Degradation Mechanisms of Urea Selective Catalytic Reduction Technology

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May 16, 2012

ACE027

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Project Overview

Timeline

- Start – December 2008
- Finish – November 2011
- 100% Complete

Budget

- Total project funding
  - DOE – $400K
  - GM – $327K
- Final year (FY11) funding:
  - $100K

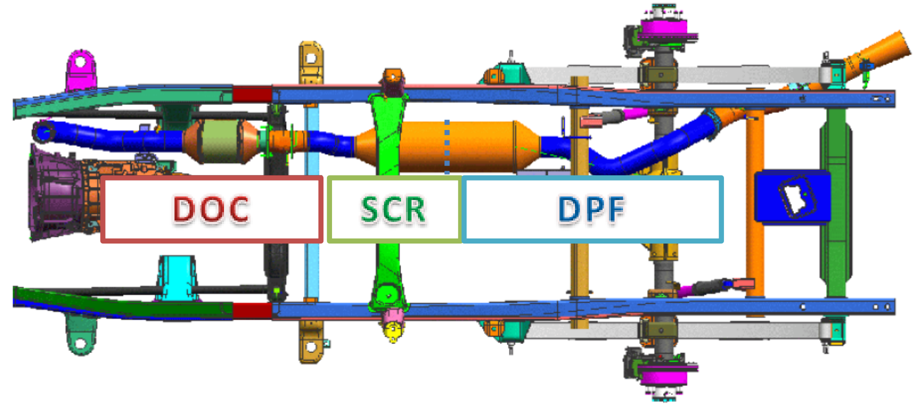
Barriers

- Discussed on next slide

Partners

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

Barriers



GM 6.6L Duramax Diesel Engine – 2011 Exhaust System Configuration

- 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.

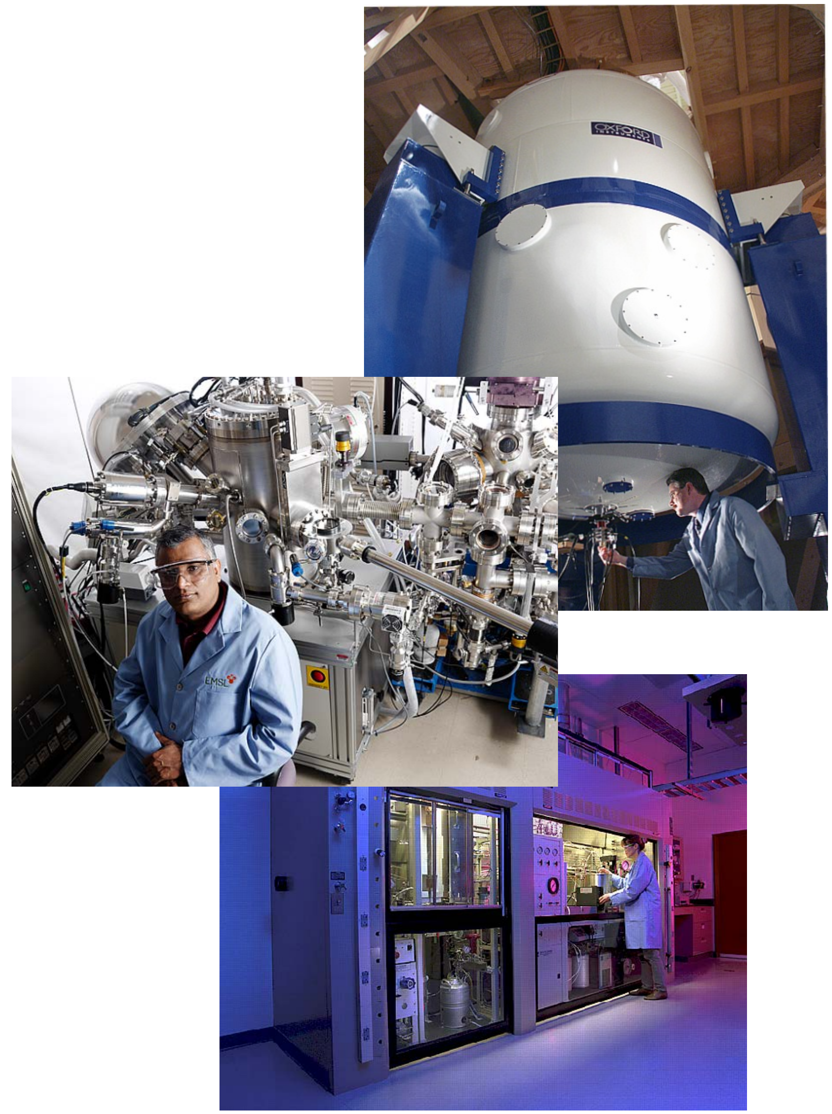
Goals and Objectives

- 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 were provided by GM in monolith form. Both “Model” and “Development” (proprietary) samples were 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

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Sample Preparation
- Laboratory Aging
- Vehicle Aging

Measurement
- Catalytic Activity
- Elemental Analysis

DEC-2008 → NOV-2011

Characterization
- *in-situ* XRD
- TEM/EDX
- XPS
- NMR
- EPR
- TPD/TPR

- ***Jointly use the new understanding to develop correlations relating the degree of performance deterioration to the catalyst aging parameters.***

- **Conference calls were held 5-7 times a year to discuss the results.**
- **Once a year ‘face-to-face’ annual reviews are held. The final (close-out) review was held at GM Research in Warren, MI, October 21, 2011.**
- **Time-line for program was developed and followed (see extra slides below).**

Thermal Durability of Cu-CHA NH_3-SCR Catalysts for Diesel NO_x Reduction

- Laboratory Aging Test Results
  - Reactor and oven aging matrix
  - 4-step SCR test protocol results (NO oxidation, NO_x conversion, NH_3 oxidation, NH_3 storage)
  - Characterization results (XRD, ^{27}Al-NMR, XPS, TEM/EDX)
- Comparison of Vehicle-Aged and Laboratory-Aged Catalysts

Catalyst Samples

Model Catalyst Formulations		
Component	**Washcoat Technology**	**PGM Loading (g/ft^3)**
DOC	PGM w/ zeolite	50 g/ft^3 10 Pt/1Pd
DOC	PGM w/ zeolite	50 g/ft^3 5 Pt/1Pd
DOC	PGM w/ zeolite	50 g/ft^3 2 Pt/1Pd
DOC	PGM w/o zeolite	50 g/ft^3 5 Pt/1Pd
SCR	**Cu-zeolite**	
SCR	**Fe-zeolite**	

PGM RATIO EFFECT

ZEOLITE EFFECT

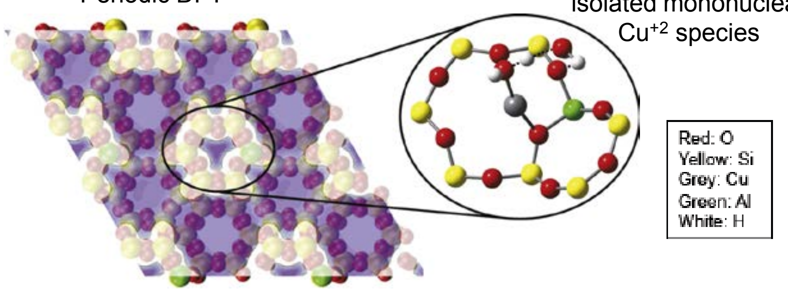
large pore zeolite ~7Å

- HC poisoning issues
- Thermal durability issues

2011 Duramax Catalyst Formulations		
Component	**Washcoat Technology**	**PGM Loading (g/ft^3)**
DOC	PGM w/ zeolite	49 g/ft^3 7 Pt/1Pd
SCR	**Cu-zeolite**	

small pore CHA zeolite ~3.8Å

Periodic DFT



J.-S. McEwan et al. [http://dx.doi.org/10.1016/j.cattod.2011.11.037]

Reference: **BASF Corporation,** US Patent 7,610,662 (2009) – 100% ion exchanged chabazite: 2.8% Cu as copper metal, silica to alumina molar ratio ~ 35:1

