doi:10.1017/S1431927614009556
Microsc. Microanal. 20 (Suppl 3), 2014

Operando TEM of Ru/RuO_2 Catalyst Performing CO Oxidation

B.K. Miller and P.A. Crozier

School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ 85287-6106

CO oxidation is a model reaction that is ideally suited for performing *operando* TEM. Several catalysts for oxidizing CO to CO_2 have been extensively studied, including ruthenium and its oxide. Despite these efforts, there has still been considerable debate regarding the most active structure for this system [1,2,3]. In fact, many of the fundamental studies performed on this ruthenium catalyst were surface science studies focused on individual crystal facets. An industrial catalyst will be composed of supported nanoparticles, and it is important to study the structure of these particles at the atomic scale, in a gas environment identical to that used in real-world applications, like hydrogen fuel cells. Environmental TEM (ETEM) can be used to study nanoparticles in a gaseous environment. *Operando* TEM goes beyond standard *in-situ* techniques, because the activity of the catalyst is monitored concurrently with the structure [4]. This allows unambiguous determination of active structures, since the activity of the exact structure observed under some experimental condition is known.

We have used electron energy-loss spectroscopy as well as mass spectrometry to determine the gas composition inside an FEI Tecnai F20 ETEM, and thus the activity of the catalyst, as seen in figures 1 and 3. Monitoring the catalytic activity in this way is made possible through the use of a novel sample preparation technique [5], which increases the amount of catalyst present in the microscope by at least an order of magnitude over a traditional powder TEM sample. In a typical *operando* experiment performed here, the catalyst is either fully oxidized to RuO_2 or fully reduced to Ru metal prior to exposing the catalyst to the CO/O_2 gas mixture. In an atmosphere of 1-2 Torr of a stoichiometric ratio of CO and O_2, the catalyst is heated up to a maximum temperature of 450^{o}C, and then cooled back to room temperature. High resolution images as well as electron diffraction patterns taken at several temperatures, allow direct observation of the morphology and crystal structure of the catalyst before and after it becomes active. As seen in figures 1 and 3, the (pre-oxidized) catalyst's activity shows a hysteresis behavior, so it should be possible to observe the catalyst at 250^{o}C in both a more active and less active state. Figure 1 also shows an image of the catalyst at 3 different conditions; at low temperature, we observed a core-shell structure in some of the catalyst particles (which were oxidized prior to exposure to CO/O_2), while at high temperature, the catalyst is reduced to Ru metal.

Operando experiments will also be performed on our new FEI Titan aberration corrected ETEM. This will provide much higher resolution images, as seen in Figure 2, and allow the active surface structures present at different experimental conditions to be determined.

References:
[1] D.W. Goodman, *et al.* Surface Science **601,** (2007a), p.L124-L126.
[2] D.W. Goodman, *et al.* Surface Science **601,** (2007b), p.5663-5665.
[3] H. Over, *et al.* Surface Science **601,** (2007), p.5659-5662.
[4] B.K. Miller, P.A. Crozier Microscopy and Microanalysis (submitted)
[5] Miller and Crozier, ibid (these proceedings)

[6] The support from US Department of Energy (DE-SC0004954) and the use of ETEM at John M. Cowley Center for HR Microscopy at Arizona State University is gratefully acknowledged.

