2009 DOE OVT
Merit Review

# Diesel Soot Filter Characterization and Modeling for Advanced Substrates

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**ace_23_gallant**



Pacific Northwest
NATIONAL LABORATORY
*Proudly Operated by* Battelle *Since 1965*

# Overview

## Timeline

- March, 2005
- September, 2009
- 90%

## Budget

- Total project funding
  - DOE $1,100,K
  - DOW >$1,100,K
- Funding received in FY07
  - $303K
- Funding for FY08
  - $267K

## Barriers

- Accurate representation of the substrate
- Accurate representation of a catalyzed washcoat.
- Chemical LNT Kinetic model

## Partners

- CLEERS

# Objectives

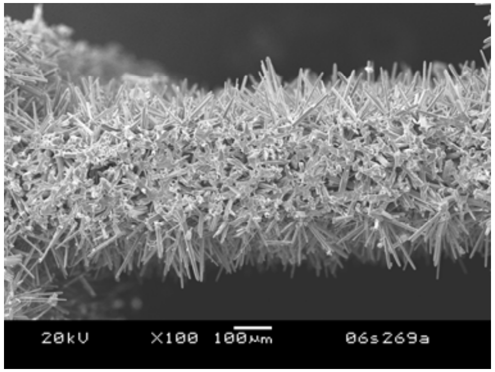


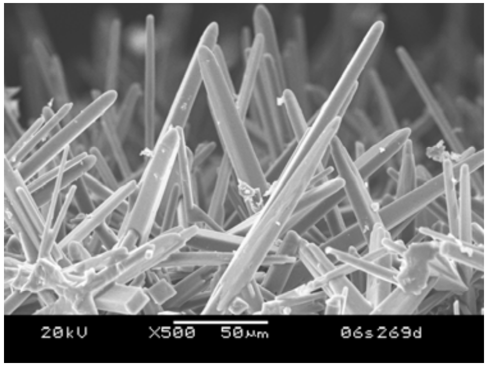
## Overall Objective:

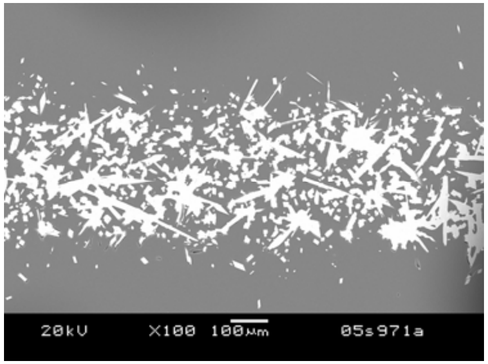
- Adapt the micro-modeling capabilities *developed by the CLEERS Program* to investigate substrate characteristics and spatial location of catalyzed washcoat on back pressure, soot regeneration and LNT function.

## ’09 Objectives:

- Compare ‘flow through’ to ‘wall flow’ ACM performance
- Incorporate LNT kinetics into the micro-model to answer key questions on ACM substrate attributes.



