Degradation Mechanisms of Urea Selective Catalytic Reduction Technology

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Control of Chemical Transformations for a Secure Energy Future

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

June 9, 2010

ACE027

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Project Overview

Timeline

- Start – December 2008
- Finish – November 2011
- 47% Complete

Budget

- Total project funding
  - DOE – $400K
  - GM – $327K
- DOE funding received in FY10:
  - $100K

Barriers

- Discussed on next slide

Partners

- Pacific Northwest National Laboratory
- General Motors R&D

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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.

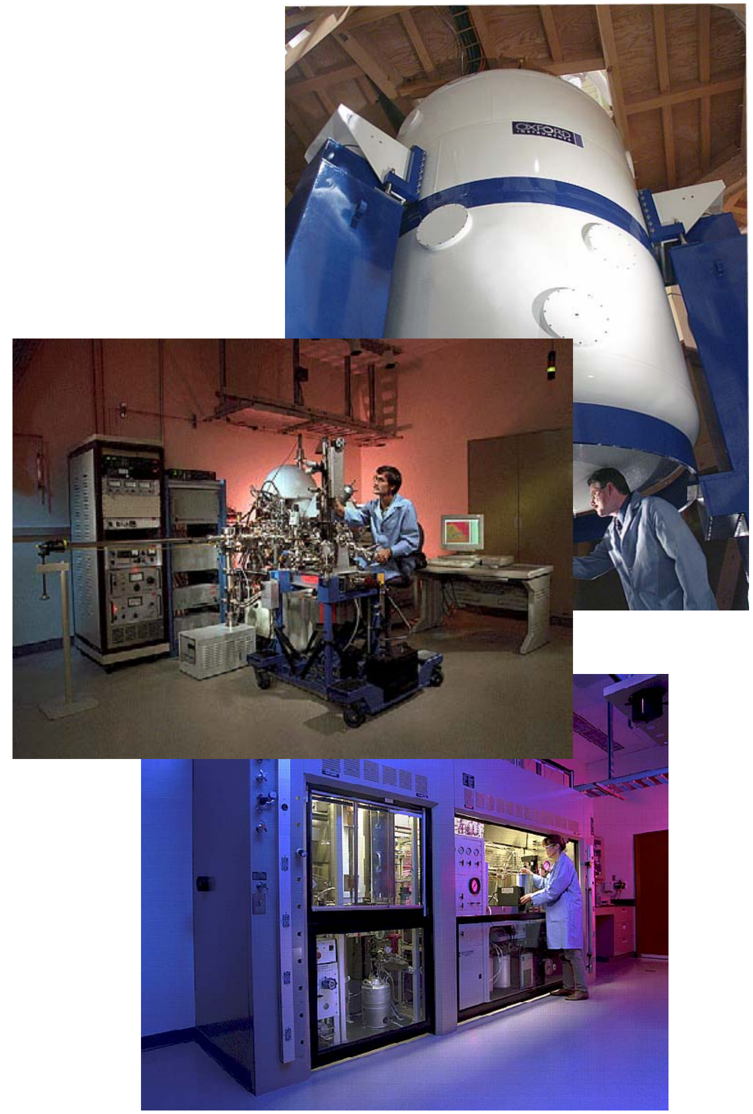
Goals and Objectives

- 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, EPR, 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.

