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CLEERS: Aftertreatment Modeling and Analysis

FENG GAO, KEN RAPPE, MARK STEWART (CO-P.I.), JANOS SZANYI, CHUCK PEDEN, DIANA TRAN, YILIN WANG, YONG WANG (CO-P.I.)

PACIFIC NORTHWEST NATIONAL LABORATORY

JUNE 8, 2016

ACE023

Overview

Timeline

- Status: On-going core R&D
- DPF activity originated in FY03
- Now also includes LNT (and PNA), SCR, and LTAT technologies

Budget

- FY15 funding - $750K
- FY16 funding - $770K
  - SCR task
  - DPF task
  - PNA task (limited)
  - LTAT activities

Barriers

- Emission controls contribute to durability, cost and fuel penalties
  - Low-temp performance is now of particular concern
- Improvements limited by:
  - Available modeling tools
  - Chemistry fundamentals
  - Knowledge of material behavior
- Effective dissemination of information

Partners

- DOE Advanced Engine Crosscut Team
- CLEERS Focus Group
- 21CTP partners
- USCAR/USDRIVE ACEC team
- Oak Ridge National Lab
- University of Wisconsin, Madison
- NSF/DOE-funded program with partners at Purdue, Notre Dame, WSU, Cummins, and ANL

Relevance (and Goals)

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- "CLEERS is a R&D focus project of the Diesel Cross-Cut Team. The overall objective is to promote development of improved computational tools for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems."

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 identify 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 cross-cut meetings
  - yearly workshops and surveys
  - ongoing discussions on program priorities with the VT office

Technical Milestones (FY2015/2016 Scope Objectives)

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- 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
- Selective Catalytic Reduction (SCR)
  - ✓ Developed a general guiding principle for the rational design of selective, active, and durable Cu/SSZ
  - ✓ Identified the active sites for Fe/SSZ catalysts
  - ✓ Partnered with ORNL to incorporate mechanistic understanding into global kinetics models, using new ammonia storage isotherm and CLEERS SCR protocol data obtained at Oak Ridge
- Low-temperature (LT) Aftertreatment (LTAT)
  - ✓ Participated in the round robin test of low temperature oxidation catalysts
- Passive NOx Adsorber (PNA)
  - ✓ Completed HC and NOx storage and release protocol
- Diesel Particulate Filter (DPF)
  - ✓ Obtained commercial light duty SCR-filter for analysis

Approach/Strategy

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Approach - "Science to Solutions"

- Build off of our strong base in fundamental sciences and academic collaborations
  - Institute for Integrated Catalysis (IIC)
  - Environmental Molecular Sciences Laboratory (EMSL)
- Orient strongly towards applications and commercialization
  - OEMs
  - TIER 1 suppliers
- Work closely with our partners and sponsors
  - ORNL (coordination of website, workshops, etc.)
  - DOE Advanced Engine Cross-Cut Team

Foundational (CLEERS)
- SCR
- LTAT
- PNA
- DPF

↔

CRADA Activities
- Standard LT SCR (FCA)
- Standard LT fast SCR (Cummins/JMI)
- Advanced emission controls (Cummins/JMI))
- LT oxidation (GM)
- SCR dosing system (USCAR)
- Fuel neutral particulate studies (GM)
- SCR-DPF (PACCAR)

Strategy – "Balanced portfolio"

- Utilize open CLEERS work to support industry CRADA activities, e.g., fundamental SCR studies led to the new CRADAs with FCA and Cummins
- Maintain clear separation between CLEERS and CRADA activities

(only CLEERS project scope covered in this presentation)

Technical Accomplishments

SCR

- Mechanistic understanding of model Cu/SSZ-13 catalysts led to the development of a general rational design principle for active, selective and durable Cu/SSZ-13 catalysts with Si/Al ratio (12-20) and Cu/Al ratio (0.2-0.3).
- Preparation and mechanistic understanding of model Fe/SSZ-13 catalysts helped identify the active sites for low temperature SCR activity and understand the deactivation mechanisms.
- Participated in collaboration with ORNL on the transient kinetic modeling of new NH_3 storage isotherm data.

LTAT

- Participated in round robin testing of oxidation catalyst protocol.

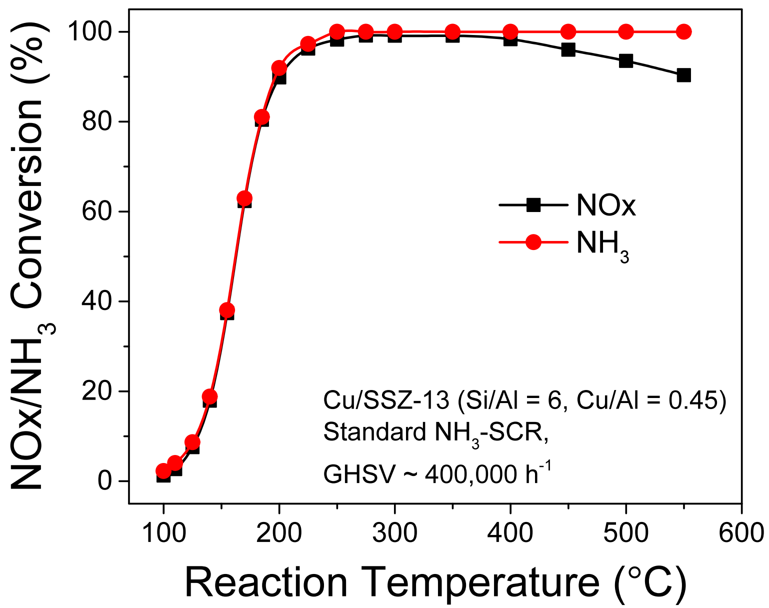
PNA

- With ACEC LTAT team, completed low temperature HC and NOx storage and release protocol, pending APTLC approval.
- With the guidance of DFT calculations, identified the IR vibrational signatures of NO_x species formed on CeO_2 after exposure to NO and $NO+O_2$ in a wide range of temperatures, and determined their thermal stabilities.

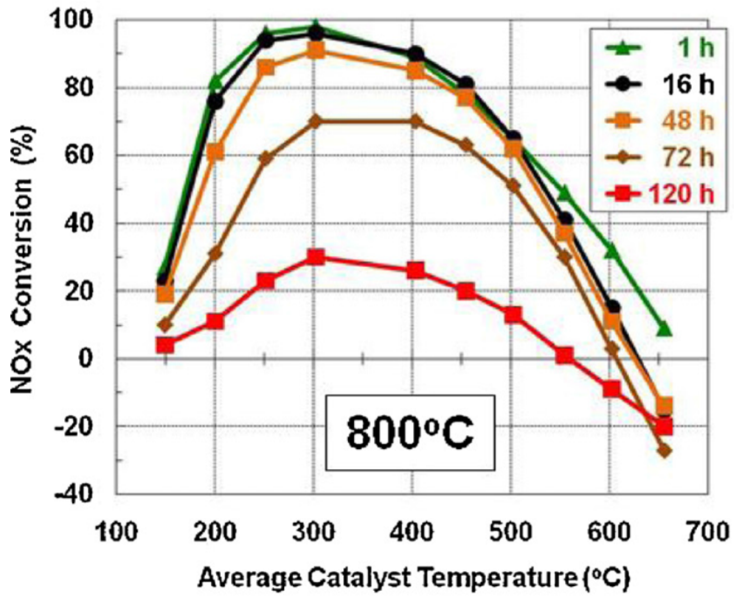
DPF

- Participated in collaboration with University of Wisconsin, Madison to examine possible effects of low-porosity surface features in ceramic exhaust filter walls.
- Obtained micro X-Ray CT data for commercial SCR-filter.

Technical Accomplishments (SCR task): Determination of Optimized Compositions from Rational Design of Cu/SSZ-13 Catalysts



Typical properly formulated fresh Cu/SSZ-13 catalysts at high loadings



Typical Cu/SSZ-13 catalysts after hydrothermal aging indicating the presence of CuOx clusters.

- Mechanistic understanding of model Cu/SSZ-13 catalysts led to the development of a general rational design principle for active, selective and durable Cu/SSZ-13 catalysts with Si/Al ratio (12-20) and Cu/Al ratio (0.2-0.3).

