Application Note

Aduro™

Visualizing Temperature Evolution of Metal Nanoparticle Catalysts in High Resolution

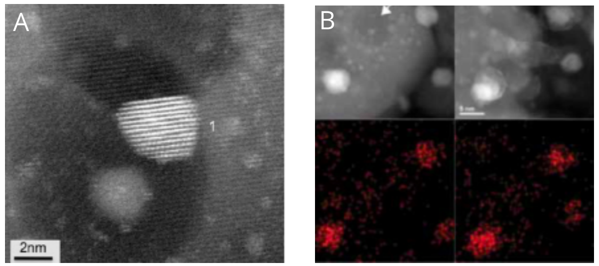
Introduction

Nanoscale metal catalysts, including gold and platinum, show promise in many high impact applications such as fuel cells, water gas shift reactions, catalytic converters, oxidation reactions and a host of other chemical reactions. To optimize the performance of nanoparticle catalyst systems for commercial applications, the nanoparticle structure and nanoparticle-substrate interface must be fully understood at the atomic level.

Researchers must effectively correlate the structure and interfaces to the rate and efficiency of the reaction. To visualize these important atomic scale features, transmission electron microscopy (TEM) is often used because it can routinely resolve features as small as individual atoms. Traditionally TEM imaging and analysis is performed in vacuum at room temperature, however, to fully understand catalysis behavior, the catalyst material must be imaged in real world operating environments. Many catalysts require elevated temperatures to operate efficiently.

In situ TEM provides highly beneficial information about the evolution of nanoparticle catalysis at relevant temperatures. Traditionally, at the elevated temperatures where the reactions occur, image resolution is compromised. The Aduro heating and electrical biasing system does not compromise resolution, and maintains the full resolution capability of the TEM at temperatures up to 1200 °C.

Atomic scale features in materials can be resolved *in situ* at high temperatures, including crystal facet evolution, atomic rearrangement and nanoparticle-substrate interactions. Aduro provides a platform to image and analyze catalyst materials as they evolve in a highly controlled temperature environment, providing quantitative and actionable data sets.



Experiment

In the first experiment very small gold nanoparticles (<1 nm) on larger iron oxide nanoparticles (>10 nm) were imaged. This material shows promise as a catalyst in water-gas shift (WGS) and CO oxidation reactions. The evolution of individual gold atoms and substrate were imaged as a function of temperature, up to 700 °C. At temperatures of 250 °C and above, individual gold atoms were seen to aggregate into larger clusters and nanoparticles. In the second experiment, the evolution of crystal facets on platinum nanoparticles (~5 nm) on larger alumina nanoparticles (>10 nm) at 1000 °C were studied.

Like many nanomaterials, catalyst samples are often powders, either dry or suspended in liquid. Liquid suspensions may be applied by pipette, and dried to the Aduro Thermal E-chips™. Dry powders may be ground and sprinkled on a device, or the device dipped in a small vial of the material. With either technique, good dispersion is easy to obtain. For the experiments described here, the samples were applied to an Aduro Thermal E-chip using both the liquid and the dry dispersion methods.

Experiments were performed on a JEOL 2200FS TEM at 200 kV, which was operated in STEM mode. The TEM had a CEOS aberration corrector on the probe forming optics.

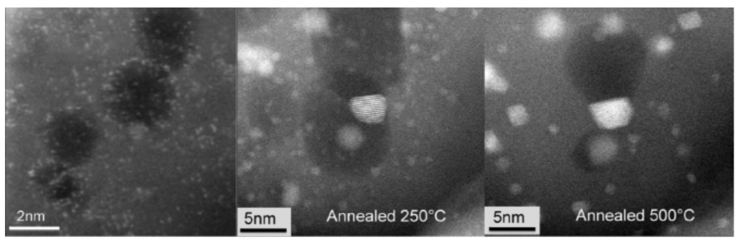
Discussion

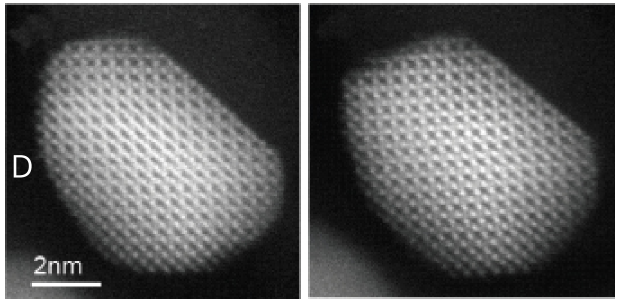
In the first experiment small gold clusters and individual atoms were initially on the surface and within the iron oxide nanoparticles. In this form the WGS reaction was active, and the CO oxidation reaction was not. As the temperature increased from room temperature gold atoms were drawn to the surface and began coalescing into clusters and particles. High-resolution EDS shows the gold nanoparticles moving and coalescing into larger particles. Upon further increase to 250 and 500 °C the individual gold atoms evolved to form larger nanoclusters and nanoparticles. As the temperature increased from 500 to 700 °C the particles grew and coalesced further. At 700 °C the gold nanoparticles became faceted and topotactically aligned with the underlying iron oxide substrate. As the gold grew into nanoparticles the CO oxidation reaction became active, and the WGS reaction was not.

The second experiment details the evolution of a platinum nanoparticle surface. It is important to understand the correlation

Reference: L.F. Allard et al., J. Elec. Micro. 58, pp. 199-212, 2009. Image courtesy Dr. Larry Allard, Oak Ridge National Labs. The two HAADF images taken as 20 second STEM scans at 1000 °C.

between the evolution of faceting in nanoparticles and the efficiency of a chemical reaction. The two images in Figure D were taken approximately 1 minute apart to demonstrate that the nanoscale Pt particle undergoes significant structural changes at 1000 °C.





Applications

Nanoparticles play a critical role in catalysis, but much work is still needed to understand and characterize these materials before they can become commercially viable. The TEM, especially when equipped with an aberration corrector, is a powerful tool that can resolve the atomic scale features important in catalytic activity. Combined with high stability and precise temperature control, Aduro adds critical functionality to the TEM, allowing users to visualize their materials in real world environments, without compromising data quality.

Contact us to discuss the full range of capabilities of Aduro with the Thermal E-chip sample supports. We can be reached at (919) 377-0800 or contact@protochips.com.

Protochips