Application Note

Atmosphere™

In situ environmental study of perovskite-noble metal catalysts for automotive exhaust control using a Cs corrected TEM

Introduction

Catalytic converters are an essential component of an automobile exhaust system. They control highly polluting gases, such as NOx, CO and hydrocarbons, emitted from the engine changing them into more benign gases including N_2, H_2O and CO_2. Noble metals, such as Pt, Pd and Rh, have been successfully used in catalytic convertors for decades. Although excellent catalysts, they suffer a serious drawback in terms of cost, and methods to reduce material required for sufficient activity has been a research focus for many years.

The catalytic activity depends on the catalyst material's surface area where chemical reactions occur. Significant effort by scientists and engineers worldwide have attempted to create catalyst materials with an increased surface area to volume ratio, which decreases the amount of material required and cost. Nanoparticles in particular, owing to their high surface to volume ratio, exhibit enhanced catalyst properties over bulk material, and are much more cost effective. However, critical hurdles must be overcome before nanoparticle catalysts see widespread industrial and commercial use.

Most catalyst materials, especially those in a catalytic converter, operate at temperatures of around 500 °C and above and must operate efficiently for years. At these temperatures, nanoparticles may become mobile and coalesce forming larger nanoparticles, which reduces surface area significantly degrading performance. The support material also plays an important role in catalytic activity, as metal nanoparticles can strongly interact with the support. In certain perovskite materials, such as $CaTiO_3$ (CTO), $BaCeO_3$ and $LaFeO_3$, the interaction is particularly unique and has been the subject of study for many years. Studies using bulk measurement techniques have shown that noble metals dissolve and reform under high temperature and reduction/oxidation conditions in a self-regenerative process. This process helps avoid excessive particle coalescence, overcoming a fundamental problem with nanoparticle catalysts.

Most researchers have studied these materials via bulk methods, and while very successful, these methods do not explore the nanoscale behavior. TEM provides a way to view samples directly down to the atomic scale, and allows crystallographic measurements and element identification through EDS and EELS. The TEM only provides a means to analyze a sample in high vacuum, therefore only *ex situ* experiments could previously be carried out. This means users must initially analyze a sample, expose it to relevant catalyst conditions in a separate reaction chamber, image again, and repeat as necessary. This can be time consuming, and possibly very expensive, and critical information may be missed during a process step. With the introduction of the Protochips Atmosphere E-cell system, researchers can now expose catalyst samples to gas and temperature conditions that closely match the real world catalyst environment. Atmosphere provides a means to visualize atomic scale processes in real time, so more meaningful and relevant information can be extracted from experiments with minimal additional effort.

Experiment

Researchers in the Xiaoqing Pan group at University of Michigan performed *in situ* high-temperature reduction experiments on a $CaTi_{0.95}Rh_{0.05}O_3$ catalyst sample. The powder sample was dispersed from solvent suspension directly onto a temperature-controlled support, or thermal E-chip. The E-chip has a thin, ceramic heating membrane, which is actively controlled with the Atmosphere software to automatically adjust the temperature in different gas environments and pressures (up to 1 atm). A second window E-chip with a SiN membrane sits on top of the thermal E-chip in the TEM holder creating a thin gas cavity sealed from the high vacuum of the TEM column. During the experiment the sample was imaged under 1 atm (760 Torr) forming gas (5% H_2 in N_2) at temperatures between 300 °C and 550 °C. A JEOL 2100F Cs corrected TEM at the University of Michigan's EMAL facility was used and operated in STEM mode at 200 kV.

Discussion

Katz, et al., demonstrated that Rh in $CaTi_{0.95}Rh_{0.05}O_3$ migrates under reducing conditions at elevated temperature.[2] The figure below corroborates this result *in situ*. In Figure 1A, a HAADF STEM image shows the sample at 250 °C in 1 atm of forming gas. Rh shows up as bright contrast spots in the image. After a few minutes at 500 °C, Figure 1B, Rh clearly has formed into small nanometer sized particles and clusters. This experiment could take several hours via traditional means. With Atmosphere only minutes have elapsed, and meaningful data is collected at relevant pressures and temperatures and the process visualized in real time.