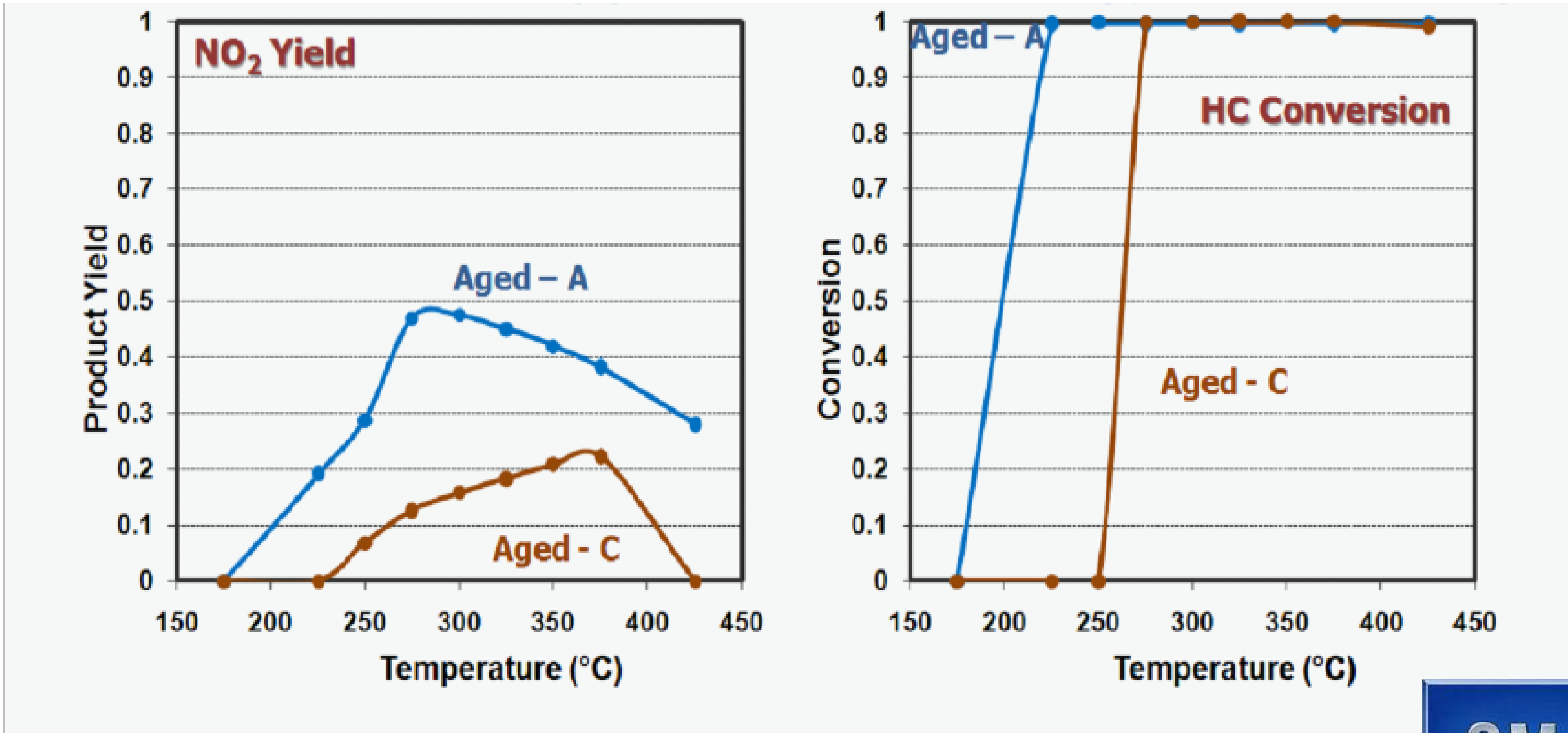
- ***Conference calls are held 8-10 times a year to discuss the results.***
- ***Once a year 'face-to-face' annual reviews are held. Second of these was held in the Detroit area, April 21, 2010.***

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, NMR, EPR 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 at various temperatures*.
  - SCR: *Focusing on the zeolite structure stability and the behavior of the ion-exchanged metal as a function of time and temperature.*

DOC: Severe Aging Effects on oxidations



- 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.