Technical Accomplishments (SCR task): Characterizations of Fe/SSZ Catalysts

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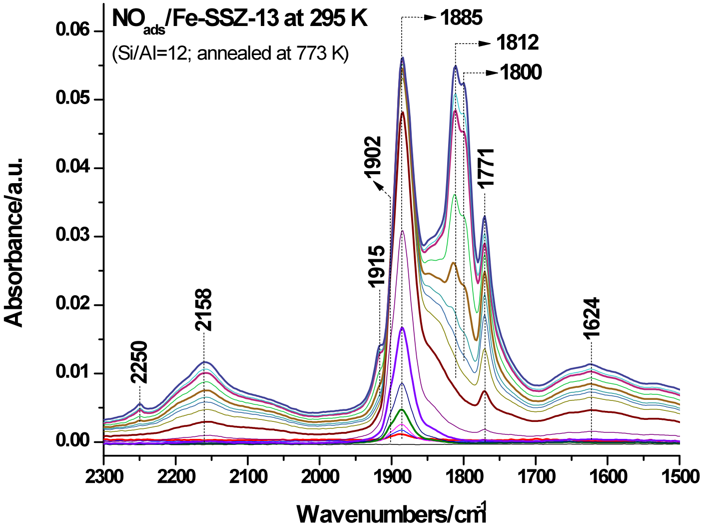
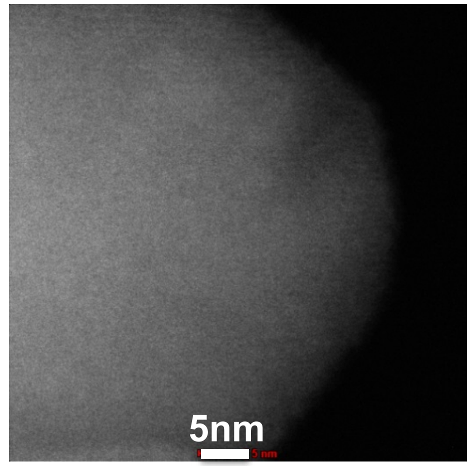
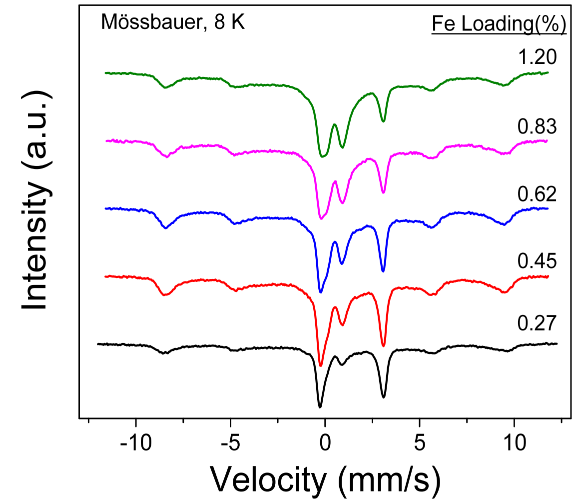


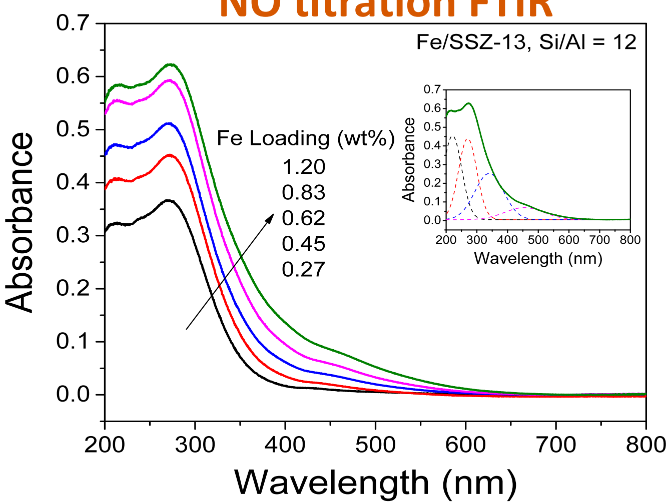
NO titration FTIR



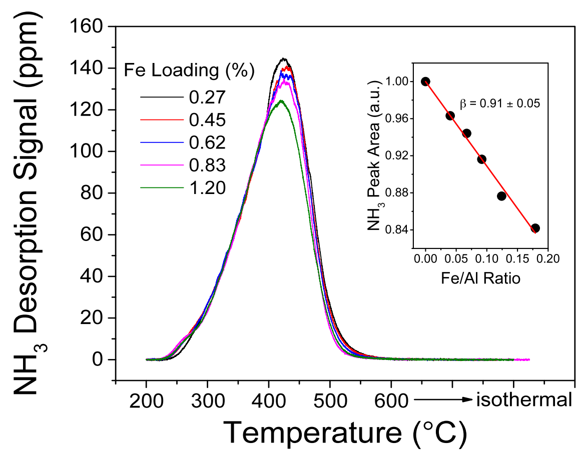
TEM Imaging



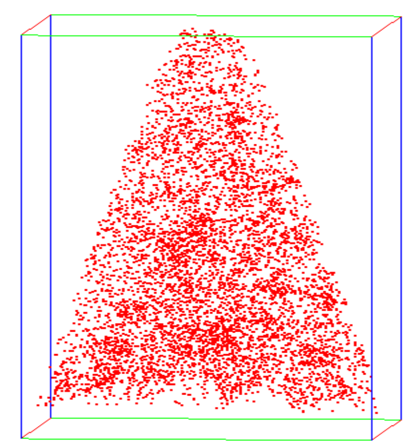
Mössbauer spectroscopy



UV-Vis Spectroscopy



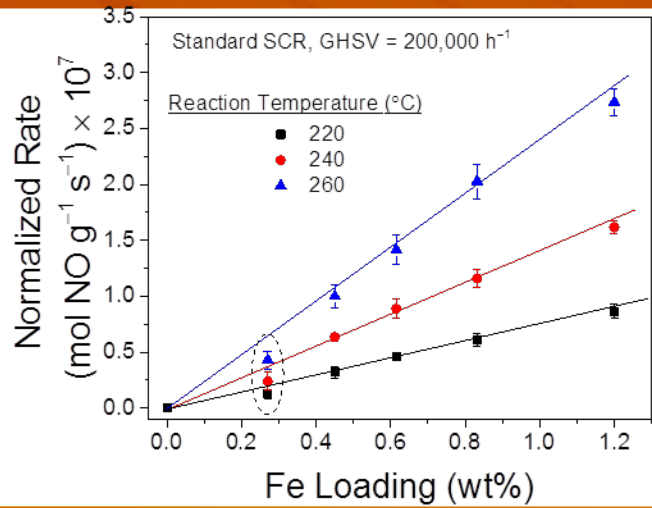
NH_3-TPD

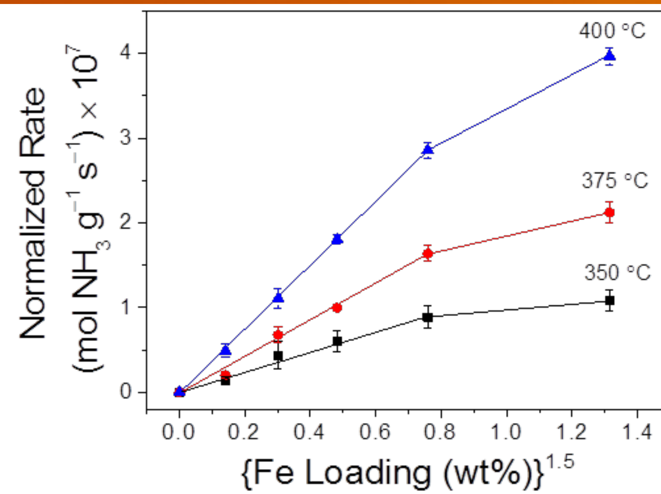


Atom probe tomography

- Fe/SSZ is shown as an example about how advanced characterizations help understand the nature of active sites and deactivation mechanisms .

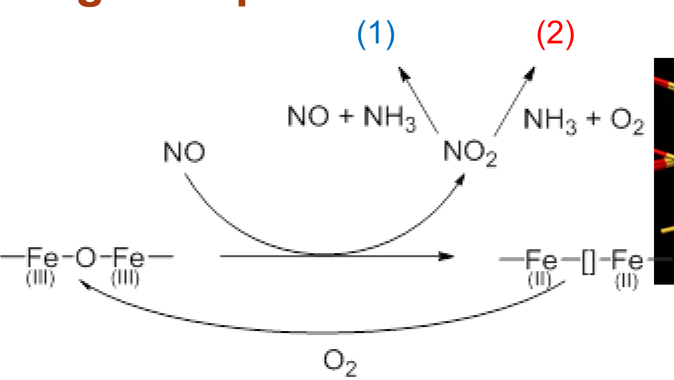
Technical Accomplishments (SCR task):
Identification of Active Sites of Fe/SSZ Catalysts





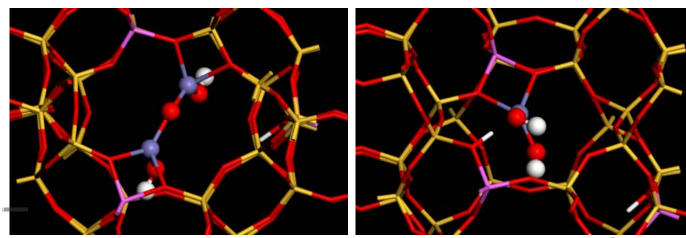
High-temperature Less Selective Pathways

