CLEERS: Aftertreatment Modeling and Analysis

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ACE023

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Overview

- **Timeline**
  - Status: On-going core R&D
  - Originated FY03 with DPF
  - Now also includes LNT, SCR and DOC technologies
- **Budget**
  - FY10 funding - $750K
  - FY11 funding allocation $750K
    - Split between SCR, LNT, DOC and DPF focus areas

CLEERS

- 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

Goal and Relevance

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.

- **VT 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 VT office**

Technical Milestones & Approach

- 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
  - 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 VT
- Approach - “Science to Solutions”

PNNL FY11 Portfolio

CLEERS activity

Integrated Systems – John Lee

- DPF subtasks* – Mark Stewart
- SCR subtasks* – John Lee
- LNT subtasks – Chuck Peden

*PNNL-led subteam
**Past activities

CRADA activities

DPF – DOW Automotive (Stewart)**

SCR/DPF – PACCAR (Rappe)

SCR, HC – Ford Motor Company (Peden, Lee)

SCR, DOC – General Motors (Peden)

LNT – Cummins Inc. (Peden)

Oxidation Catalysts

– General Motors (Lee)

– SDC Materials (Herling)

– Caterpillar (Rappe)**

FY2010/2011 Scope Objectives

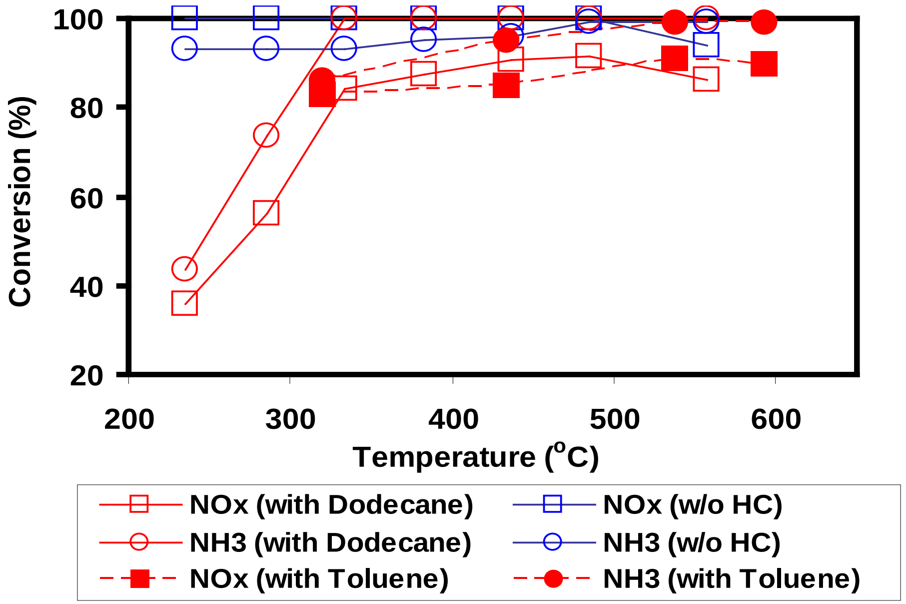
- Selective Catalytic Reduction (SCR)
  - Update our SCR model for the state-of-the-art Cu SCR catalyst, and develop kinetics models to describe the performance degradation due to the competitive adsorption and catalyst aging
  - Conduct detailed characterization of the Cu SCR catalyst with emphasis on the active sites and its deactivation
- Lean NOx Trap (LNT)
  - Complete the investigation of CO_2 and H_2O effects on BaO morphology changes and NOx storage properties
  - Fundamental studies of novel high-temp LNT catalyst materials
- Diesel Particulate Filter (DPF)
  - Evaluate the accuracy of unit collector model with respect to nano-sized particulates, and improve the accuracy of mico-scale model for prediction of soot-catalyst contact
  - Characterize soot chemistry and structure relevant to exhaust system performance and regeneration

Technical Accomplishments Outline

- SCR
  - Developed single site kinetic models to describe the effects of competitive adsorption on NOx reduction on Fe SCR catalyst
  - Currently developing Cu SCR model with ORNL, and conducting detailed characterization of the state-of-the-art Cu SCR catalyst with emphasis on the active sites
- LNT
  - Demonstration of significantly enhanced high temperature performance for a $K/MgAl_2O_4$ LNT material
  - Fundamental studies of complex morphology changes in K-based LNT materials have been initiated
- DPF
  - Currently evaluating the accuracy of unit collector model with respect to nano-sized particulates
  - Recently collected soot from HDD engine at MTU for characterization of soot chemistry and structure

Selective Catalytic Reduction

Effect of Hydrocarbon on SCR Reactions



Feed Conditions

175 ppm NO

175 ppm NO_2

350 ppm NH_3

14% O_2

2% H_2O

50 ppm toluene (350 C1)

29 ppm dodecane (350 C1)

29k h^{-1}

- The effects of HC on Fe SCR catalyst examined using model HC species for combustion products and unburned fuel
- Detrimental effects of toluene & n-dodecane on SCR reactions
- Models developed to investigate the effects of HC on SCR reaction pathways quantitatively

Overview of PNNL 1-D SCR Model

- Gas phase, surface phase concentrations and NH_3 storage as states
- Coded as ‘C’ S-functions and developed in Matlab/Simulink
- Optimized and validated using steady state and transient reactor data

No	Reaction Name	Reaction	Reaction Rate
1	NH_3 Adsorption	$NH_3 + S \rightarrow NH_3^*$	$R_1 = k_1 C_{s,NH3}(1-\theta)\,\Omega$
2	NH_3 Desorption	$NH_3^* \rightarrow NH_3 + S$	$R_2 = k_2\,\theta\,\Omega$
3	Fast SCR	$2NH_3+NO+NO_2 \rightarrow 2N_2+3H_2O$	$R_3 = k_3 C_{NO} C_{NO2}\,\theta\,\Omega$
4	Standard SCR	$4NH_3+4NO+O_2 \rightarrow 4N_2+6H_2O$	$R_4 = k_4 C_{NO}\,\theta\,\Omega$
5	NO_2-SCR	$4NH_3+3NO_2 \rightarrow 3.5N_2+6H_2O$	$R_5 = k_5 C_{NO2}\,\theta\,\Omega$
6	NH_3 Oxidation	$2NH_3+3/2O_2 \rightarrow N_2+3H_2O$	$R_6 = k_6 C_{O2}\,\theta\,\Omega$
7	NO-NO_2 Oxidation	$NO+1/2O_2 \Leftrightarrow NO_2$	$R_7 = k_{7,f} C_{NO} C_{O2}^{1/2} - k_{7,b} C_{NO2}$

