CLEERS Activities: Diesel Soot Filter Characterization & NOx Control Fundamentals

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Overview

- **Timeline**
  - Status: On-Going
  - Focus area starts vary (DPF, LNT, SCR)
- **Budget**
  - FY08 funding - $750K
  - FY09 funding allocation $750K
    - Split between DPF, LNT, SCR focus areas

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- **Barriers**
  - Limitations on:
    - available modeling tools
    - chemistry fundamentals
    - knowledge of material behavior
  - Effective dissemination of information
  - Technical “Valley of Death”
- **Partner**
  - Diesel Crosscut Team
  - 21CT partners
  - USCAR partners
  - Oak Ridge National Lab

iic Institute for Interfacial Catalysis
Control of Chemical Transformations for a Secure Energy Future

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Goal and Objectives

CLEERS PNNL Subprogram Goal

Working closely with our National Lab partners, the CLEERS industrial/academic team and in coordination with our CRADA portfolio, PNNL will…

…provide the practical scientific understanding and analytical base required to enable the development of efficient, commercially viable emissions control solutions and modeling tools for ultra high efficiency vehicles.

- OVT program goals are achieved through these project objectives:
  - interact with technical community to indentify relevant technological gaps
  - understand fundamental underlying mechanisms and material behavior
  - develop analytical and modeling tools, methodologies, and best practices
  - apply knowledge and tools to advance technologies leading to reducing vehicle emissions while improving efficiency
- Specific work tasks in support of the objectives are arrived at through:
  - focus group industrial monthly teleconferences, diesel x-cut meetings
  - yearly workshops and surveys
  - submission of SOW to the OVT office

Milestones & Approach

- Approach - “Science to Solutions”
- The overall performance measure of the project is inextricably linked to the interests of industry.
  - PNNL CLEERS activities have resulted in the formation of new CRADAs
  - PNNL has received formal letters of gratitude from Cummins and DOW for their commercial successes:
    - Cummins for the NOx adsorber for the Dodge RAM
    - DOW for the soot filter success with the Audi Racing team
  - Tremendous success of the annual workshops
  - Strong participation in the monthly teleconferences
- Specific performance measures are developed with the industrial/academic partners and captured in SOW
  - Specific technical targets and major milestones are described in our AOPs and annual reports to OVT

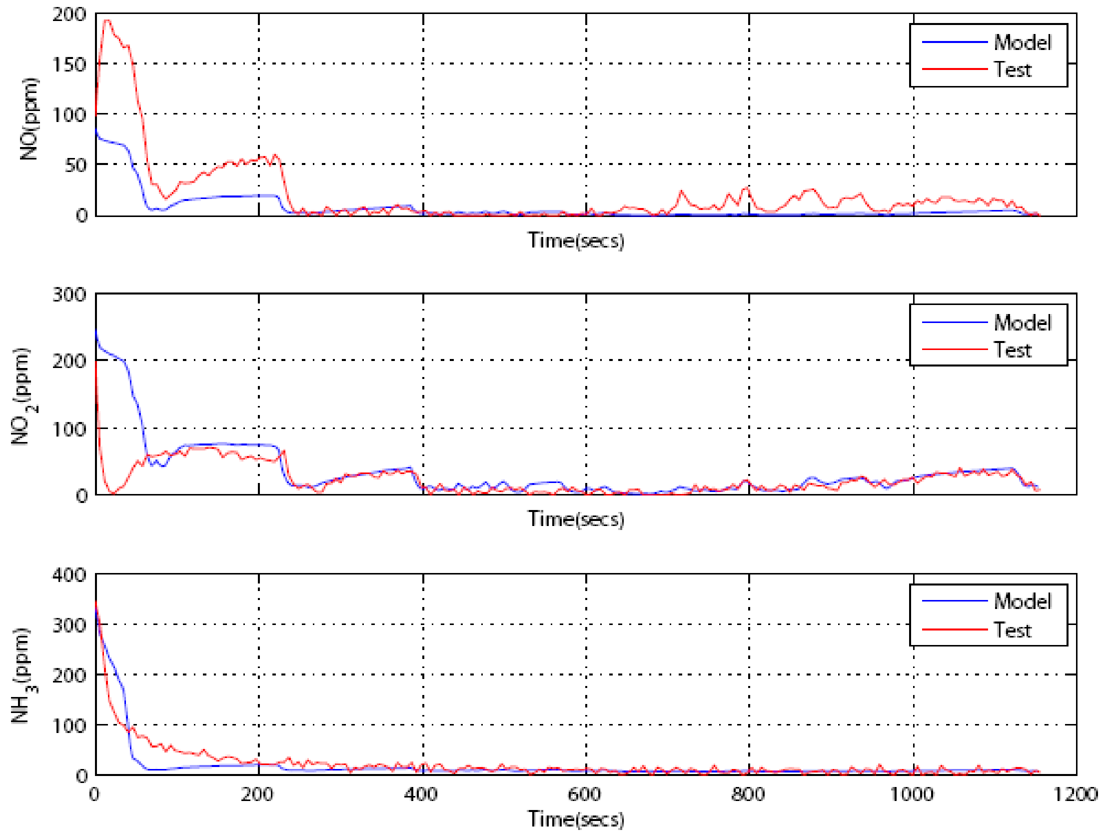
Technical Accomplishments – Summary

- NOx Control Fundamentals
  - Developed and validated thermal transient micro-reactor model
  - Characterized and modeled steady-state oxidation performance over Fe-zeolite
  - Characterized and modeled NH3 adsorption/desorption
  - Initiated baseline SCR tests and investigation into inhibition reactions (HC perf. impact)
  - Setup test bench capability for NH_4NO_3 studies
- Soot Filtration Characterization
  - Reviewed background on pore-scale filter simulations
  - Increased fidelity for micro-geometry modeling
  - Explored fundamental physical and modeling artifacts in micro-scale filtration simulations
  - Analyzed passive regeneration simulations and comparisons to experimental measurements