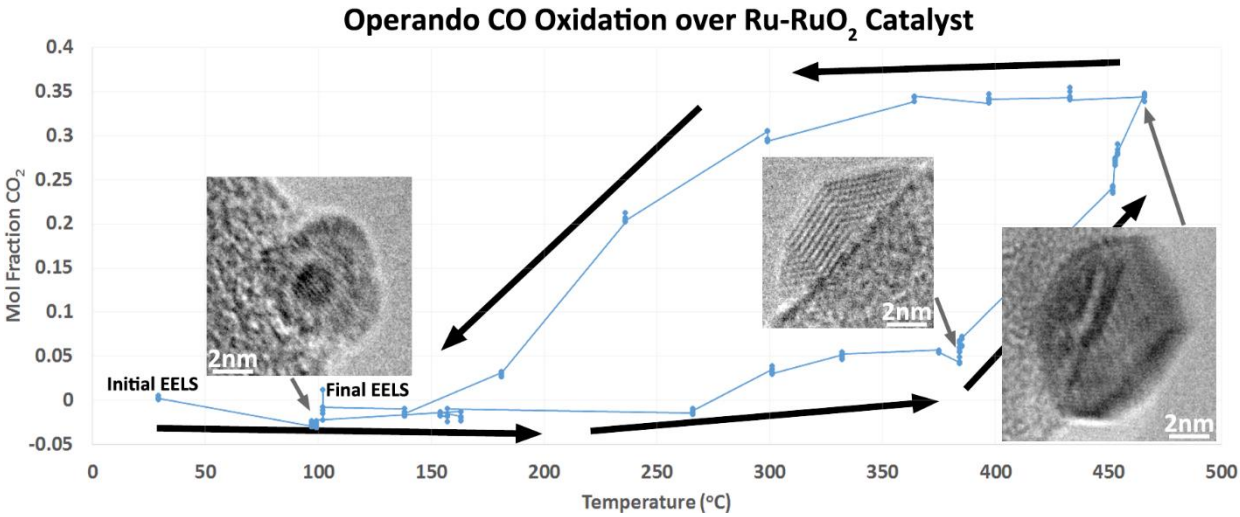

Figure 1. Plot showing results from an *operando* experiment in which the Ru-RuO_2 catalyst was heated from room temperature to 460°C, and then cooled back to 100°C. Energy-loss spectra were acquired at various temperatures during the ramp up and down, and the analysis of these yields the gas composition at those temperatures. A clear hysteresis is observed, indicating that the catalyst is activated as the temperature rises above 350°C in the CO/O_2 gas. Images were acquired as the temperature was ramped up, and several structures were observed including, from left to right, Ru core-RuO_2 shell structures, highly crystalline RuO_2, and fully reduced Ru.

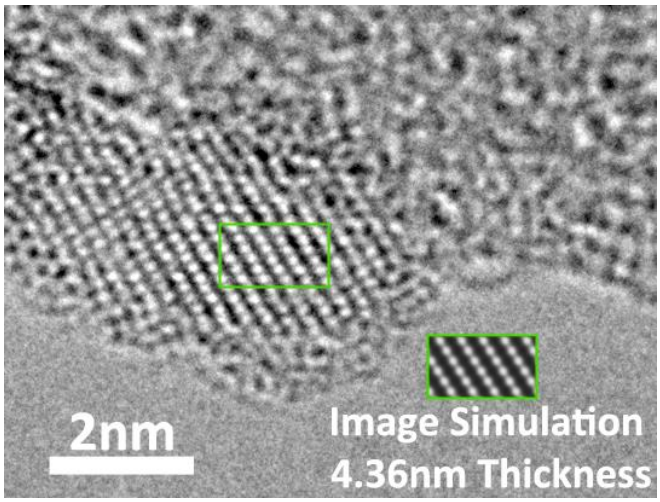

Figure 2. Aberration corrected image of RuO_2 catalyst particle supported on amorphous SiO_2 taken in an FEI Titan 80-300 at 300kV, with an inset showing a multislice simulation performed using JEMS.

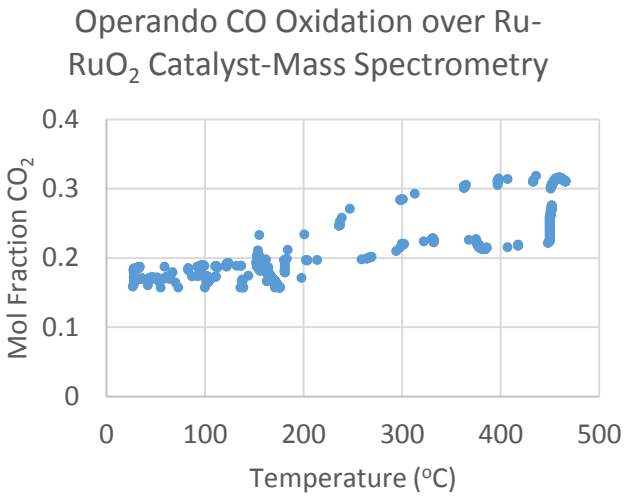

Figure 3. Mass spectrometry data from the experiment shown in Figure 1, showing a similar hysteresis behaviour.

https://doi.org/10.1017/S1431927614009556 Published online by Cambridge University Press