GM

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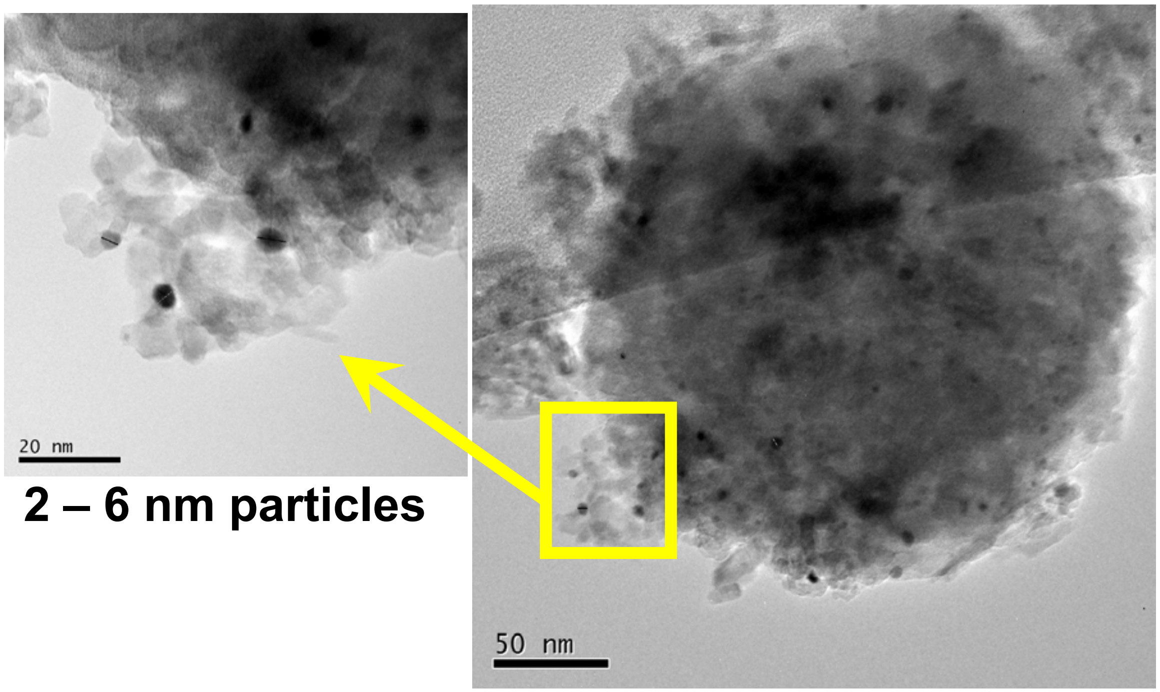
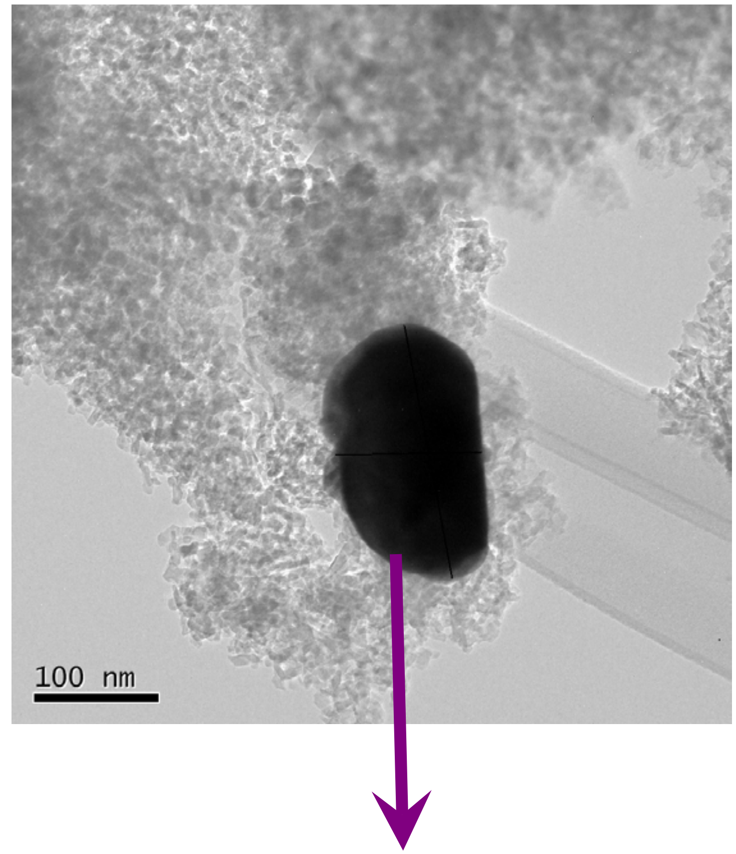
TEM analysis: aged A vs. aged C