Thermal Transient Micro-reactor Modeling

- Characterize and model steady state reactor
- Develop dynamic reactor model, simulated in Matlab/Simulink
- Steady state data from micro-reactor used for parameter identification and transient data is used for validation

Transient Reactor Model Validation



- Still some issues with the model at low temperatures, during the start of the test
- Needs further tuning based on steady state tests on an Fe-zeolite

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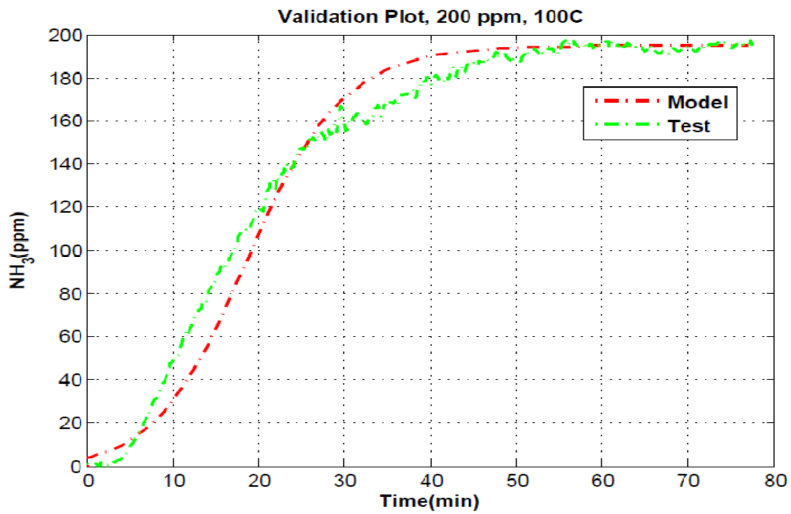
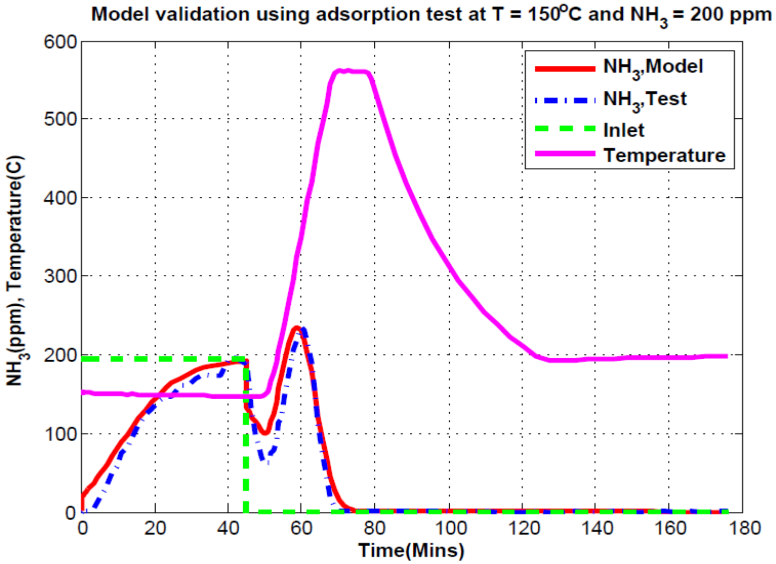
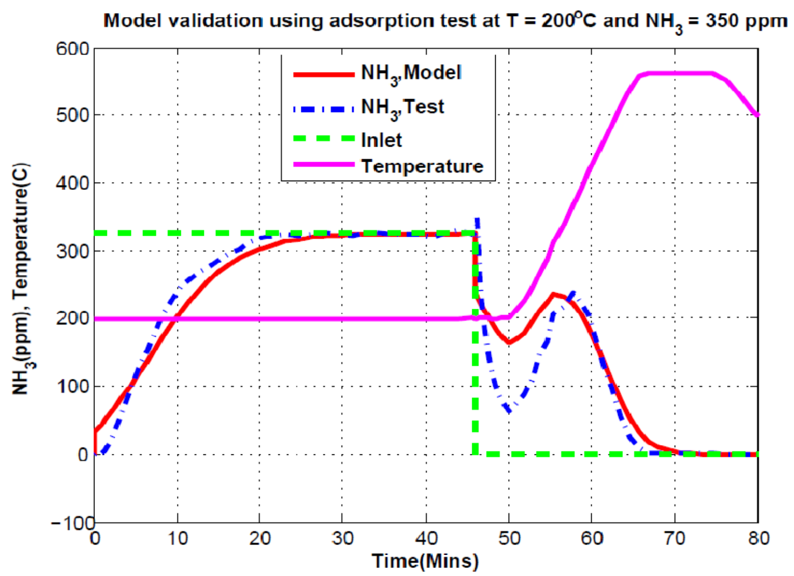
NH_3 Adsorption-Desorption Model Validation

