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Degradation Mechanisms of Urea Selective Catalytic Reduction Technology

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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.

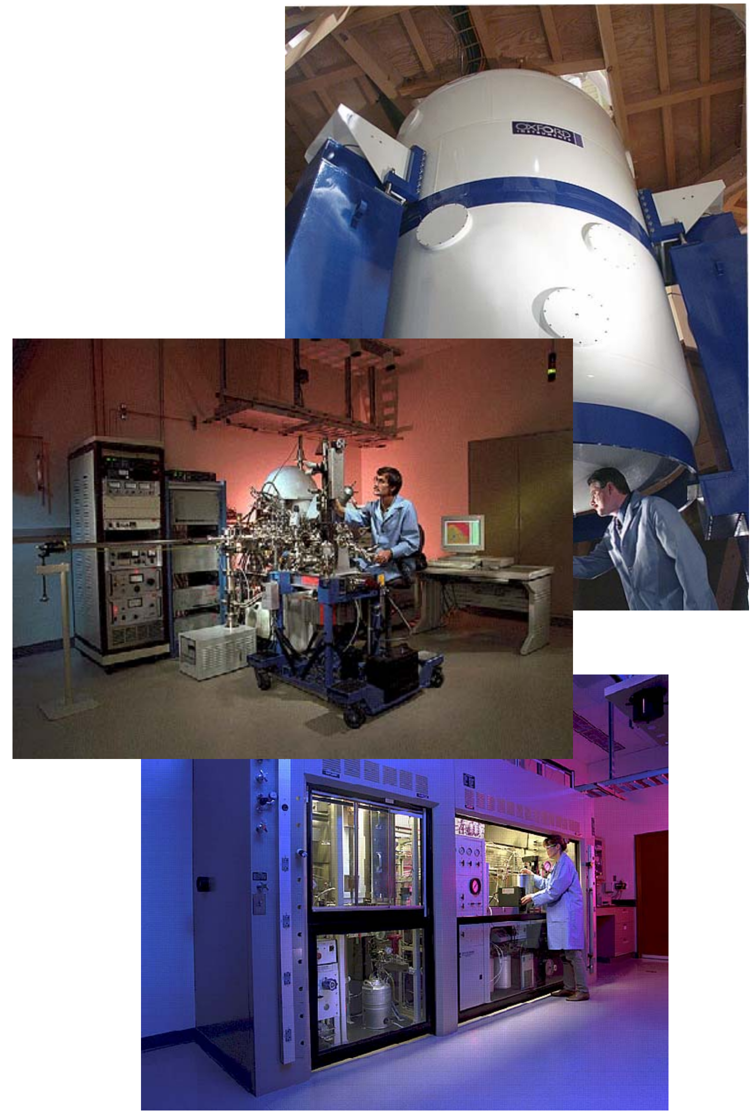
Goals and Objectives

- 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, H_2 TPR
    - Lab reactor studies



Collaborations/Interactions

GM

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

Joint Activity

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

PNNL

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

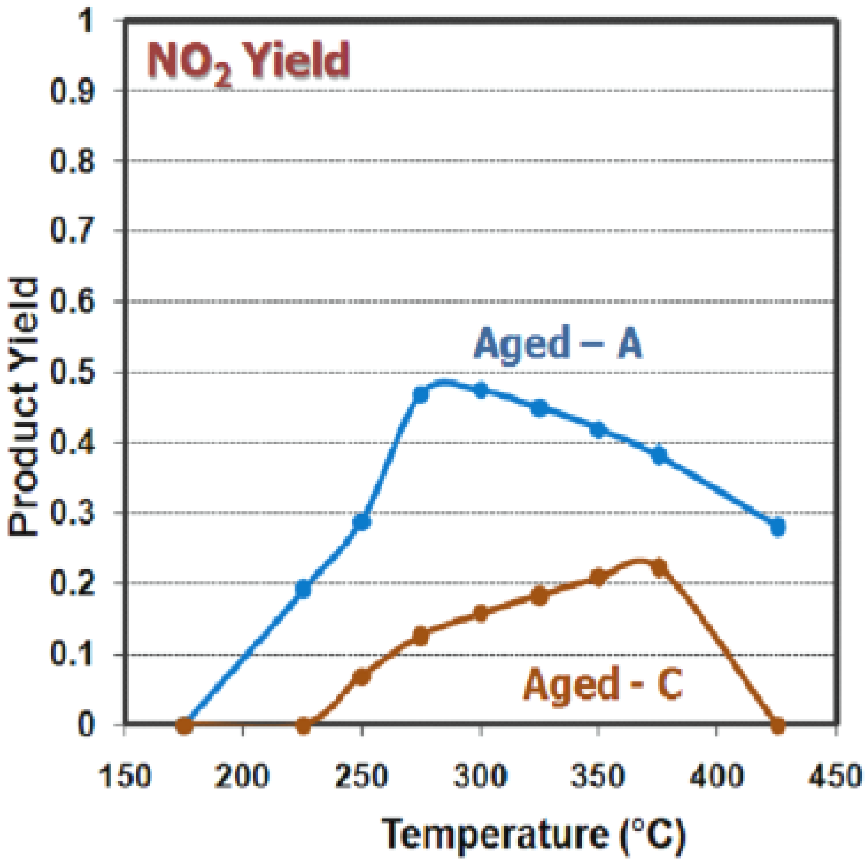
- ***Conference calls are held at least once a month to discuss the results.***
- ***Once a year 'face-to-face' annual reviews are planned. First of these was held in Detroit, April 29, 2009.***