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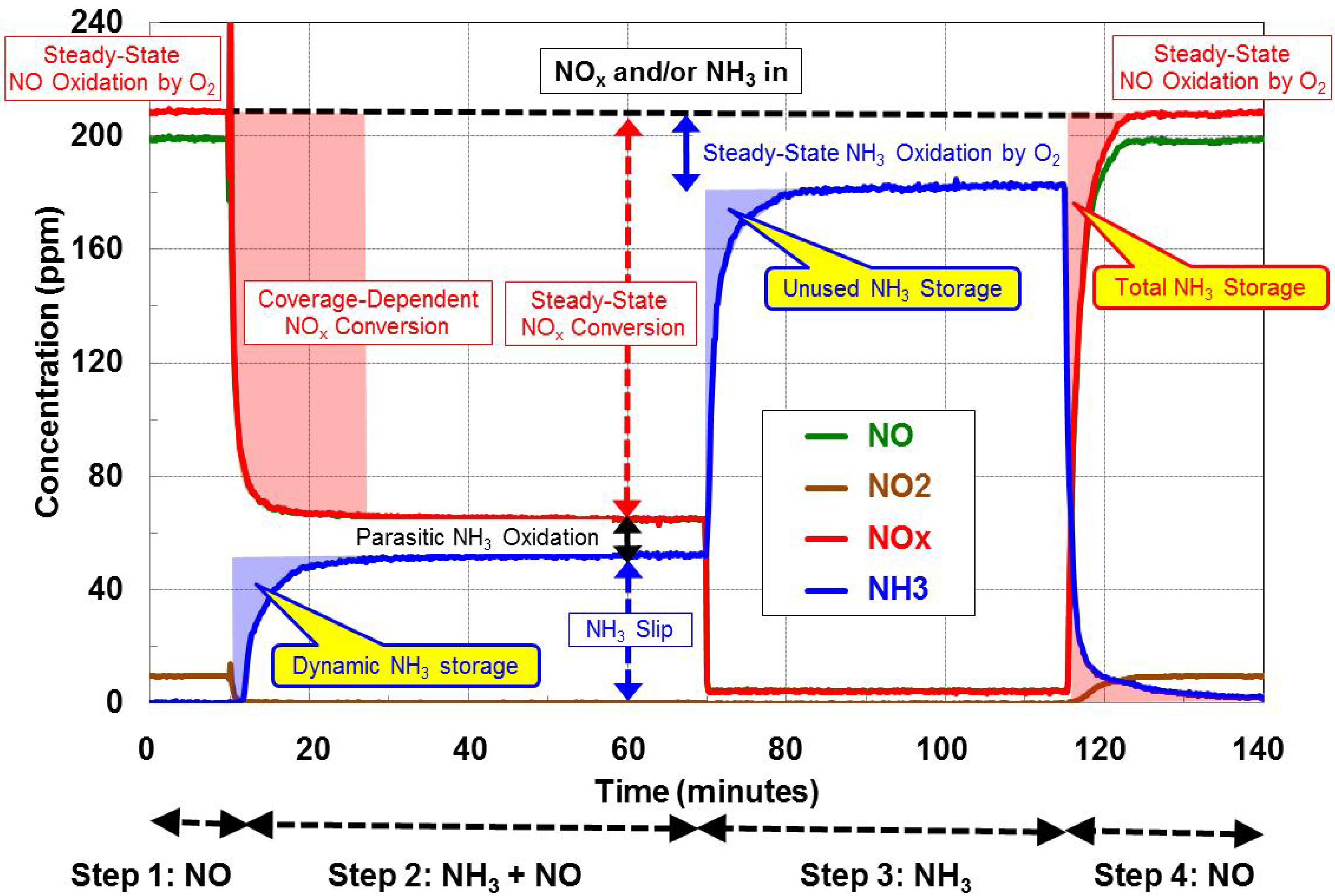
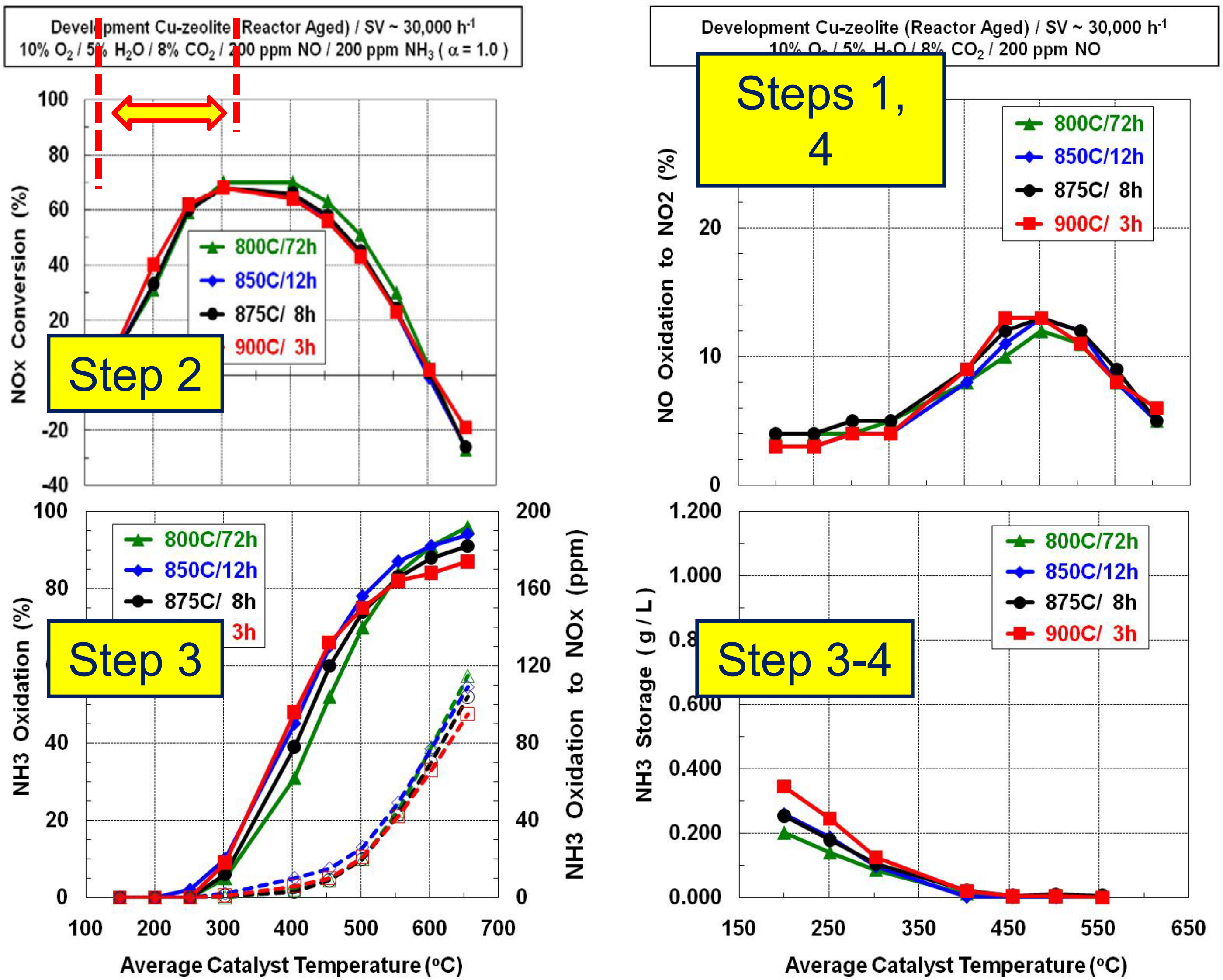
4-Step SCR Test Protocol Used



Reference: K. Kamasamudram, N.W. Currier, X. Chen, and A. Yezerets, Catalysis Today, 151 (2010) 212-222.