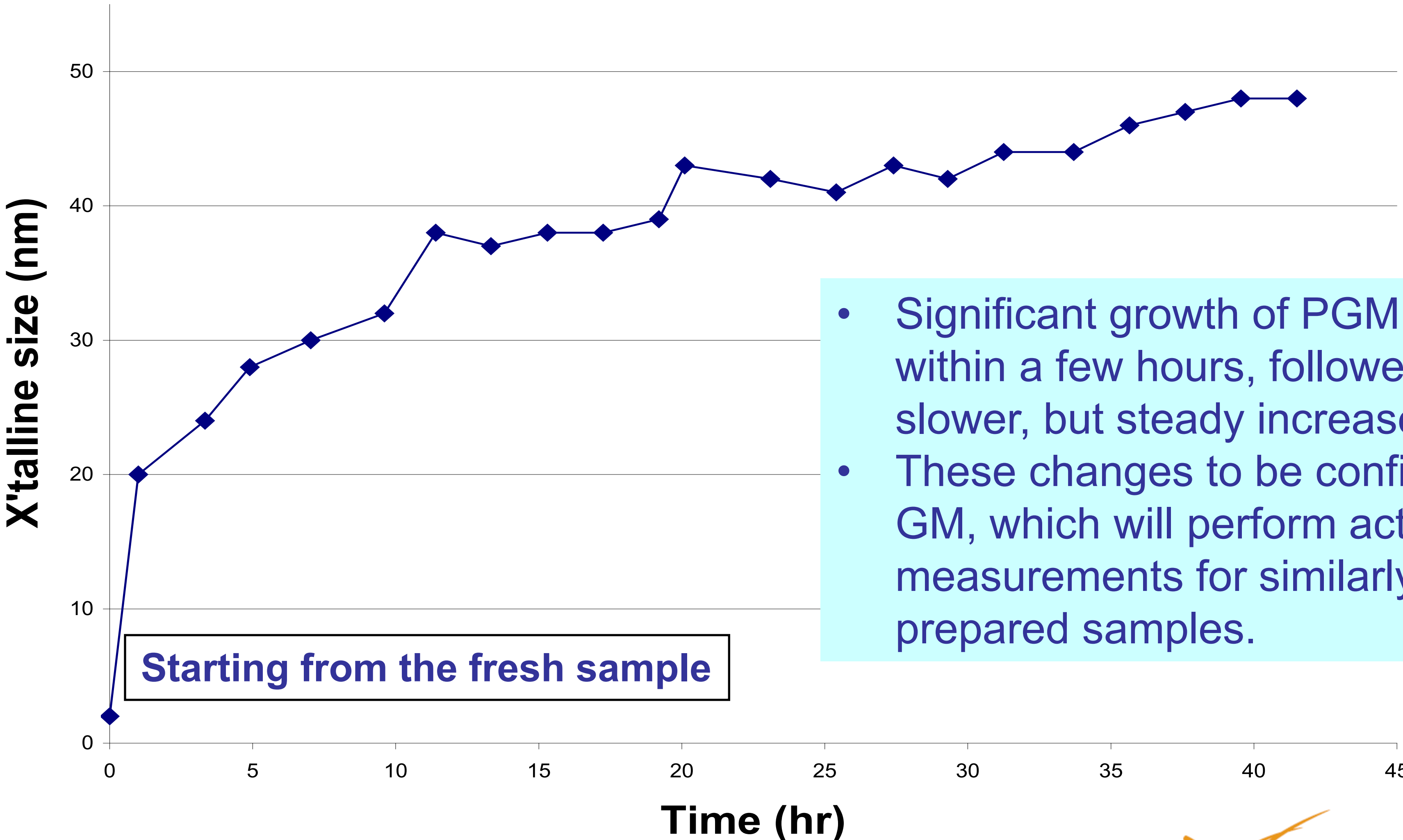


2 – 6 nm particles



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

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

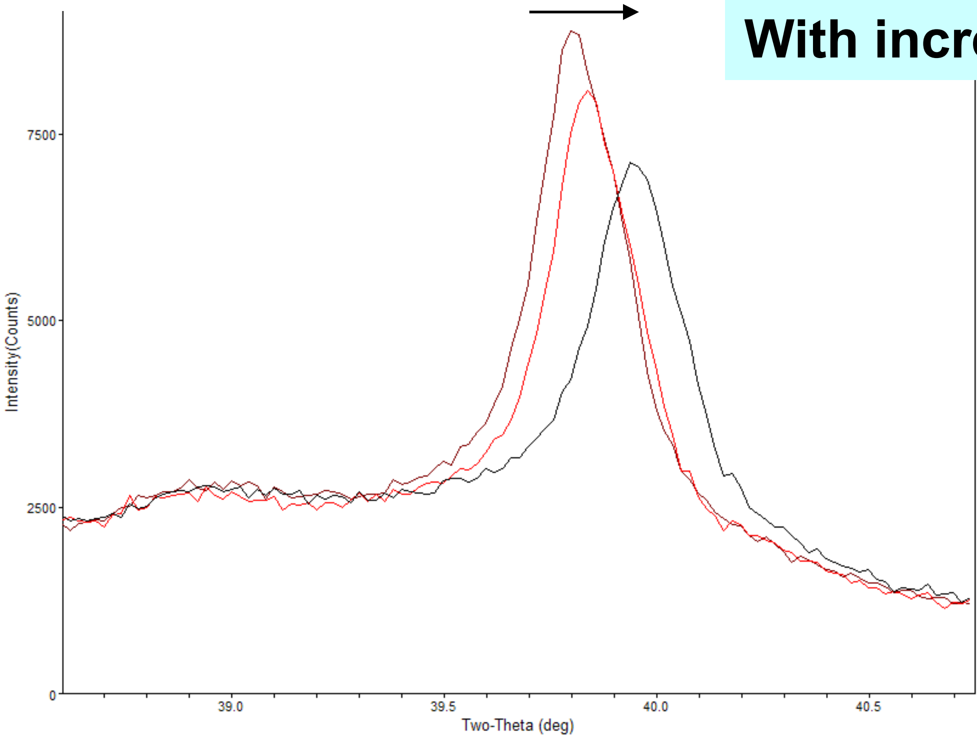


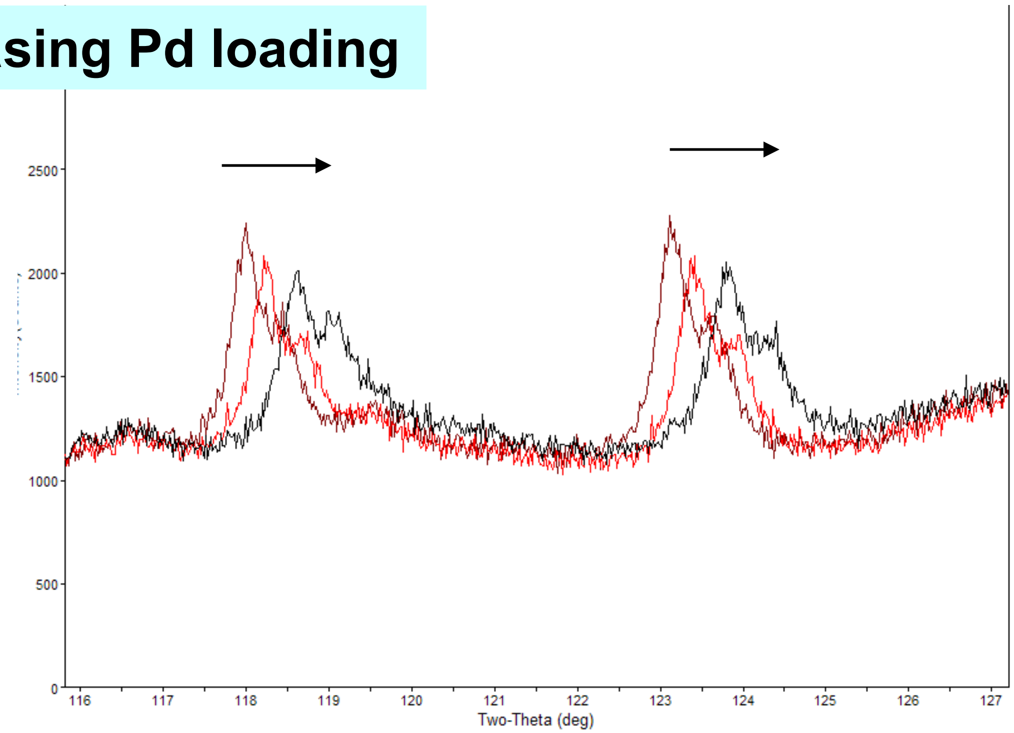
- Significant growth of PGM size within a few hours, followed by slower, but steady increase.
- These changes to be confirmed by GM, which will perform activity measurements for similarly prepared samples.

Technical Accomplishments/ Progress/Results

Can XRD tell us whether a Pt-Pd alloy is formed on aged DOC samples with different Pt/Pd ratios?

With increasing Pd loading





- **Peaks are located between Pd and Pt → formation of Pt-Pd alloy**
- **Symmetry of the peaks → homogeneous phase**
- **Higher 2 theta with more Pd → alloy formed corresponding to Pt/Pd**

Thermal aging induced the formation of Pt-Pd alloy particles in DOC samples.