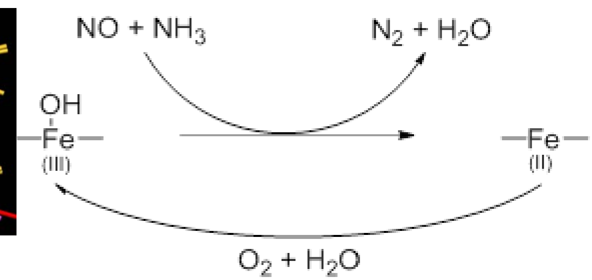
Low-temperature Selective Pathways

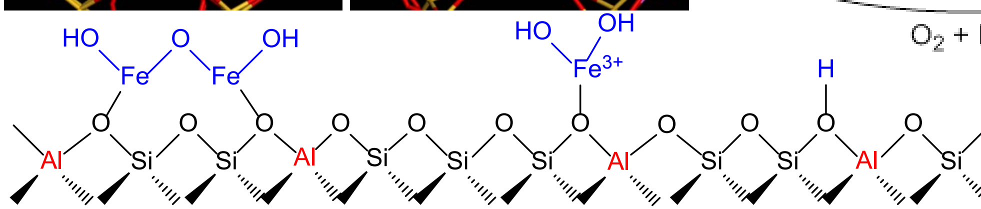


(1) $NO + NO_2 + 2NH_3 = 2N_2 + 3H_2O$

(2) $NO_2 + 2NH_3 + O_2 = NO + N_2 + 3H_2O$



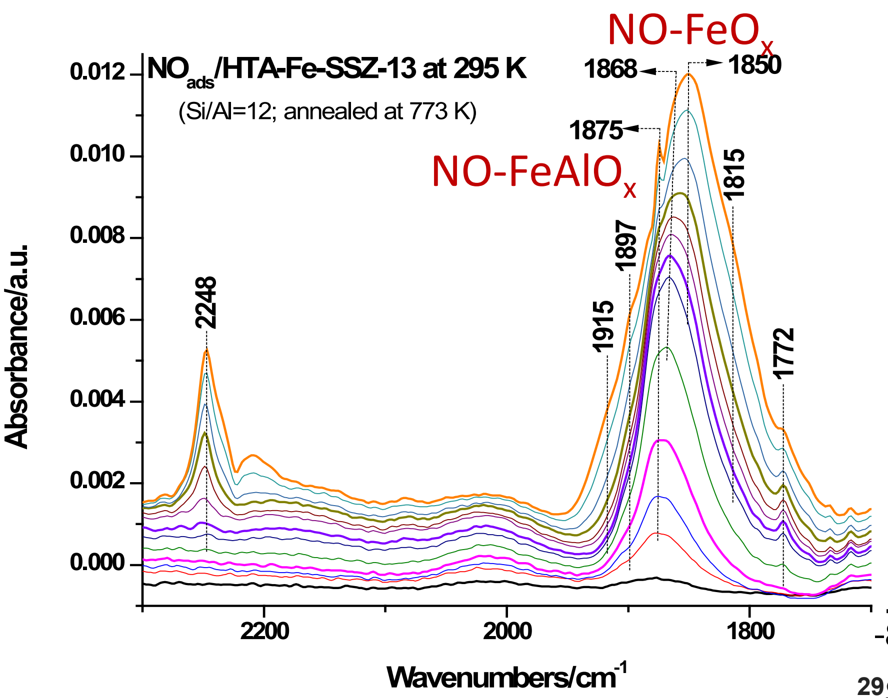




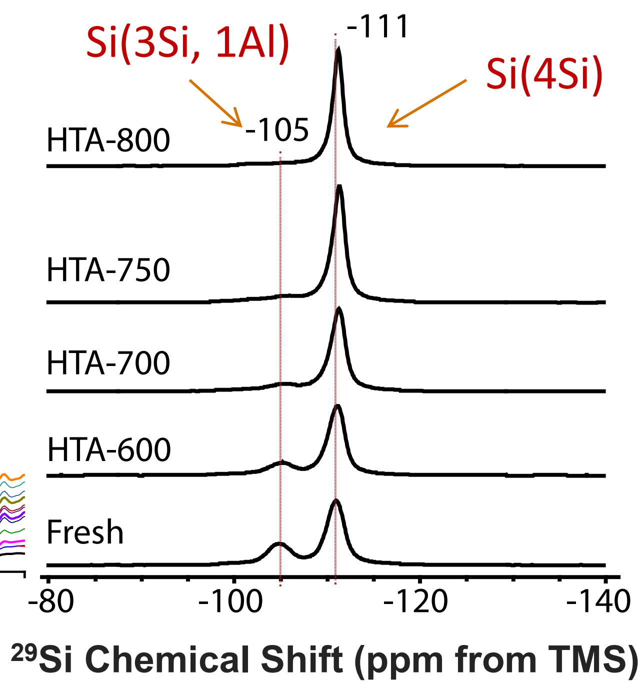
- Isolated $Fe(OH)_2$ monomers responsible for low-temperature activity.
- Dimers/higher oligomers responsible for high-temperature activity and side reactions.

Technical Accomplishments (SCR task):
Deactivation Mechanisms of HTA Fe/SSZ Catalysts

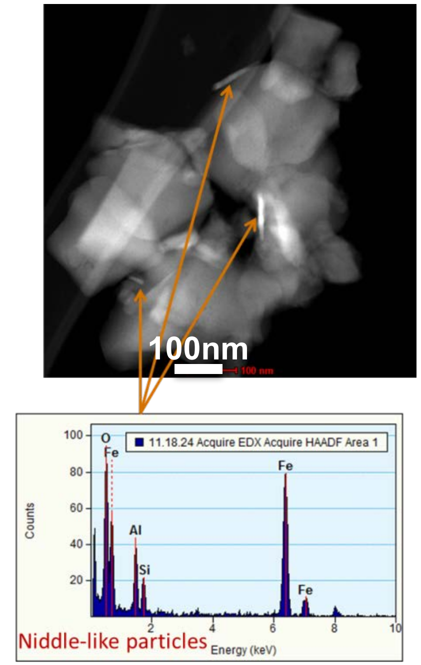
NO titration FTIR Spectroscopy



^{29}Si NMR



TEM

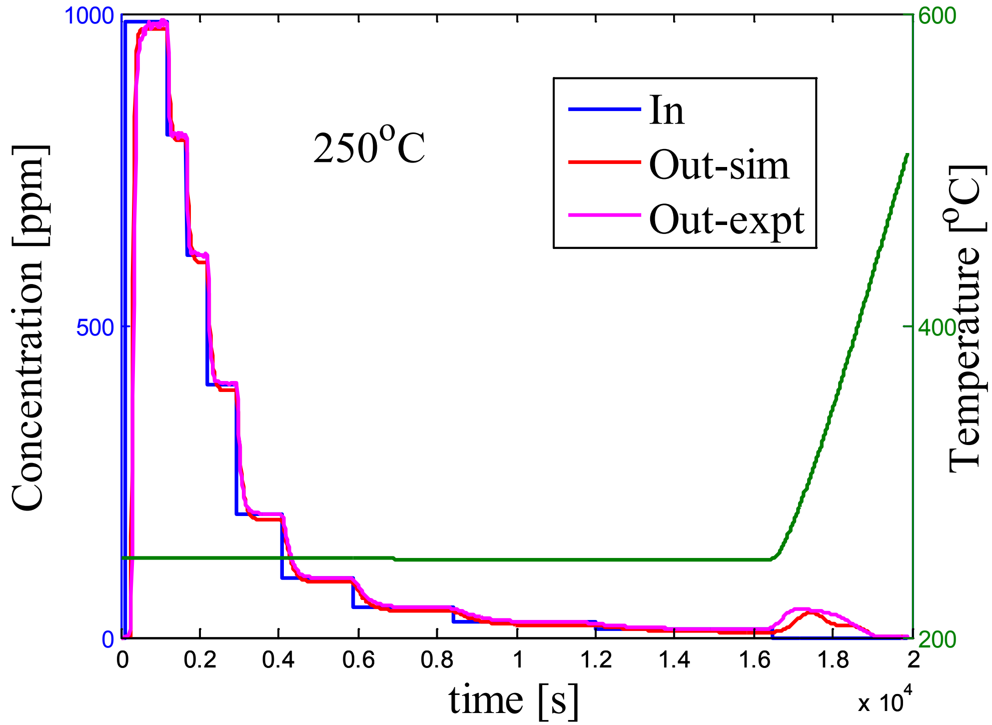


- Under hydrothermal aging conditions, dealumination causes extra-framework $Fe(OH)_2$ monomers to migrate and agglomerate.
- Detached $Al(OH)_3$ interacts with Fe-oxides to form Fe aluminates ($FeAlO_x$), leading to decreased low temperature SCR activity.

Technical Accomplishments (SCR task):

SCR Modeling in Collaboration with ORNL

- ORNL has generated an extensive dataset using updated CLEERS SCR and NH_3 storage protocols at a range of aging states
- Seeking to complement equilibrium storage model developed at ORNL with an improved global transient model
- Starting point: three site NH_3 storage model proposed by Olsson *et al*. (2015)*
  - Site 1 – Acid Site (Tempkin)
  - Site 2 – Acid Site (Langmuir)
  - Site 3 – Weak physisorption



- The three site model provides a reasonable structure to fit the latest storage data
- Other schemes are being considered to incorporate recent mechanistic understanding

* Olsson, L., K. Wijayanti, K. Leistner, A. Kumar, S. Y. Joshi, K. Kamasamudram, N. W. Currier and A. Yezerets (2015). "A multi-site kinetic model for NH3-SCR over Cu/SSZ-13." Applied Catalysis B-Environmental **174**: 212-224.

Technical Accomplishments (LTAT task): Participated in Round Robin Testing of OC Protocol