Benchmark for SCR Catalyst Failure (OBD)

Vehicle Technologies Program



- Selection criteria of 70% NO_x conversion based on:
  - typical operating T ~ 200 – 400°C
  - 1.0 g/mi engine out NO_x
  - 0.2 g/mi emission standard
  - OBD limit at 0.3 g/mi (1.5x standard)

Similar activity loss occurs at shorter times as aging temperature increases

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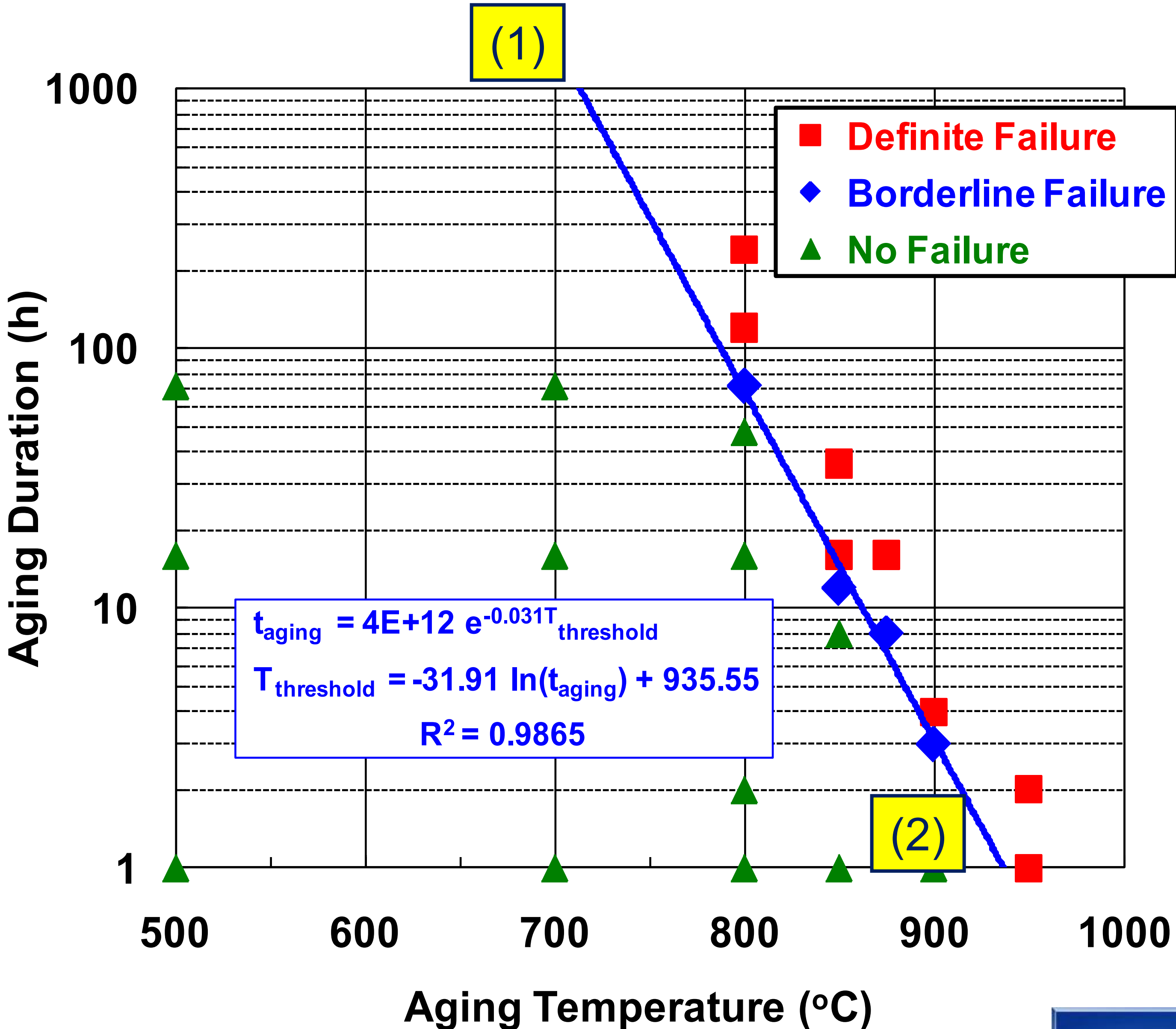
SCR Reactor Aging Matrix

Aging Temperature (°C)	Aging Duration (h) [Reactor Aged: 6 L/minute AIR + 12.5% H_2O]											
	1	2	3	4	8	12	16	36	48	72	120	240
500	✓						✓			✓		✓
700	✓						✓			✓		✓
800	✓	✓			✓		✓	✓	✓	✓	✓	✓
850	✓	✓		✓	✓	✓	✓	✓				
875				✓	✓		✓					
900	✓	✓	✓	✓								
950	✓	✓										

→ 33 catalysts aged and tested

Damage Equation for Reactor Aging



Implications for operation of SCR catalyst:

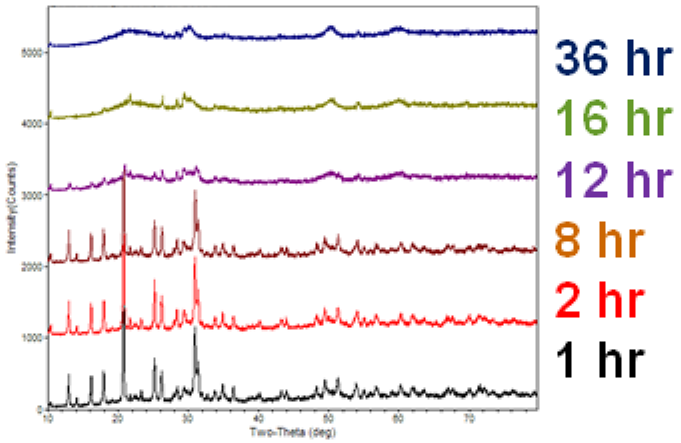
(1) Catalyst would still provide sufficient NO_x conversion efficiency up to 1000 h at 700°C

(2) The "not-to-exceed" operating temperature of this catalyst would be 935°C

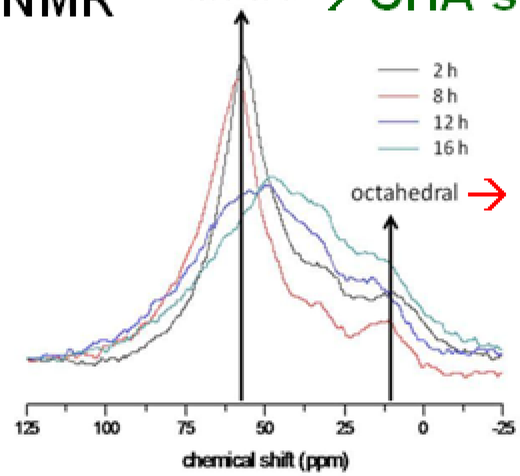
Analysis of Samples Aged at 850ºC

1. Changes in zeolite structure → abrupt collapse

XRD

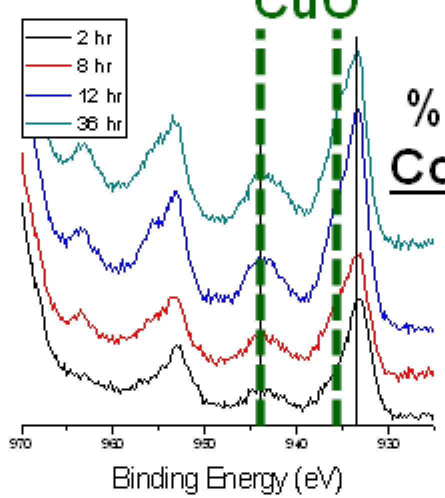


^{27}Al NMR



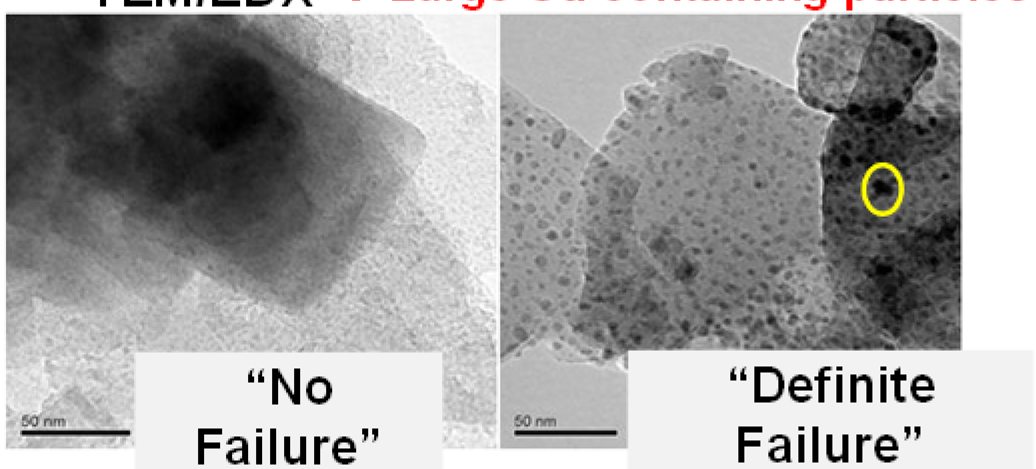
2. Changes in Cu sites → CuO agglomeration