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OVERVIEW OF DOC studies

DOC samples with different ratio of Pt/Pd

- Fresh
- Thermal aging at various T

Activity measurement at GM

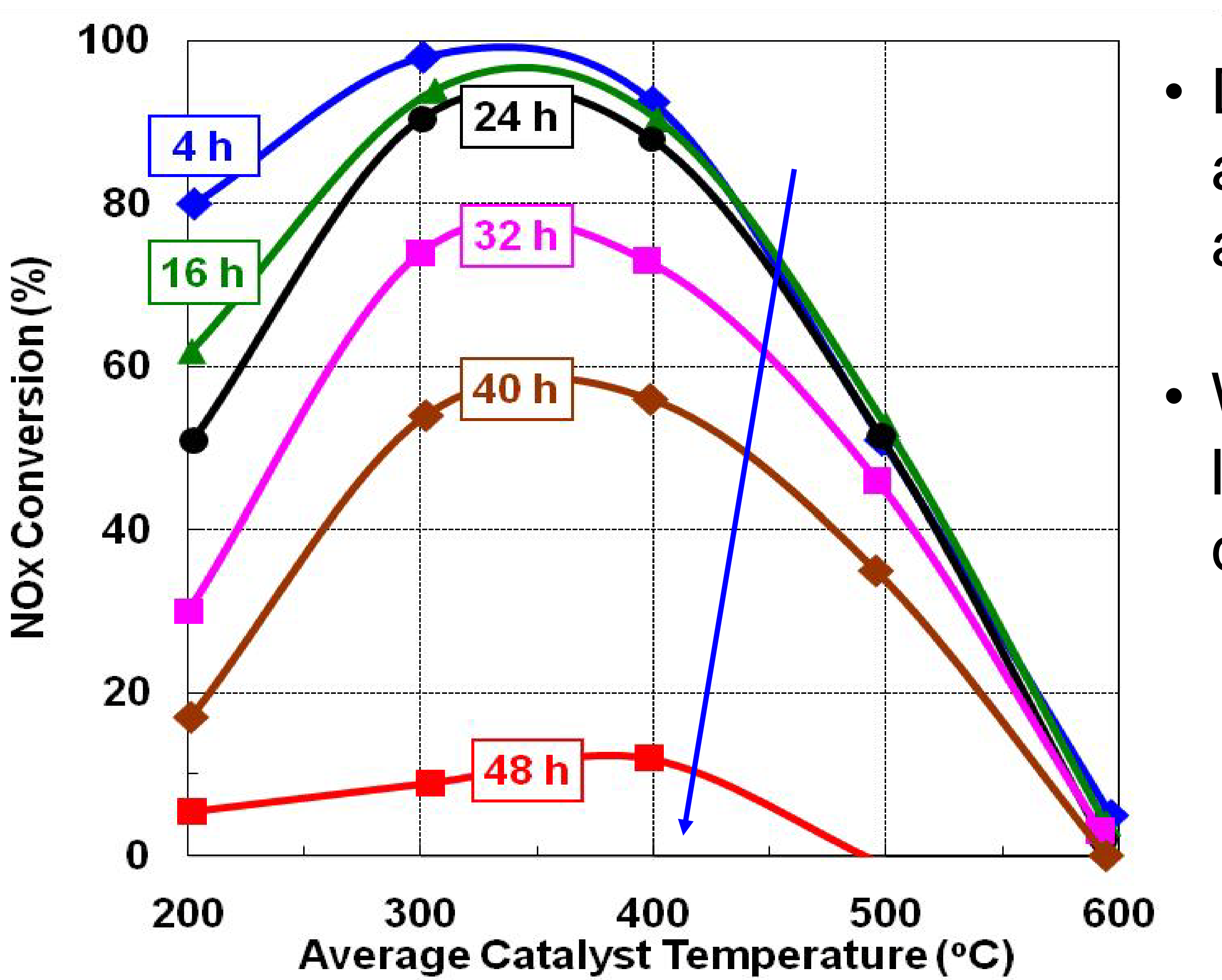