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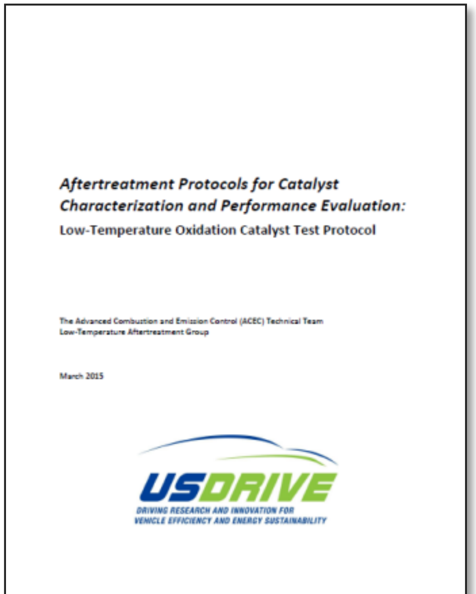
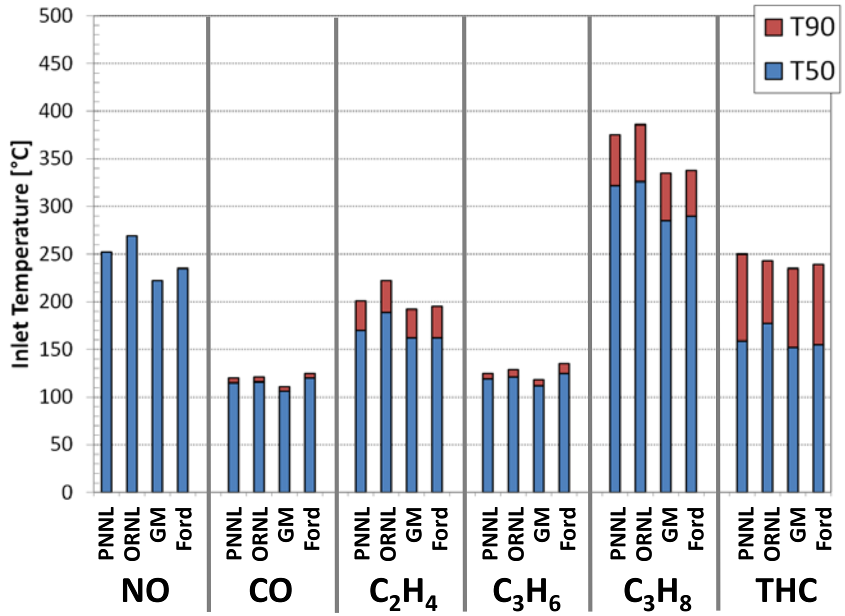
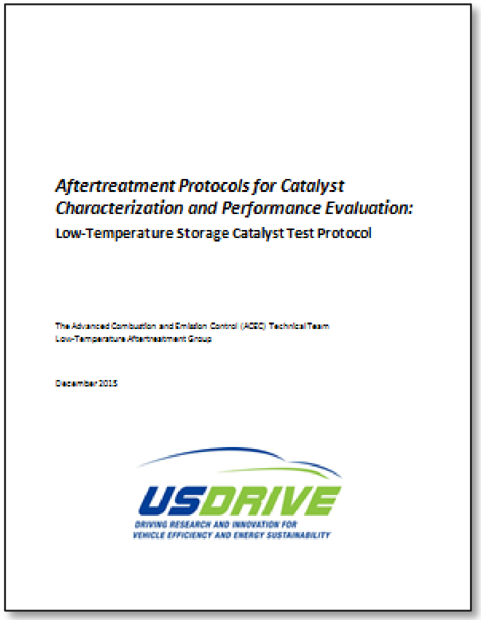




Org.	Representatives
FCA	Craig DiMaggio
Ford	Joe Theis
GM	Se Oh Wei Li
PNNL	Ken Rappe Mark Stewart
ORNL	Jim Parks Josh Pihl
UM	Galen Fisher
DOE	Ken Howden

- Evaluated impact of reactor setup
  - Example: found that inert core upstream of catalyst has no effect
- Identified protocol revisions to improve clarity
- Shared data with members of LTAT team for comparison of reproducibility across labs

Technical Accomplishments (PNA task): Completed Storage and Release Protocol



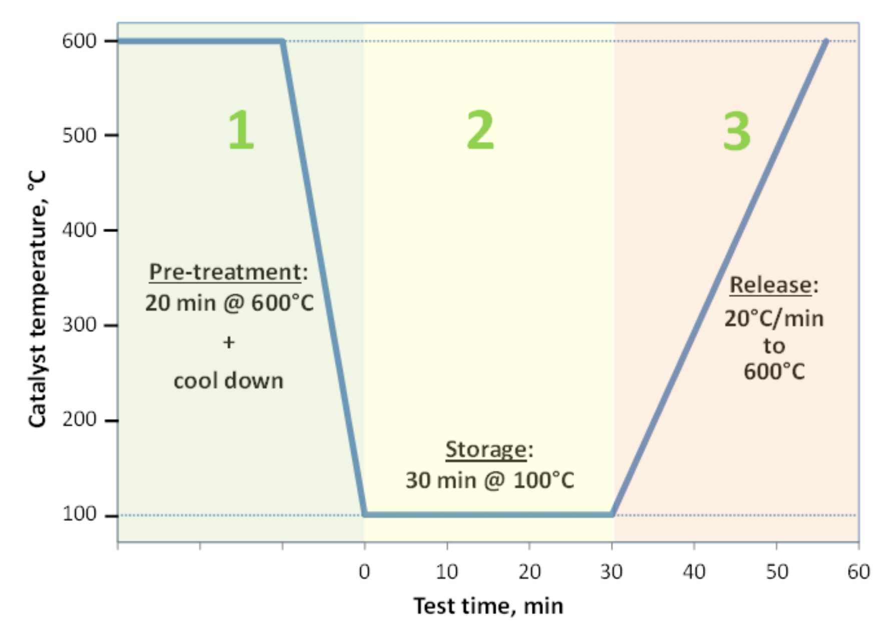
Aftertreatment Protocols for Catalyst Characterization and Performance Evaluation:
Low-Temperature Storage Catalyst Test Protocol

The Advanced Combustion and Emission Control (ACEC) Technical Team
Low-Temperature Aftertreatment Group

December 2015

Test sequence consists of 3 components

1. Pretreat
2. Storage
3. Release



- Storage and Release Protocol – complete, pending APTLC approval
- Focused on HC and NO_x storage and release/react catalysts
  - Simple to execute, comprehensive enough to encompass many scenarios
- Comparison to oxidation catalyst protocol
  - Same document structure
  - Differences in testing structure to account for transient storage/release/react
    - Versus steady-state reaction (i.e., oxidation)
  - Reactor design/operation different due to time-sensitive transient events

Technical Accomplishments (PNA task): Fundamental Understanding of Interaction of NO and NO+O_2 with CeO_2

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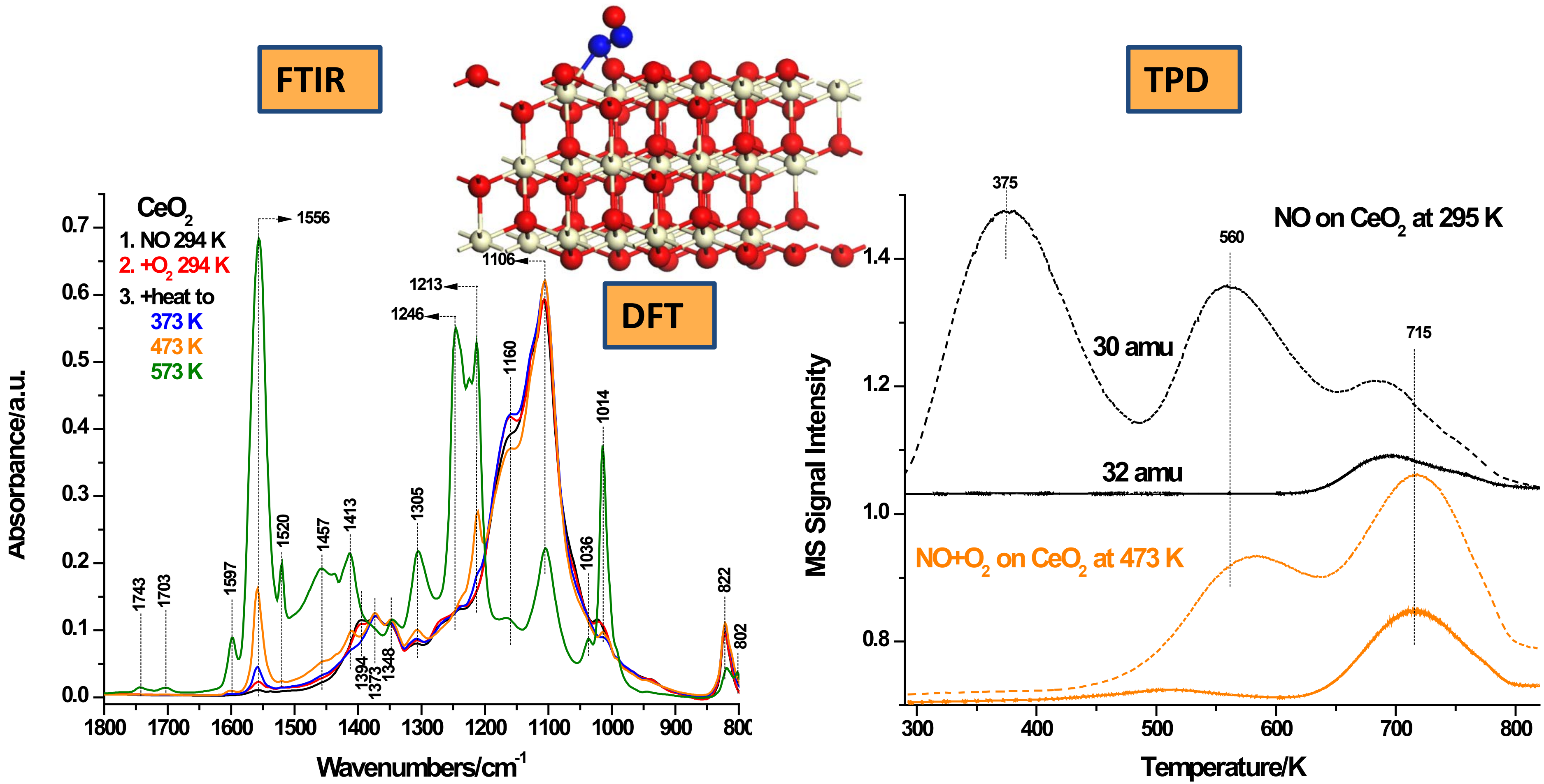
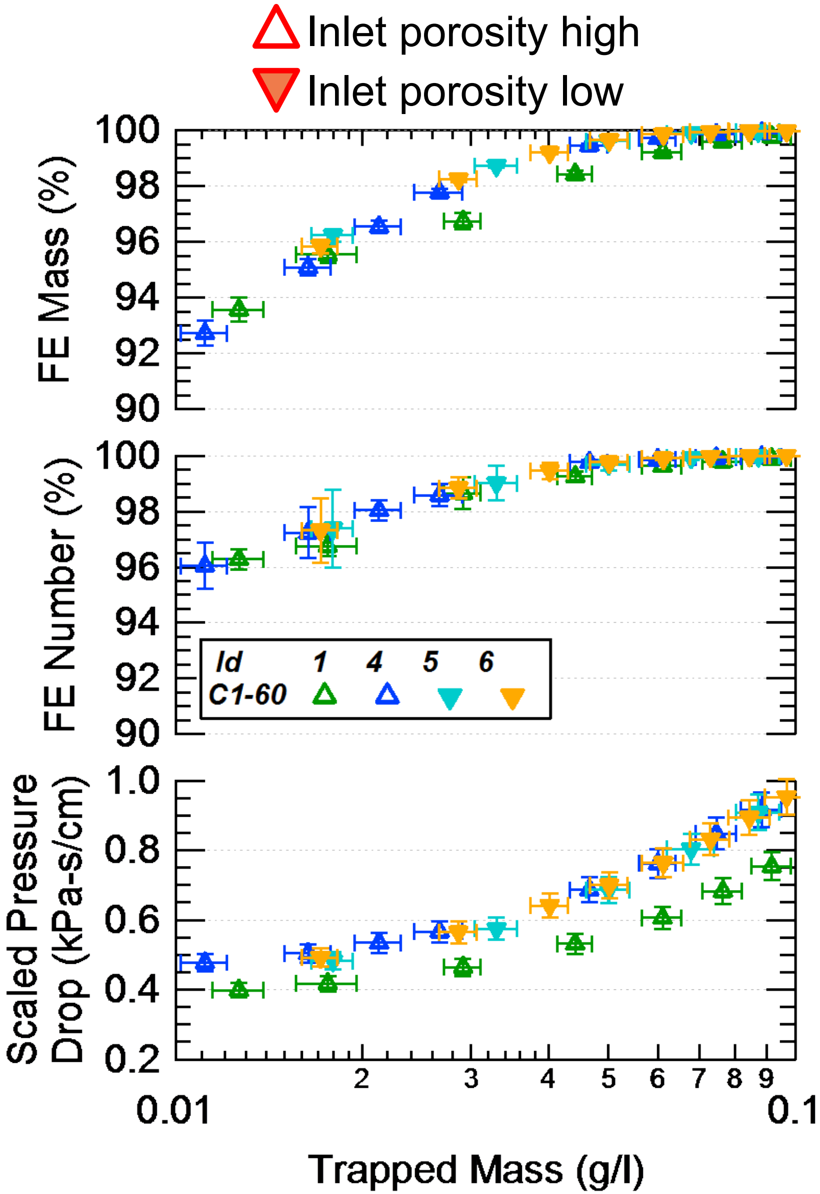