Modeling Competitive Adsorption

- Single site storage model was first developed , and parameters were obtained from the Langmuir isotherms.
- Assuming the adsorbates, such as NH_3, NO, NO_2, H_2O and hydrocarbons (toluene, n-dodecane), competing for the same active site, single site kinetics for each species and the respective surface coverage are defined as follows:

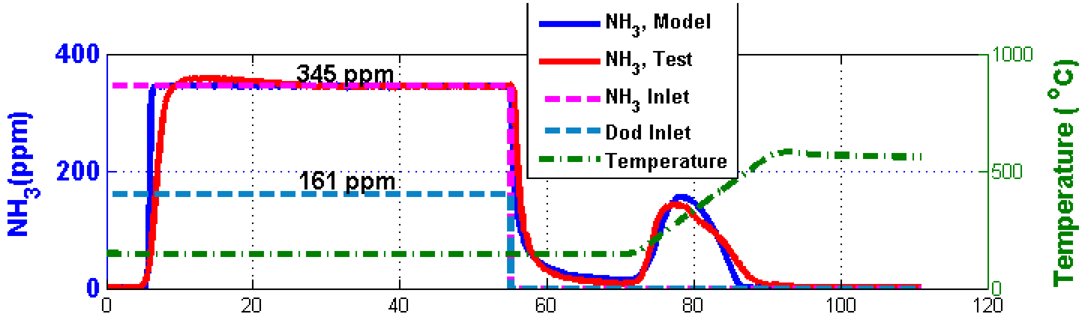
$$\frac{d\theta_i}{dt} = \frac{1}{\Omega_i}[k_{ads,i}(1-\theta_i - \sum_{j=1}^{N-1+P}\theta_j)c_{s,i}\Omega_i - k_{des,i}\theta_i\Omega_i - \sum_{k=1}^{M} n_{i,k}r_{i,k}]$$

$$\varepsilon\frac{\partial c_{g,i}}{\partial t} = -\varepsilon u\frac{\partial c_{g,i}}{\partial x} - \beta_i A_g(c_{g,i} - c_{s,i})$$

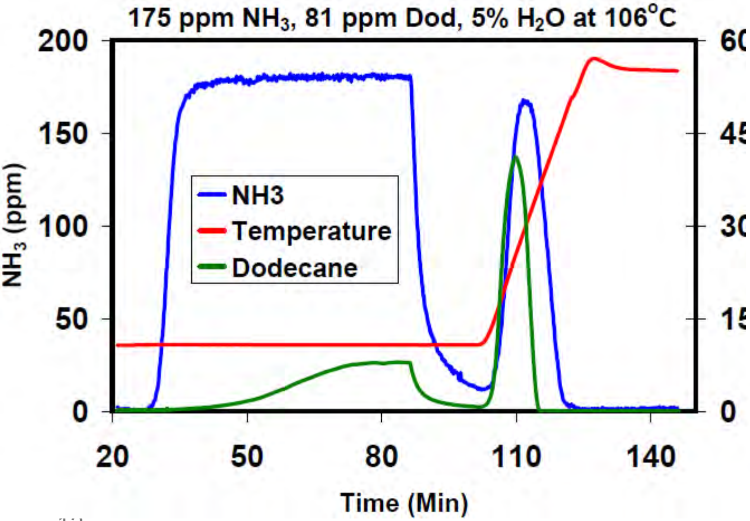
$$(1-\varepsilon)\frac{\partial c_{s,i}}{\partial t} = \beta_i A_g(c_{g,i} - c_{s,i}) + \sum_k r_{i,k}n_{i,k}$$

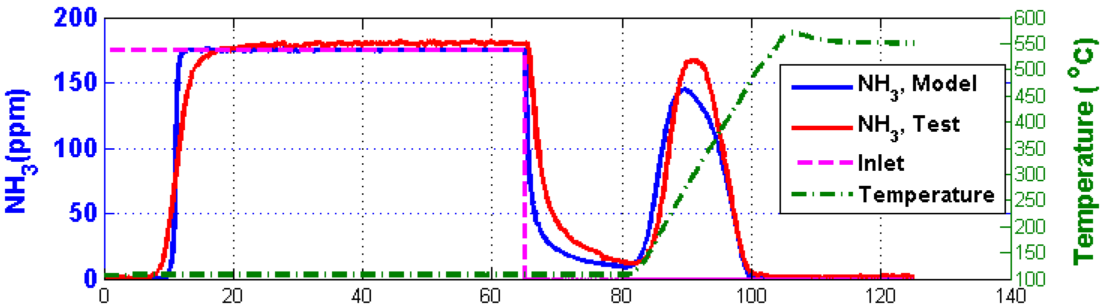
CA Model Validation: NH_3, H_2O, Dodecane

- Competitive adsorption (CA) model development using data for NH_3 vs. H_2O, NH_3 vs. HC



- CA model validation for full competitive adsorption of NH_3, H_2O, and dodecane

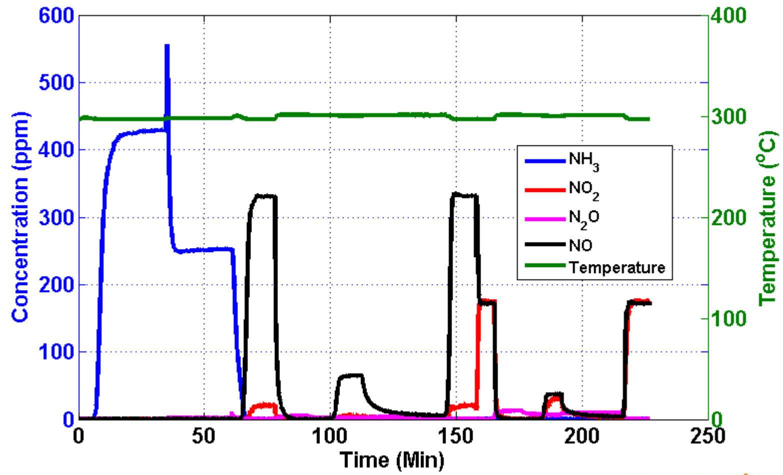




CLEERS Cu SCR Model Development

- Commercial Cu SCR catalyst evaluation
  - Cu SCR being used by most OEMs in North America
  - Lab reactor testing currently being conducted at ORNL using the CLEERS Transient reactor test protocol
- PNNL's 1-D Cu SCR catalyst model
  - Same strategy used for the Fe SCR catalyst model
  - Cu catalyst model being developed entirely in Matlab/Simulink
  - Autonomie being considered as platform to share CLEERS SCR catalyst model with the others