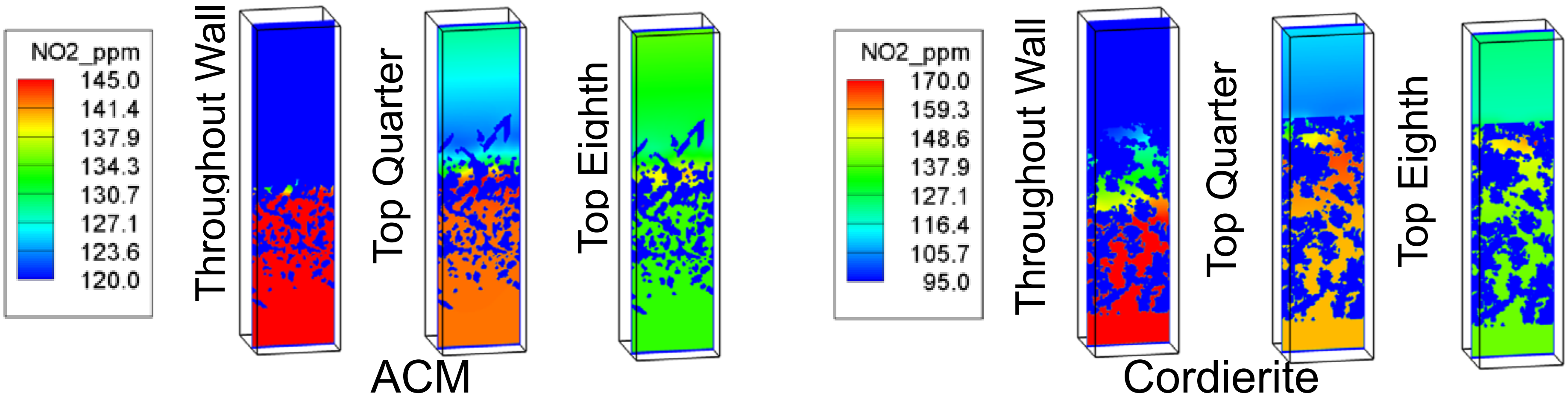
# ‘09 Milestones

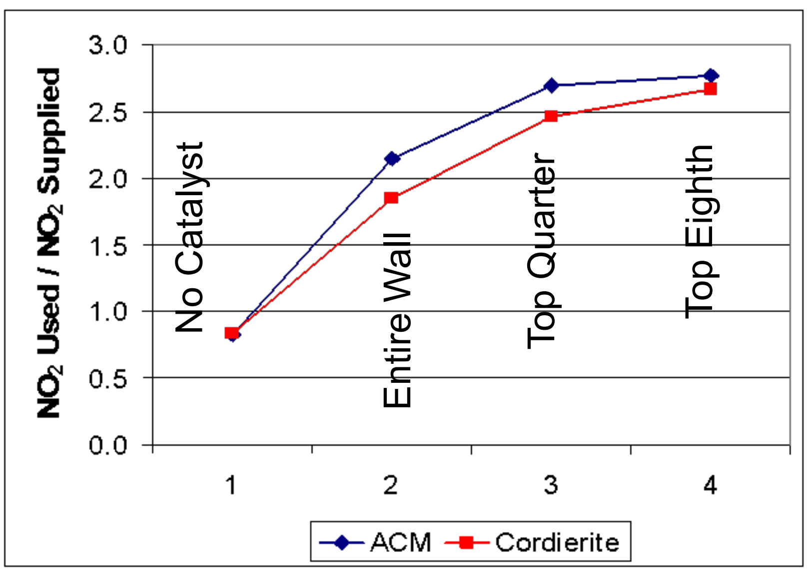
- Compare LNT ‘flow-through’ versus ‘wall-flow’ using single / mini  channel reactor – June ’09
- Incorporate LNT kinetics into Micro model and exercise model– July ’09
- Final report – September ‘09

# ’09 Approach
# LNT Concept

- Establish a substrate / LNT model to be investigated.
- Develop a list of Key Questions to be answered by the micro model or by experimentation.
- Investigate kinetic models and incorporate into micro-model.
- Mini brick LNT washcoated samples for investigating coupled reactions and 1-D transport across the thickness of the wall.
- Validate modeling with single / mini channel reactor

# '08 Accomplishments
## DOC Catalyst Distribution




- Some back-diffusion of $NO_2$ from catalytic reactions within wall.
- Wall provides significant resistance to diffusion.
- $NO_X$ recycle promoted by placing catalyst close to soot

# '08 Accomplishments

## Single Channel – DOC Kinetics Validation

### Reaction Order of NO and O2

$O_2$ order: 300 ppm of NO with 5 – 15% of $O_2$
NO order: 10% of $O_2$ with 50 – 500 ppm of NO

| Catalyst | NO order | $O_2$ order |
|---|---|---|
| Fresh | 0.51 | 0.51 |
| Aged | 0.52 | 0.53 |

According to Mulla, et al. J. Catal. 241 (2006) 389,

| | NO | $O_2$ |
|---|---|---|
| Fresh $Pt/Al_2O_3$ catalyst | 1.09 | 0.86 |
| Sintered $Pt/Al_2O_3$ catalyst | 1.12 | 0.69 |

Kinetics from single channel experimental setup using DOW DOC provide reasonable results as compare to published value.

# '09 Accomplishments LNT Washcoat Concept

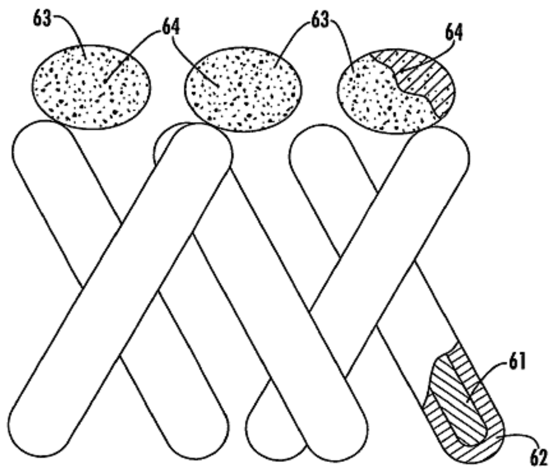



FIG. 6

US 2006/0193757 A1

62: Combined NOx adsorber and 3 Way catalyst
63: Alumina/DOC
64: DOC

- Mini brick samples ( with and w/o DOC) which are representative of LNT catalyst.
- Collaborate on techniques for characterizing the catalyst surface layer.
- Design experiments and micro modeling to answer key questions

