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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Project Overview

Timeline

- Start – December 2008
- Finish – November 2011
- 80% Complete

Budget

- Total project funding
  - DOE – $400K
  - GM – $327K
- FY11 funding:
  - $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 and time.

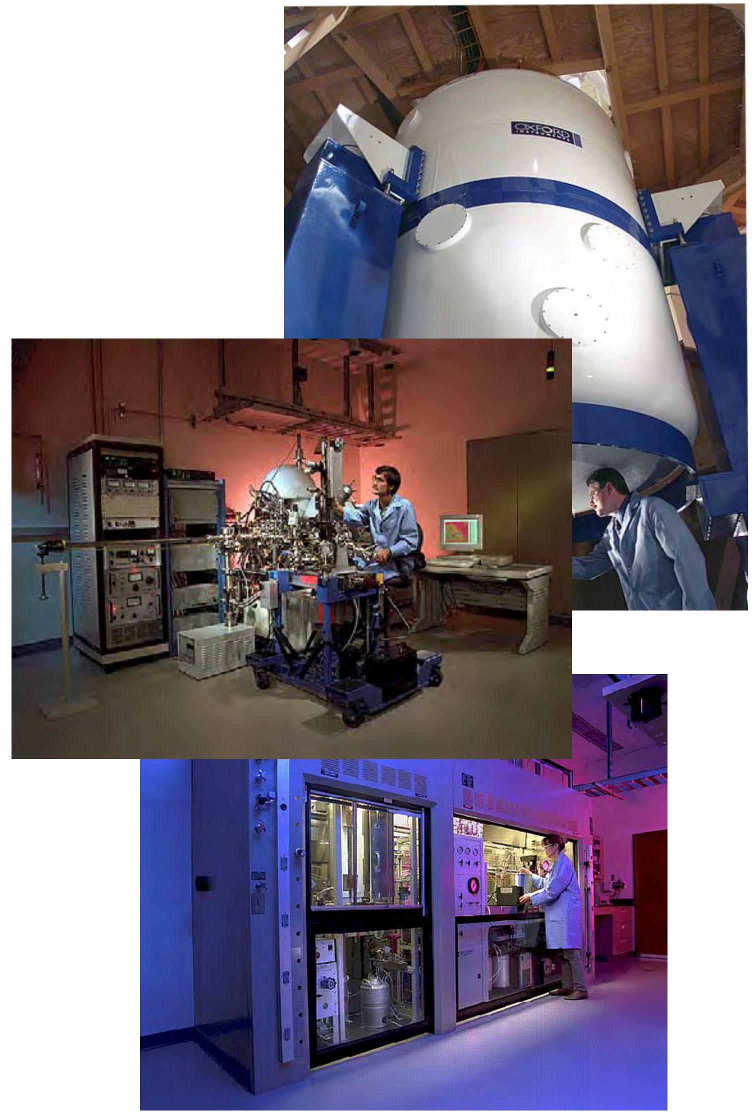
Goals and Objectives

- Develop an understanding of the deactivation mechanisms of and interactions between the diesel oxidation catalyst (DOC) and the urea selective catalytic reduction (SCR) catalyst 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).
- Catalyst 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 5-7 times a year to discuss the results.***
- ***Once a year 'face-to-face' annual reviews are held. Most recent of these was held in the Detroit area, April 20, 2011.***

Focus of Current Activities

Two 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.
  - Comparison between lab-aged and vehicle-aged (135,000 miles) samples.
- 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.*