Step	Description	NO (ppm)	NO_2 (ppm)	NH_3 (ppm)	O_2 (%)	H_2O (%)	CO_2 (%)
a	cool + stabilize	0	0	0	10	5	5
b	NH_3 adsorption	0	0	420	0	5	5
c	NH_3 oxidation	0	0	420	10	5	5
d	NH_3 desorption	0	0	0	10	5	5
e	NO oxidation	350	0	0	10	5	5
f	SCR α=1.2	350	0	420	10	5	5
g	SCR α=0.8	350	0	280	10	5	5
h	SCR α=1.0	350	0	250	10	5	5
i	NH_3 inventory	350	0	0	10	5	5
j	NO2/NOx = 1	175	175	0	10	5	5
k	SCR α=1.2	175	175	420	10	5	5
l	SCR α=0.8	175	175	280	10	5	5
m	SCR α=1.0	175	175	250	10	5	5
n	NH_3 inventory	175	175	0	10	5	5



State-of-the-art Cu SCR Catalyst Research

- First open literature studies of the latest Cu SCR catalyst
  - The current production Cu SCR catalyst is based on CHA zeolite.
  - Cu-SSZ-13 prepared and evaluated for various SCR reactions
    → J. Catal. 275 (2010)187-190

- Detailed characterization of active sites in progress
  - TPD, TPR of model Cu-zeolite catalysts
  - In situ XRD and EXAFS experiments at Brookhaven's NSLS

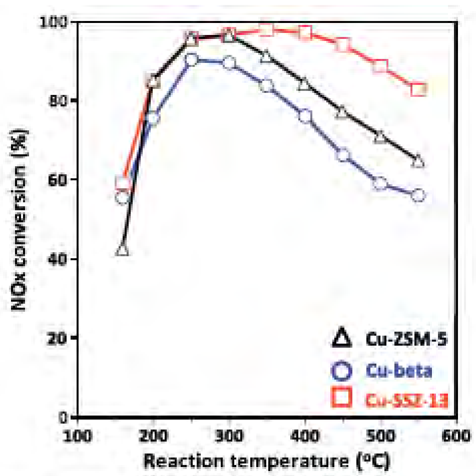


Fig. 1. NO_x conversion profiles for Cu-SSZ-13 (squares), Cu-beta (circles), and Cu-ZSM-5 (triangles) at various temperatures in a gas mixture containing 350 ppm NO, 350 ppm NH_3, 14% O_2, and 2% H_2O with a balance of N_2.

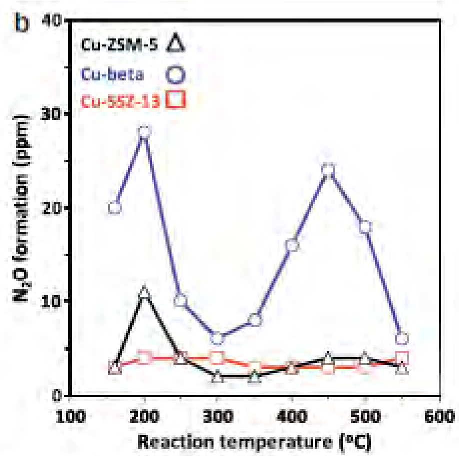


Fig. 2. NO_2 (a) and N_2O (b) formation profiles during NH_3 SCR on Cu-SSZ-13 (squares), Cu-beta (circles), and Cu-ZSM-5 (triangles) at various temperatures in a gas mixture containing 350 ppm NO, 350 ppm NH_3, 14% O_2, and 2% H_2O with a balance of N_2.

Lean NOx Traps

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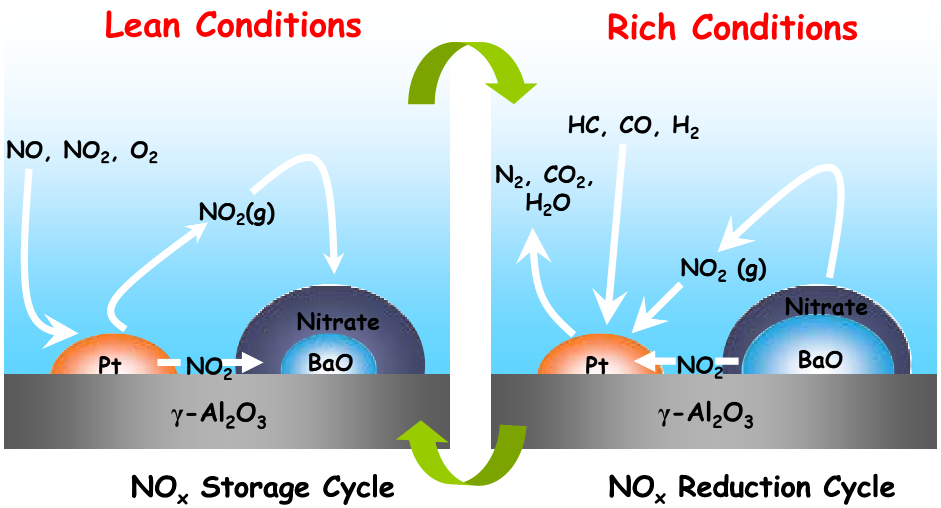
  - Characterize soot chemistry and structure relevant to exhaust system performance and regeneration