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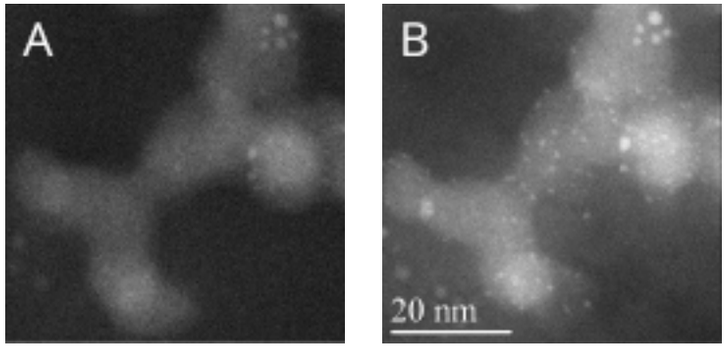

Figure 1: HAADF STEM images of CaTi0.95Rh0.05O3. The left image shows initial Rh migration and coalescence into nanoparticles and clusters at 250 °C in 1 atm forming gas. The right image shows significant Rh migration at 500 °C in 1 atm forming gas.

Increasing the magnification on an individual CTO nanoparticle on zone axis revealed that Ca and Ti in the crystal lattice could be distinguished using Z-contrast, Figure 2A, though they are only separated by one element on the periodic table. Clusters of Rh appear as bright clouds, however, it is difficult to determine whether these clusters are crystalline, as they may not be oriented along a zone axis and do not appear epitaxial with the CTO. In Figure 2B, alternating Ca and Ti columns are readily apparent, and Rh atoms could be identified as a result of their higher relative atomic mass. This demonstrates that noble metal catalyst atoms in the lattice can be tracked during oxidation and reduction experiments in real time using high-resolution STEM techniques coupled with Atmosphere, allowing researchers to understand how the self-regeneration process occurs at the atomic scale.

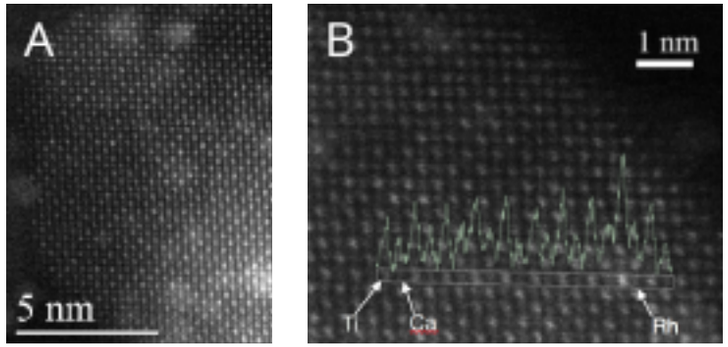

Figure 2: STEM HAADF images of $CaTi_{0.95}Rh_{0.05}O_3$ at 500 °C in 1 atm of forming gas. The left image shows Z-contrast indicating the positions of the Ca and Ti atomic columns. The right image is at higher magnification. A line scan indicating pixel intensity shows the positions of Ca and Ti, as well as where Rh atoms appear and show up as brighter contrast due to the higher atomic number.

Applications

Catalyst materials used for automotive applications as well as a myriad of industry sectors are critical components in creating consumer and industrial products and materials. Nanoparticle catalysts show exceptional promise in these applications and processes if critical hurdles can be overcome. TEM analysis of nanoparticle catalysts has shown extraordinary results in spite of the high vacuum conditions found in the column of the TEM. Atmosphere builds on those results by providing the means to apply accurate temperatures over a wide pressure range, without degrading the performance of the most powerful TEMs on the market today. A holder based system, Atmosphere is compatible with most modern TEMs, and can be added to new and existing instruments usually with no special modifications whatsoever. Contact us to discuss the full range of capabilities of the Atmosphere E-cell System for your applications. We can be reached at (919) 377-0800 or contact@protochips.com.

References:
Y. Nishihata et al., Nature, 418, p164, 2002
M.B. Katz et al, J Catal, 293, p145, 2012

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