

***In Situ* EELS Analysis of Gas Mixtures in the Environmental TEM**

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Environmental TEM is a powerful tool for understanding gas-solid interactions in nanomaterials. This approach allows us to follow structural and composition changes in materials as a result of changes in the surrounding gas pressure and composition. In fields such as heterogeneous catalysis, it is often desirable to vary the gas composition during an experiment in order to understand the evolution of the material under varying reactor conditions. While such gas analysis may be performed with residual gas analyzers, we are investigating the possibility of performing gas analysis in the ETEM using *in situ* electron energy-loss spectroscopy (EELS). This approach allows real time analysis of the volume of gas in direct contact with the TEM sample and can be performed rapidly with typical acquisition times being a few second (or less for low-loss spectroscopy).

In situ EELS analysis of various gases was performed on a FEI Tecnai F20 field emission environmental transmission electron microscope (ETEM) operating at 200kV. The microscope was equipped with a Gatan Imaging Filter and spectra were acquired from gas samples in the cell at pressures of a few Torr. Inner-shell spectra were recorded with the microscope operating in diffraction mode with a convergence semi-angle of about 1 mrad, a collection semi-angle of 8 mrad and a dispersion of 0.5 eV. Low-loss spectra were recorded in EFTEM image mode with a convergence semi-angle of about 1 mrad, a collection semi-angle of 50 mrad and a dispersion of 0.05 eV and an energy resolution of 1 eV. Spectra were acquired from gases and gas mixtures of interest to our research on energy related catalysts and included H₂, H₂O, O₂, CO, CO₂, CH₄.

Figure 1 shows inner-shell spectra from CO and CO₂ demonstrating the presence of large π^* peaks at the front of the carbon K-edges in agreement with previously published data from Hitchcock [1,2]. These spectra were used as calibration standards to determine the O/C concentration ratio using standard EELS analysis procedure. The background was removed from the C and O edges and the signal was integrated over 100 eV. The signal ratio was converted to elemental ratios using hydrogenic cross sections in Gatan DigitalMicrograph software. The resulting average O/C ratios were 0.77 ± 0.02 and 1.52 ± 0.03 for CO and CO₂ respectively showing that the analysis gives values that are systematically low by about 25%. Excluding the white lines from the C and O edges only increases the ratios by a few percent. The reason for the discrepancy is not clear at present; the background removal is rather straightforward, plural scattering can be excluded because the scattering parameters (t/λ) ~ 0.1 and the K-shell ionization cross sections are suppose to be accurate to within 5% for these two elements. However, the signal ratios scale correctly between CO and CO₂ (i.e. $1.52/0.77 \sim 2$ as it should be) so we use the spectra to derive a k-factor for quantifying mixtures of gasses involving carbon and oxygen containing molecules. We tested this on a mixture of methane and oxygen (3 Torr of 2CH₄ + O₂) and got a value of C/O of 1.1 ± 0.04 which is within 5% percent of the nominal value.

The inner-shell edge approach does not work for gas mixtures containing H₂ because the hydrogen “edge” is located in the low-loss region of the spectrum and may overlap severely with the valence-

loss spectra from other gases in a mixture. One approach to quantify gas mixtures containing H_2 is to fit the low-loss spectrum from the gas mixture to a linear combination of valence loss spectra from each of the component gases. Figure 3 shows an example of such an analysis for a gas sample consisting of 2.8 Torr of $CO + 2H_2$. In this case, the spectra are fitted over the range 7 – 20 eV and the correction for the zero-loss tails is ignored. The H_2/C ratio determined from the fitting procedure is 1.5 ± 0.1 compared to the nominal concentration from partial pressures of 2. We will discuss the source of the discrepancy and compare different approaches for quantifying the low-loss spectra.

References:

[1] Hitchcock, A. P. and Brion, C. E. J. Elec. Spec. Rel. Phenom. 18 (1980) 1.

[2] Hitchcock, A. P. J. Elec. Spec. Rel. Phenom. (2000) **112** 9.

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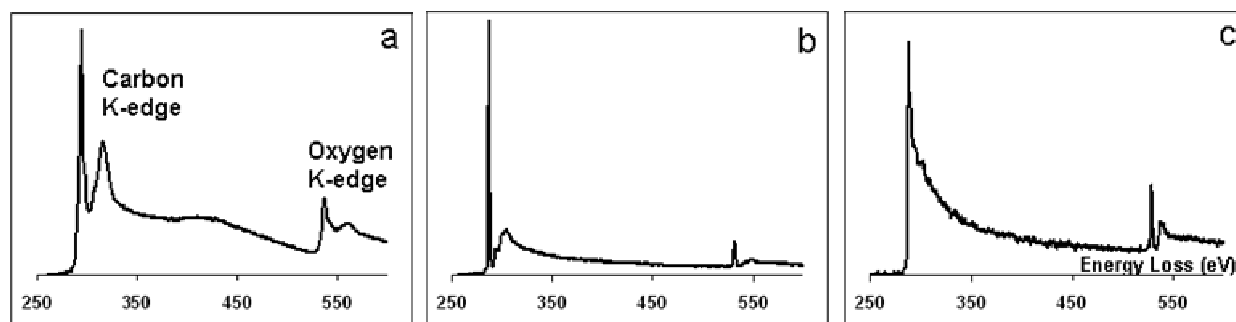


FIG 1: Background subtracted energy-loss spectra from a) 2.5 Torr CO_2 and b) 2.5 Torr of CO showing carbon and oxygen K-edges. c) Energy loss spectrum from 50%/50% mixture of CH_4 and O_2 .

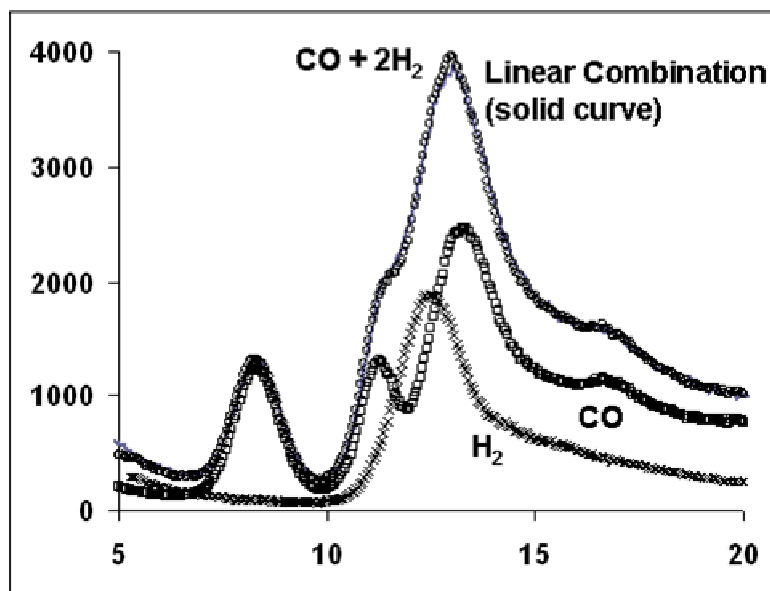


FIG 2: Low-loss spectra from CO , H_2 and $CO + 2H_2$ mixture all at about 2 Torr pressure. The solid curve is the linear combination of the individual spectra from CO and H_2 .