Approach

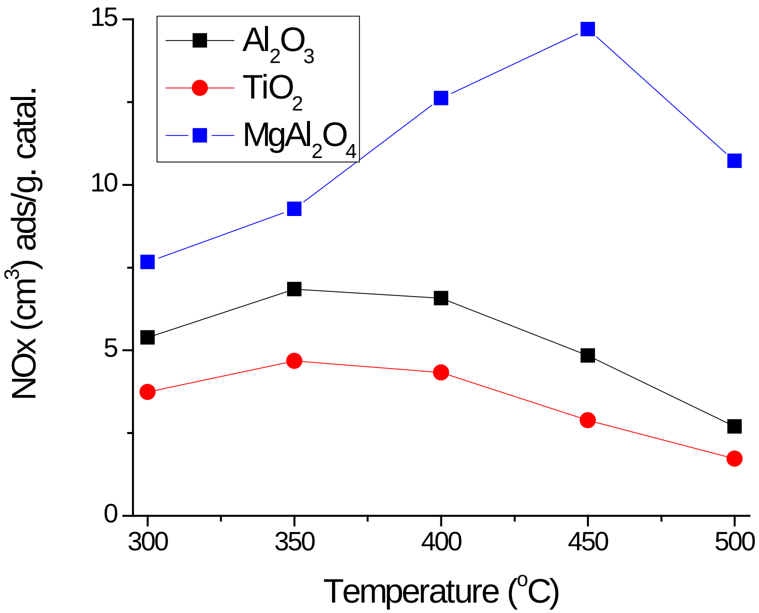
- Higher temperature NOx reduction performance required for:
  - Difficult to meet “not to exceed” regulations during desulfations
  - Possible use of LNTs for lean-gasoline applications



- PNNL/Cummins/JM CRADA focusing on degradation of possible materials for next-generation high temperature LNTs.
- CLEERS studies are addressing more fundamental issues of these potential new LNT materials related to composition, morphology, and chemical reaction kinetics and mechanisms.
- For these studies, PNNL has prepared a range of materials based on literature and prior CLEERS work at PNNL.

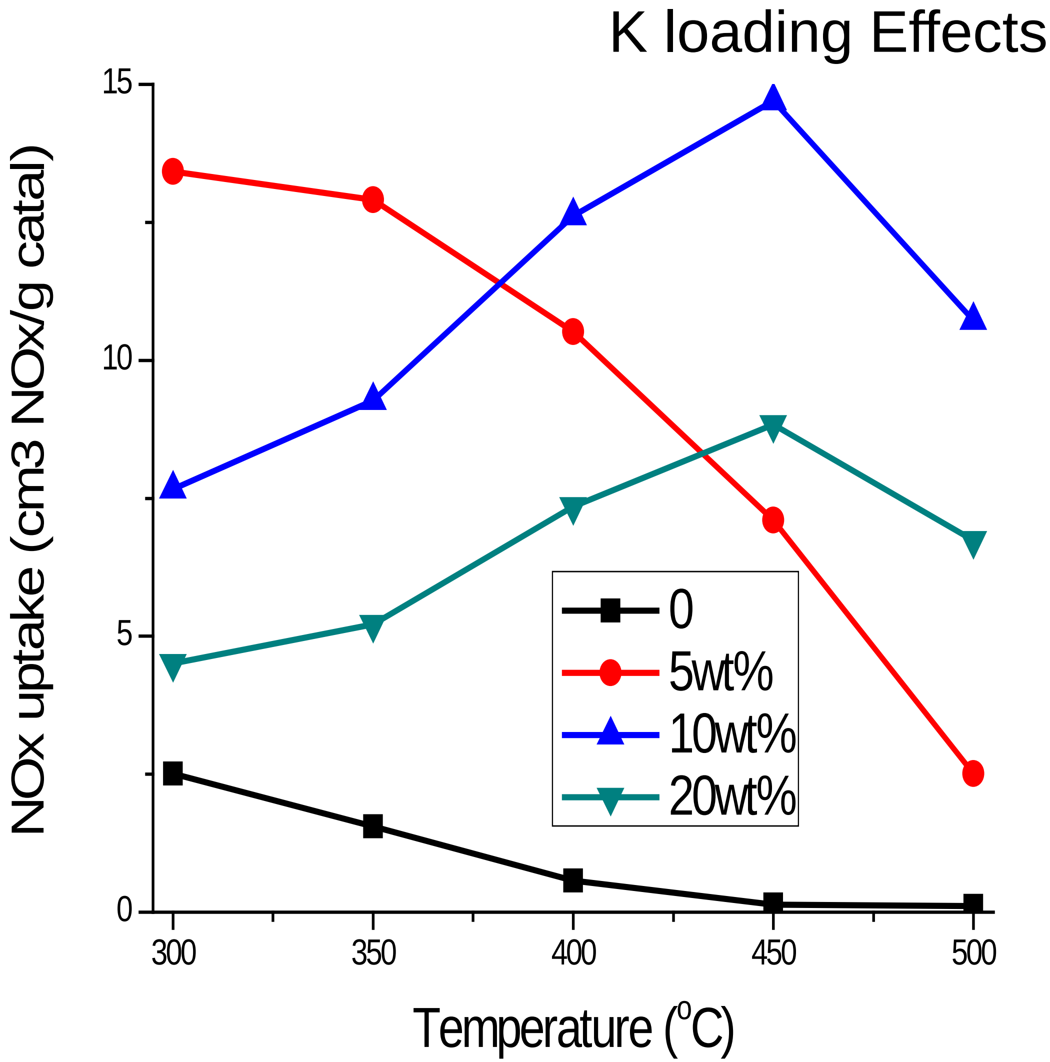
High Temperature LNT Catalyst Materials

- K-based LNTs known to exhibit higher temperature performance
- Recent literature reports suggest titania (TiO_2) may be a better support for K-based LNTs than alumina (Al_2O_3)
- Prior CLEERS studies on Ba-based LNTs at PNNL have suggested $MgAl_2O_4$ as a promising support material for high temperature application



- Superior activity of $MgAl_2O_4$-supported LNT relative to Al_2O_3- and TiO_2-supported samples over all temperatures.
- Moreover, maximum NOx uptake activity at a considerably higher temperature of 450 ºC.

K-loading effects on $MgAl_2O_4$ support materials



- We're not aware of prior systematic studies of K-loading.
- Negligible $MgAl_2O_4$ contribution in NOx uptake at high temperature
- Drastic difference between 5 wt% and 10 wt%
- Higher loading than 10 wt% does not improve the activity.