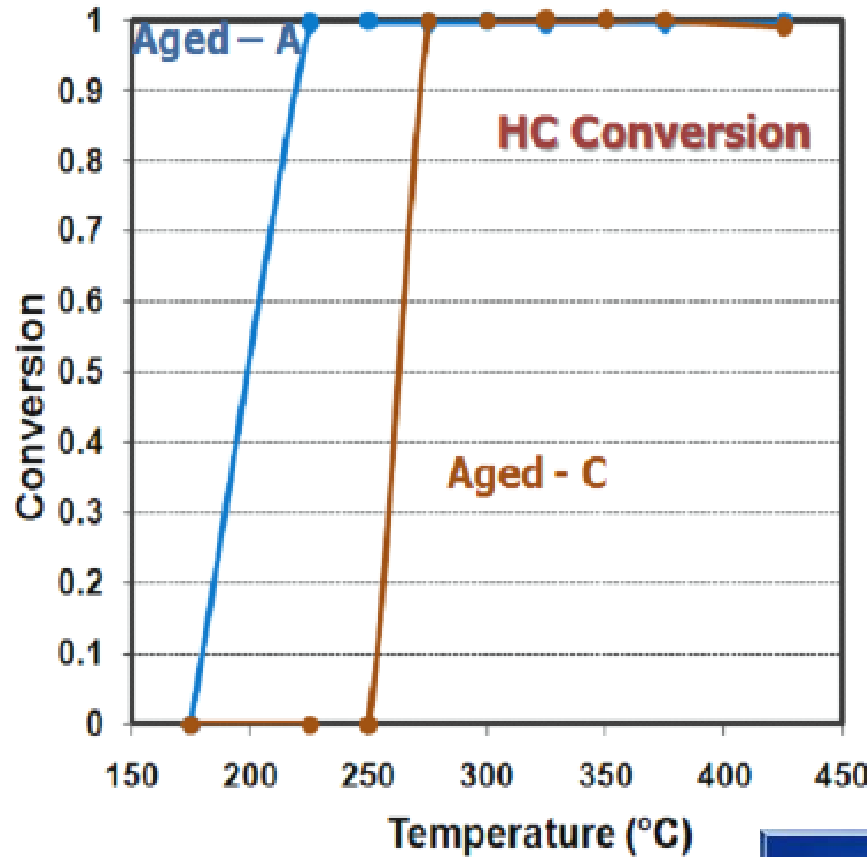
Focus of Current Activities

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.*

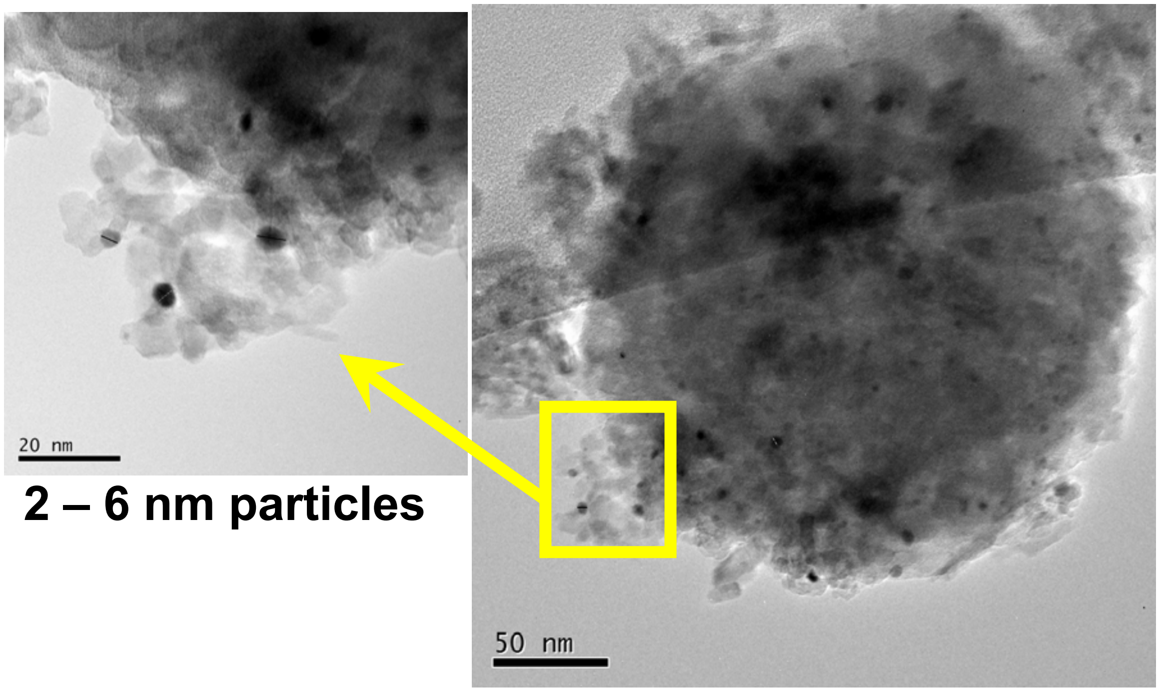
DOC: Severe Aging Effects