Adsorption Validation



Overall Model Validation





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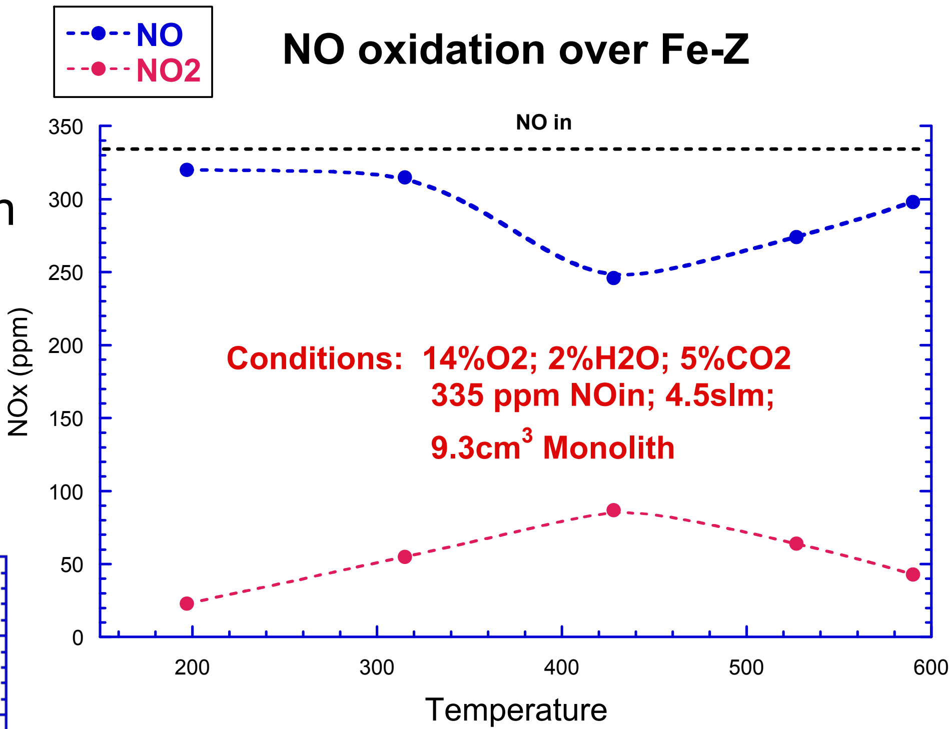
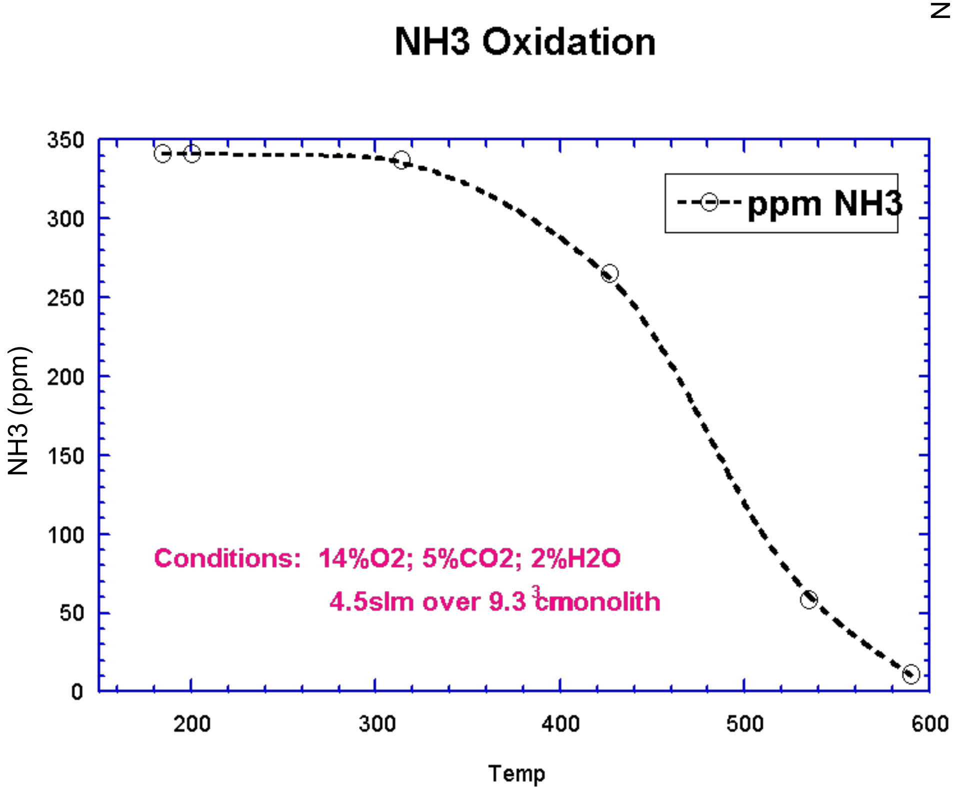
NO & NH_3 Oxidation over Fe-zeolite