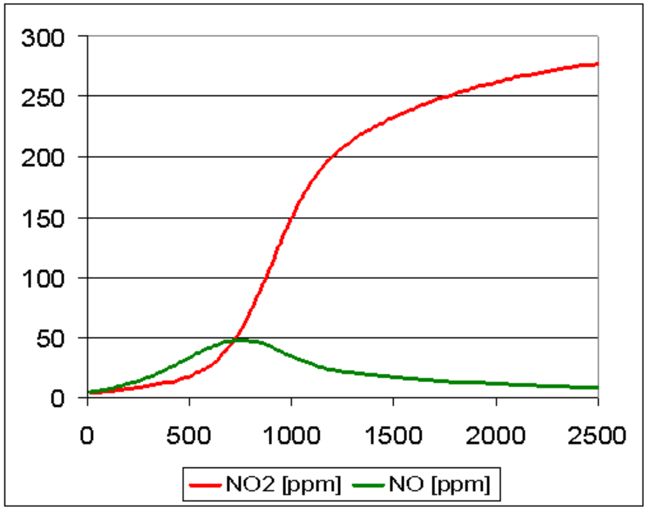
# '09 Accomplishments
# Key Questions – LNT Concept

- Is there an advantage of additional oxidation catalyst upstream versus uniformly dispersed?
- What is the performance difference between "Flow Through' versus 'Wall Flow' conversion for ACM.
- What is the impact on adsorption of $NO_x$ on passive soot oxidation rates?
- Does reduction of $NO_2$ to NO by soot oxidation inhibit rates of $NO_X$ adsorption in subsequent catalyst?
- Is the oxidation of reductants by upstream precious metal catalysts a significant barrier to $NO_X$ reduction during rich phases?

# '09 Accomplishments
## $NO_x$ Adsorber Kinetics

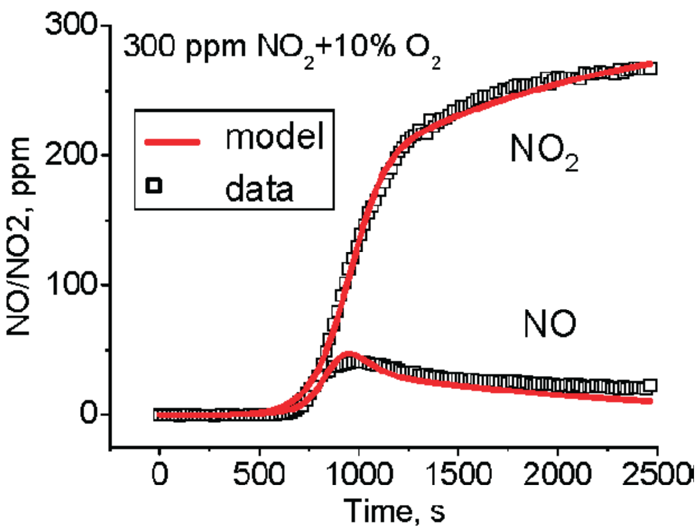
- A literature survey of 16 recent papers
- Review Criteria:
  - Simplest possible kinetic model for $NO_X$ adsorption
  - Model parameters should be documented
  - Generic catalyst, such as $Pt/BaO/Al_2O_3$
  - Catalyst composition and loading should be documented
  - Realistic operating conditions
  - Generalized model covering the widest possible range of operating parameters
- Top pick:
  - Cao, L., et al., *Kinetic Modeling of NOx Storage/Reduction on Pt/BaO/Al2O3 Monolith Catalysts.* Industrial & Engineering Chemistry Research, 2008. **47**(23): p. 9006-9017.