OVERVIEW OF DOC studies

DOC samples with different ratio of Pt/Pd

- Thermal aging at various T
- Field-aged sample

Activity measurement at GM

- HC oxidation
- NO oxidation

Physicochemical characterization at PNNL

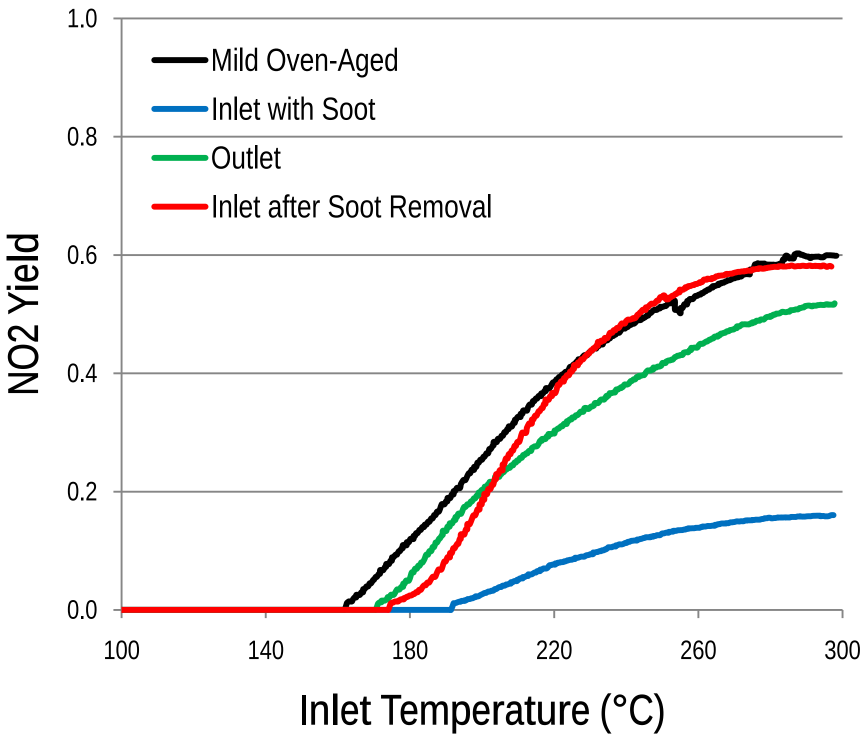
- Focusing on PGM

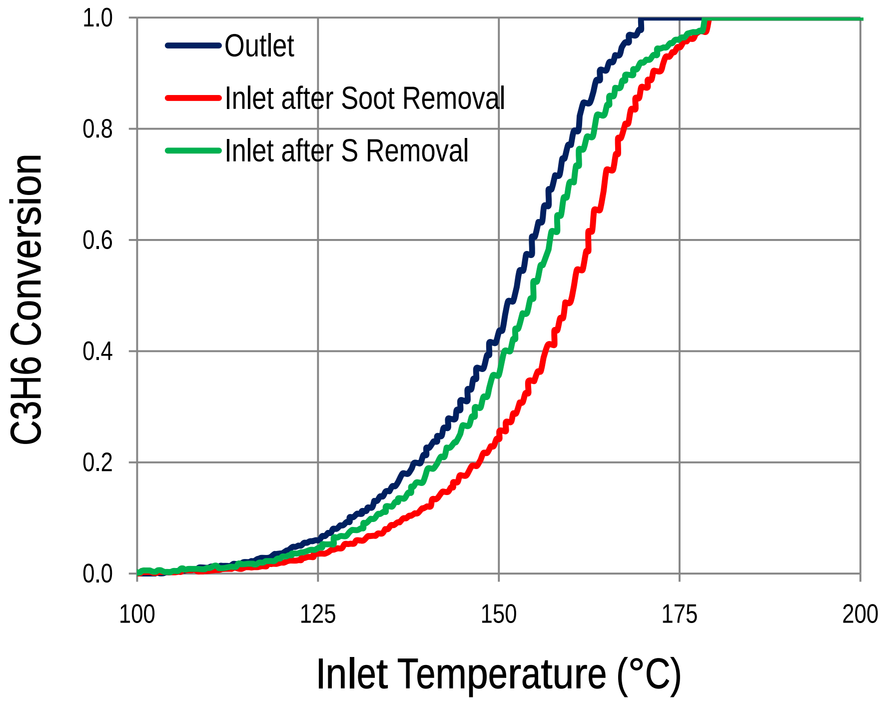
Relationship between activity and active sites as a function of <u>Pt/Pd ratio</u> and <u>aging T</u>