XPS

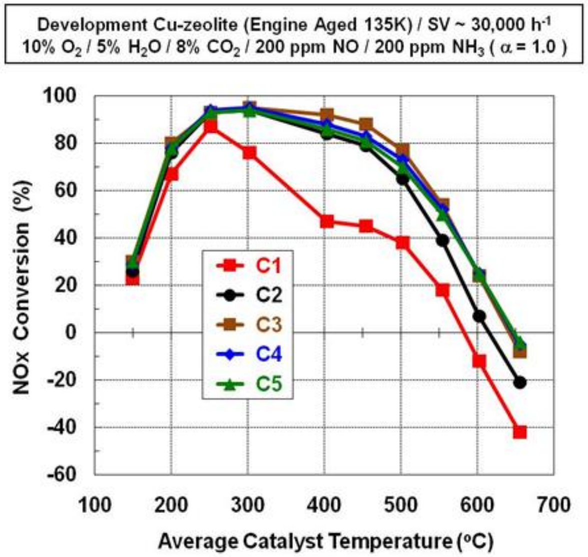


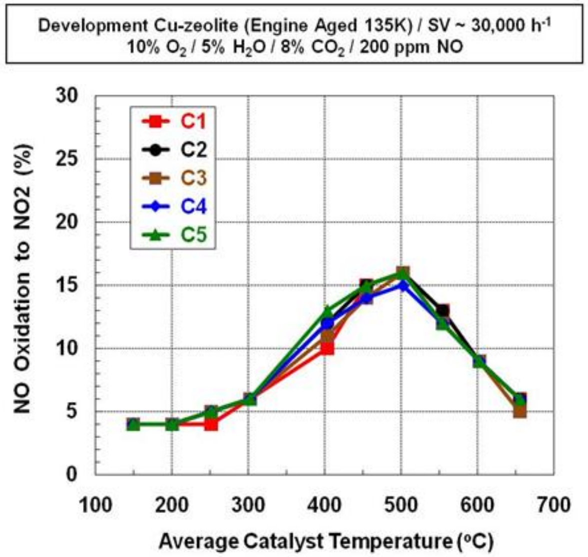
% Cu Surface Concentration
1.36
1.29
0.91
0.70

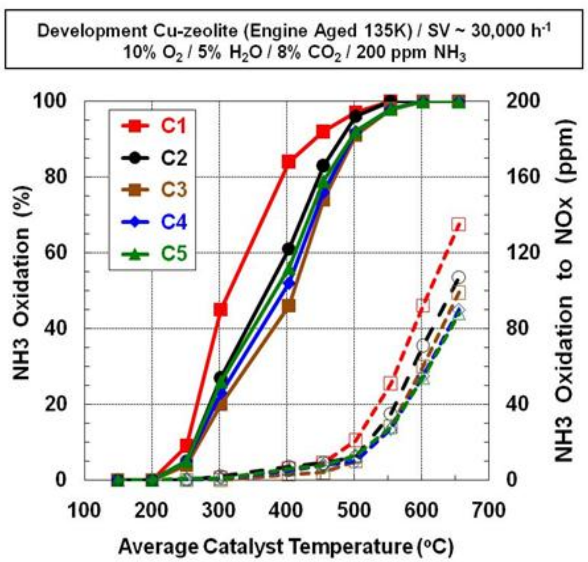
TEM/EDX → Large Cu-containing particles

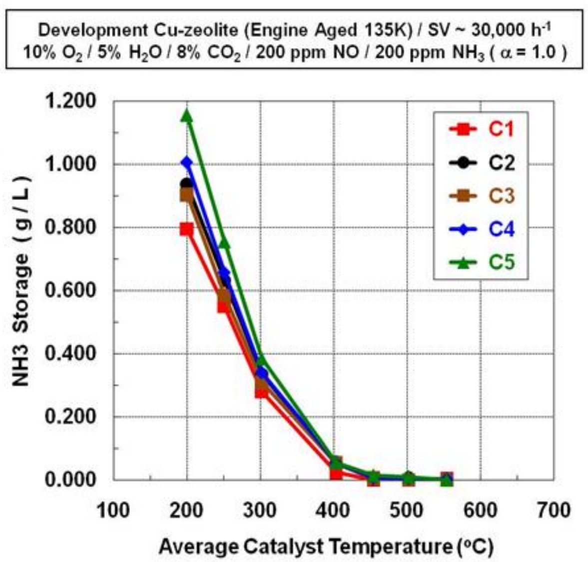


135,000 Mile Vehicle Aged SCR Catalysts









As function of axial position:

- NO_x conversion decreases with first inch (C1) much worse at high T
- No difference in NO oxidation
- NH_3 oxidation and NO_x formation worse for C1
- NH_3 storage decreases C5-C1
- XRD results indicate C1 slightly more thermally damaged

→ **C4** selected as representative of vehicle aging

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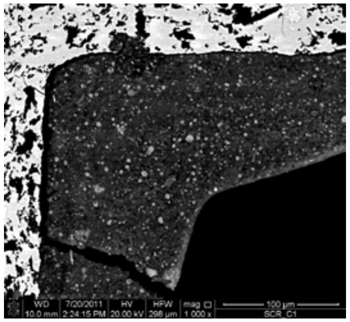
SCR Summary and Conclusions

1) Primary deactivation modes are the destruction of the zeolite structure and the agglomeration of the active metal, well correlated with $DeNO_x$ activity.
2) Damage equation for laboratory aging with respect to time and temperature was obtained.
3) Determined reactor aging conditions and oven aging conditions required to reproduce vehicle aged and threshold aged (OBD) catalyst performance:

Reactor Aged: 135,000 Mile = 16h / 800°C , OBD Threshold = 12h / 850°C
Oven Aged: 135,000 Mile = 72h / 700°C , OBD Threshold = 54h / 850°C

4) Detailed XRD, XPS, ICP and SEM measurements of the vehicle-aged catalysts (not shown) showed high concentrations of Pt and engine oil components on at the front end of the monolith.



Analyzed for C, O, Al, Si, P, S, Cl, Ca, and Zn as a function of depth for monolith cores from the front to the back of the brick.

