

SOFT X-RAY MICROANALYSIS AND MICROSCOPY: A UNIQUE PROBE OF THE ORGANIC CHEMISTRY OF HETEROGENEOUS SOLIDS

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INTRODUCTION

Many problems in fuel chemistry relate directly to the heterogeneous nature of materials such as coals and cokes. Recent advances in X-ray micro-focusing techniques coupled with synchrotron light sources have resulted in a scanning transmission X-ray microscope (STXM) located at the National Synchrotron Light Source at Brookhaven National Laboratory. Carbon's 1s near absorption edge region is rich with fine structure associated with photo-excited transitions to various low lying, unoccupied molecular orbitals. Preliminary carbon near edge absorption micro-spectroscopy (C-NEXAFS) and microscopy on complex organic solids such as coal has been performed using the scanning transmission microscope on the X1A beamline at NSLS. In many cases, spectacular chemical heterogeneity was observed down to the submicron level using the intensity of the prominent absorption fine structure on carbon's absorption edge for contrast.¹⁻³ STXM/C-NEXAFS has also been applied to biological specimen^{4,6} and heterogeneous polymers.⁷

In the present paper, the STXM and C-NEXAFS microanalysis will be used to analyze the microchemistry of cokes and highly carbonaceous materials. The issue of molecular orientation will be addressed by using the intrinsic polarization of the X-ray beam at X1A.

EXPERIMENTAL

Sample: Two samples of carbonized materials were selected for STXM analysis. The first is a naturally coked coal from western Pennsylvania. The other is a laboratory derived sample of carbonized (1000 °C) pyrene.

Sample Preparation: A crucial aspect of STXM and C-NEXAFS is the necessity of preparing extremely thin specimens. The relatively high molar absorption coefficient of carbon at these wavelengths, $\mu = 1 \times 10^4 \text{ cm}^2/\text{g}$, and the high bulk density of carbon in coal requires that sample thicknesses be less than 800 nm. There are a variety of methods available to obtain specimens of this thicknesses, however, ultra-microtoming was found to yield the most favorable results. Thicknesses in the range of 100 to 200 nm were readily produced. Artifacts associated with the technique, for example, scoring marks paralleling the cutting direction of the diamond knife and chatter marks perpendicular to the cutting direction, were readily identifiable.

Scanning Transmission X-ray Microscopy: The microscope, a scanning transmission X-ray microscope (STXM), is located at the terminus of the X1A beam line at the National Synchrotron Light Source (NSLS). The elements of the STXM relevant to this paper are described as follows. At the head of the instrument, soft X-rays are generated using an undulator which resides on the 2.5 GeV electron storage ring. Energy selectivity (0.3 eV resolution) is controlled with a tunable spherical monochromator. X-ray micro-focusing is managed with near field optics, i.e., a Fresnel phase zone plate and an order sorting aperture.⁵ Currently, the STXM has a resolution limit of 55 nm, however, in the future, the resolution down to 10 nm may be possible.⁹ X-ray transmission is detected using a gas-filled proportional counter. Details on the instrument's specifications have been reported elsewhere.⁸

C-NEXAFS: The physics of NEXAFS is similar to valence shell electronic state spectroscopy, with one important distinction, the initial state of the photo-ionized electron is in an atomic, not molecular, orbital. Herein lies the major advantage of inner shell over valence shell spectroscopy, the photo-ionized core hole is highly localized, thus, the initial orbital is more readily identified and, in principle, specific information on functional groups may be obtained. Absorption of X-rays occurs through the interaction of an X-ray photon with an electron in an atomic core resulting in the promotion of the inner shell electron to a relatively low-lying unoccupied molecular orbital (LUMO). Molecules containing π orbitals generally have their lowest energy inner shell transition to the first unoccupied, or antibonding, π^* orbital.

In alkanes, a relatively intense absorption band is observed which correspond to the transition from carbon's 1s to a 3p Rydberg-like orbital which overlaps with a C-H σ^* transition. These transitions are referred to as 1s - 3p/ σ^* transitions.¹⁰

The intensity of a given electronic transition is a function of its dipole moment. Given some preferred orientation in a molecular assemblage, linear dichroic effects are expected and can be measured. For aromatic systems, the 1s - π^* transitions are naturally polarized in the direction of the 2p_z orbitals, i.e., out of the ring. The 1s - σ^* transitions are polarized parallel with the 2p_{x,y} plane, i.e., opposite that of the 1s - π^* transitions. Degrees of preferred orientation can be calculated from the change in intensity with orientation via the relationship,

$$I_{\parallel}/I_{90} = \cot^2\alpha \quad (1)$$

where α is the angular degree of preferred orientation, i.e., $\alpha = 45$ is completely random, while $\alpha = 0$ is perfectly aligned.