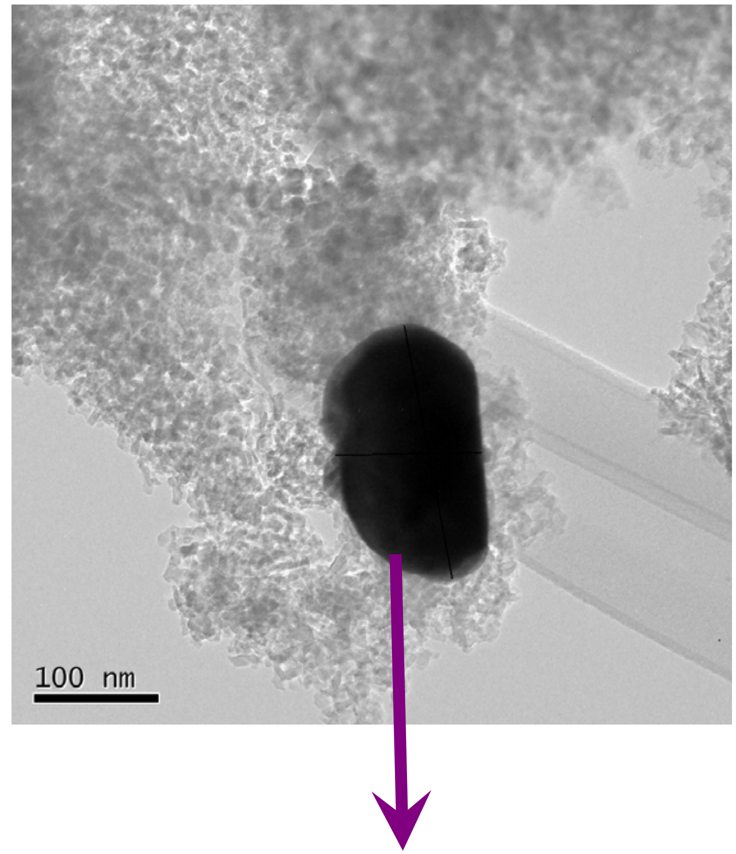


- Sample C aged at 250 °C higher temperature than sample A. Both NO oxidation (NO_2 yield) and HC oxidation performance decreased with increasing aging temperature.