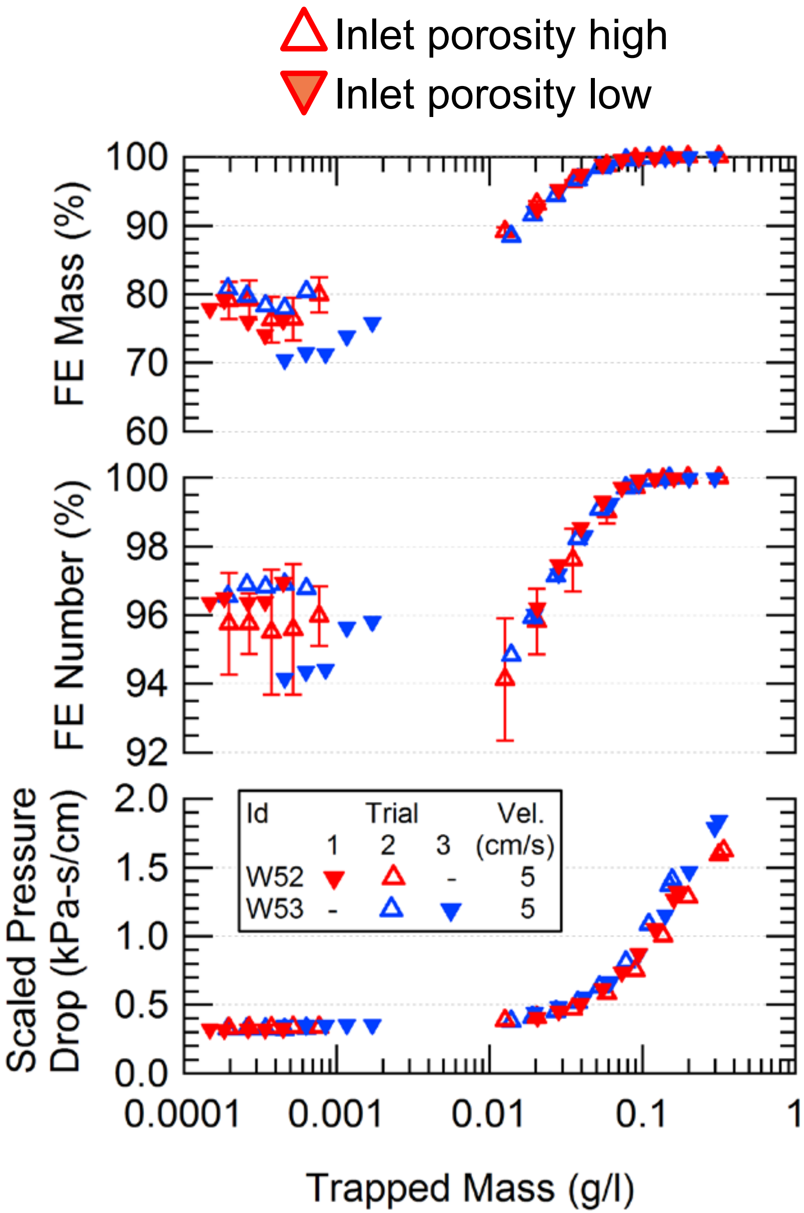
- Guided by DFT on IR peak assignments, it was found that NO adsorbs on CeO_2 as nitrites and hyponitrites, and, in the presence of O_2 at elevated temperatures, nitrites and hyponitrites convert to nitrates.
- TPD after NO adsorption yields low T NO desorption with some of the adsorbed NO being converted to nitrates even in the absence of gas phase O_2, and nitrates decompose at high T as NO + O_2.

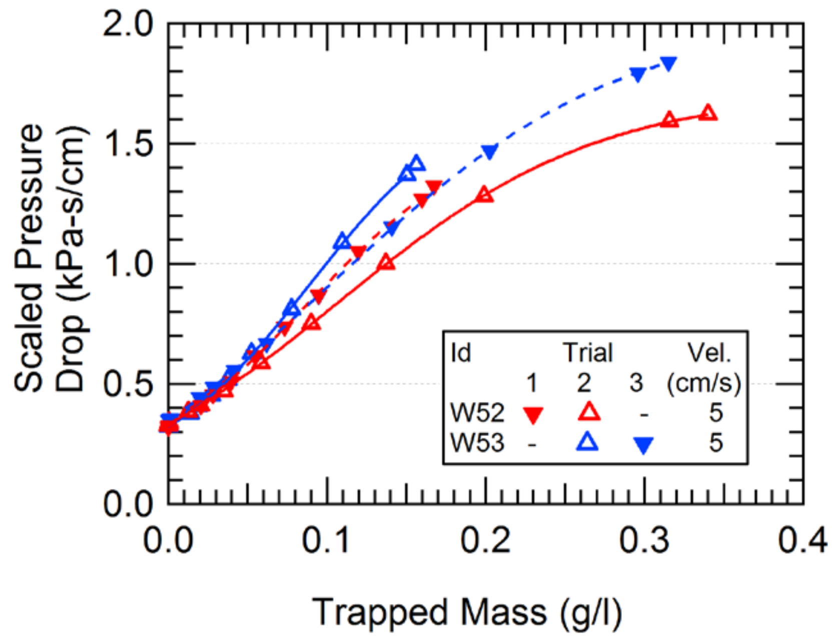
Technical Accomplishments (DPF task): Fundamental Studies of Filter Characteristics in Collaboration with U of Wisconsin, Madison



- New techniques for analyzing CT data had identified a common feature in cordierite and aluminum titanate filter materials: thin, low porosity layers on filter wall surfaces.
- “C1” cordierite wafer samples had been ground to thickness, removing the low porosity layer from one side.
- Using the EFA system at U of Wisconsin, the same wafer samples were repeatedly loaded with soot and regenerated, flipping the sample between experiments.
- Different behavior between initial and subsequent loadings show measurable effect of ash from very first loading.
- However, no significant difference in behavior was observed between loading the low and high porosity surfaces.