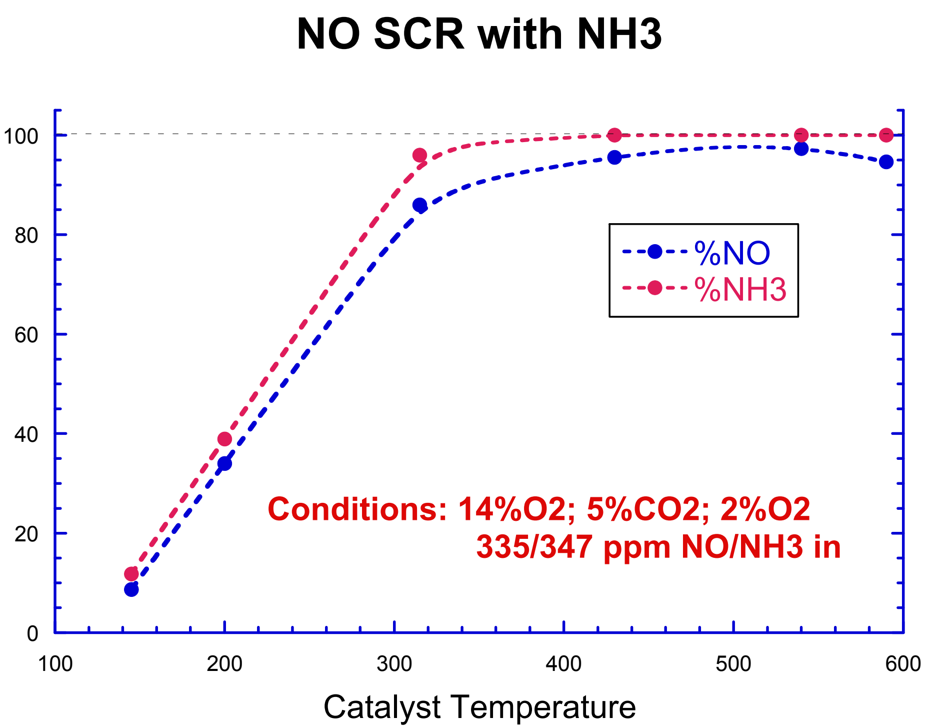
- NO oxidation slow at low temperature
- NO favored thermodynamically at high temperature