Similarities and differences between <u>lab-aged and vehicle-aged samples</u>

Technical Accomplishments/ Progress/Results

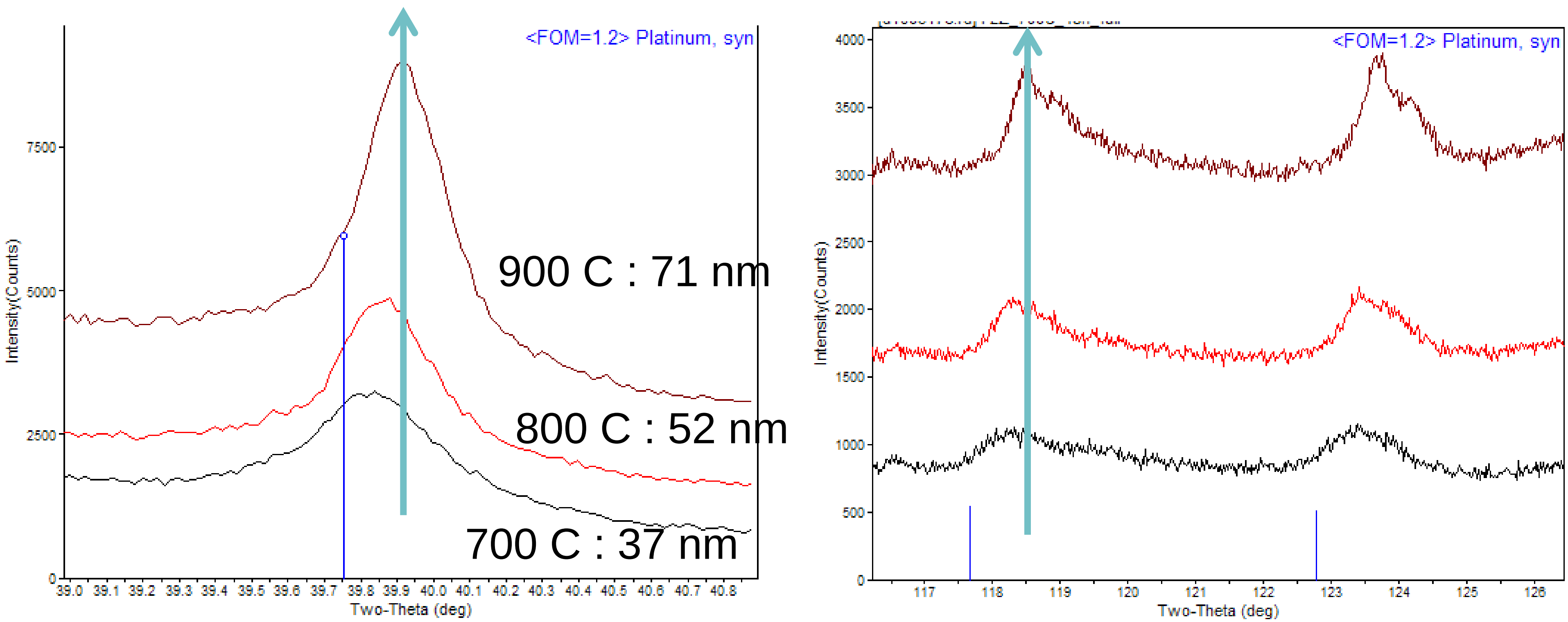
Vehicle-aged (135,000 mile) samples: Inhibition by soot





Physicochemical characterization in progress!

Model DOC: P2Z sample (Pt/Pd=2)



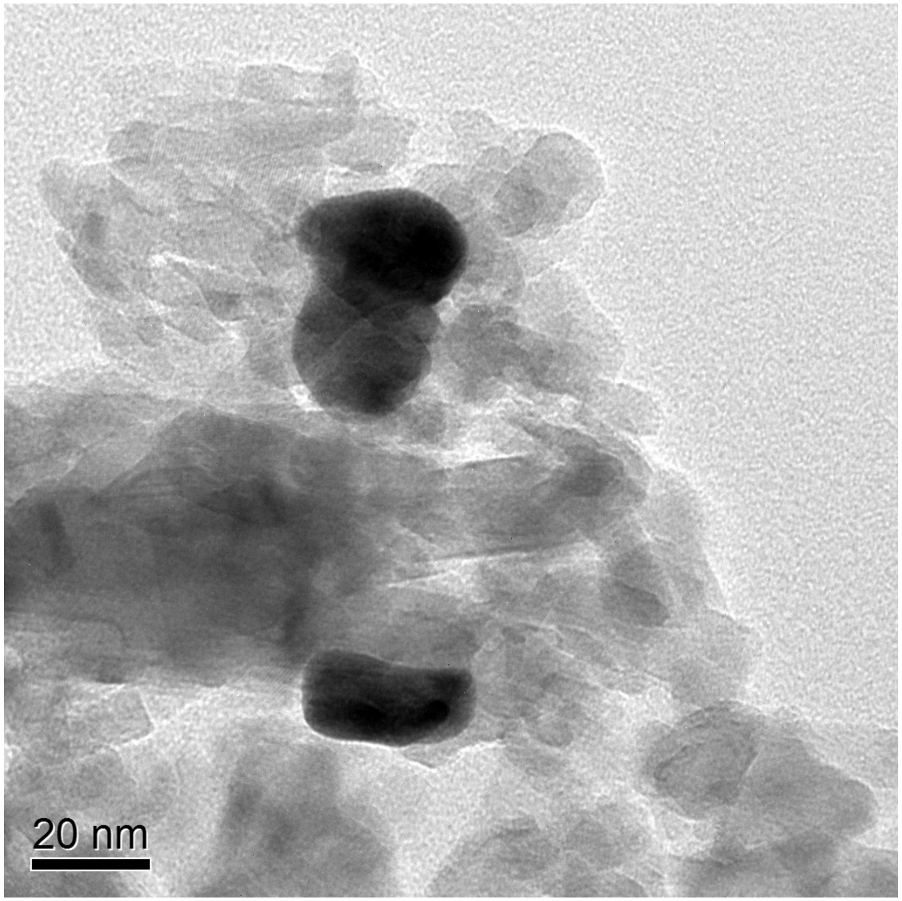
With increasing aging temperature:

- Crystalline size increases
- More Pd-rich Pt-Pd alloy particles are formed, based on XRD peak shifts toward higher 2-theta.