TEM analysis: aged A vs. aged C



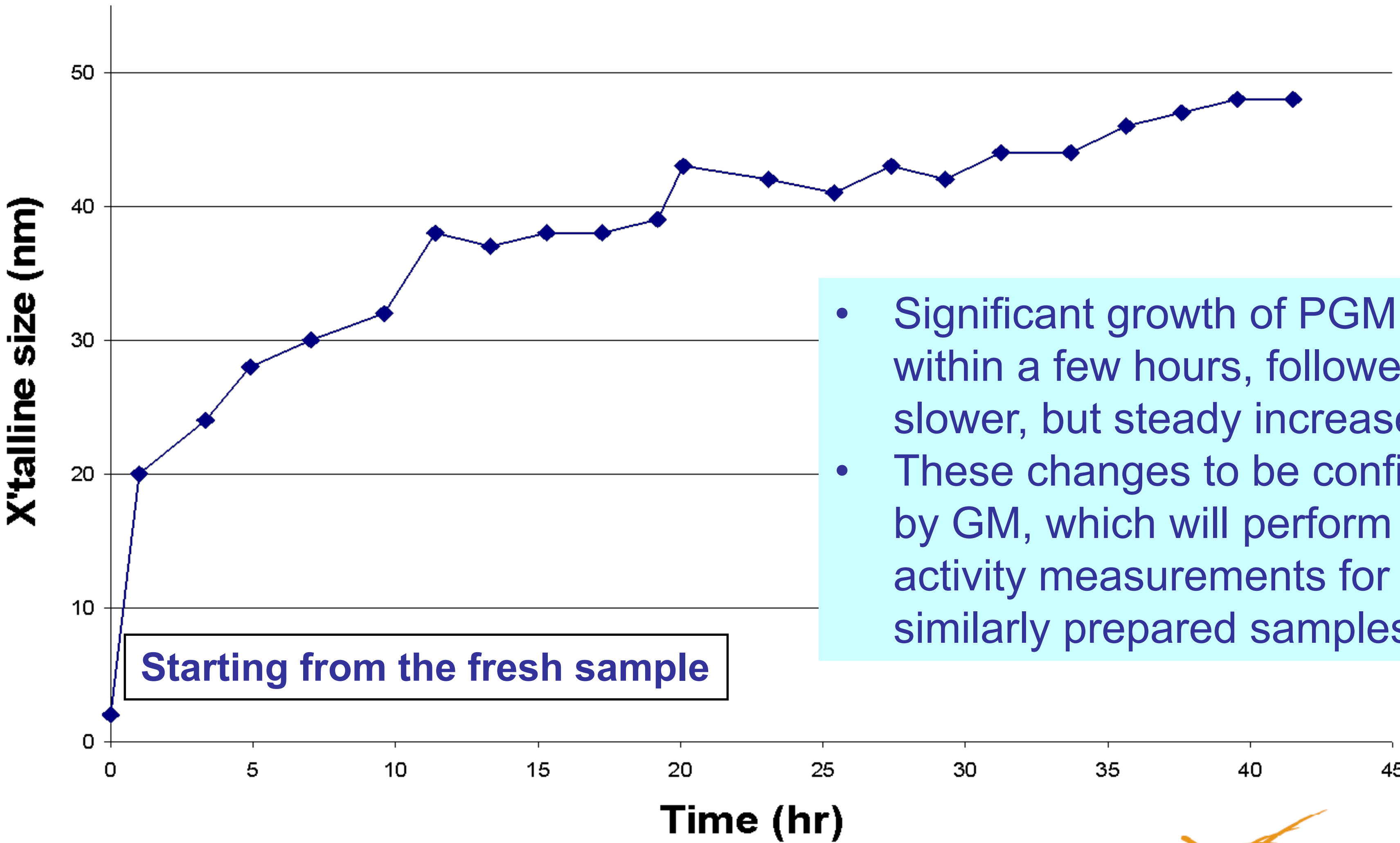
2 – 6 nm particles



PGM severely sinters to form crystallites about 100 nm in size → these results fully consistent with XRD results (~90 nm)