- HC oxidation
- NO oxidation

Physicochemical characterization at PNNL

- Focusing on PGM

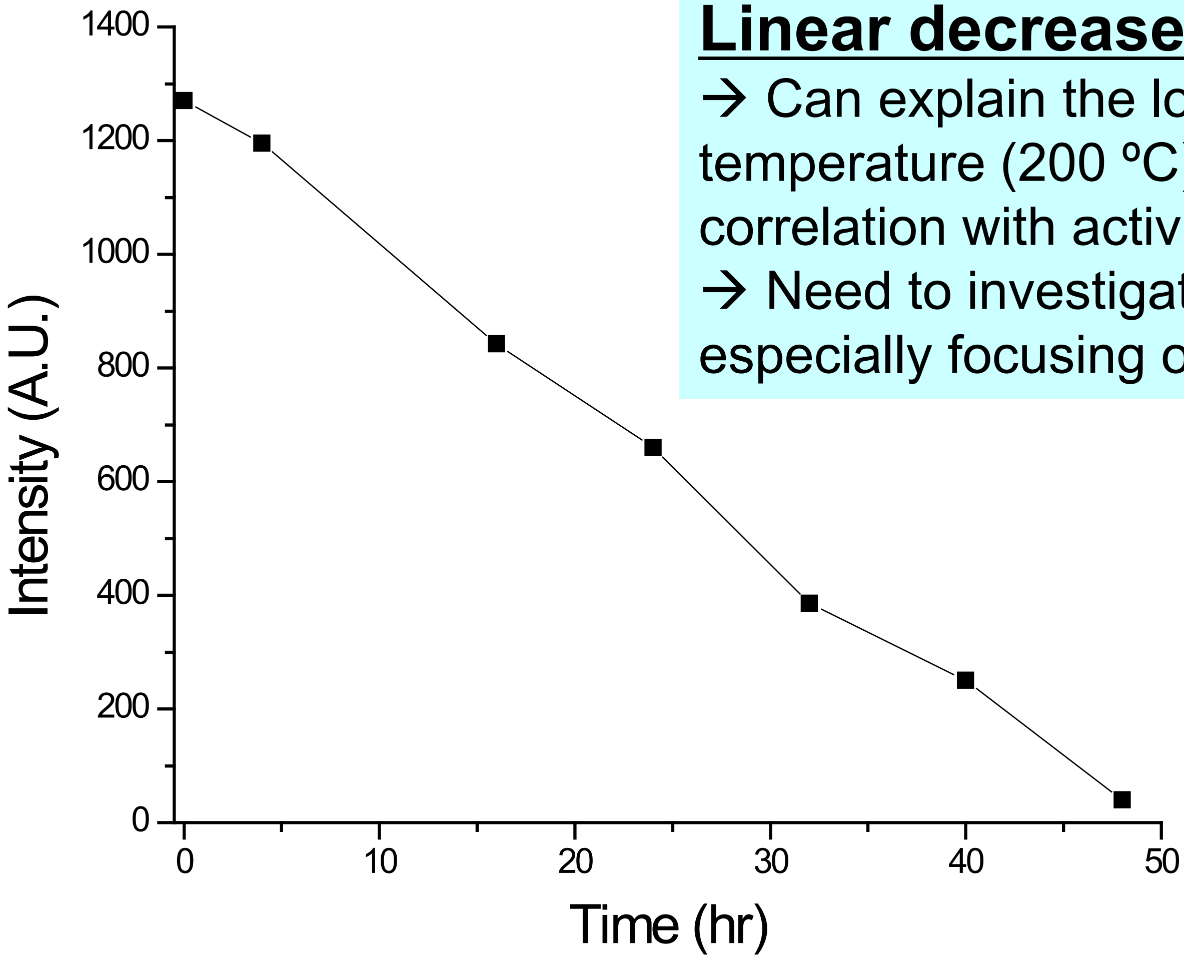
Relationship between activity and active sites as a function of <u>Pt/Pd ratio</u> and <u>aging T</u>