Technical Accomplishments/ Progress/Results

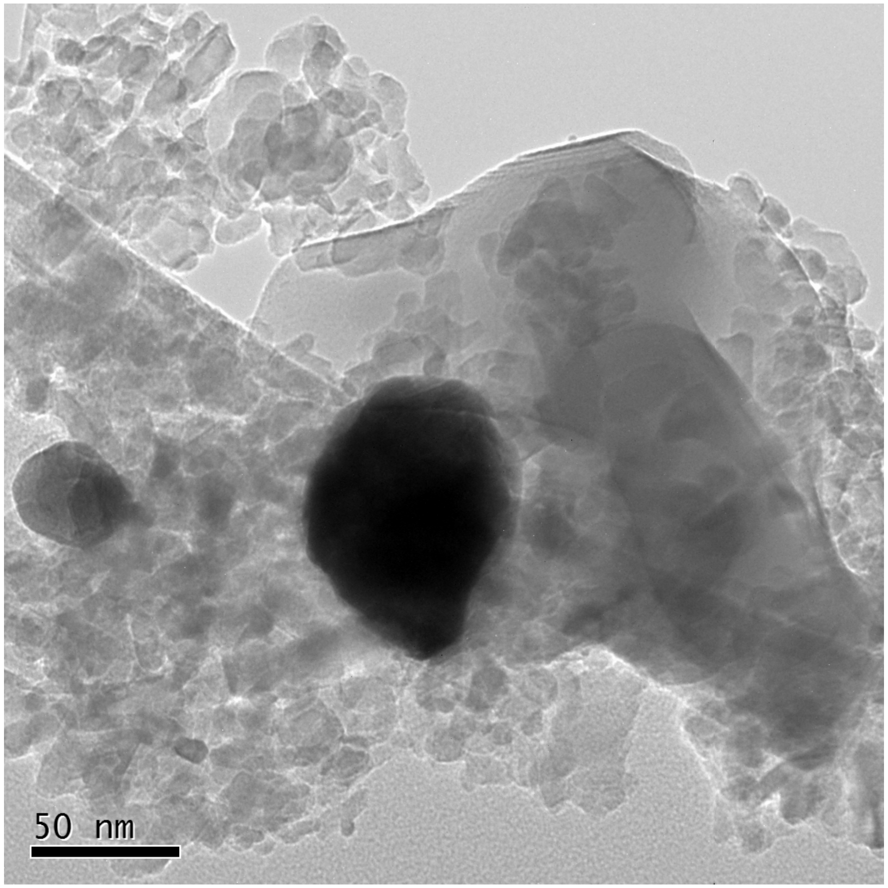
Vehicle Technologies Program

P2Z-700



Size of particles: 15 - 80 nm
Average Pt/Pd = 84/16

P2Z-900



Size of particles: 30 – 100 nm
Average Pt/Pd = 74/26

TEM/EDX show the more enrichment of Pd in the severely aged particles.