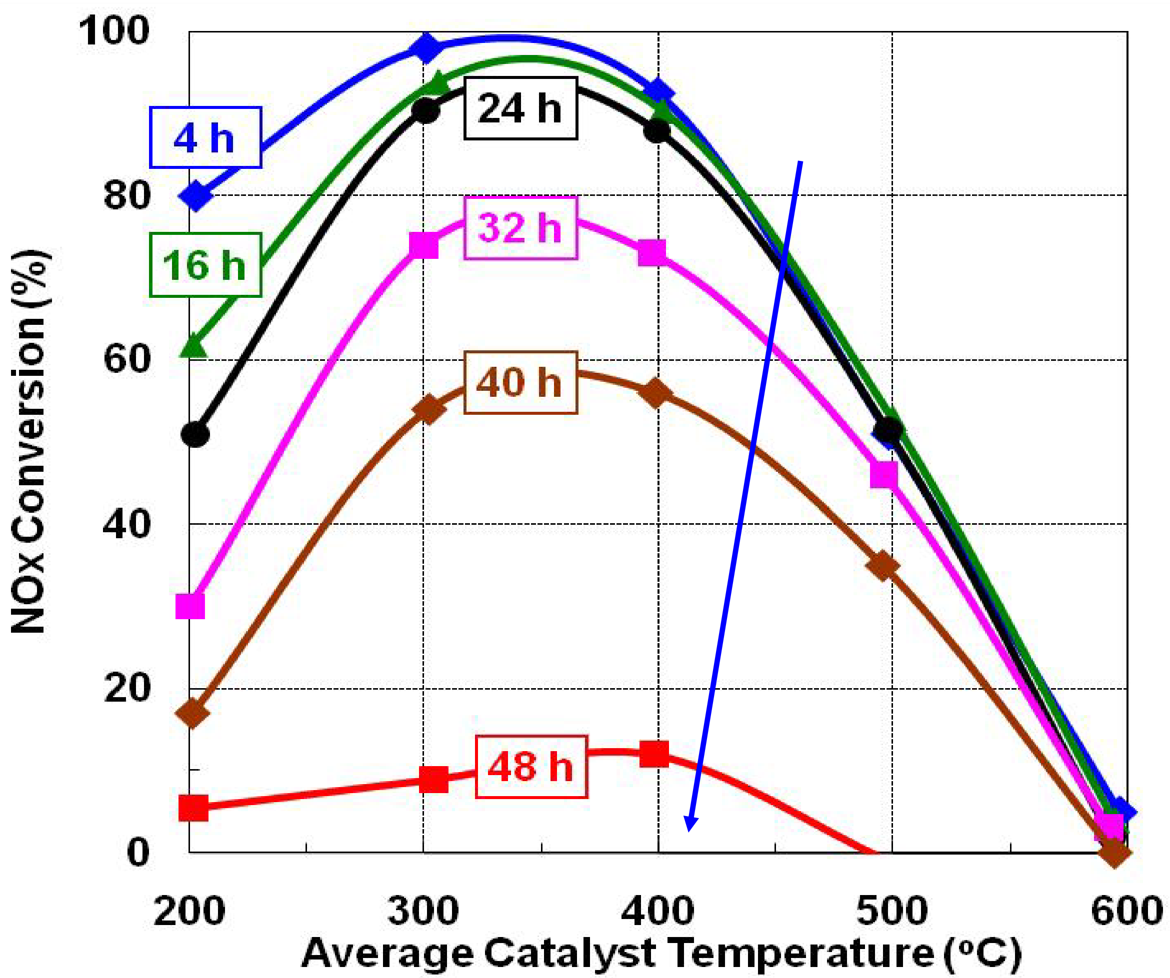
Technical Accomplishments/ Progress/Results

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



- 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.

