

## ***Operando* TEM - Detection of Gas Phase Catalysis in an Environmental TEM with EELS**

S. Chenna,\* and P.A. Crozier

\* School of Mechanical, Aerospace, Chemical and Materials Engineering, Arizona State University, Tempe, AZ, 85287-6106

*In-situ* environmental transmission electron microscopy (ETEM) is a powerful tool for obtaining atomic scale structural and chemical information under reacting gas conditions. We have shown the significance of *in-situ* ETEM studies in developing the structure-activity relationship in supported metal catalysts for heterogeneous catalysis [1]. However in this case, the catalytic measurements were performed in an *ex-situ* reactor. Ideally we would like to perform an *operando* experiment where we observe the nanostructural changes taking place in the catalyst while simultaneously measuring the catalyst activity and selectivity. We have shown that the reactant gas composition around the TEM sample can be monitored by using electron energy-loss spectroscopy (EELS) [2]. Here we demonstrate that EELS can also detect product gas formation over a catalyst thus opening up the possibility of performing true *operando* microscopy. As a preliminary test we performed CO oxidation on a Pt mesh inside the ETEM, we will extend this approach for studying catalytic reactions on supported metal catalyst.

*In-situ* environmental catalysis was performed in an FEI Tecnai F20 field emission environmental transmission electron microscope operating at 200kV. This microscope is equipped with a Gatan imaging filter and with a differentially pumped environmental cell. A 3 mm disk of Pt mesh was loaded into a Gatan inconel heating holder. Electron energy loss spectra were recorded with the microscope in diffraction mode with an energy dispersion of 0.1 eV. Spectra were acquired from pure gases and gas mixtures for calibration purpose. For the CO oxidation reaction, CO and O<sub>2</sub> were mixed in a 2:1 ratio and the catalytic reaction was performed on Pt mesh at 1 Torr gas pressure inside the environmental cell. Similar experiments were performed on the same Pt mesh on an *ex situ* microreactor.

Figure 1a and 1b, shows the background subtracted inner-shell spectra from pure CO and CO<sub>2</sub> respectively showing the presence of large  $\pi^*$  peaks in front of the carbon K-edges [3,4]. The  $\pi^*$  peak positions are calibrated with the C K-edge from an amorphous carbon film (284 eV). The C  $\pi^*$  peaks are at 287.0 eV for CO and 290.2 eV for CO<sub>2</sub>. Figure 2a, shows the background subtracted energy-loss spectra of C  $\pi^*$  peaks obtained while heating the Pt mesh inside the environmental cell. No catalytic conversion of CO was observed until 350°C. A small peak started to appear at 290.2 eV at 400°C corresponding to CO<sub>2</sub>  $\pi^*$  peak, indicating the formation of CO<sub>2</sub> by the CO oxidation reaction. This observation confirms that the catalysis has been detected inside the TEM. The  $\pi^*$  peak at 290.2 eV gradually increases with increasing temperature, which is expected as the increase in temperature increases the catalytic activity. In order to remove the affect of the inconel furnace on catalysis, similar experiments were performed on the holder without the presence of Pt mesh. No CO<sub>2</sub> formation was observed even at 500 °C on the inconel furnace indicating that the product gas measured is due to the catalytic activity of Pt for CO oxidation to CO<sub>2</sub>.

Linear curve fitting procedures were used to quantify the gas composition [2]. Figure 1c, shows the normalized reference spectrum from a mixture of CO and CO<sub>2</sub> in 1:1 ratio (solid curve). Dotted curve shows the simulated composite spectra from the linear combination of CO and CO<sub>2</sub> individual spectra. The spectra from the gas mixture and the composite spectra are almost indistinguishable indicating that a good fit has been achieved. The ratio of linear coefficients gave a CO<sub>2</sub> to CO ratio of 0.95 which is within 5% of the expected value of 1. Figure 2b, shows the corresponding plot of CO<sub>2</sub> to CO ratio during catalysis at different temperatures, obtained from the curve fitting procedures described above. We will present the similar experiments on supported metal catalysts along with the nanoscale structural and chemical information of the catalyst during the catalytic reaction.

## References

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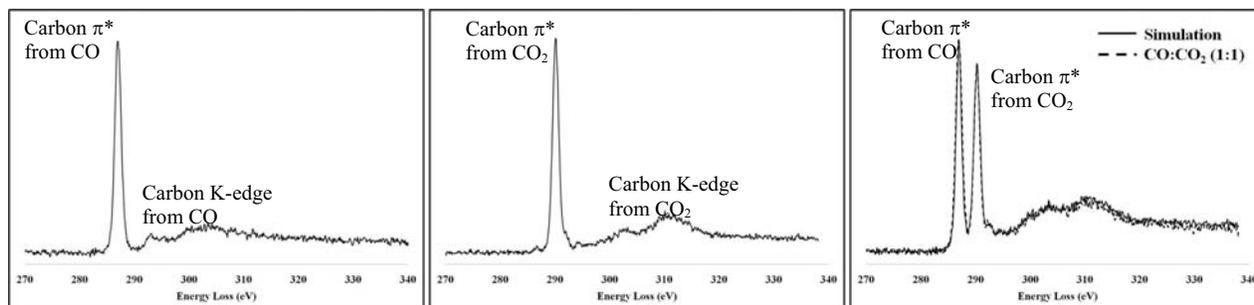


FIG. 1. Background subtracted energy-loss spectra from a) 1 Torr of CO and b) 1 Torr of CO<sub>2</sub> and c) normalized EELS spectra from a mixture of CO and CO<sub>2</sub> in 1:1 ratio at 1 Torr pressure (solid curve). The dotted curve is the linear combination of the individual spectra from both CO and CO<sub>2</sub>.

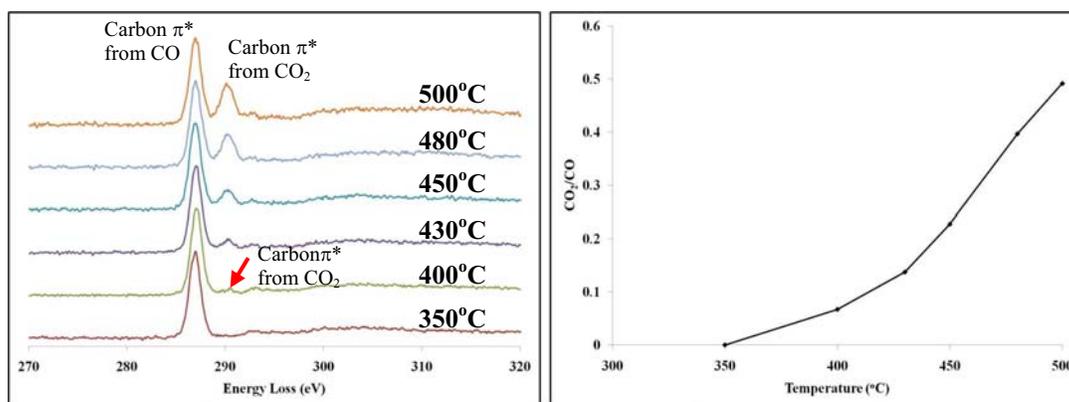


FIG. 2. a) Background subtracted energy-loss spectra acquired at different temperatures during CO oxidation on Pt mesh, b) plot showing the ratio of CO<sub>2</sub> to CO with increase in temperature.