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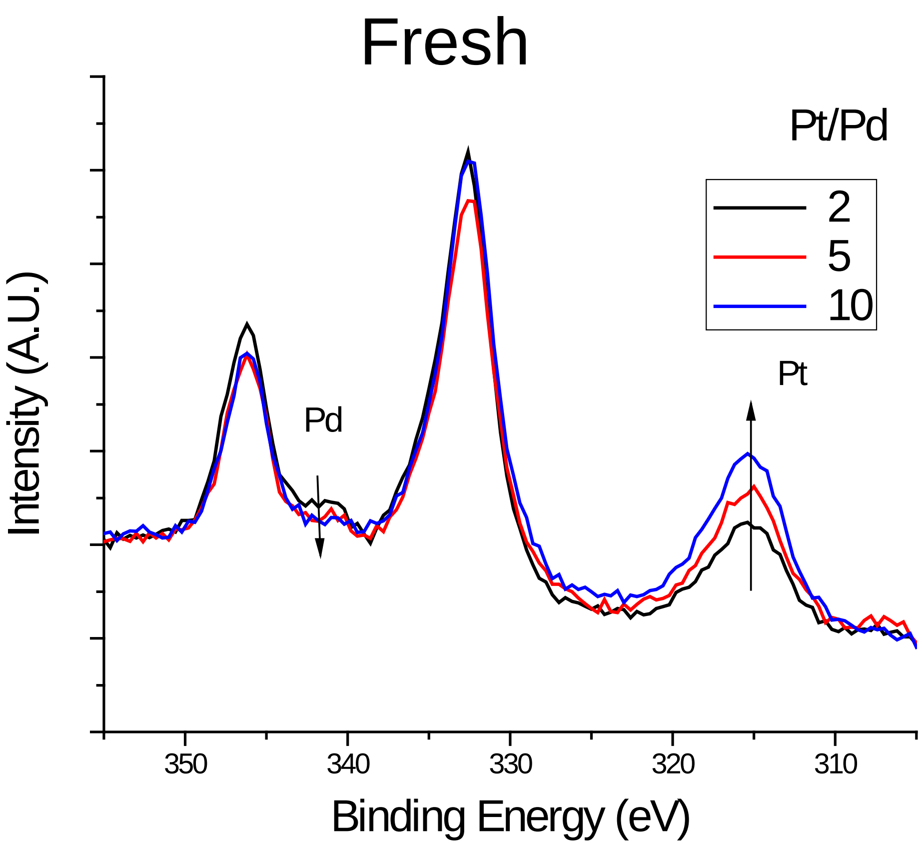
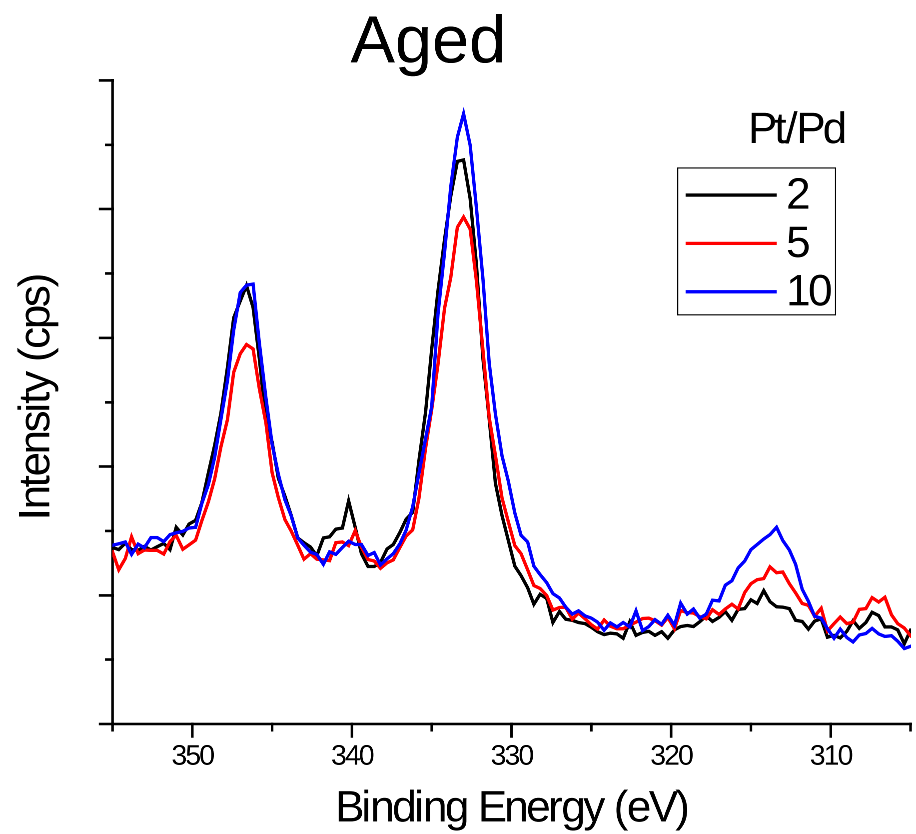
XPS analysis: Pd and Pt behavior of Fresh and Aged samples





- For the case of fresh catalysts, surface concentrations follow those expected for the bulk.
- Thermal aging gives rise to a Pd-enriched surface relative to Pt, compared with fresh samples.

OVERVIEW OF SCR catalyst studies

SCR samples

- Lab-aged at various T and time
- Vehicle-aged samples

Activity measurement at GM

- SCR reaction
- 4-step experiments

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?
→How does it relate to real vehicle-aged samples?