Technical Accomplishments (DPF task):
Fundamental studies of Filter Characteristics

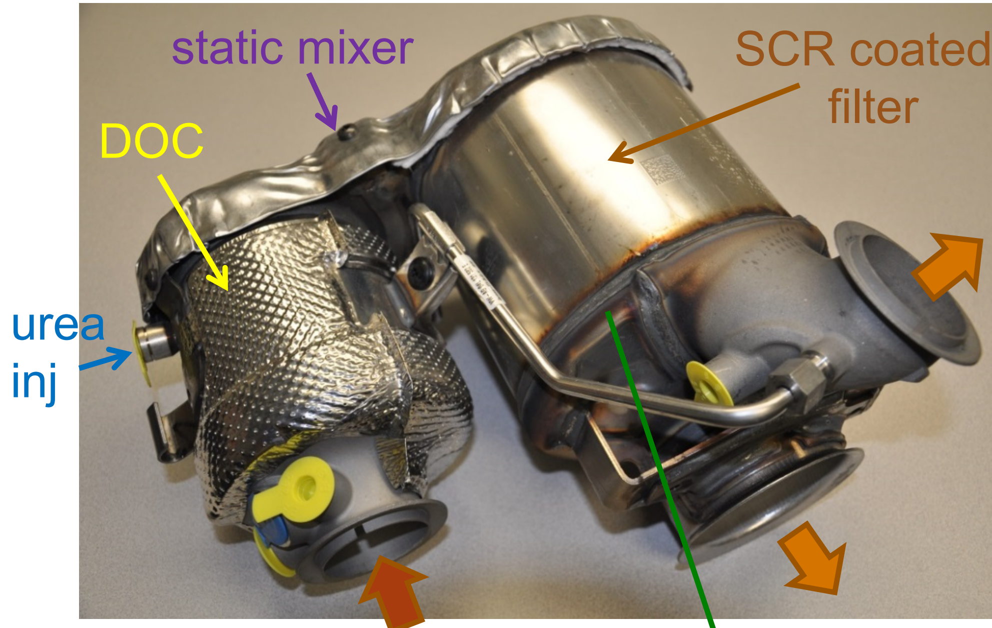


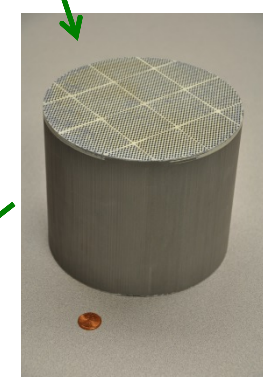


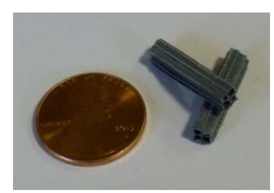
- Additional experiments were run at higher flow rates and for longer durations to increase loading
- No conclusive impact of filter orientation was observed on capture efficiency or pressure drop

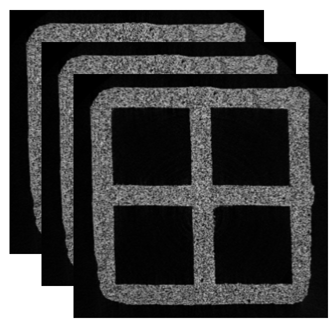
Examination of Multi-functional Filters

- One of the first commercially deployed SCR-filters was used with the VW 2.0T TDI Clean Diesel EA288 (2015 Jetta, Passat, etc.)
- No defeat device with this system
- Innovative compact system includes DOC, static mixer, filter with Cu-zeolite SCR coating
- Filter:
  - 165mm diameter x 140mm
  - Segmented silicon carbide
  - ~300/12, asymmetric channels
- Samples from various locations in the brick have been submitted for X-Ray micro CT scans
- Will attempt to image SCR coating within/upon filter walls









(Example images from a different SiC filter)

Response to Previous Year Reviewers' Comments

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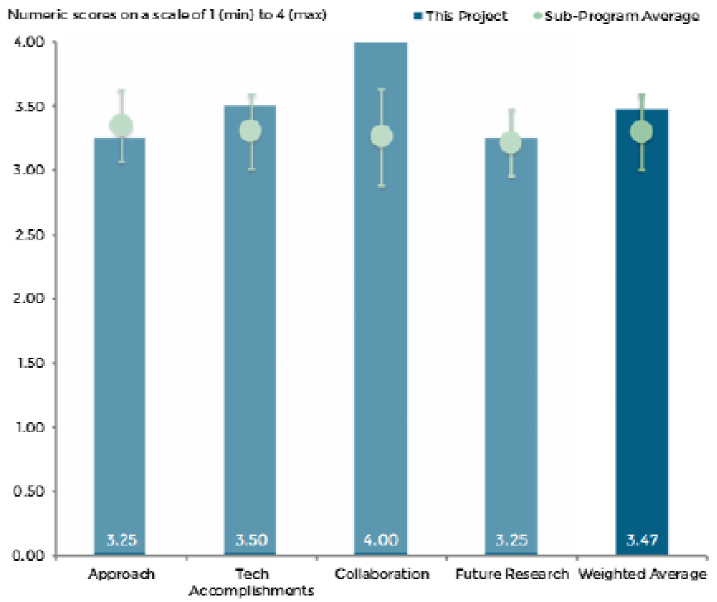
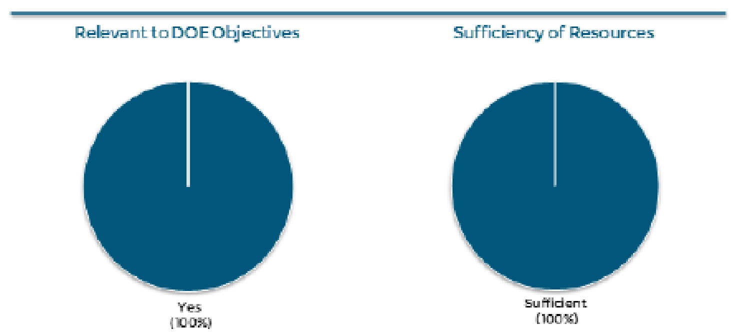
- Nearly all the comments from the reviewers last year were very supportive and complimentary.
- Some comments/recommendations included:
  1. ..focus on generating knowledge on the reaction kinetics and mechanism.. Not on developing new catalyst preparation methods..
  2. What's next for X-ray/CT analyses.
  3. Add sulfur tolerance studies.
- PNNL response:
  1. SCR effort is primarily focused on the elucidation of active sites, mechanistic and kinetic studies to guide the rational design of Cu/SSZ and Fe/SSZ catalysts.
  2. Will attempt to image the first commercially deployed multi-functional filters.
  3. PNNL's studies of aging and tolerance of SCR catalysts are carried out as part of a CRADA program with Cummins.





Collaboration and Coordination with Other Institutions

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Collaborators/Coordination

- DOE Advanced Engine Crosscut Team (this group is the primary sponsor and overseer of all activities)
- CLEERS Focus Groups
- USCAR/USDRIVE ACEC team
- 21CTP partners
- Oak Ridge National Lab
- U of Wisconsin, Madison
- Very active collaboration with an NSF/DOE-funded program with partners at Purdue, Notre Dame, WSU, Cummins and ANL

Acknowledgements

- PNNL: Haiying Chen (Johnson Matthey), Laura Righini (Politechnico Milano), John Luo (Cummins), Gary Maupin, Alla Zelenyuk, Jacqueline Wilson
- ORNL: Stuart Daw, Jim Parks, Josh Pihl, John Storey, Vitaly Prikhodko, Samuel Lewis, Mary Eibl, and support from the ORNL team
- DOE Vehicle Technologies Program: Gurpreet Singh and Ken Howden

Remaining Challenges and Barriers

SCR

- Understand the nature and location of the active Cu species in Cu-CHA SCR catalysts during operation.
- Elucidate the exceptional stability of SSZ zeolites.
- Improved global models for NH_3 storage and kinetics in aged and poisoned catalysts.

LTAT

- Low temperature oxidation of short-chain HCs including methane.

PNA

- Insufficient sulfur tolerance of CeO_2-based NO_x materials requires the search for new type of materials that is able to store NO_x at low temperature and release them at elevated temperatures, e.g., metal ion exchanged zeolites.

DPF

- The three-way collaboration between OEM’s, filter manufacturers, and catalyst coaters would benefit from more open dialog concerning the design and optimization of multi-functional filters.

Proposed Future Work

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SCR

- Experimentally address the continuing fundamental issues being identified in modeling studies.
- Comprehensive studies of SCR mechanisms and kinetics on Cu/SSZ using an integrated theoretic and experimental approach, i.e., to fully describe Cu^{1+} oxidation to Cu^{2+}, Cu loading dependence, and temperature dependence.
- In collaboration with collaborators on NSF/DOE-funded program, understand the similarity and difference, i.e., the nature and stability of the active Cu species, in the SSZ-based and SAPO-34 zeolite-based catalysts.
- Understand the exceptional stability of SSZ as compared to other zeolites.
- Use knowledge of detailed reaction mechanisms and intermediates to propose improved global kinetics models for aged catalysts, in coordination with extensive experimental effort at ORNL.

LTAT

- Low temperature CH_4 and HC oxidation.

PNA

- Mechanistic and kinetic studies of NOx storage/release on precious metals (Pd, Pt, Pd/Pt alloy) on zeolites.

DPF

- Complete analysis of commercial SCR-filter using micro X-Ray computed tomography.

Summary

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SCR

- A general rational design principle for Cu/CHA catalysts is provided based on the mechanistic studies of model Cu/SSZ-13 catalysts, which suggests Si/Al ratio of 12-20 and Cu/Al ratio of 0.2-0.3 for active, selective and durable Cu/SSZ-13 catalysts.
- Mechanistic studies of model Fe/SSZ-13 catalysts suggest that isolated $Fe(OH)_2$ monomers are active sites for low temperature SCR while dimer/higher oligomers of Fe species are responsible for high temperature SCR and undesired reactions.
- Hydrothermal aging studies of Fe/SSZ-13 catalysts indicate that extra-framework $Fe(OH)_2$ monomers can readily migrate and agglomerate to form Fe oxide clusters which can react with $Al(OH)_3$ from dealumination to form Fe aluminates ($FeAlO_x$), leading to the loss of low temperature SCR activity.

LTAT

- Participated in round robin testing of low temperature oxidation catalyst protocol.

