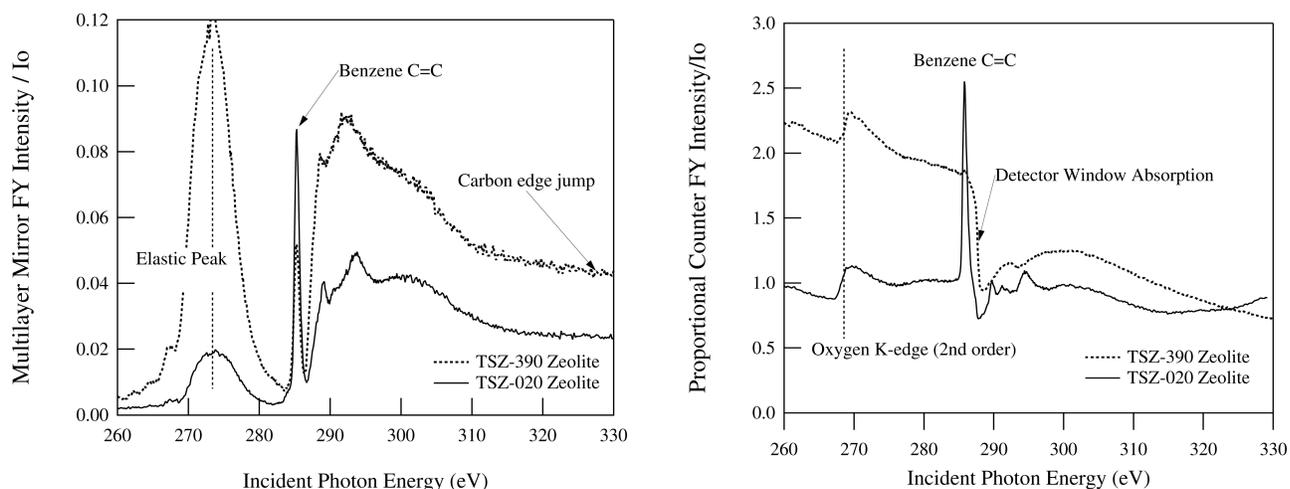


Figure 3. Fluorescence yield (FY) carbon K edge NEXAFS spectra for benzene-dosed zeolites TSZ-20 (solid) and a TSZ-390 (dashed) utilizing the graded MLM prototype (left panel) and the proportional counter (right panel).

about 25 minutes and provide a carbon sensitivity nearly 1000 times that of a typical laboratory infrared absorption spectrometer for bulk materials.

In the above example we have focused our discussion on benzene-dosed zeolites as an effective demonstration of the wavelength dispersive MLM detection method for carbon NEXAFS of adsorbates in "real" catalysts. The novel graded d spacing spherical multilayer mirror effectively discriminates against the background fluorescence and scattered light signals originating at the sample during a carbon K edge soft x-ray absorption experiment. Signal to background in excess of 100 is possible for these very dilute carbon samples. This enables a whole new class of in-situ photon-in photon-out soft x-ray absorption measurements of carbon chemistry in catalysts to be made, even in a reactive chemical environment.

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