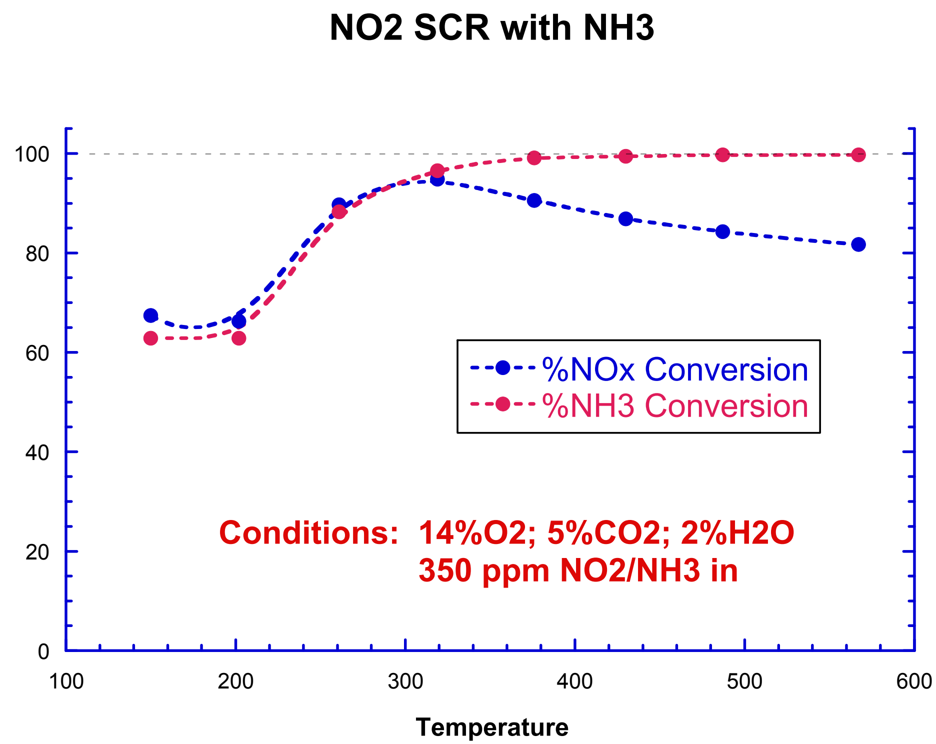




- NH_3 oxidizes to N_2 – no NO, NO_2, N_2O formed

Steady-State SCR over Fe-zeolite





- No NO_2 or N_2O formed with NO/NH_3 feed- presume NOx and NH_3 go-to N_2

2.2 cm dia x 2.5 cm long core
9.3 cm3 or ~30000/Hr GHSV

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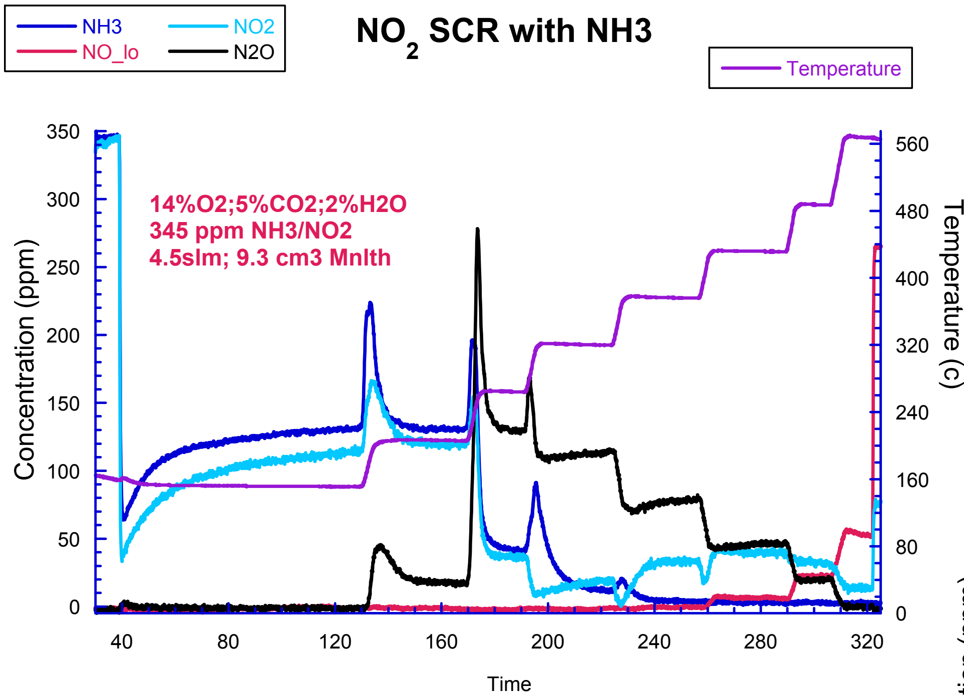
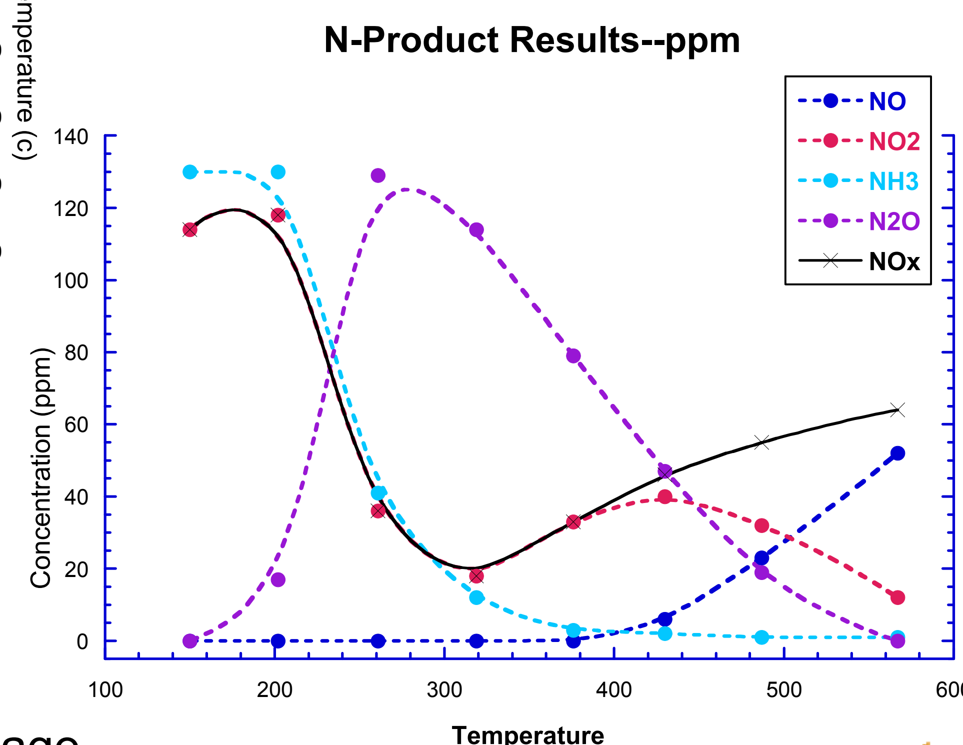
Products of NO_2 SCR over Fe-zeolite





- N_2O formed at low T; NO at high T;
- NH_3 and NO_2 release during heating stage
- NH_3 oxidation evident at high T

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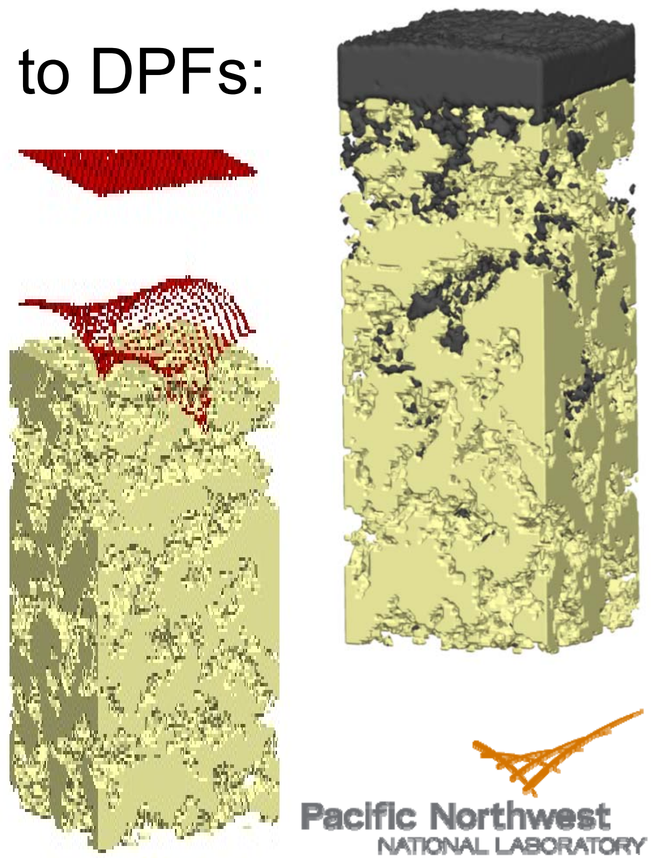
Pore-Scale Filtration Simulations