Lab-aged samples: SCR Aging Matrix

Aging Temperature (°C)	Aging Conditions: AIR + 10% H_2O at 6 L/minute Hydrothermal Aging Duration (h)											
	1	2	3	4	8	12	16	36	48	72	120	240
500	✓						✓			✓		✓
700	✓						✓			✓		✓
800	✓	✓					✓	✓	✓	✓ x	✓	✓
850	✓	✓		✓	✓	✓ x	✓	✓ xx				
875				✓	✓ x		✓ xx					
900	✓	✓	✓ x	✓ xx								
950	✓ xx	✓ xx										

Legend	
✓	aged / tested
x	SCR failure benchmark
xx	complete deactivation

→ **32 catalysts aged/tested & XRD …**

[< 70% NO_x conversion (200 - 400°C)]

[< 10% NO_x conversion (200 - 600°C)]

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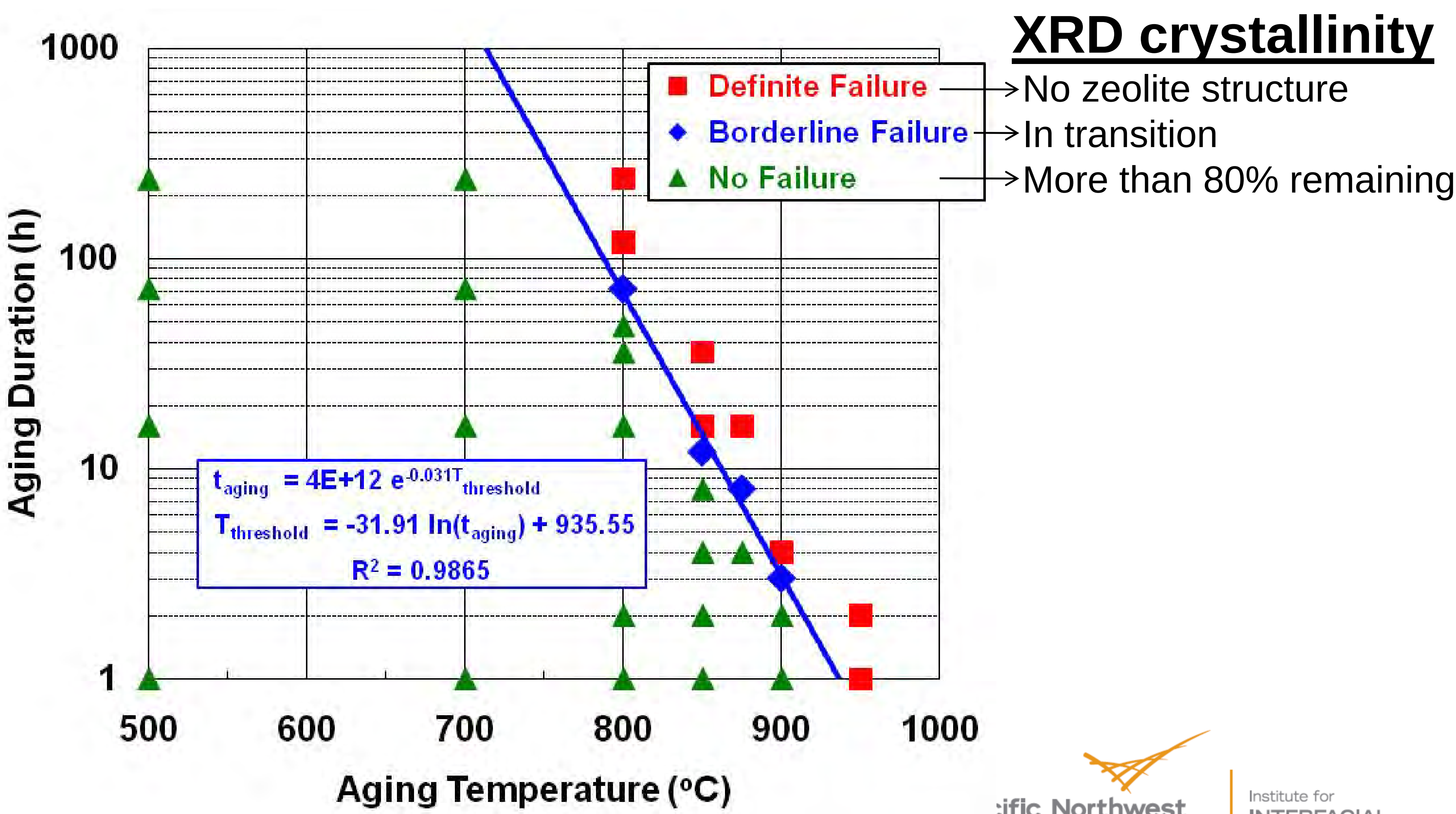
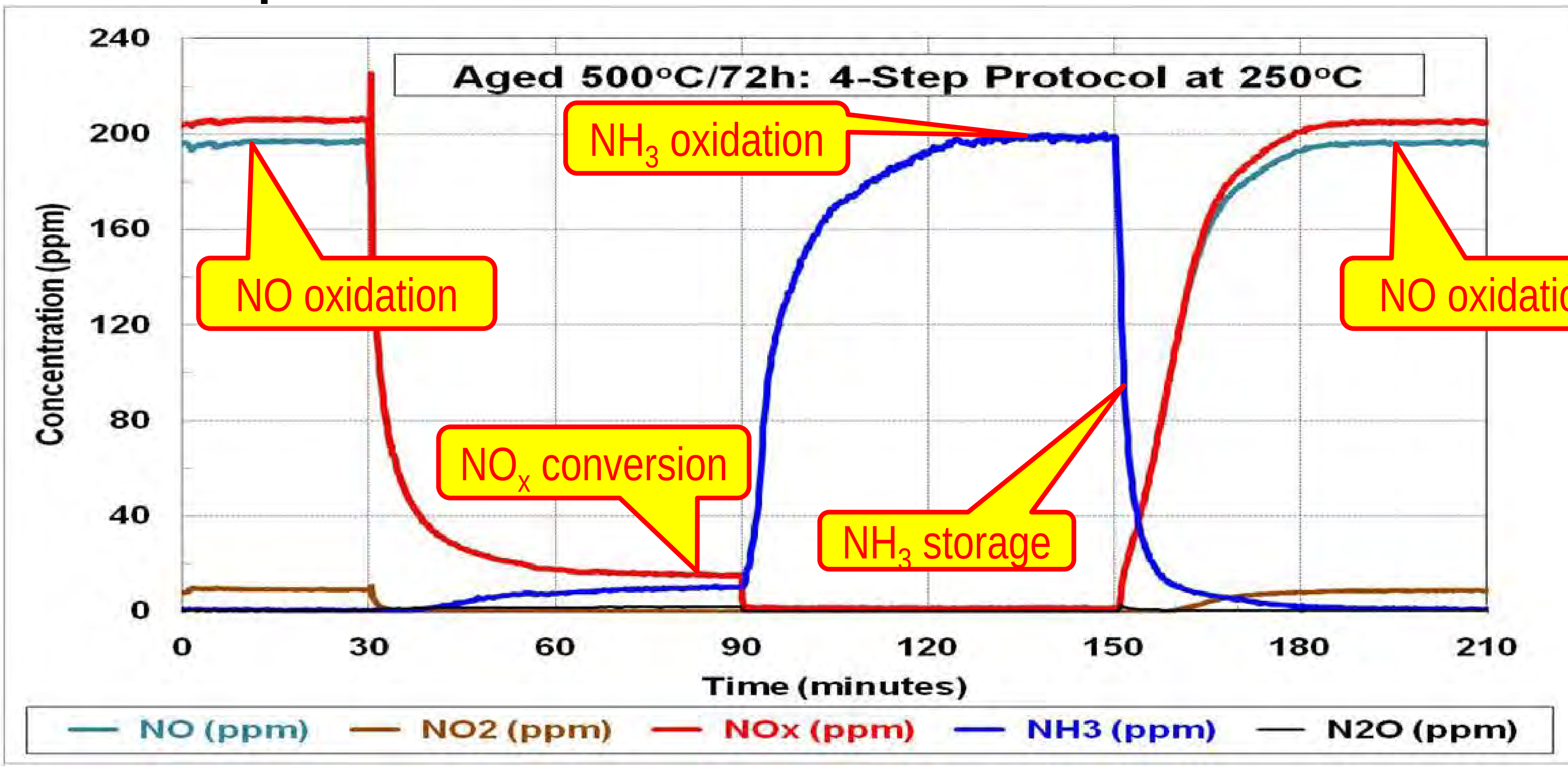
Obtaining the universal curve to determine the failure of catalyst