PNA

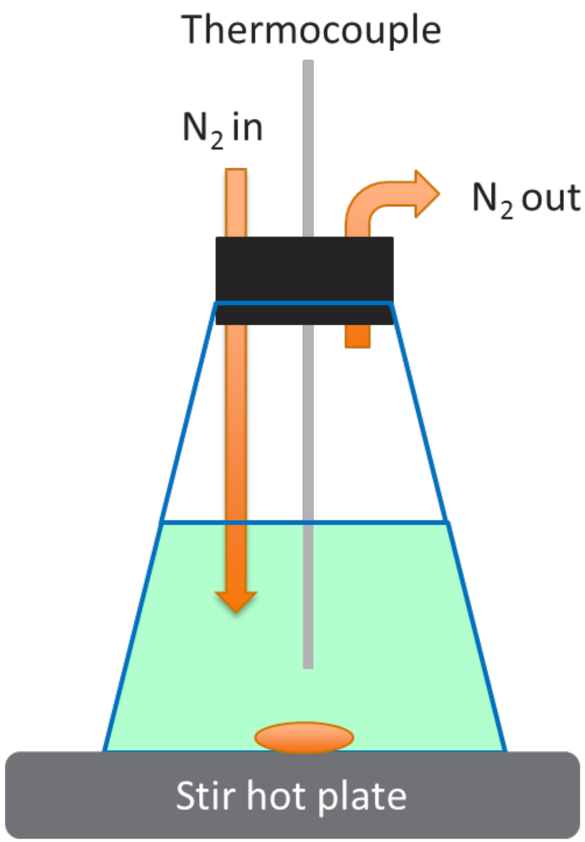
- Completed HC and NOx storage and release protocol.

DPF

- Initial studies suggest that the low-porosity wall surface layers observed in many porous ceramic filter substrates do not have a significant impact on filter performance.

Technical Back-Up Slides

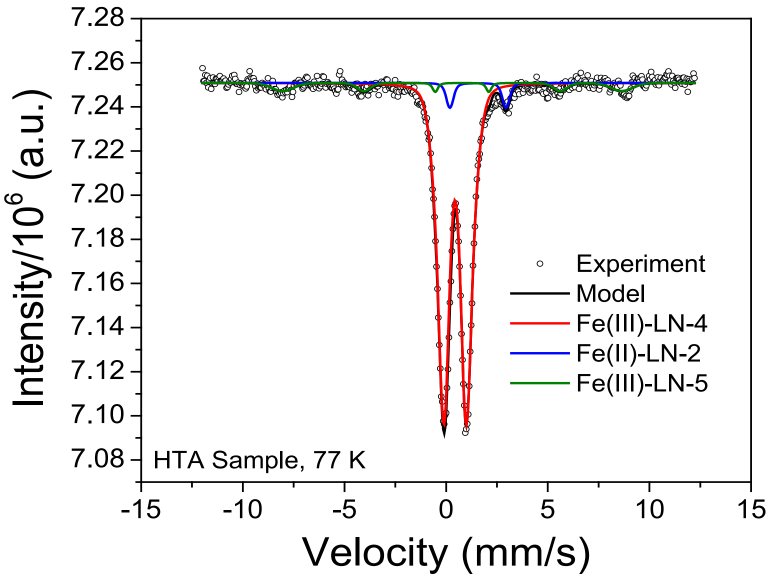
Fe/CHA: Catalyst Synthesis



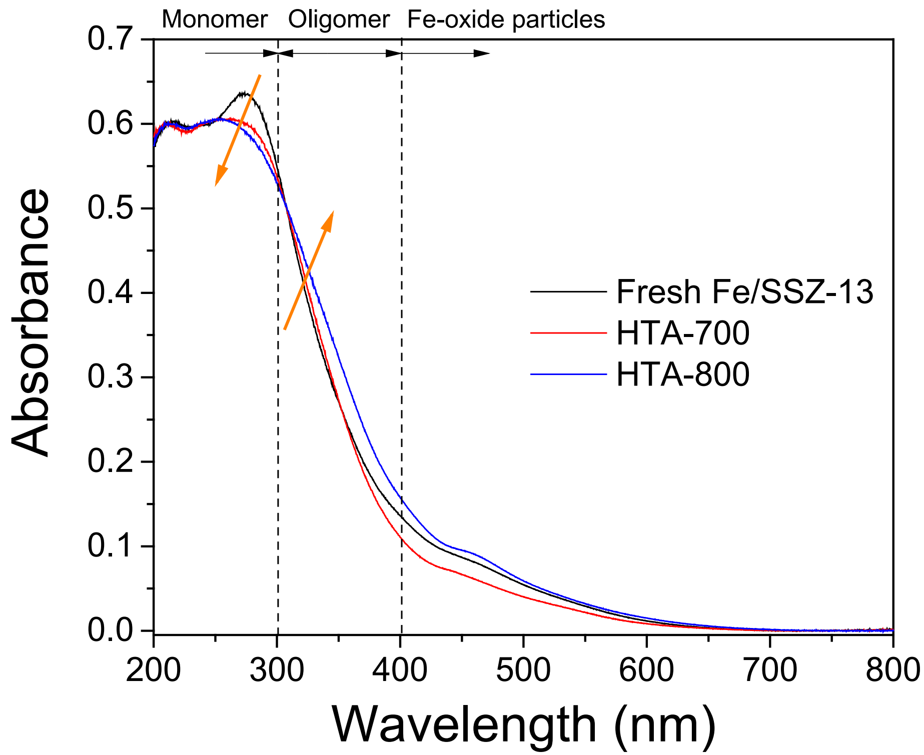
- Solution ion-exchange between NH_4/SSZ-13 and $Fe(NO_3)_2$ at 80 °C for 1h.
- Maintain a low pH of ~3.0.
- Under the protection of pure N_2.
- Fe/SSZ-13, Fe = 0.27-1.20 wt%, Si/Al = 12;
- Fresh catalysts hydrothermally aged at 600/700/750/800 °C for 16 h in flowing air containing 10% of H_2O.

Nature of Fe species in HTA samples

Mössbauer Spectroscopy



UV-Vis Spectroscopy

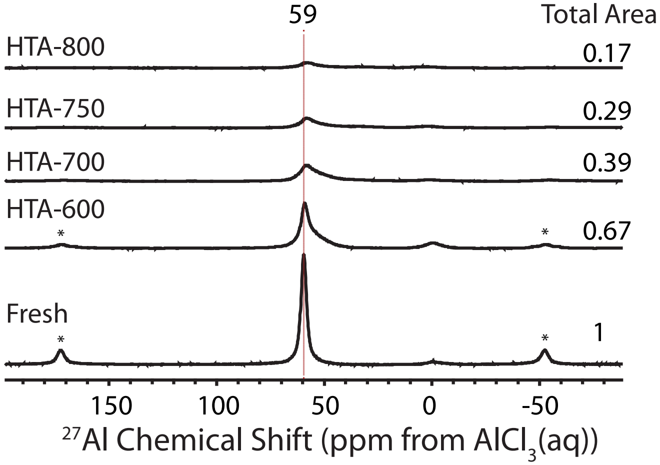


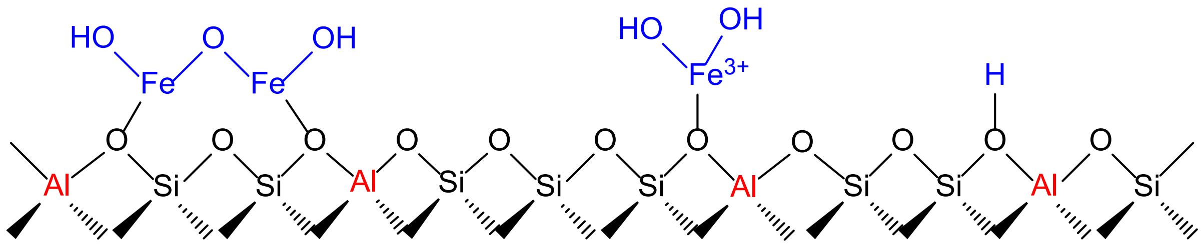
- Mössbauer indicates (1) Fe species are structurally similar to Fe-oxides; (2) there may be Al incorporation into Fe-oxides.
- UV-vis results suggest monomers are less stable

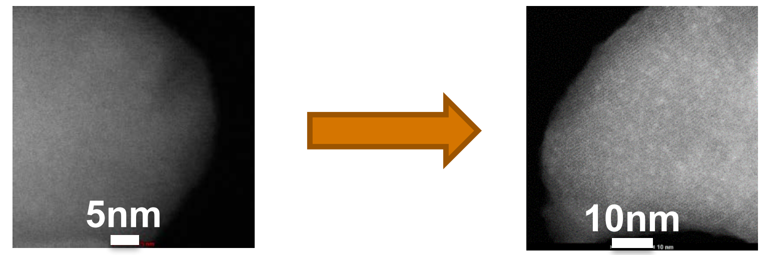
F. Gao, M. Kollar, R.K. Kukkadapu, Y. Wang, J. Szanyi, C.H.F. Peden, *Applied Catalysis B* **164** (2015) 407-419.
R. Kefirov, E. Ivanova, K. Hadjiivanov, S. Dzwigaj, M. Che, Catal. Lett. **125** (2008) 209-214.