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Thermal Durability of Diesel Oxidation Catalysts

- Laboratory Aging Test Results
  - Deactivation as a function of PGM Ratio
  - Effects of the additional zeolite
  - Characterization results (XRD, XPS, TEM/EDX)
- Deactivation of Vehicle-Aged Catalysts
- Comparison of Vehicle-Aged and Laboratory-Aged Catalysts
  - Accelerated aging protocol

Catalyst Samples

Model Formulations		
Component	**Washcoat Technology**	**PGM Loading (g/ft^3)**
DOC	**PGM w/ zeolite P10Z-F**	**50 g/ft^3 10 Pt/1Pd**
DOC	**PGM w/ zeolite P5Z-F**	**50 g/ft^3 5 Pt/1Pd**
DOC	**PGM w/ zeolite P2Z-F**	**50 g/ft^3 2 Pt/1Pd**
DOC	**PGM w/o zeolite**	**50 g/ft^3 5 Pt/1Pd**
SCR	Cu-zeolite	N/A
SCR	Fe-zeolite	N/A

PGM RATIO EFFECT

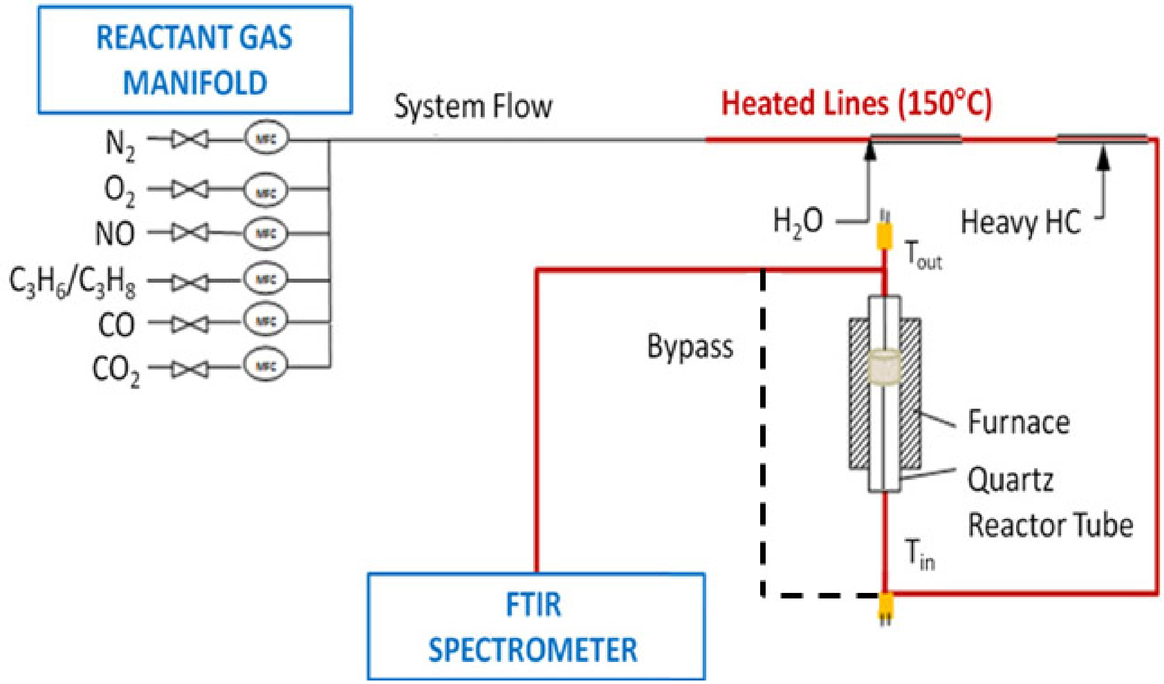
ZEOLITE EFFECT

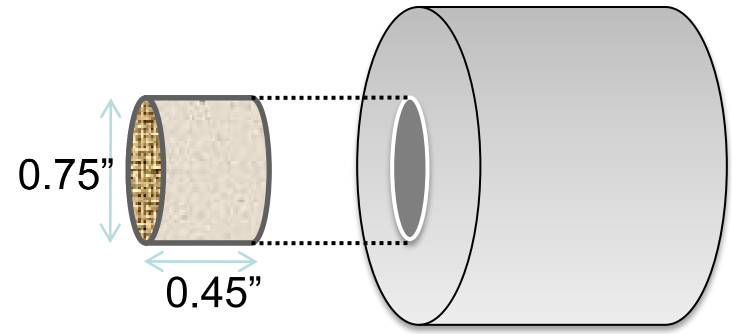
2011 Duramax Catalyst Formulations		
Component	**Washcoat Technology**	**PGM Loading (g/ft^3)**
DOC	**PGM w/ zeolite**	**49 g/ft^3 7 Pt/1Pd**
SCR	Cu-zeolite	N/A

2011 DURAMAX FORMULATION

DOC Lab Reactor Measurements

Vehicle Technologies Program





- GHSV: 30,000 h^{-1}

NO	HC(C_1)	C_3H_6:C_3H_8	O_2	H_2O	N_2
200 ppm	1050 ppm	2.9 : 1	8 %	8 %	Balanced

- Measured Components: $NO/NO_2/HC/CO/CO_2/H_2O$

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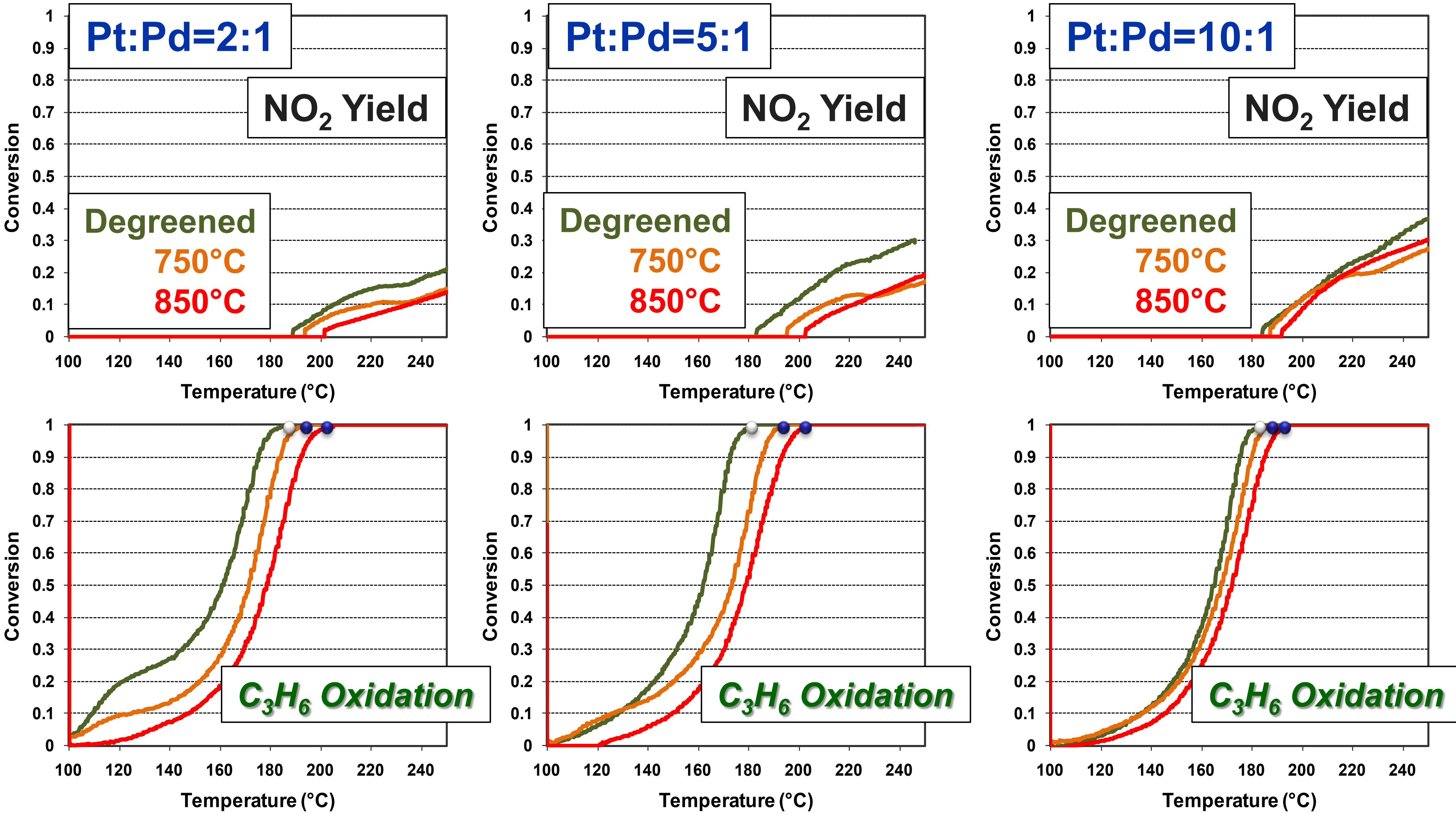
HC and NO Oxidation – Model Catalysts