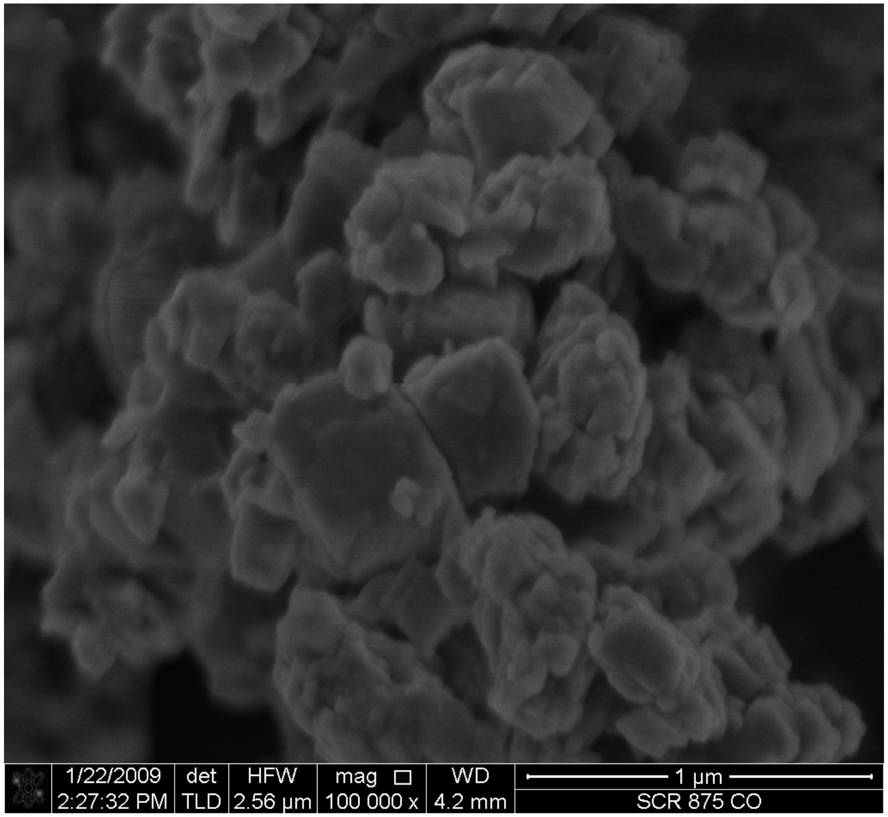
4-Step SCR Test Protocol



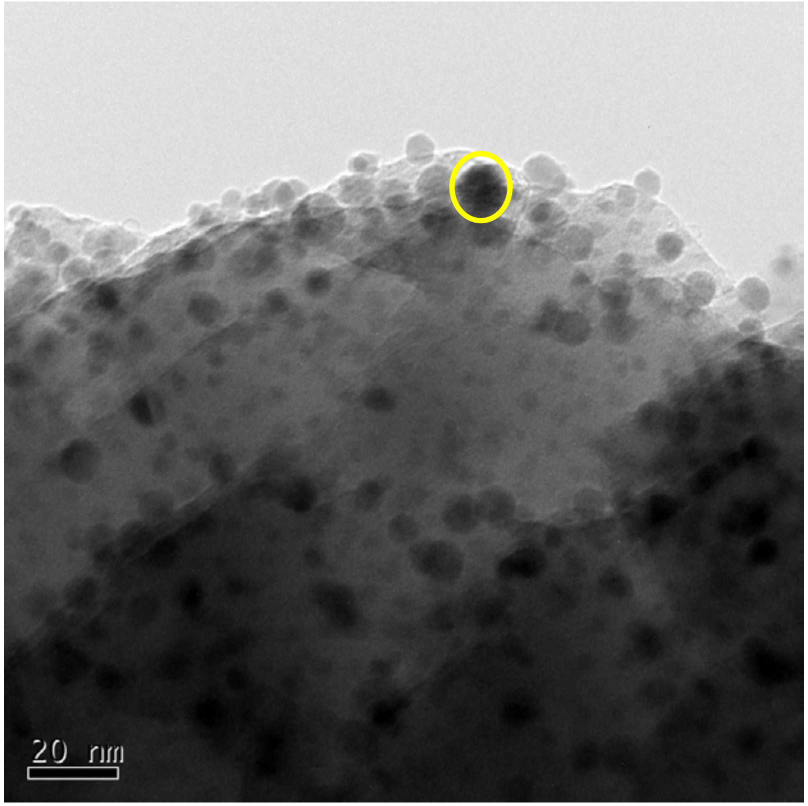
How are the aging-induced changes in the individual reaction steps related to the overall NOx performance deterioration?

→ **In progress**

SEM & TEM: After aging for 40 hrs at 875 ^oC



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.

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 and NMR: structural and catalytic phase information
  - XPS and EPR: 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 modes of 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 lab-aged and vehicle-aged samples, detailed characterization and activity experiments focusing on molecular level active phase changes are in progress:
  - *XPS, XRD, TEM, TPD …*
  - Probe reactions

Activities for Next Fiscal Year

- Full analysis of vehicle-aged samples and comparison with lab-aged samples: similarities and differences
  - Which lab-aging conditions are most appropriate for modeling real world behavior?
  - Effects of poisoning from vehicle-aged samples on:
    - Elemental distribution within the monolith (XPS, SEM/EDX)
    - Catalyst performance (SCR and DOC)
- Complete studies of DOC and SCR degradation mechanisms
  - Analysis and interpretation of the results: comprehensive summary of the correlation between changes in active sites and reaction/adsorption behavior
  - Define "optimized" rapid aging protocols to fit the vehicle aging

Summary

- The Urea SCR technology coupled with a DOC system is being implemented 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 mechanisms through the use of state-of-the-art catalyst characterization methods, with the ultimate goal of developing a "damage equation" relating performance deterioration to the catalyst aging parameters..
- 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.
  - Correlation between lab-aged and vehicle-aged samples is in progress.
- This is a highly interactive and collaborative program between GM and PNNL.

GM

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