- Objective: allow prediction of filtration and regeneration performance from the detailed micro-structure and composition of filter
- Application of pore-scale simulations to DPFs:
  - Konstandopoulos, CERTH/CPERI
  - Yamamoto, Nagoya University
  - Rief, Fraunhofer Institute
- Significant progress made, but several challenges remain:
  - Adequacy of geometric reconstructions
  - Capture of critical particle transport and deposition phenomena



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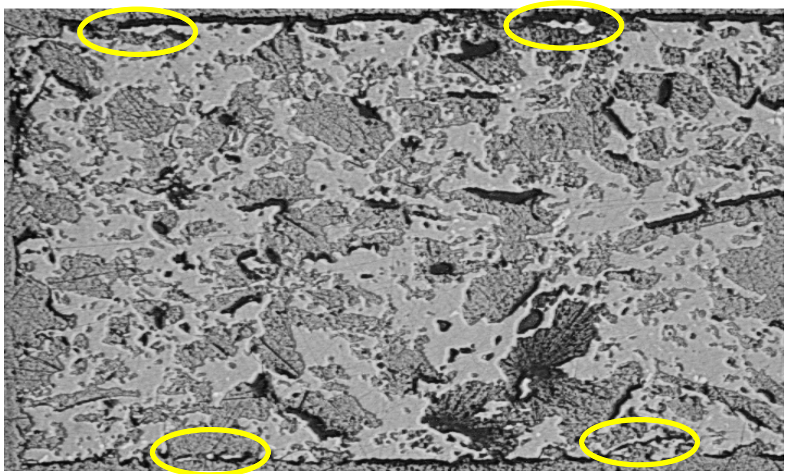
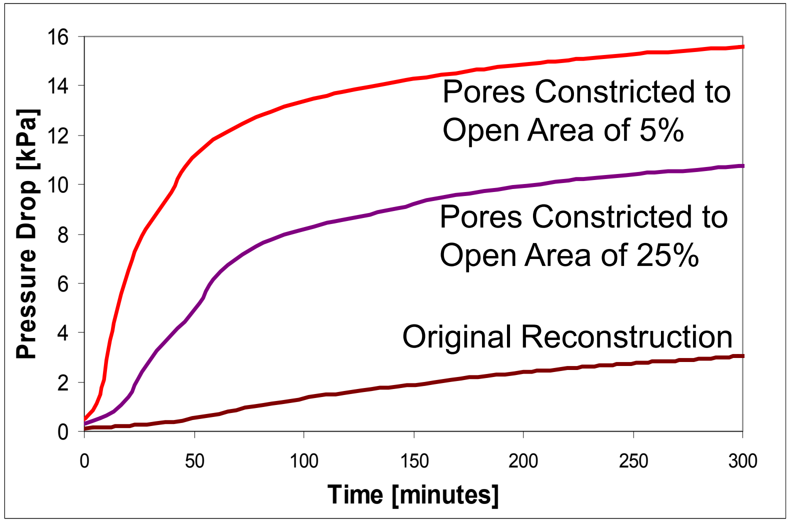
Reconstructions of Pore Geometry



Micrograph of cordierite wall cross-section showing fine structures at wall surface



- Methods to obtain geometries
  - Interpolation between 2D micrographs
  - Stochastic reconstruction
- Must capture details representative of bulk
- Methods have limitations
  - Stochastic reconstructions relies upon comparison with statistical metrics
  - 2D micrographs requires interpolation between images and is time consuming
  - Are these metrics adequate?

