Iin-situ TEM for studies of morphological changes in emission control catalysts during operation

C. Wang[1]; J.H. Kwak[1]; D.H. Kim[1]; J. Szanyi[1]; R. Sharma[2]; S. Thevuthasan[1]; C.H.F. Peden[1]

[1] Institute for Interfacial Catalysis and Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, USA.
[2] Center for Solid State Science, Arizona State University, Tempe, AZ, USA.

Catalysis is one of the most valuable contributors to the World economy, as it is integral to chemical processing and petroleum refining, plays a key role in emission control from manufacturing, energy production and transportation, and is critical to proposed advances needed to secure a sustainable energy future.

Manipulation of catalyst materials at the nanoscale has long been and continues to be essential to this critical technology. Catalysis is also a dynamic process and information about catalyst morphology changes during reaction is critical to understanding and improving catalyst materials and processes. Thus, many recent workshop reports [1-3] have emphasized the need for greatly improved methods for observing catalyst materials at the nanoscale as they are operating in a catalytic process.

We have discovered a dramatic example of the importance of morphology changes in a catalytic process that involves the storage, release and reduction of nitrogen oxides (NOx), one of the most harmful gases emitted by internal combustion engines. The reduction of NOx from an exhaust gas mixture that contains an excess amount of oxygen, as in the case of diesel engines, remains a particularly difficult challenge. One of the most promising technologies under consideration for this problem is the NOx storage/reduction (NSR) method. This process is based on the ability of certain oxides, in particular alkali and alkaline earth oxide materials, to store NOx under lean conditions and release it in rich (excess reductant) engine operation cycles. The most extensively studied catalyst systems for this purpose are based on BaO supported on Al_2O_3. During the NOx uptake, BaO/$BaCO_3$ phases are converted to $Ba(NO_3)_2$ which, in turn, releases NOx in the rich cycle and reforms the active NOx storage phase of BaO/$BaCO_3$. We have followed these processes on model catalyst materials with infrared (FTIR) and ^{15}N solid-state NMR spectroscopies, temperature-programmed desorption (TPD), *ex-situ* TEM, and *in-situ* time-resolved x-ray diffraction (TR-XRD) techniques. The results from these experiments suggested rather profound morphology changes in the Ba-containing phases during reaction; thus, this seemed an excellent system for study by *in-situ* TEM. In this presentation we will discuss some of our initial results from such experiments, and some possible future experiments that would be of special interest.

[1] JM White and J Bercaw, US Department of Energy Office of Science (2002). *Opportunities for Catalysis Science in the 21st Century.*
[2] ME Davis and TD Tilley, National Science Foundation (2003). *Future Directions in Catalysis: Structures that Function at the Nanoscale.*
[3] D Ray and CHF Peden, Pacific Northwest National Laboratory (2005). *Advanced Resources for Catalysis Science: Recommendations for a National Catalysis Research Institute.*