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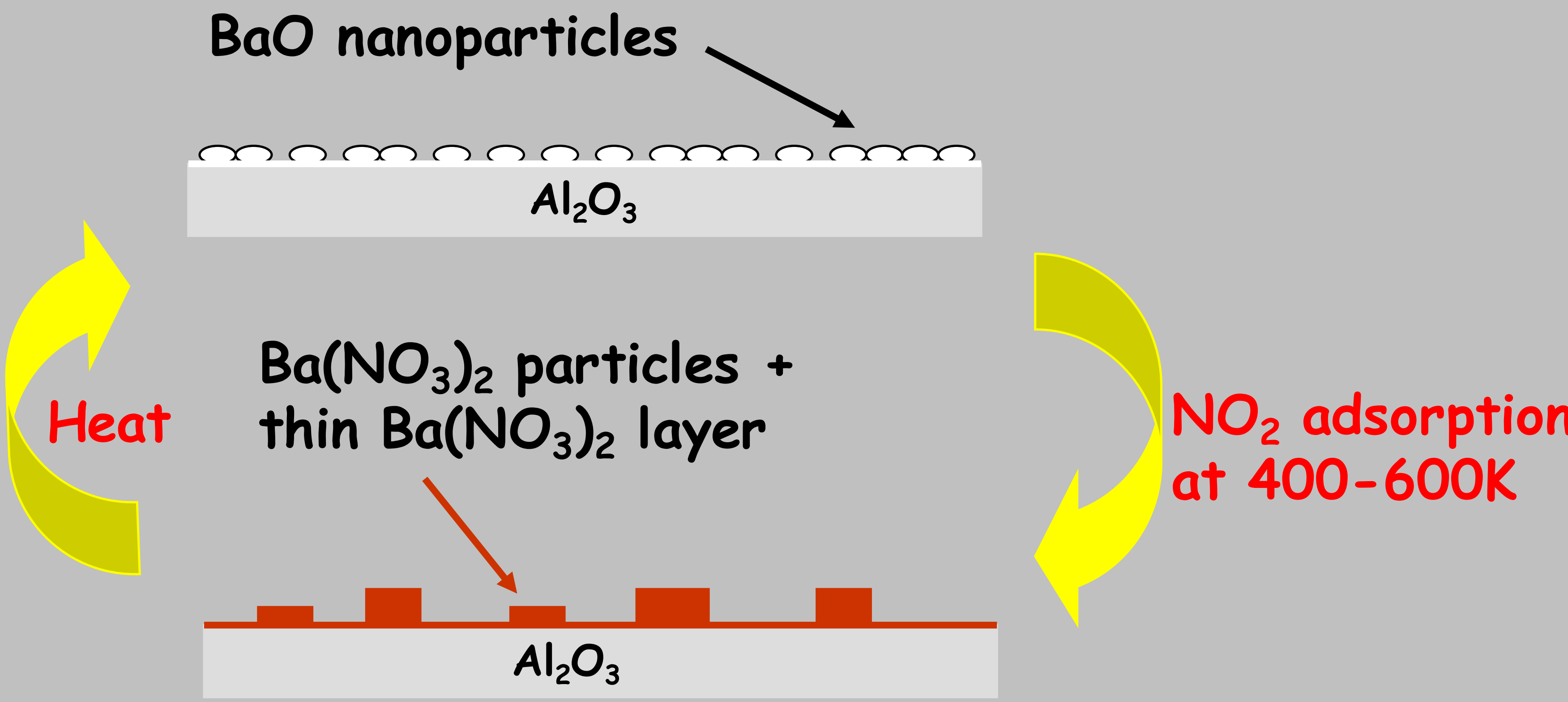
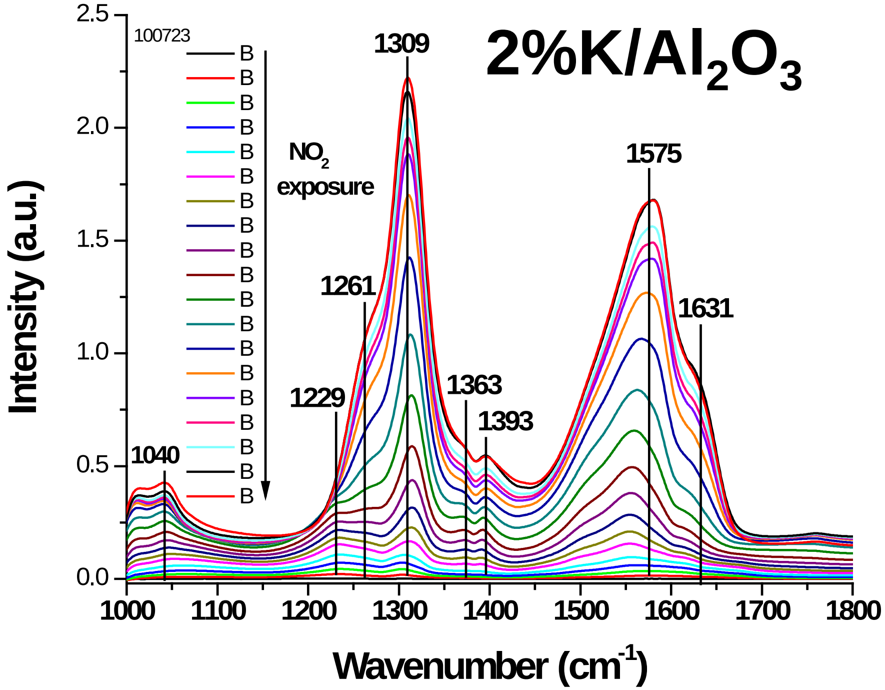
Significant Morphology Changes During Operation of Ba-Based LNTs Were Observed in our Prior CLEERS Studies