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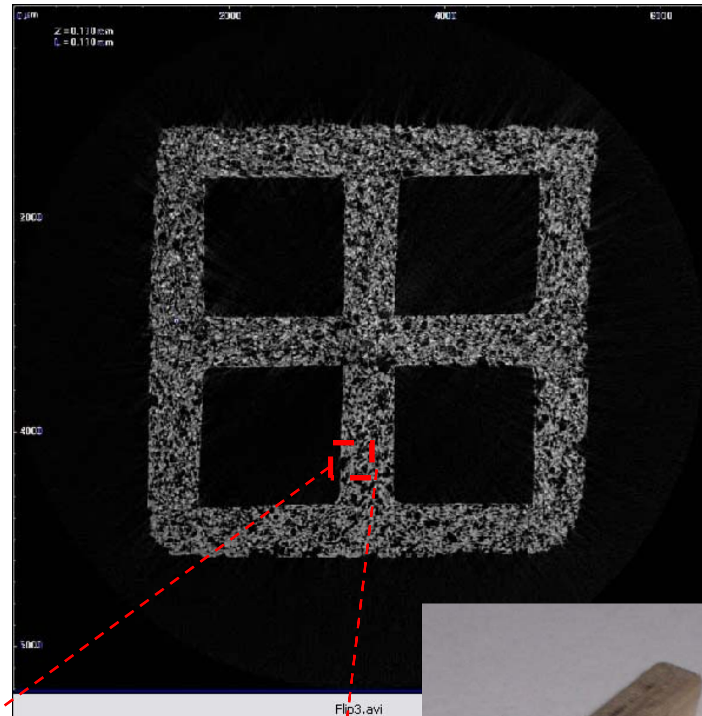
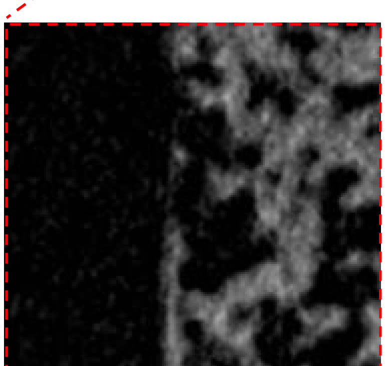
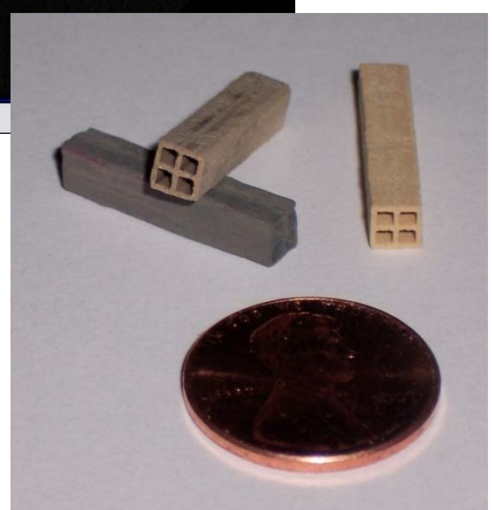
Micro-Computed Tomography







- Micro-CT scans of commercial substrates
  - 1.5 um resolution
  - four complete channels
  - SiC and cordierite
- Analysis of results
  - stochastic reconstructions
  - 2D "layers"
  - cracks or unusually large pores
- Effect of catalyst washcoat on pores near wall surface will be examined

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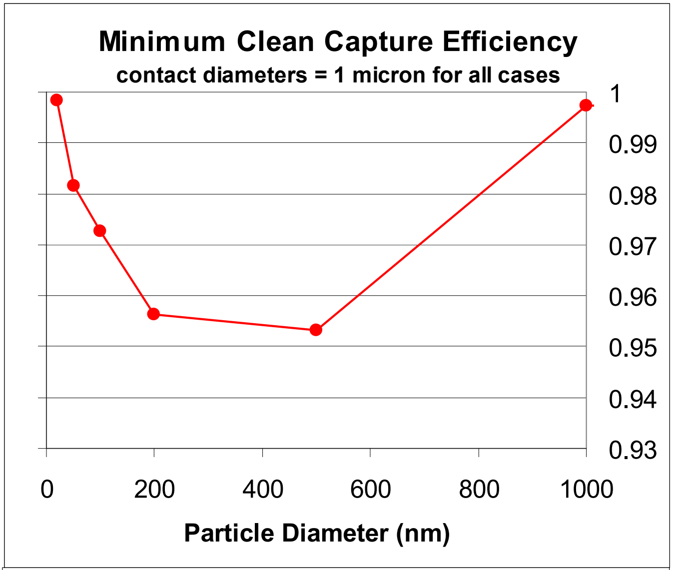
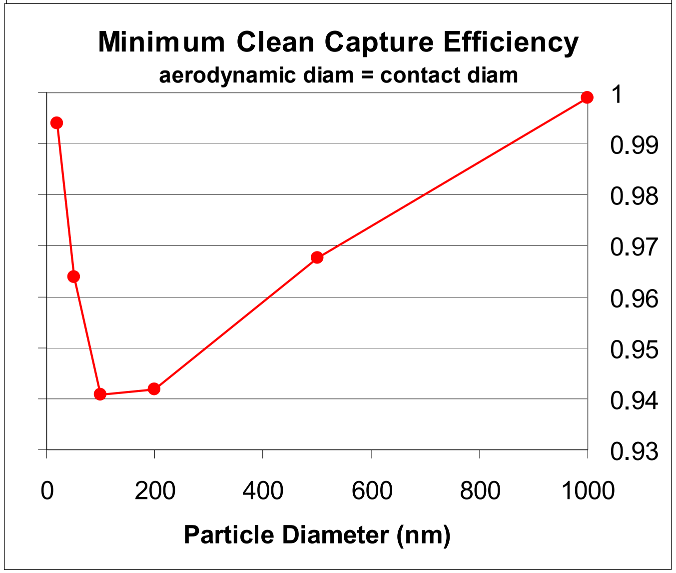
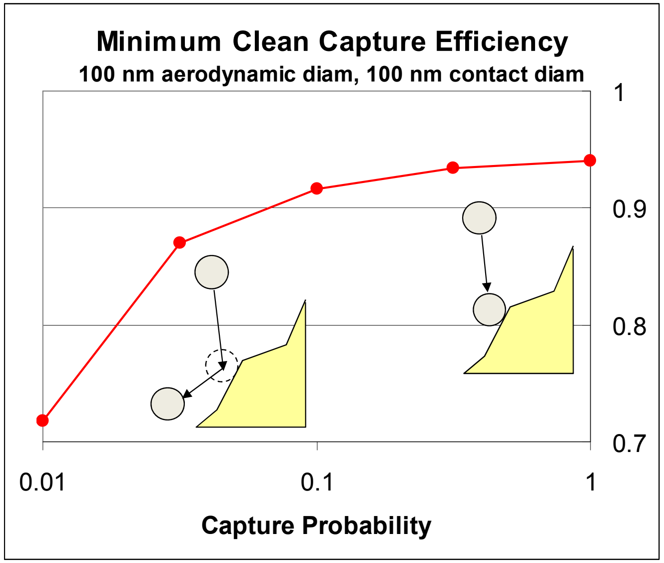
Predicting Clean Capture Efficiency