SCR: Severe Aging Effects



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

Zeolite XRD peak intensity with exposure time



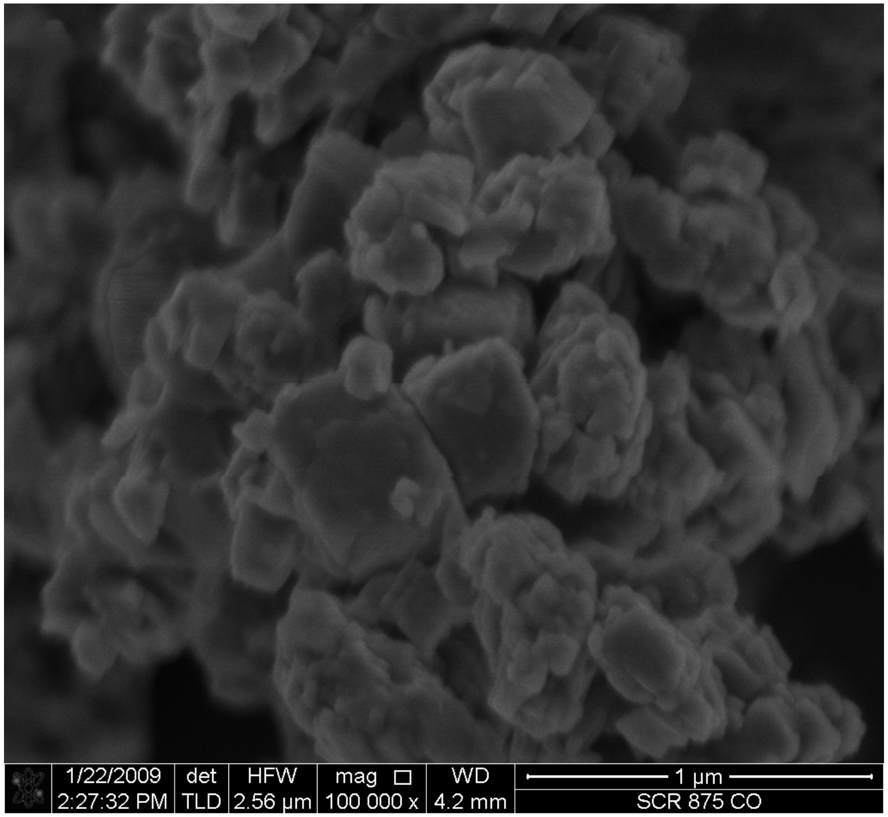
Linear decrease with time

→ Can explain the loss of activity at low temperature (200 ºC). However, not a good correlation with activity changes above 300 ºC

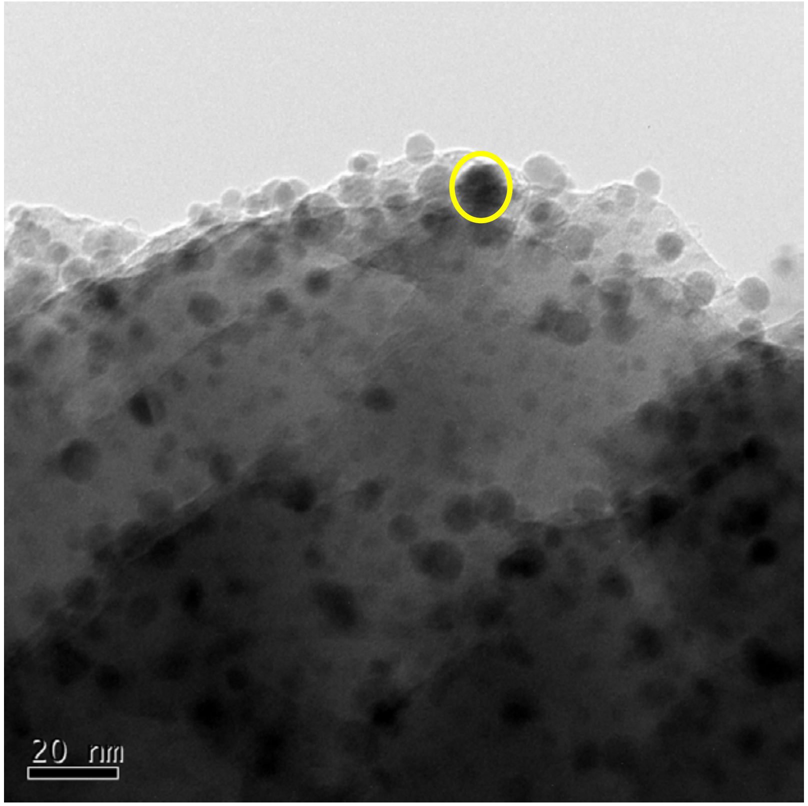
→ Need to investigate catalyst further, especially focusing on active sites.

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

In addition, XPS, NMR and EPR proved to be useful for investigating material changes in these samples.

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OVERVIEW OF SCR catalyst studies

SCR samples

- Fresh
- Thermal aging at various T and time

Activity measurement at GM

- SCR reaction

Physicochemical characterization at PNNL

- physical properties
- active sites

Relationship between activity and active sites as a function of aging time and temperature

→ What is the "not-to-exceed" temperature and time?

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, *in-situ* XRD, EPR and ^{27}Al NMR
  - Probe reaction

Activities for Next Fiscal Year

- Complete characterization and performance evaluation of the lab-aged of DOC and SCR catalysts
  - GM: laboratory reaction testing of fresh and aged samples.
  - PNNL: characterization of these samples.
- Revise the initial laboratory aging protocol and compare results to the vehicle-aged samples
  - Based on the evaluation of the first round of DOC and SCR catalysts, current laboratory aging protocols were revised and are being tested.
  - Apply the established protocol and characterization tools to the vehicle aged samples for validation.
- 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 an effective 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.

GM

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