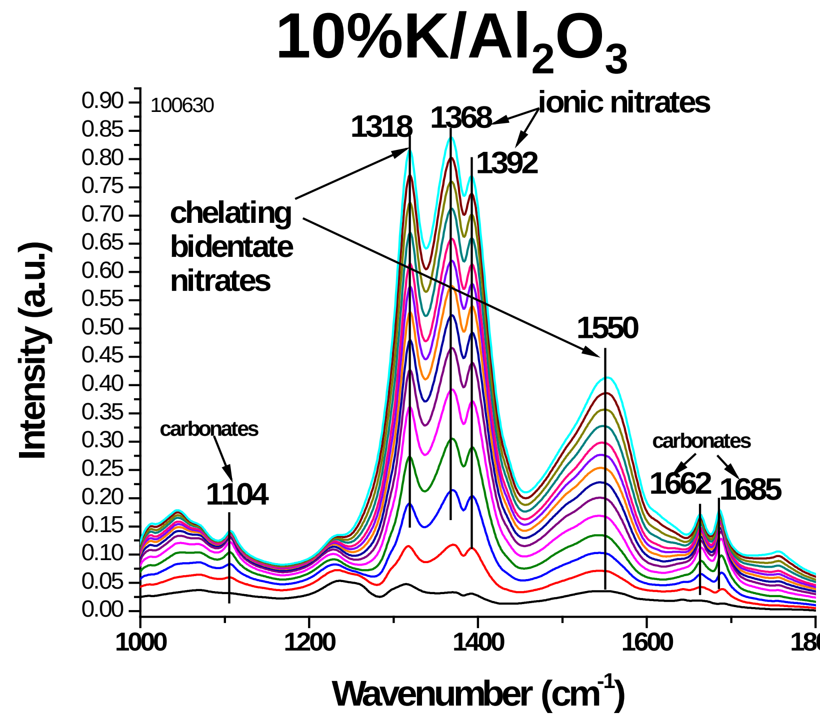


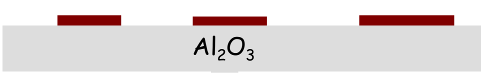
Szanyi, Kwak, Hanson, Wang, Szailer, Peden,
J. Phys. Chem. B 109 (2005) 7339-7344.

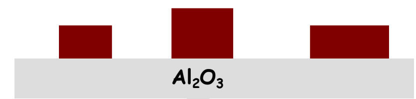
Similar to Ba, FTIR Spectral Changes Consistent with Multiple K-oxide Phases

FTIR spectra of NO_2 adsorbed on K(2 or 10)/Al_2O_3 samples





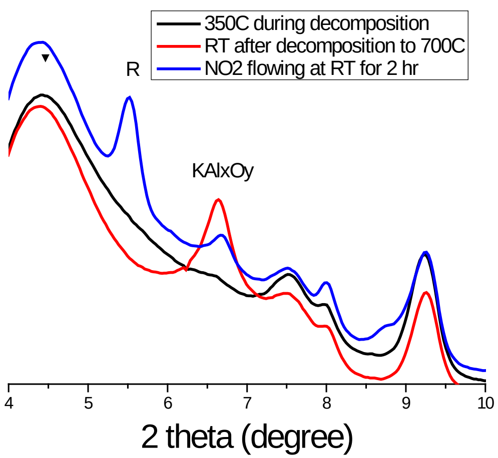


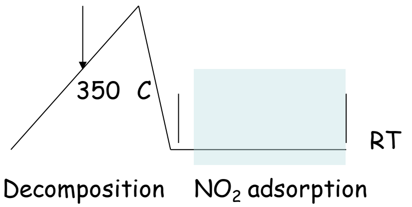


2 wt% K: mostly bidentate nitrates → surface nitrates?
10 wt% K: ionic nitrates and bidentate nitrates → surface and bulk nitrates?

Complex Morphology Changes in K/Al_2O_3

Morphology change of K phase during decomposition and formation of nitrate





- At 350 °C, only Al_2O_3
- At 700 °C, KAl_xO_y phase formed.
- NO_2 transformed KAl_xO_y phase into rhombohedral KNO_3 phase (no orthorhombic phase).

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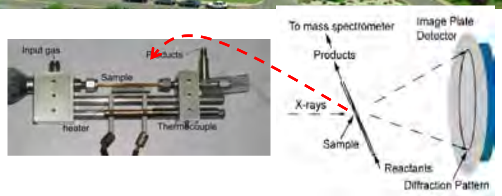
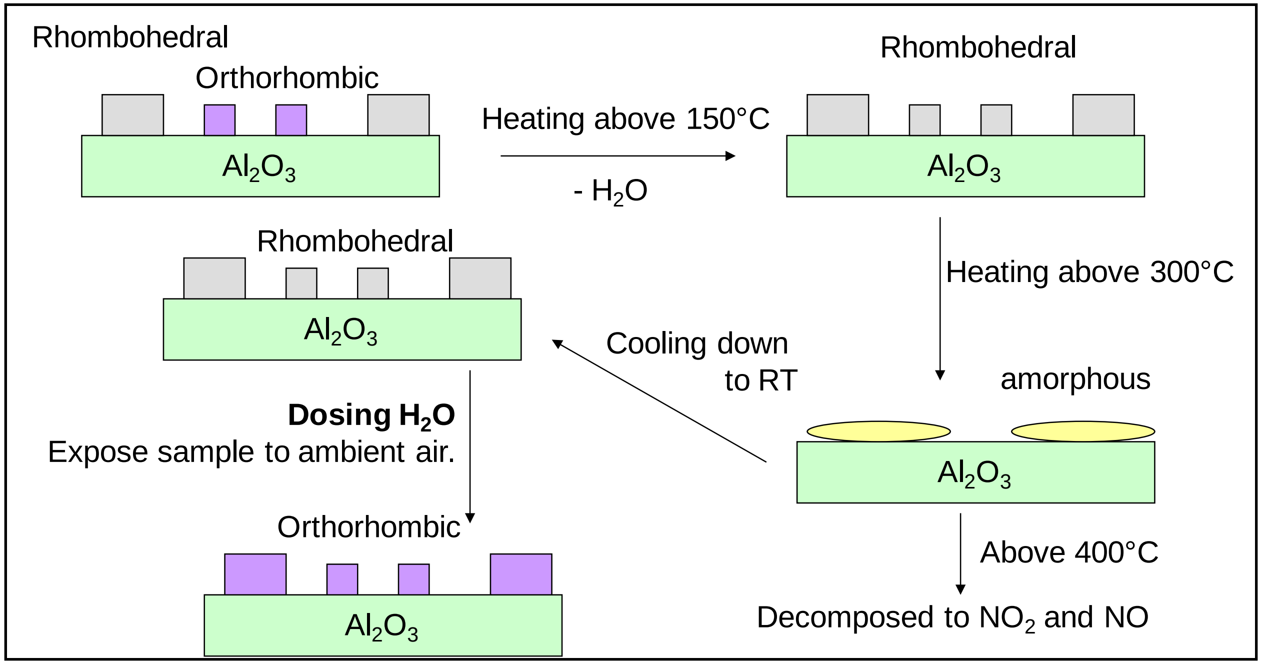
NSLS NATIONAL SYNCHROTRON LIGHT SOURCE





Synchrotron XRD at the NSLS is being used to study the complex morphology changes in K-based LNTs