RESULTS AND DISCUSSION

Figure 1 presents a reasonably high resolution image of the naturally coked coal acquired with the monochromator tuned to the 1s - π^* transition of aromatic carbon. Clearly there is considerable microstructure which may be related to either chemistry or molecular orientation. Figure 2 presents the laboratory carbonized material. In this sample, there is also considerable microheterogeneity, with a domain scale somewhat finer than the coke (Figure 1).

The C-NEXAFS spectra of light and dark regions in Figure 1 are presented in Figure 3. At the low energy end, enormous differences in intensity of the 1s - π^* transitions are clearly evident. At the high energy end of the near edge region, the 1s - σ^* transitions also exhibit significant differences in intensity. The fact that the two types of transition exhibit a contrast reversal indicates that the differences in absorption are related to molecular orientation. Using Equation 1, we calculate an preferred orientation of 20 degrees off of completely random.

The C-NEXAFS spectra of the laboratory coke is presented in Figure 4. In this case, there are also significant differences in absorption; however, there is no contrast reversal between the 1s - π^* and 1s - σ^* transitions. This indicates that the contrast evident in Figure 2 is related to variation in the chemistry and density, but not to variations in molecular orientation.

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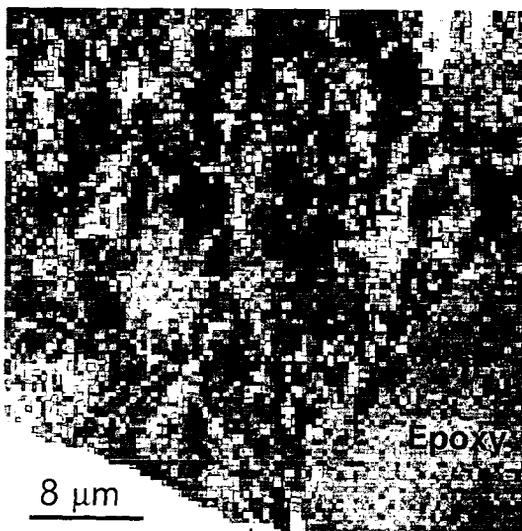
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$E = 285.5 \text{ eV}$

$8 \mu\text{m}$

Figure 1. X-ray image of the naturally coked coal. Monochromator tuned to the aromatic $1s\text{-}\pi^*$ electronic transition.



$8 \mu\text{m}$

$E = 285.5 \text{ eV}$

Figure 2. X-ray image of the carbonized pyrene sample. Monochromator tuned to the aromatic $1s\text{-}\pi^*$ electronic transition.

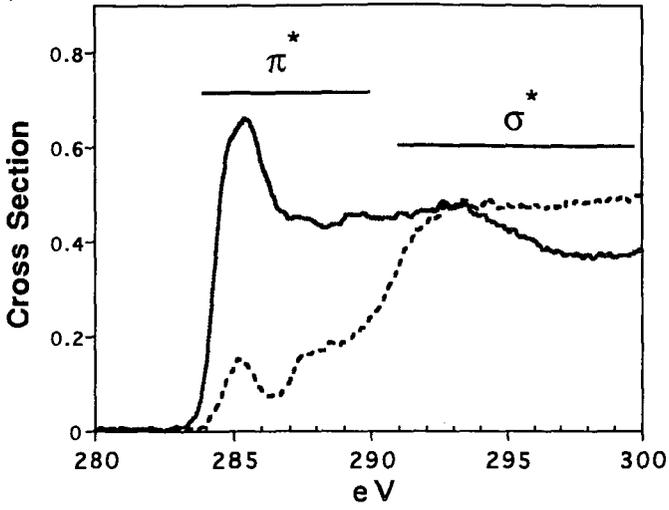


Figure 3. The C-NEXAFS spectra of light and dark regions in Figure 1.

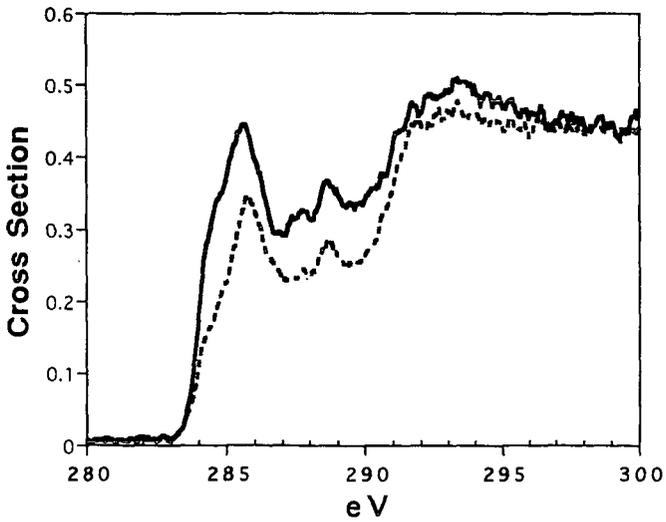


Figure 4. The C-NEXAFS spectra of the laboratory coke.