Ex-situ Reactor Enabled Microstructural Monitoring: Elucidating Lean NOx Trap Deterioration Parameters

Melanie J. Moses, Chaitanya K. Narula[*] and Lawrence F. Allard
Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN
*narulack@ornl.gov (corresponding author)

Introduction

The lean NO_x trap (LNT) strategy has received extensive attention for treating NO_x emissions from lean-burn gasoline and diesel engines [1, 2]. In this strategy, the NO_x is collected during lean engine operation and then reduced during a brief rich engine operation. The mechanism is believed to involve oxidation of NO, conversion of NO_2 to NO_3, and storage of the NO_3 in the lean cycle and the reduction of NO_3 in rich cycle [1-3]. The precious metal component of the LNT catalyzes both oxidation and reduction steps. However, the rapid loss of performance, attributed to precious metal sintering, limits LNT deployment to only specialty vehicles such as gas-electric hybrids [1, 2]. This correlation of performance deterioration with precious metal sintering is based on the microstructural analysis of samples obtained from bench-top reactors, dynamometers, and on-vehicles after testing. Thus, the microstructural analysis is limited to fresh samples and fully deteriorated samples because the destructive nature of characterization techniques prevents periodic monitoring of microstructural changes throughout a testing protocol.

We present a unique method employing an *ex-situ* reactor that allows us to expose catalyst samples on TEM grids to operating conditions using simulated exhaust and analyzing microstructural changes by electron microscopy [4]. The ORNL *ex-situ* reactor is very versatile and has gas flow cycling capability. This permits the design of studies to elucidate the parameter(s) responsible for microstructural changes in catalysts. This is demonstrated by monitoring Pt sintering in LNT catalysts under various operating conditions i.e. lean, rich, lean-rich cycling conditions, SO_2, temperature, etc.

Materials and Methods

The model LNT, $2\%Pt\text{-}98\%[10\%CeO_2\text{-}ZrO_2\text{-}90\%(2\%La_2O_3\text{-}98\%BaO\cdot 6Al_2O_3)]$, and $2\%Pt/\gamma\text{-}Al_2O_3$ catalysts were prepared by stepwise impregnation on commercial γ-alumina [4]. Samples were prepared by depositing the catalysts via dry-dipping on stainless steel TEM grids coated with a conductive film of holey $LaCrO_3$ [4]. The samples on TEM grids were aged under simulated lean, rich and lean-rich cycled diesel exhaust on the *ex-situ* reactor. The Pt sintering was monitored by imaging the fresh and aged samples on a Hitachi HD-2000 scanning transmission electron microscope (STEM), in the high-angle annular dark-field (HA-ADF) mode.

Results and Discussion

The STEM imaging of model LNT catalysts before and after exposure to simulated lean, rich, or lean-rich cycled diesel exhaust (without sulfur) at standard diesel engine operating temperatures (500°C) in the ex-situ reactor showed a lack of Pt sintering in model catalysts. This observation is not surprising since we did not expect significant sintering after aging for only 4 hours under normal operating conditions, especially, because samples were not exposed to desulfation conditions (SO_2 in simulated exhaust, 700ºC).

While low-sulfur fuel (15-30 ppm) has reduced sulfur poisoning, it is still necessary to carry out periodic desulfation of LNTs to reclaim lost NO_x trapping performance. The desulfation requires high-temperature (~700°C) operation of LNTs to decompose sulfates. In order to isolate the roles of sulfation-desulfation and thermal effects under exhaust, we carried out accelerated aging of model LNTs using simulated exhaust (with and without SO_2) on our *ex-situ* reactor. Figure 1 shows a model LNT catalyst area (and Pt particles) that was monitored throughout the accelerated aging test (700ºC) without sulfur in simulated exhaust. The results of the accelerated aging tests show that the bulk of the Pt sintering occurs during the early stages of testing. Repeating this test with simulated exhaust containing SO_2 showed an identical Pt sintering pattern. The bulk of precious metal sintering in the early stages of aging has also been observed in LNT tests carried out on vehicles [5]. Our study suggests that sulfation-desulfation itself has little impact on the precious metal sintering, and the temperature of desulfation is the primary cause of Pt sintering.

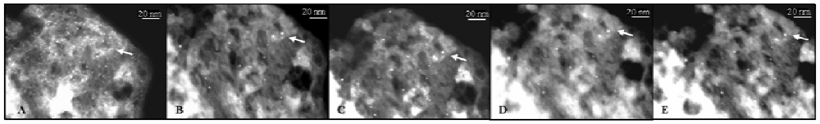

Figure 1. STEM images of the exact same area of the model LNT before accelerated aging without SO_2 (A), after 4hrs aging (B), after 8hrs aging (C), after 12hrs aging (D) and after 16hrs aging (E). Arrows point to the same area on each image.

Significance

The *ex-situ* reactor in conjunction with electron microscopy allows monitoring of catalyst microstructural changes under various operating conditions. As illustrated by the example in this presentation, this technique adds to the arsenal of methods available for understanding microstructural changes that occur in catalysts under operating conditions. A correlation of microstructure with catalyst activity can make this technique suitable for rapid screening of catalysts.

References

1. Liu, Z. and Woo, S.I. *Catal. Rev*., 48, 43 (2006).
2. Narula, C.K., Daw, C.S., Hoard, J.W., and Hammer, T., *Int. J. Appl. Ceram. Tech*. 2, 452 (2005).
3. Fridell, E., Persson, H., Westerberg, B., Olsson, L., and Skoglundh, M. *Catal. Lett.* 66, 71 (2000).
4. Narula, C.K., Moses, M.J., and Allard, L.F. *SAE paper no.2006-01-3420* (2006).
5. Narula, C.K., Allard, L.F., Moses, M., Xu, Y., Shelton, W., Schneider, W.F., Graham, G.; and Hoard, J. DEER 2005, Palmer Hilton, Chicago, Aug. 21-25, 2005.

This research is sponsored by the Heavy Vehicle Propulsion Materials Program, DOE Office of FreedomCAR and Vehicle Technology Program, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.