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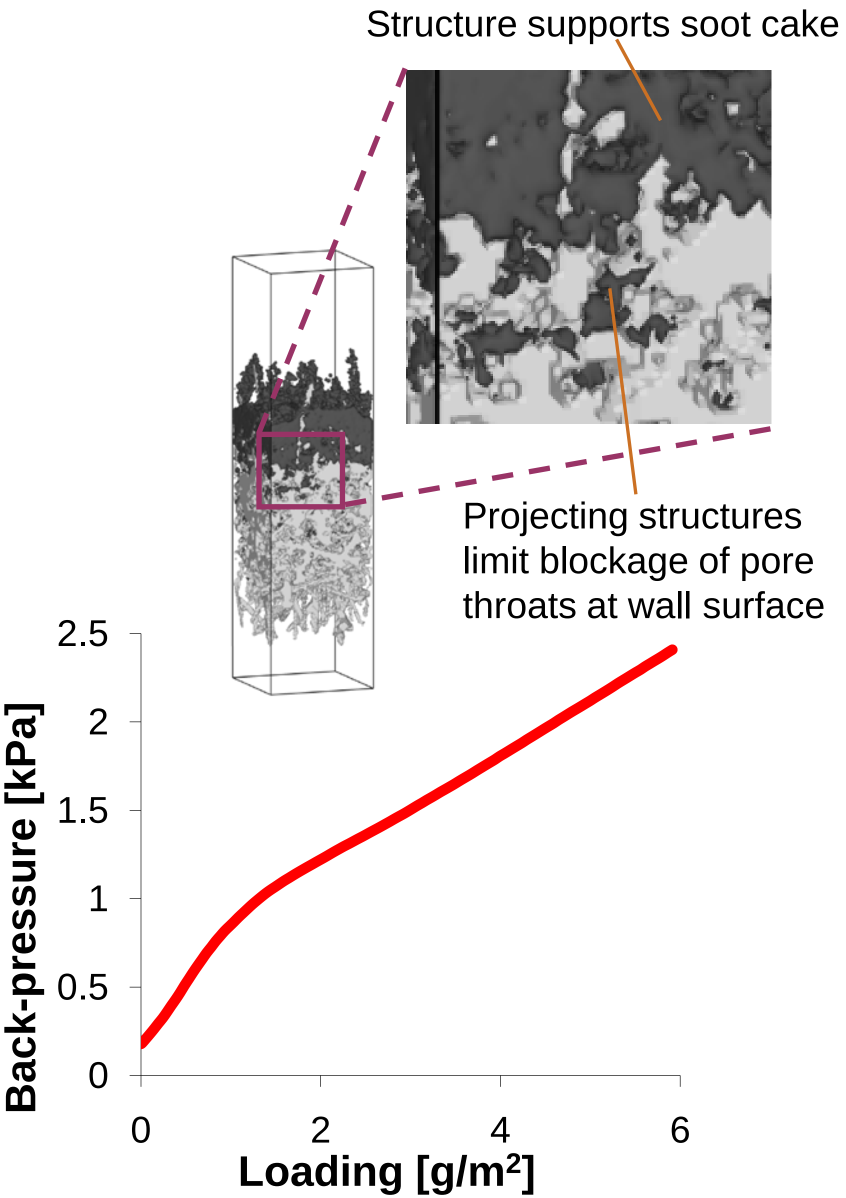
Diesel Particulate Filter

Approach

- Conduct bench reactor soot experiments
  - Soot oxidation w/ NOx correlated by surface area
  - HC Absorption
- Examine soot nano-structure using TEM and advanced image analysis techniques
- Improve pore-scale filter dynamics tools through:
  - Characterization of necessary microstructure resolution and sample size for accurate predictions in various media
  - Validation and enhancement of particle capture mechanics
  - Validation of particle motion Brownian dynamics algorithm
- Collect structural data for filter substrates using:
  - Micro/nano X-ray computed tomography
  - Porosimetry
- Carry out fundamental single cell filtration experiments using reproducible lab-generated aerosols

Pore-Scale DPF Model Development

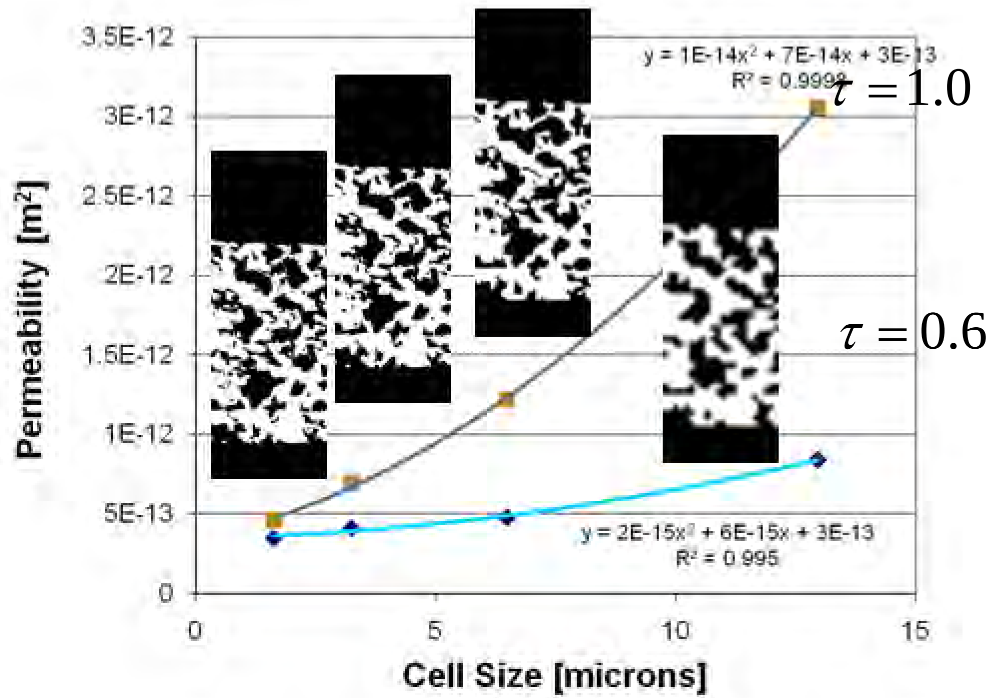
- Numerous pore-scale DPF simulations have been carried out to date using the Lattice-Boltzmann method
- Pore networks have been resolved down to a few microns
- Qualitative features in back-pressure, deposit morphology, and soot penetration into filter walls have been reproduced
- Insight into pore-scale mechanisms has assisted in the development of systems and new materials