SCR: Severe Aging Effects



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

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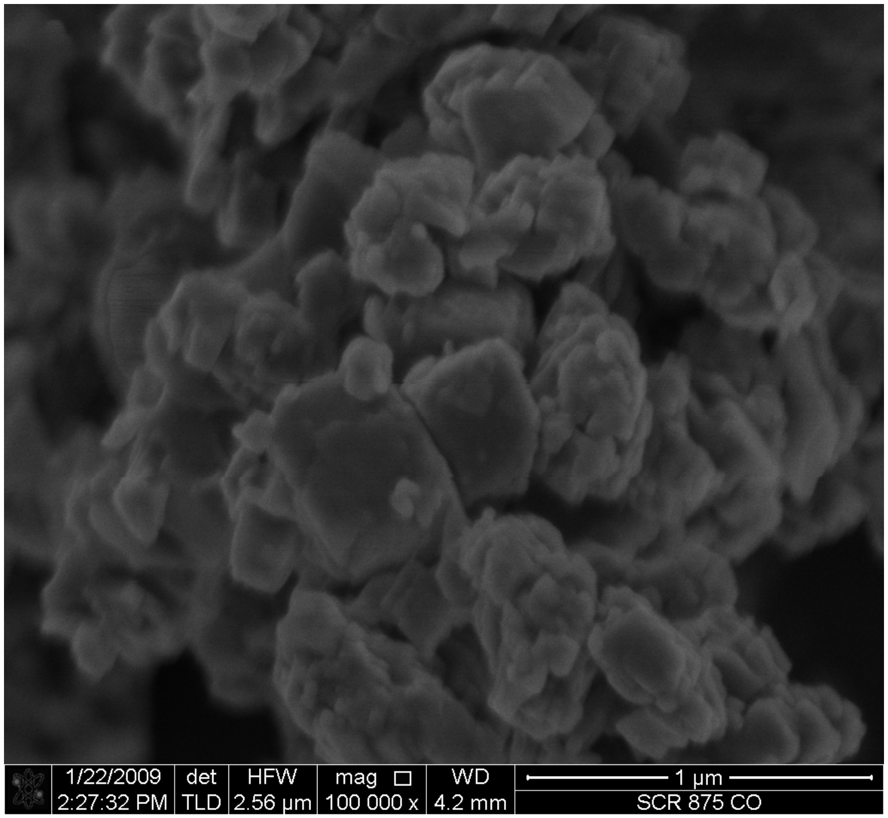
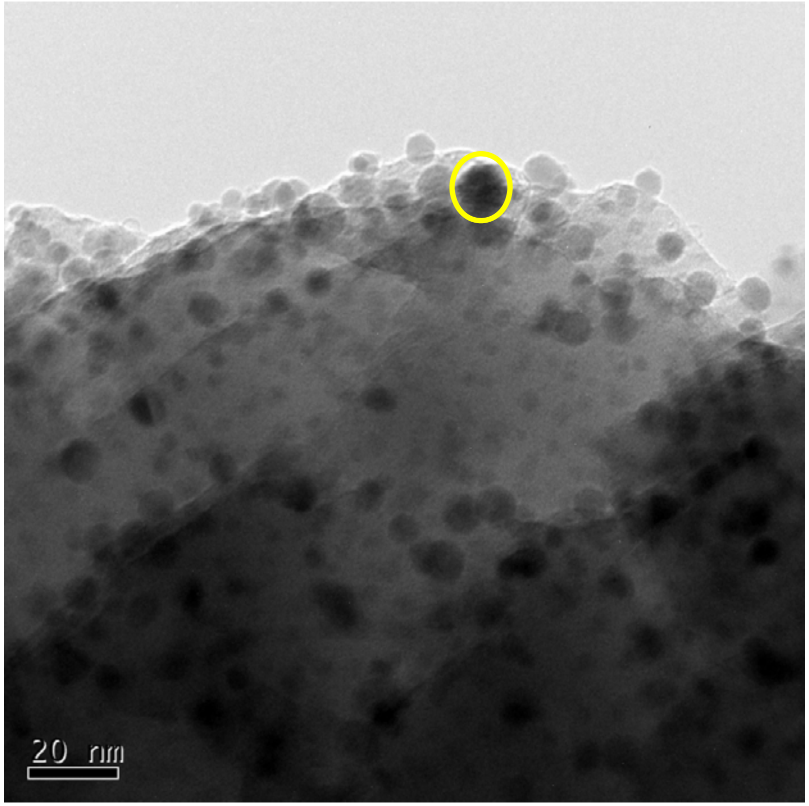
SEM & TEM: After aging for 40 hrs



Morphology becomes inhomogeneous.
Changes in zeolite structure



Growth in metal particle size to 10 nm.
Changes in the active phase

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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

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Activities for Next Fiscal Year

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- 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.