# '09 Accomplishments Micro-Model Results




**Adjusted Parameters**

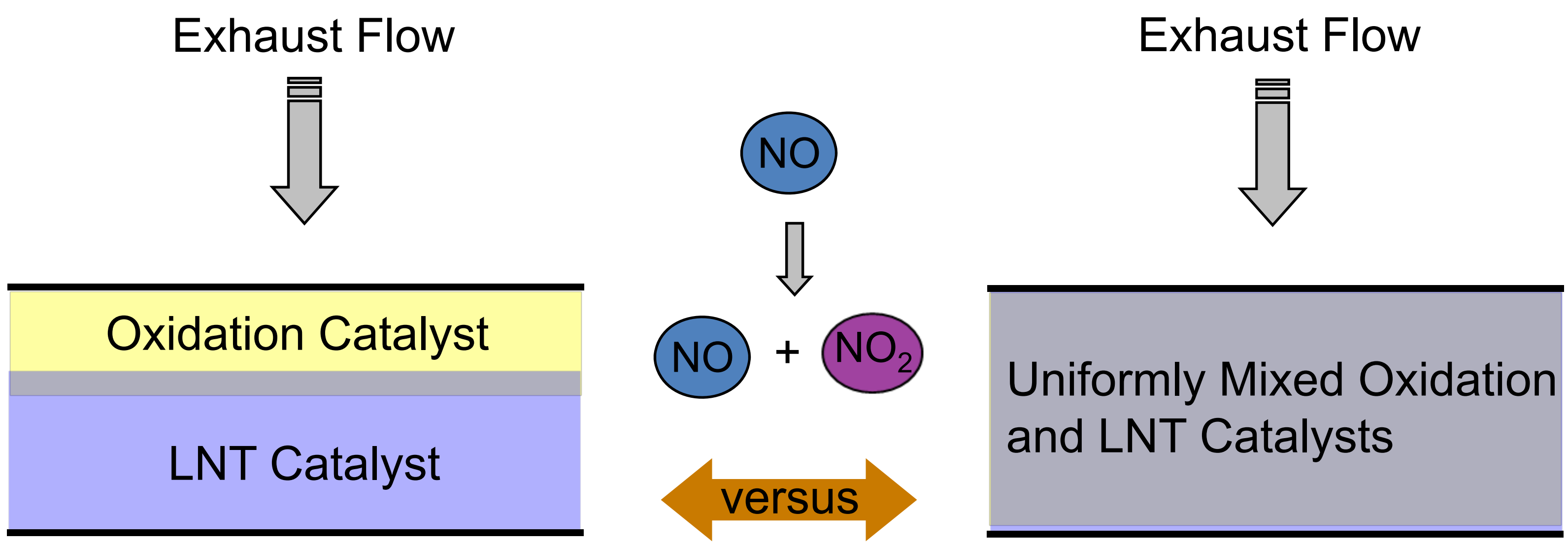
k_NO2FastAds = 3.5d0 [m3/ mole s]
NO2FastSiteC = 20.d0 [mol/m3 monolith]
k_NO2SlowAds = 0.4d0 [m3/ mole s]
NO2SlowSiteC = 15.3d0 [mol/m3 monolith]
k_NOAds = **0.15d0** [m3/ mole s]
NOSiteC = 29.7d0 [mol/m3 monolith]




- Decreased the NO direct adsorption rate to allow 50 ppm pulse to make it all the way through the monolith.
- Investigating the option of adjusting site concentrations to improve shape of NO pulse.

# '09 Future Plans
## LNT 1-D Wall-Flow Model

- Kinetics for $NO_2$ absorption are usually considered dominant over direct absorption of NO
- Oxidation catalysts are included to convert NO to $NO_2$
- Key question: Is there an advantage to separating an oxidation catalyst from an LNT catalyst through the wall thickness?
- This will be explored using a 1-D transport and reaction model

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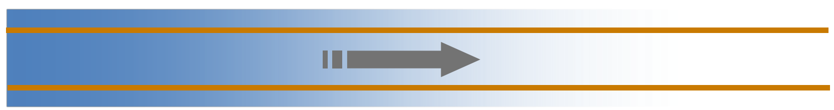
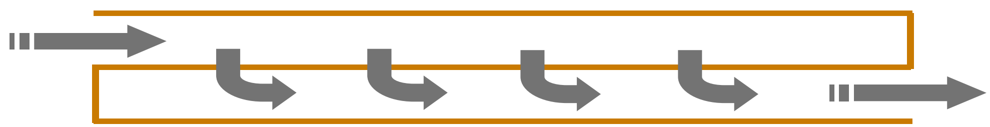
# '09 Future Plans
## Device-scale transport

- Most adsorption data and models in the literature are for flow-through devices
  - Front moves axially through monolith and assumed to be uniform in radial direction



- A simple model with a wall-flow device is more challenging.
  - Transport resistance between gas and catalyst will likely be different in the channels vs. moving through the catalyzed wall
  - What will the adsorption front look like?



- Significance will be explored by experiment:
  - Characterize $NO_x$ adsorption transient with a small core in flow-through configuration
  - Convert sample to wall-flow by plugging alternating channels and repeat experiment

# Plans for Next Fiscal Year

- This is the final year of the CRADA.
- DOW decided to invest >$100 Million of capital investments in the production of ACM substrates.

# Overall Project Summary

- Micro-Modeling has identified characteristics of an ACM substrate as it relates to back pressure.
- The high surface area provided by the needles, in conjunction with the high porosity, minimizes the exhaust backpressure.
- Micro modeling is tuned and validated by unique single channel experiments.
- Micro modeling techniques can be applied to various substrates which can be characterizes by digitized micrographs or stochastic models.
- Answering key questions to optimize ACM structure to maximum LNT performance.