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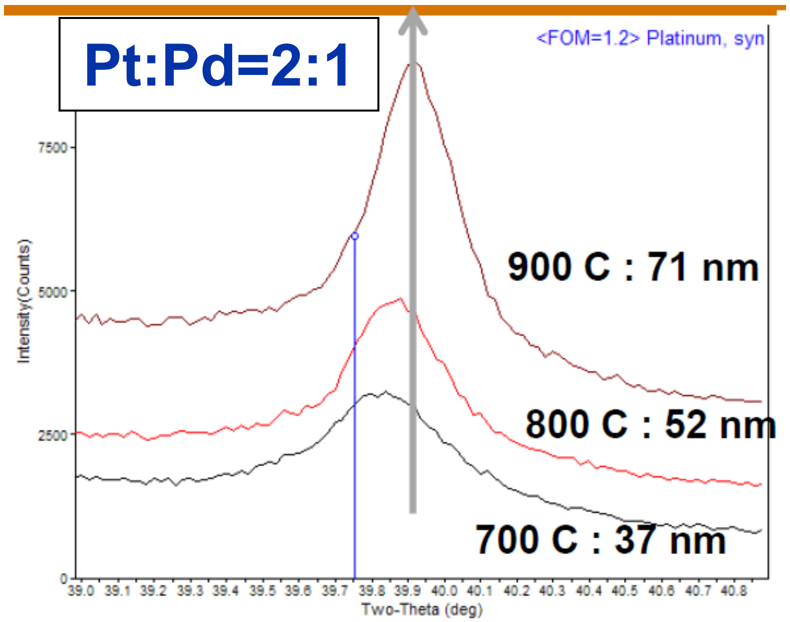
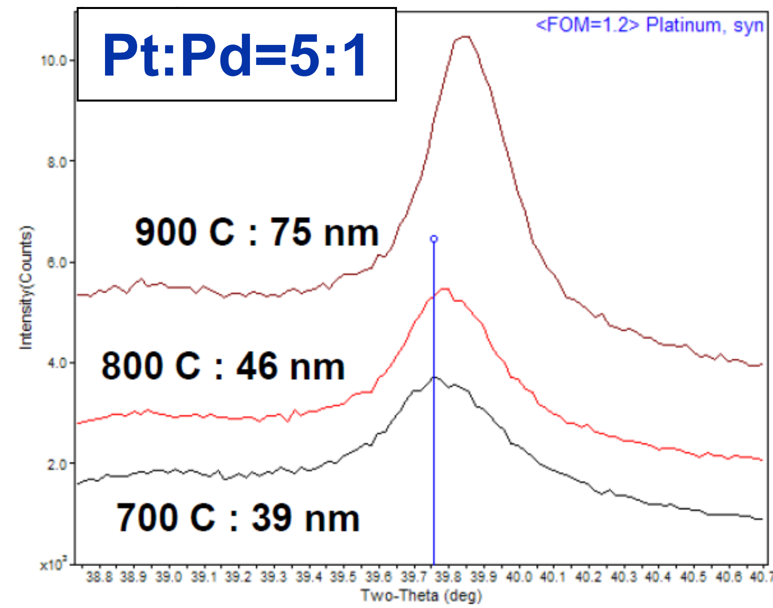
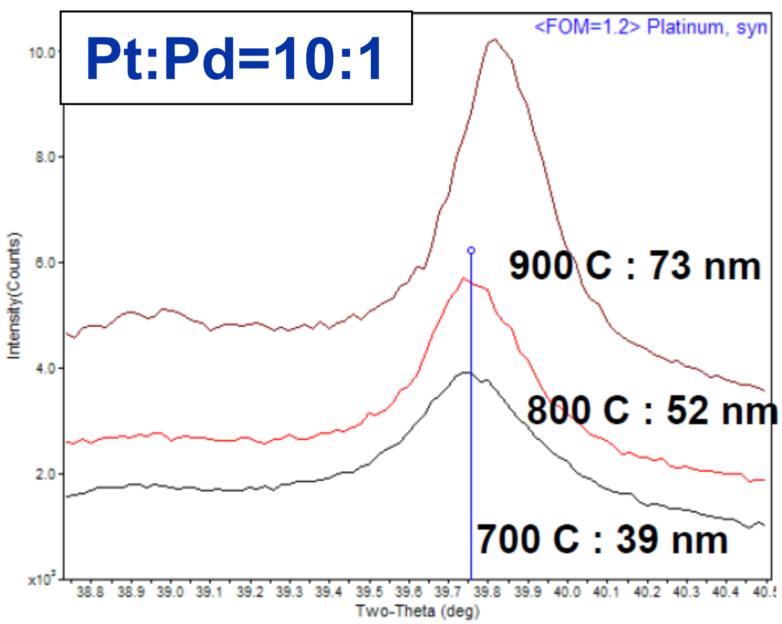
Technical Accomplishments/ Progress/Results







- XRD peak height, shape and location were used to probe deactivation.
- Both particle growth and an increase in Pd concentration occurred at temperatures above 800 °C.

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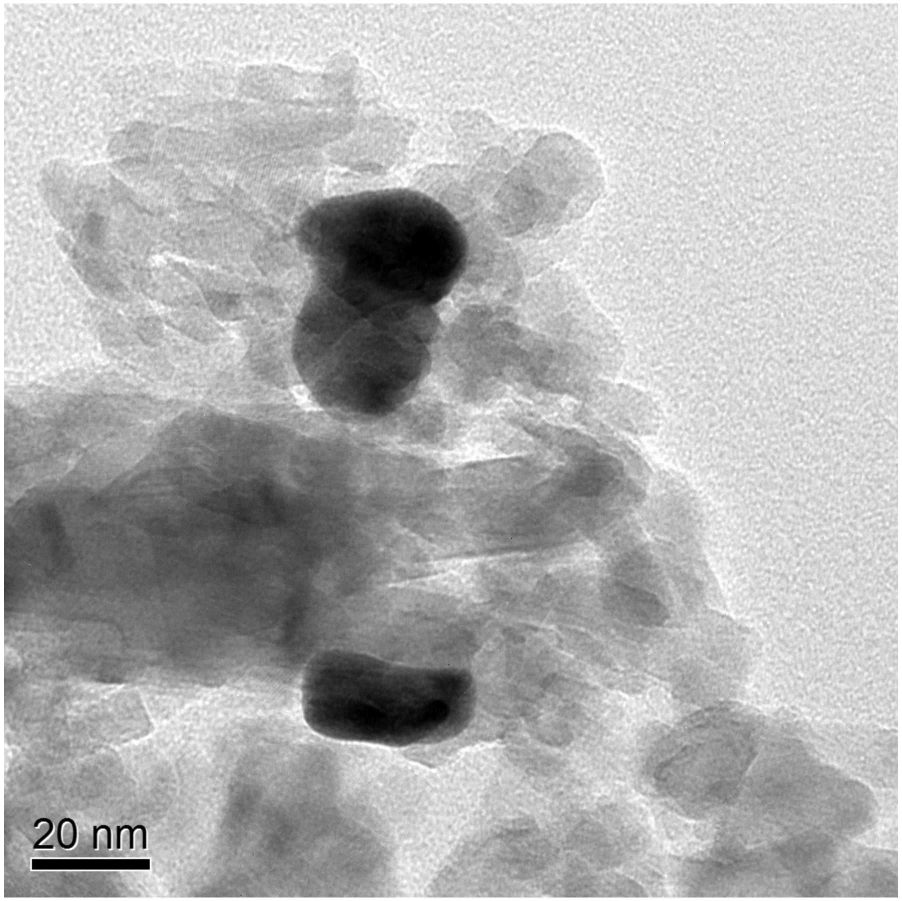
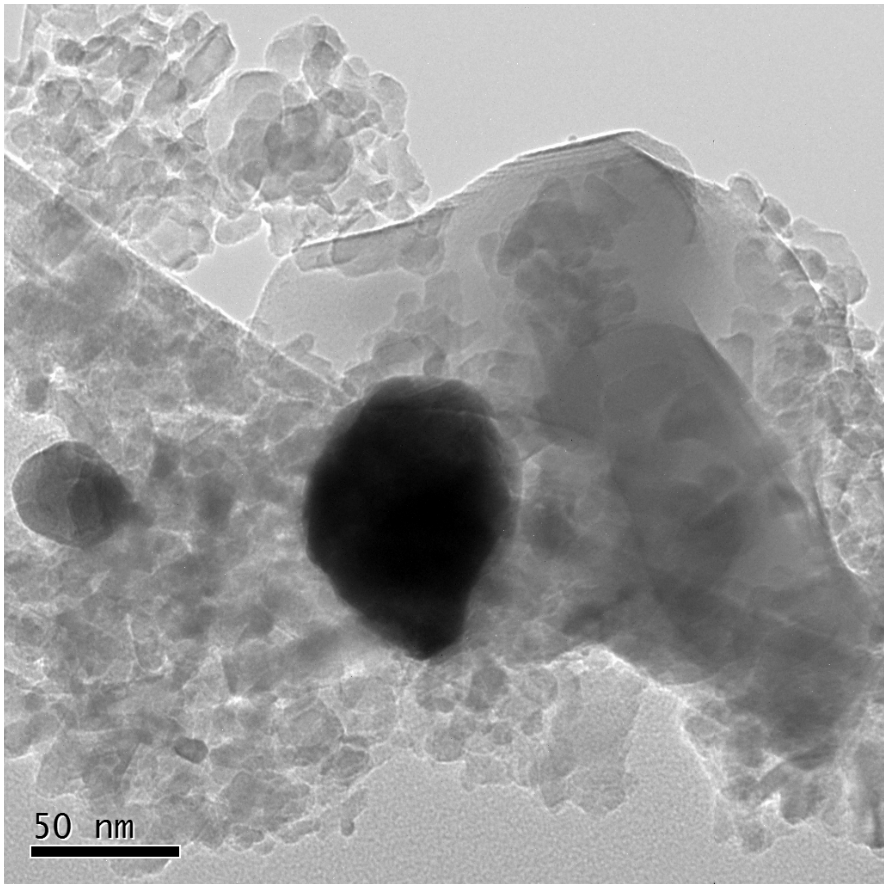
TEM Results Consistent with XRD