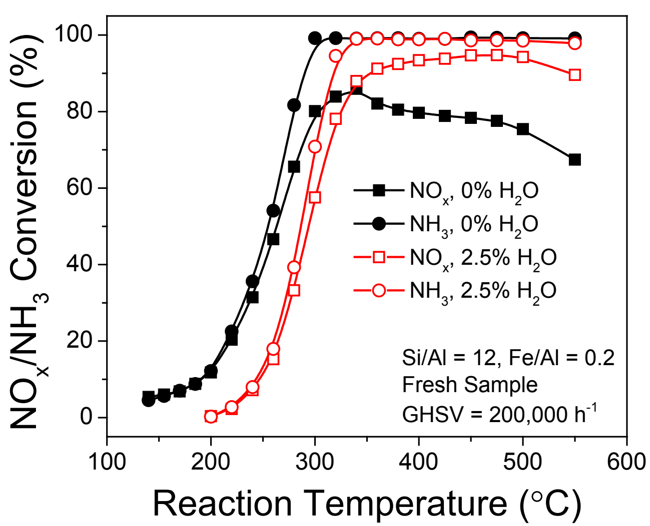
SCR Performances after HTA

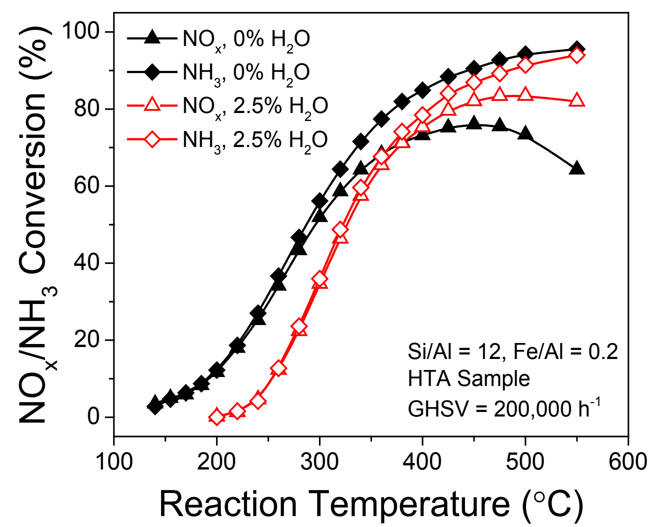
^{27}Al NMR











Low-temperature performance decreases but high-temperature performance largely maintains, consistent with the stability difference between monomers and dimers.

EFA Filtration Experiments at U of Wisconsin, Madison

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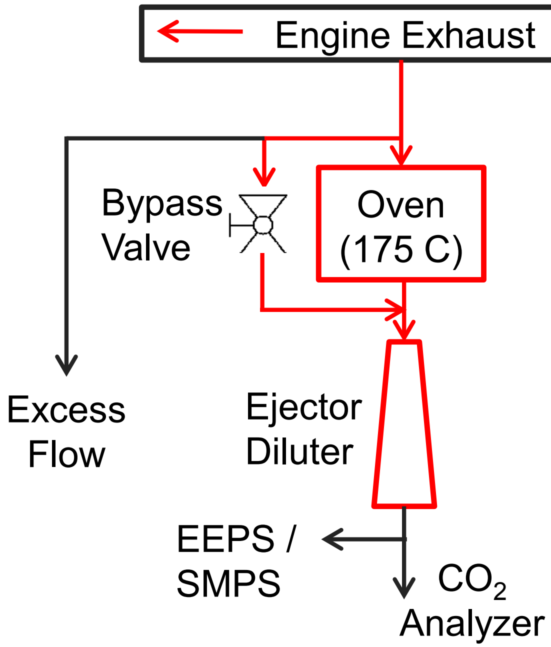
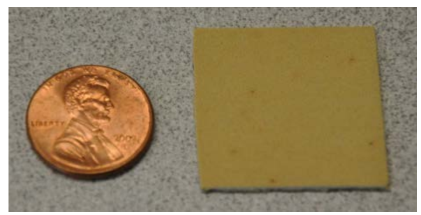
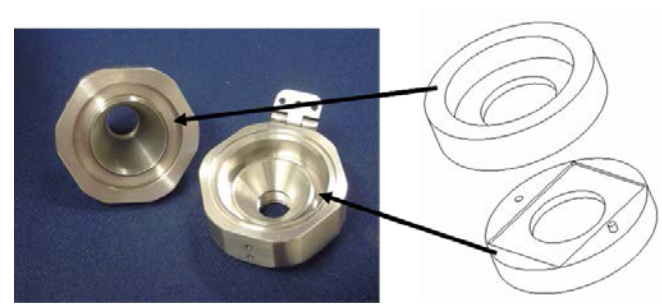
Exhaust filtration analysis (EFA) system



- Filtration experiments were carried out at the University of Wisconsin, Madison Engine Research Center using the Exhaust Filtration Analysis (EFA) system
- Particle size distributions in and out of filter sample holder are continuously measured for number and mass capture efficiency and integrated for real-time filter loading

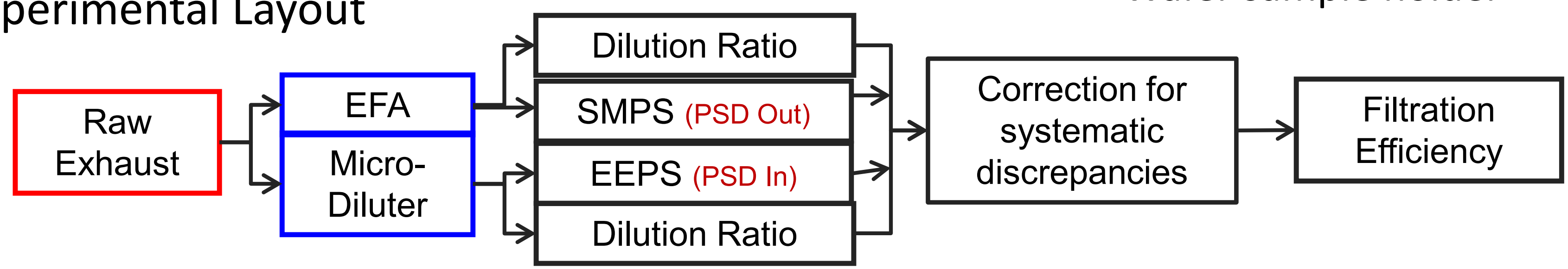


Wafer filter sample



Wafer sample holder

Experimental Layout



Fundamental Studies of Filter Characteristics

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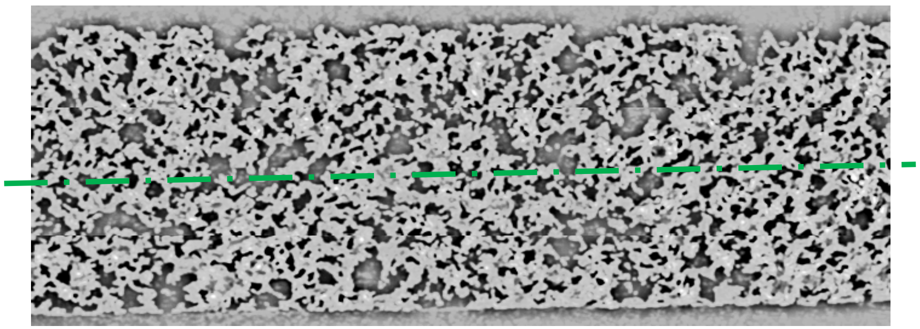
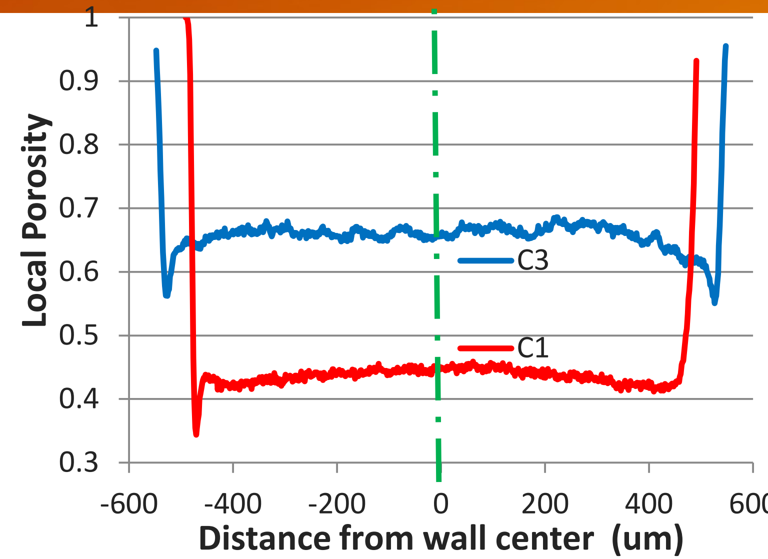
C1 (Top) – High porosity



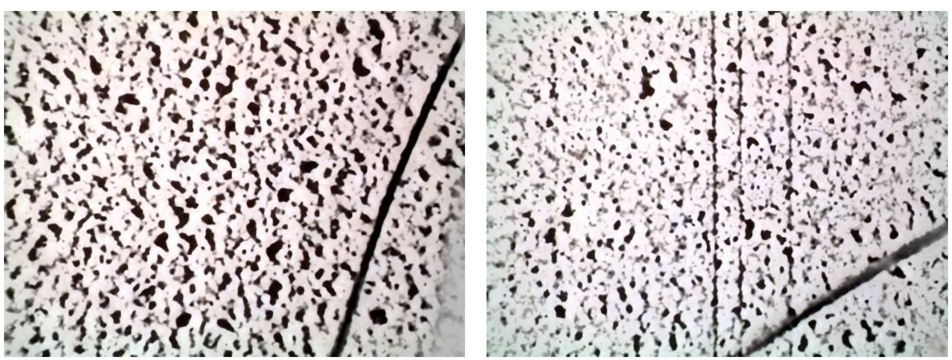
C1 (Bottom) – Low porosity

Micro-CT image (PNNL)



C1 (Top)
High porosity

C1 (Bottom)
Low porosity



Optical microscope image (50X, UW Madison)

- New techniques for analyzing CT data had quantified a common feature in cordierite and aluminum titanate filter materials: thin, low porosity layers on filter wall surfaces
- Could this feature affect behavior during filtration?
- "C1" cordierite wafer samples had been ground to thickness, removing the low porosity layer from one side