Pore-Scale DPF Model Development (cont'd)

- Recent studies suggest requirements for quantitative pore-scale simulations:
  - Sintered granular materials (SiC) are easier to simulate than cordierite
  - Cordierite may require resolutions < 1 um and domain sizes of over 1 mm (>0.5E+9 computational cells)
- Adjustment of lattice-Boltzmann parameters may allow lower resolutions at the expense of shorter time-steps

Predicted permeability vs. computational cell size for cordierite

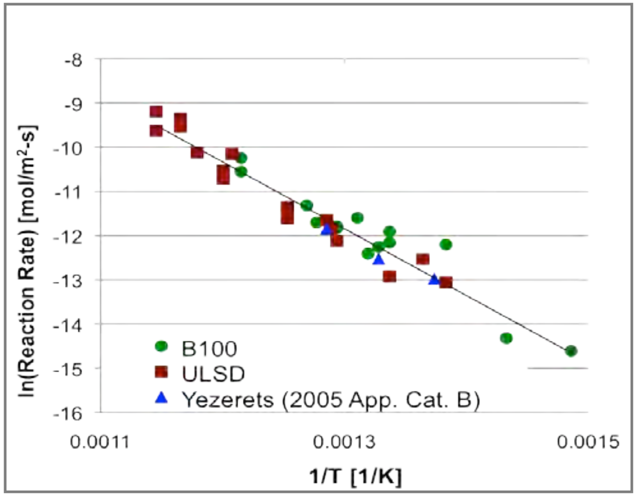


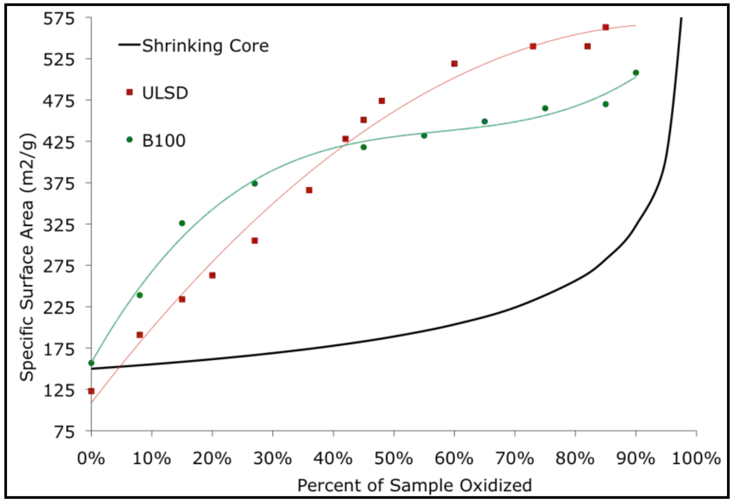
- Fortunately, cost and availability of massively parallel computational resources are rapidly becoming more favorable

  → Precise quantitative performance predictions from pore-scale simulations may be just around the corner

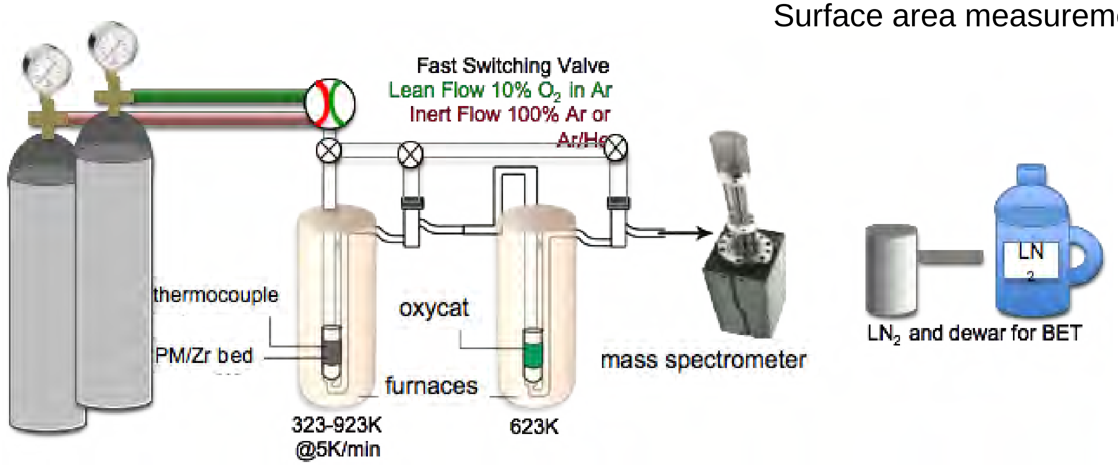
Kinetic Measurements & Surface Area

- Bench reactor soot experiments (in progress)
  - Soot oxidation w/ NOx correlated by surface area
  - HC adsorption





Surface area measurement by in situ BET



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Conclusion & Future Work

Conclusions

- SCR
  - Developed single site kinetic models to describe the effects of competitive adsorption on NOx reduction on Fe SCR catalyst
  - Currently developing Cu SCR model using data obtained by CLEERS transient reactor protocol with ORNL
  - First open literature investigation of the state-of-the-art Cu SCR catalyst with emphasis on the active sites
- LNT
  - Mg/Al_2O_4 identified as a very promising support material for K-based LNTs in high-temperature applications
  - Initial structural studies of K-based LNTs indicate very complex morphology changes
- DPF
  - Recently collected soot from HDD engine at MTU for characterization of soot chemistry and structure relevant to exhaust system performance and regeneration

Future Work

- SCR
  - Update the kinetics for Cu SCR model with ORNL's data, and develop kinetics models to describe the performance degradation due to the competitive adsorption and catalyst aging
  - Continue to conduct detailed characterization of the Cu SCR catalyst with emphasis on the active sites and its deactivation
- LNT
  - Complete studies of CO_2 and H_2O effects on BaO morphology changes and NOx storage properties
  - Continue fundamental studies of morphology changes and NOx uptake mechanisms of novel high-temp LNT catalyst materials
  - Investigate the formation and stability of PGM particles (also relevant to DOC, TWC)
- DPF
  - Evaluate the accuracy of unit collector model with respect to nano-sized particulates, and improve the accuracy of mico-scale model for prediction of soot-catalyst contact
  - Characterize soot chemistry and structure relevant to exhaust system performance and regeneration

Acknowledgements

- <u>PNNL</u>

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