Degradation Mechanisms of Urea Selective Catalytic Reduction Technology

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The work was funded by the U.S. Department of Energy (DOE) Office of FreedomCar and Vehicle Technologies.

May 20, 2009

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Project ID: acep_02_peden
Project Overview

Timeline

- Start – December 2008
- Finish – November 2011
- 14% Complete

Budget

- Total project funding
  - DOE – $400K
  - GM – $327K
- DOE funding received in FY09:
  - $100K

Barriers

- Discussed on next slide

Partners

- Pacific Northwest National Laboratory
- General Motors R&D
Barriers

• Some of the mechanisms for deactivation of urea SCR and DOC catalysts have been described. However, a detailed understanding of the main factors determining the long-term performance of these catalysts and the interplay between deactivation of the two catalyst systems has yet to be obtained.

• An especially important issue is the relationship between laboratory and vehicle aging. In particular:
  – How well do laboratory aging conditions reproduce sample deactivation in vehicle aged samples at various stages of use?

• Establishing the relevance of rapid laboratory catalyst aging protocols is essential to reducing development cost.
Goals and Objectives

• Develop an understanding of the deactivation mechanisms of and interactions between the diesel oxidation (DOC) and urea selective catalytic reduction (SCR) catalysts used in light-duty diesel vehicle applications.

• Understand the difference between vehicle aging and aging under laboratory conditions, information essential to provide a rapid assessment tool for emission control technology development.

• Determine the role of the various aging factors impacting long-term performance of these catalyst systems, in order to provide operational information about how catalyst deactivation can be avoided.
Approach

• Prepare and Process Urea SCR catalyst and DOC catalyst
  – All catalyst samples are being provided by GM in monolith form. Both “Model” and “Development” (proprietary) samples are being studied in the following forms:
    • Fresh and ‘degreened’
    • Lab reactor-aged, oven-aged, and vehicle-aged samples.

• Utilize catalysis expertise, and state-of-the-art catalyst characterization and testing facilities in PNNL’s IIC to determine deactivation mechanisms and structure/function
  • XRD, XPS, NMR, TEM/EDX and SEM/EDX
  • NO TPD, H₂ TPR
  • Lab reactor studies
Collaborations/Interactions

**GM**
- Perform catalyst aging (both laboratory aging and vehicle aging).
- Performance measurements.
- Provide the aged samples to PNNL.

**PNNL**
- Perform various catalyst characterizations on the samples provided by GM.
- Develop a fundamental understanding of major catalyst deactivation mechanisms.

**Joint Activity**
- Using the new understanding, develop correlations relating the degree of performance deterioration to the catalyst aging parameters.

- Conference calls are held at least once a month to discuss the results.
- Once a year ‘face-to-face’ annual reviews are planned. First of these was held in Detroit, April 29, 2009.
Two initial primary areas of focus:

• Determine most appropriate tools and procedures for catalyst state diagnosis of deactivation in development SCR and DOC materials.
  – Applied methods so far: BET, TEM, XRD, TPD and XPS
  – Most results on the ‘development’ catalysts contain proprietary information regarding catalyst composition and structure.
  – Still on-going with other characterization tools to be applied.

• Identify relationships between performance (as measured at GM) and physicochemical changes (by PNNL)
  – DOC: Focusing on the precious metal sintering and alloying with respect to thermal aging.
  – SCR: Focusing on the zeolite structure stability and the behavior of the ion-exchanged metal.
DOC: Severe Aging Effects

- Sample C aged at 250 °C higher temperature than sample A. Both NO oxidation (NO₂ yield) and HC oxidation performance decreased with increasing aging temperature.
TEM analysis: aged A vs. aged C

PGM severely sinters to form crystallites about 100 nm in size → these results fully consistent with XRD results (~90 nm)
**Technical Accomplishments/Progress/Results**

*In situ* high temperature XRD: changes in precious metal crystallite size with time at 900 °C

![Graph showing changes in X'talline size (nm) over time (hr)]

- Significant growth of PGM size within a few hours, followed by slower, but steady increase.
- These changes to be confirmed by GM, which will perform activity measurements for similarly prepared samples.

*Starting from the fresh sample*
Technical Accomplishments/Progress/Results

SCR: Severe Aging Effects

- Drastic decrease in DeNOx activity with laboratory aging time.
- What is the primary factor leading to this observed deactivation behavior?
Technical Accomplishments/Progress/Results

SEM & TEM: After aging for 40 hrs

Morphology becomes inhomogeneous.
Changes in zeolite structure

Growth in metal particle size to 10 nm.
Changes in the active phase
Technical Accomplishments/Progress/Results

Principal conclusions of these studies to date:

• Several state-of-the-art characterization tools were found to be useful for investigating degradation mechanisms of the ‘development’ DOC and SCR catalysts. In particular, to date we have used:
  – TEM/XRD: structural and catalytic phase information
  – XPS: chemical state of active catalytic phase

• Based on a correlation of the performance measurements (GM) and characterization results (PNNL) obtained to date, the following are indicated as the primary reasons for deactivation:
  – DOC: sintering and alloying of the active precious metals.
  – SCR: structure destruction of zeolite and agglomeration of active phase.

• In order to obtain a more precise relationship between activity deterioration and catalyst changes, detailed characterization experiments focusing on molecular level active phase changes are in progress:
  – In-situ XANES, EPR and $^{27}$Al NMR
  – $H_2$ TPR and TPD
Activities for Next Fiscal Year

• Complete characterization and performance evaluation of the first round of fresh and aged DOC and SCR catalysts
  - GM: laboratory testing of fresh and aged samples.
  - PNNL: characterization of these samples.

• Revise the initial laboratory aging protocol
  - Based on the evaluation of the first round of DOC and SCR catalysts, current laboratory aging protocols will be revised and tested.

• Continued evaluation of the most effective characterization tools in order to provide additional crucial information about materials changes in the active catalytic phases.
  - Several additional state-of-the-art characterization techniques will be applied to the evaluated catalyst materials.
Summary

• The Urea SCR technology coupled with a DOC system is being considered by GM as a primary path to meeting emission standards for 2010 and beyond for light-duty diesel vehicles.

• PNNL’s role continues to be to obtain a fundamental understanding of DOC and SCR catalyst deactivation, by correlation of catalyst characterization with GM’s performance results for lab- and vehicle-aged ‘development’ materials.

• Technical highlights from this project to date have included:
  – The primary deactivation mode identified in aged DOCs is precious metal alloying and sintering.
  – The primary deactivation modes in SCR catalysts are the destruction of the zeolite structure and the agglomeration of the active metal.
  – Detailed characterization focusing on a molecular-level understanding of the observed deactivation is in progress.

• This is a highly interactive and collaborative program between GM and PNNL.