- Previous simulations predict minimum efficiency at larger particle sizes than experimentally observed (Miyairi et al)
- Algorithm for capture mechanics updated with real contact diameters
- New simulations predict minimum efficiency closer to 100 or 200 nm
  - capture efficiency still high
  - long run times to build significant deposits



- Does capture efficiency play a role?

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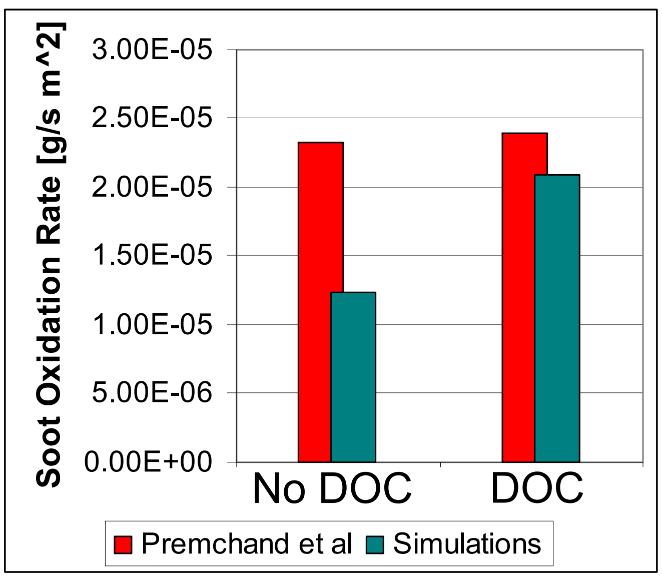
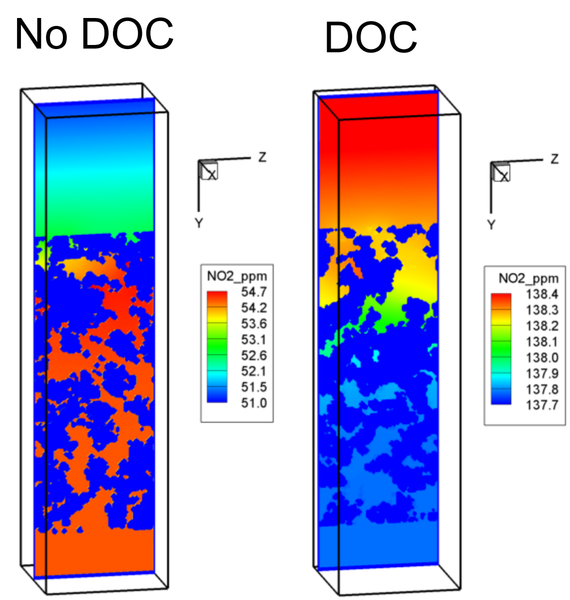
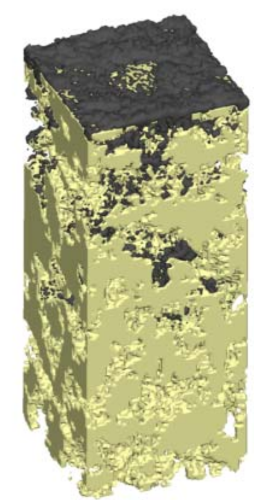
Passive Regeneration Simulations

- Passive regeneration study documented by Premchand et al SAE-2007-01-1123
- Johnson Matthey CCRT® system
- *NOT an apples-to-apples comparison*
- Simulations again assumed 120 g Pt/ft^3 in top quarter of filter wall

	No DOC	DOC
Soot loading [g/m^2]	1.4	0.87
Wall velocity [cm/s]	1.81	1.87
Temperature [°C]	250	267
NO in [ppm]	160	46
NO_2 in [ppm]	38	144
Oxygen	13%	13%







Predicted soot distribution at 0.9 g/m^2 loading

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Future Work – NOx Control

- Kinetic modeling of NH3 oxidation, NO oxidation and other SCR reactions on Fe-zeolite
- Complete NH3-SCR model calibration and validation
- Model based analysis of H2O adsorption and competitive adsorption between HC and NH3 on Fe-zeolite catalysts, thermal aging, etc.
- Isocynanic acid reagent studies
  - Steady state kinetic modeling of HNCO hydrolysis and adsorption on Fe-zeolite
  - Transient reactor modeling based on HNCO injection
- Thermal Transient Testing of Urea-SCR catalyst

Future Work – Soot Filter Characterization

- Process and analyze micro-CT data
- Continuing development of pore-scale modeling tools
  - Validate with single-fiber simulations
  - Experiment with alternate particle capture algorithms
- Application of pore-scale models
  - Examine effects of unusually large pores and cracks
  - Examine effects of catalyst washcoat on flow and filtration
- Filtration and regeneration experiments

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