In situ and operando Transmission Electron Microscopy of thermal and photocatalysts

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Environmental transmission electron microscopy (ETEM) is an important tool for in situ catalyst characterization because reactive gases may have a strong influence on the structure and composition of materials. The ability to study materials at elevated temperatures under reactive gases makes it possible to investigate the atomic scale changes taking place during materials synthesis and in materials under reactor conditions. For example, by correlating catalytic reactor data with suitably designed ETEM observations, it is possible to map out structure-property relations in catalysts [1]. In ETEM, the gas is mostly confined to the region around the TEM sample and not allowed access to the rest of the column or the electron gun. Heating can be performed up to 1000°C or higher although the thermal conductivity and gas pressure can make precise temperature determination more challenging for some configurations. We are currently extending the capability of ETEM by developing operando techniques and introducing variable wavelength light illumination.

In-situ transmission electron microscopy is a powerful tool for atomic level investigations of gas-induced structural and compositional changes taking place in high surface area materials. However, a significant problem with this approach has been the lack of any direct measurement of gas-phase products which may be generated by the catalyst during the structural observation. This limits the ability to explore the links between catalyst structure and activity. To overcome this deficiency we are developing an operando TEM technique that combines the nanostructural characterization of the catalyst during the reaction with the simultaneous measurement of the catalyst performance. We employ electron energy-loss spectroscopy (EELS) of gases [2] to detect catalytic products directly inside the microscope reaction cell while simultaneously determining the nanoscale structure of the catalyst.

One of the challenges in developing an “operando” TEM technique is associated with the TEM sample preparation. The amount of catalyst present in the TEM is very small (less than micrograms) and in most cases, product gases generated in the ETEM cannot be detected by EELS. A sample preparation technique was developed to get high catalytic loadings onto a TEM sample to make products detectable. CO oxidation on an Ru catalyst was investigated with operando TEM. A 2.5 wt% Ru/SiO2 catalyst was prepared by using an incipient wetness method, by impregnating SiO2 with RuCl3.xH2O solution. In-situ catalytic activity measurements were performed with EELS. Figure 1a shows the background subtracted energy-loss spectra of C π* peaks obtained while heating the Ru/SiO2 catalyst inside the environmental cell in the presence of CO and O2 (2:1) mixture at 1 Torr pressure. A peak started to appear at 289.7 eV at 150°C corresponding to C π* peak from CO2. This observation confirms that catalysis has been detected inside the TEM using EELS. As the temperature increases, the C π* peak from CO2 also increases. Figure 1b shows the corresponding CO conversion to CO2 on Ru/SiO2 during catalysis at different temperatures and corresponds closely to ex-situ reactor data. Catalytic conversions of about 1% can be detected with this EELS approach. A detailed discussion on the challenges associated with developing operando TEM will be presented.

Motivated by a desire to improve solar energy conversions, we have also incorporating a variable wavelength high-brightness light source into our FEI Tecnai F20 ETEM. There are many unanswered fundamental questions about the structure and property relationships in photocatalytic processes. It is critical to investigate the surface and bulk structure changes at the atomic scale that take place in the presence of reactive gases during photon irradiation. In our design, we employ an Energetiq laser driven light source and couple light into the reaction cell of the microscope using a quartz fiber. The fiber is kept some distance from the TEM sample holder so that heating in reactive
gas environments can be performed without damage to the fiber. We investigated the amorphization taking place on the surface of the anatase during exposure to light, heat and water vapour (see Figure 2). The number of (101) lattice spacings across the crystal decreased by about 4 showing that the ordered surface became disordered during in situ exposure.

References

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Figure 1. a) Background subtracted energy-loss spectra acquired at different temperatures during CO oxidation on Ru/SiO₂ catalyst in an environmental TEM. b) Plot showing the CO conversion with increase in temperature on Ru/SiO₂ catalyst measured from in-situ energy-loss spectroscopy. c) ETEM image recorded from Ru catalyst during acquisition of EELS data from product gas.

Figure 2. TEM images of anatase particles at 150°C a) start of 1 Torr water, no light b) 15hrs water, no light c) 16hrs water gas flowing, 0.5 hrs light d) 83hrs water, 68hrs light.