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

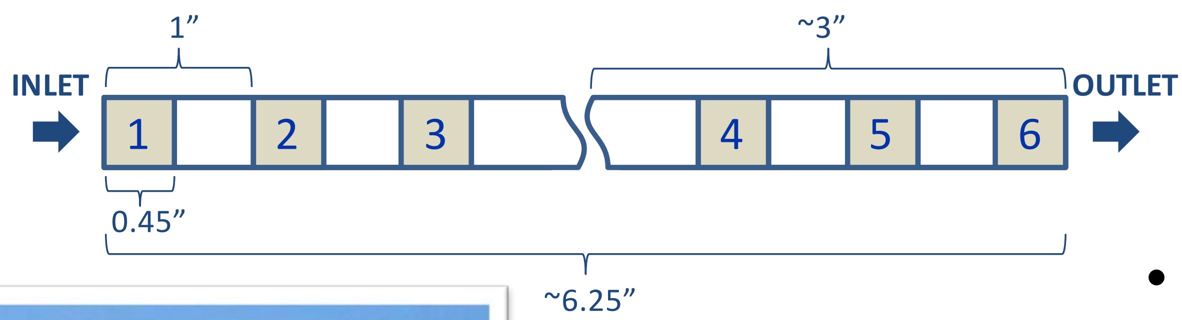
TEM/EDX show the more enrichment of Pd in the severely aged particles.

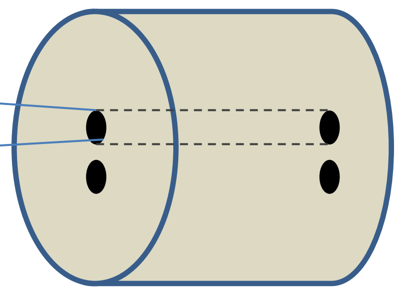
Summary of Model Catalyst Data – Effect of Pt-Pd Ratios

- Trends in performance were observed over DOC samples with different Pt-Pd ratios
- Hydrothermal stability improves when Pd is present
- Light-off performance significantly improved with presence of both Pt and Pd
- NO_2 yield depends directly on Pt-content
- These observations suggest that the Pt-Pd ratio of the DOC can be adjusted to maximize performance depending on the application

Vehicle-Aged DOC

- Full-size DOC was taken from a vehicle driven for 135,000 miles.
- One 0.75” x 0.45” piece from each inch of the core was tested.
- Both HC and NO oxidation measured as before.





CHARACTERIZATION

- XRD (1,2,3,4,5,6)
- TEM/EDX (1,3,5)
- XPS (1,3,4,6)
- In depth SEM/EDX (1, 6)
- In depth XPS (1): before and after oxidation

Accelerated Aging Protocol Development

- Activity of vehicle-aged parts falls between fresh (degreened, "F") and prior baseline ("OB") laboratory aging
- Exception – Inlet (sample 1) before soot removal
- Need an intermediate aging method in order to mimic vehicle aging

Time (h)	600°C	700°C	750°C	850°C	950°C
2.4			F		
4					
16					
24					
48					
72			OB		

All with 10% H_2O

- Too Mild
- Too Severe
- Possibly Comparable
- ***Tested***

- Shorten time for hydrothermal aging
- Improved approximation of deactivation due to vehicle aging

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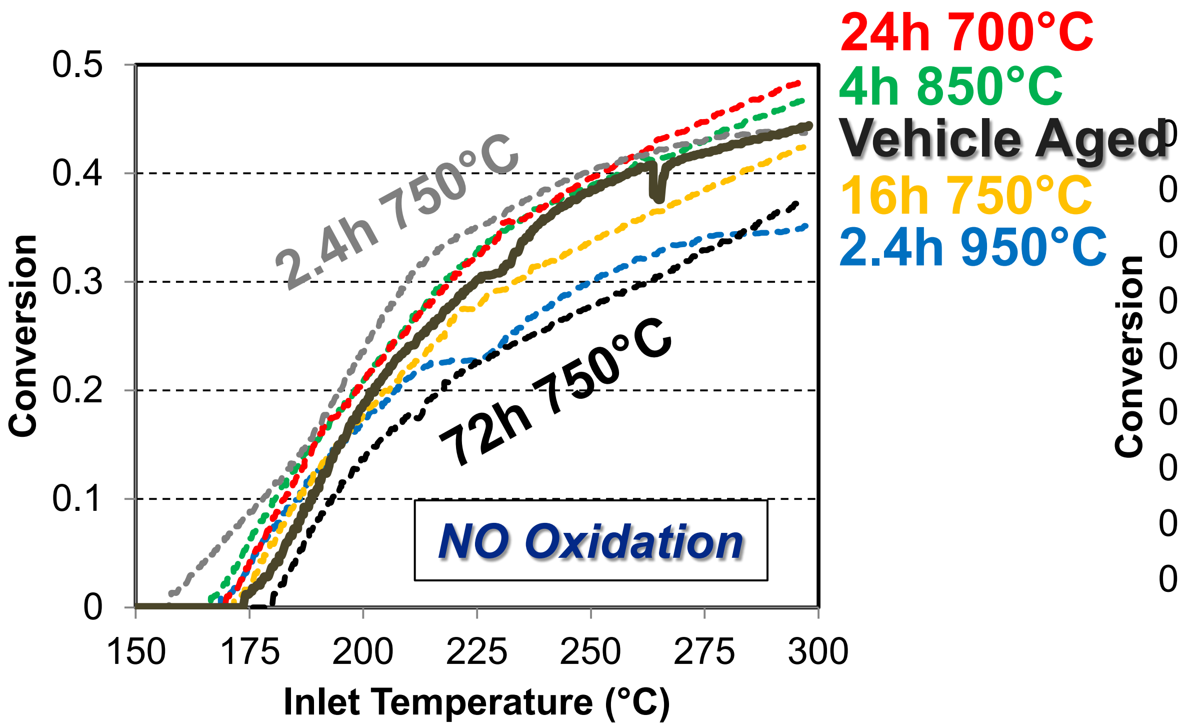
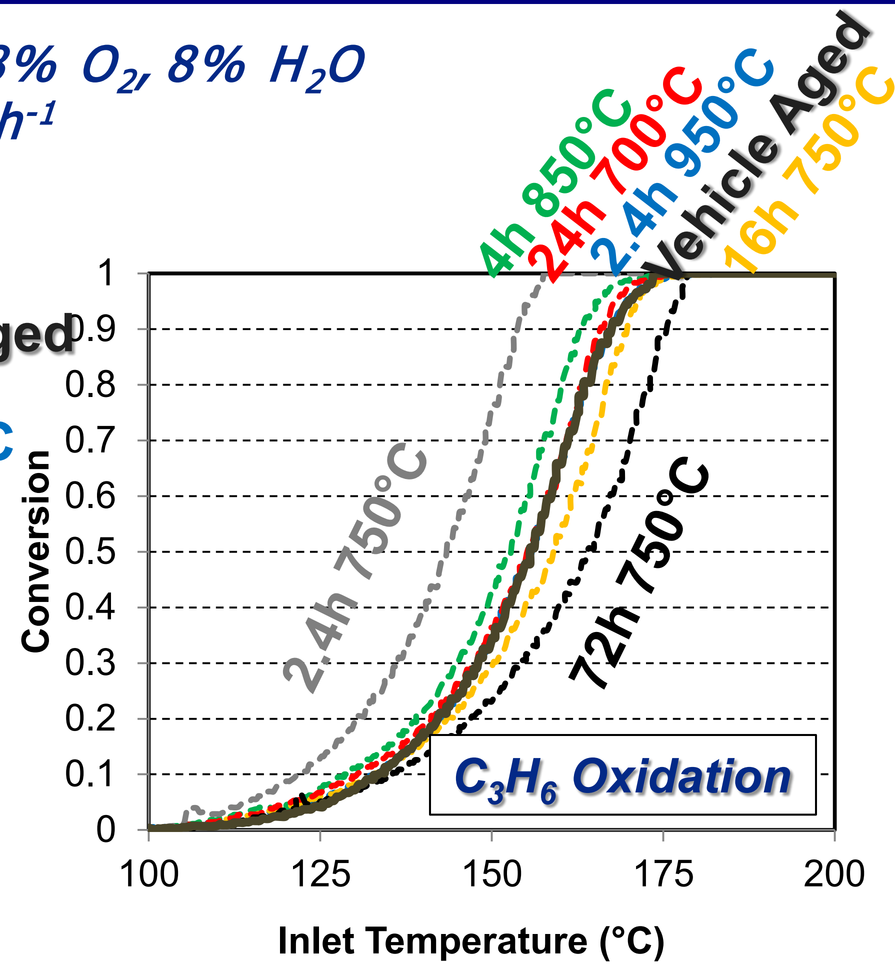
Vehicle Aging vs. Laboratory Aging

200 ppm NO, 260 ppm C_3H_6, 90 ppm C_3H_8, 8% O_2, 8% H_2O
Temp. Ramp Rate: 2 C/min, GHSV: 30,000 h^{-1}





- 24h at 700°C give similar NO and HC oxidation performance

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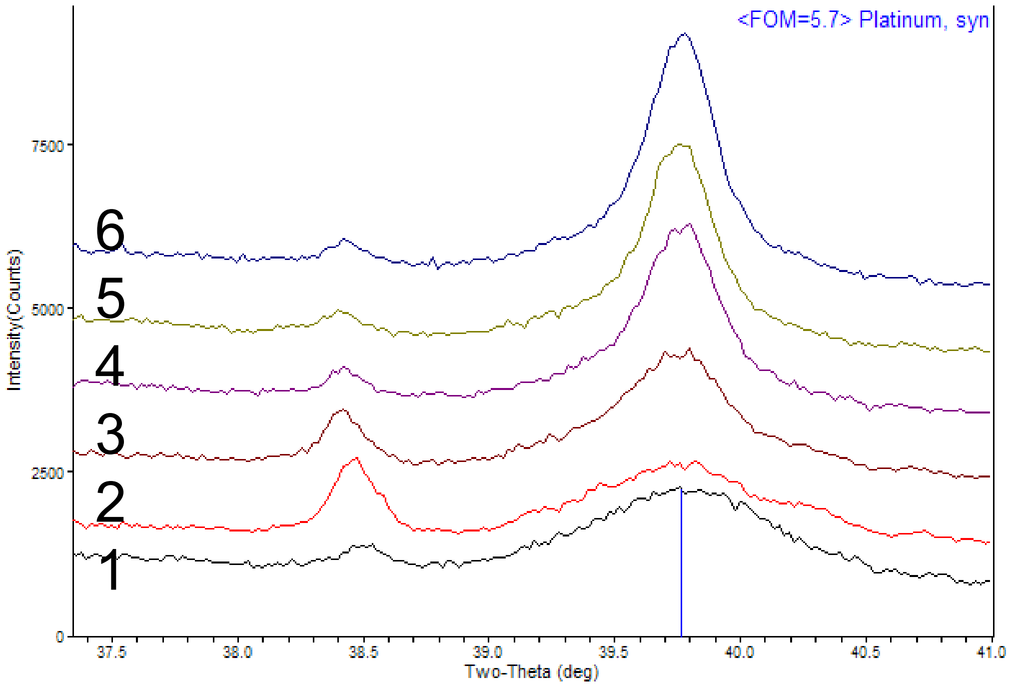
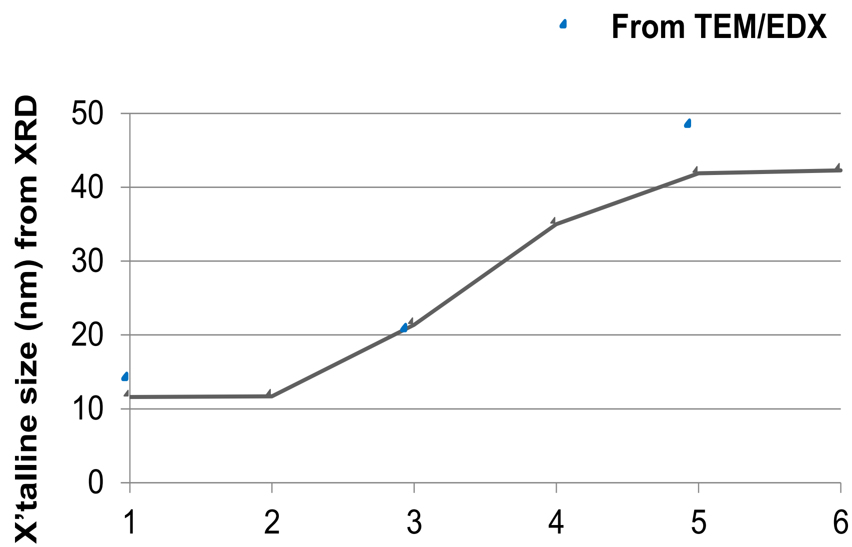
XRD and TEM of Vehicle-Aged Catalyst





- XRD and TEM results are fully consistent with each other.
- PM particles are Pd rich crystallites that increase in size towards the back end (#s 5 and 6) of the DOC monolith.

DOC Summary and Conclusions

- The cause of deactivation on the vehicle-aged DOC includes both thermal sintering as well as sulfur poisoning of the inlet. Thermal damage is more severe at the exit of the monolith, not the inlet.
- Deactivation Mechanism for NO oxidation
  - Accumulation of soot – reversible
  - Sintering of Pt-Pd particles – irreversible
- Deactivation Mechanism for CO/HC oxidation
  - Accumulation of sulfur – reversible
  - Sintering of Pt-Pd particles – irreversible
- Correlation was developed to accelerate the aging protocol, and a more accurate prediction of a 135,000 mile vehicle aged DOC was achieved.

Activities for Next Fiscal Year

- N/A – program completed

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 has been 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 has led to the development of laboratory rapid aging protocols.
- *This has been a highly interactive and collaborative program between GM and PNNL.*