CLEERS: Aftertreatment Modeling and Analysis

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Pacific Northwest National Lab

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ACE023

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Overview

- Timeline
  - Status: On-going core R&D
  - DPF activity originated in FY03
  - Now also includes LNT, SCR, DOC and LTAT technologies
- Budget
  - FY13 funding - $750K
  - FY14 funding - $750K
    - SCR task
    - DPF task
    - LNT task (limited)
    - LTAT activities initiated

CLEERS

- Barriers
  - Emission controls contribute to durability, cost and fuel penalties
    - Low-temp performance 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
  - NSF/DOE-funded program with partners at Purdue, Notre Dame, WSU, Cummins and ANL

Relevance (and Goals)

- "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 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
  - Ongoing discussions on program priorities with the VT office

Technical Milestones (FY2013/2014 Scope Objectives)

- 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)
  - ✓ Prepare a range of model SCR catalysts for fundamental studies ; to include Fe-SSZ-13, Cu-SAPO-34 with varying Cu loading, and Cu-SSZ-13 with varying Si/Al ratios and Cu loadings.
- NO_x Storage-Reduction (NSR) Catalysts
  - ✓ Complete fundamental studies of novel high-temp LNT catalyst materials
  - ✓ Initiate studies of low temperature passive NOx adsorbers
- Diesel Particulate Filter (DPF)
  - ✓ Use advanced analytical techniques to examine particulates produced by state-of-the-art lean gasoline direct injection engine
  - ✓ Use high resolution micro X-Ray Computed Tomography to study multi-function filters coated with a current commercial SCR catalyst in order to better understand how the catalyst affects filtration and backpressure

Approach/Strategy

- **Approach - "Science to Solutions"**
  - We build off of our strong base in fundamental sciences and academic collaborations
    - Institute for Integrated Catalysis (IIC)
    - Environmental Molecular Sciences Laboratory (EMSL)
  - With a strong pull towards industrial applications and commercialization
    - OEMs
    - TIER 1 suppliers
  - Working closely with our partners and sponsors
    - ORNL (coordination of website, workshops, etc.)
    - DOE Advanced Engine Cross-Cut Team
- **Strategy – "Balanced portfolio"**
  - Utilize open CLEERS work to support industry CRADA activities

CLEERS activity

Integrated Systems – George Muntean

- DPF subtasks* – Mark Stewart
- SCR subtasks* – George Muntean
- LNT subtasks – Chuck Peden
- LTAT activities – George Muntean

*PNNL-led subteam
**Past activities

CRADA activities

DPF – DOW Automotive (Stewart)**

Fuel Neutral Particulate study (Stewart)

SCR/DPF – PACCAR (Rappe)

SCR/DPF – Ford Motor Company (Peden)

Low T Oxidation – General Motors (Peden)

SCR Dosing Systems – GM & Ford (Karkamkar)

SCR and LNT – Cummins Inc. (Peden)

Oxidation Catalysts**

– General Motors (Herling)

– SDC Materials (Herling)

– Caterpillar (Rappe)

Technical Accomplishments (Outline)

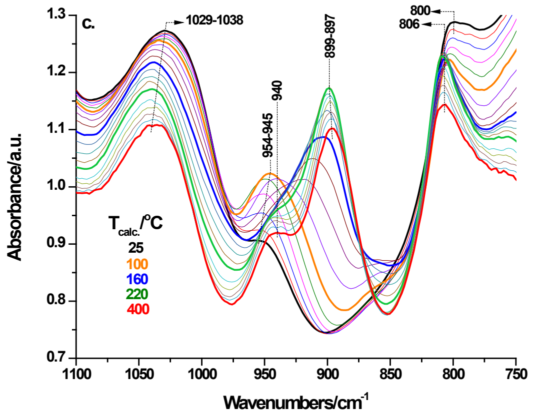
- SCR
  - Assisted ORNL in continuing development and improvement of SCR protocol experiments
  - Materials characterization/mechanistic studies
    - state-of-the-art characterization data of Cu-zeolite – Cu mobility during SCR
    - detailed kinetics studies for structure/function determination – likely explanation of "seagull" shaped performance curves
    - hydrothermal deactivation – effects on ammonia storage
- NSR
  - Completed studies of K-based LNT materials. Even promising titanate-based supports don't solve the K-mobility issues.
  - Initiated fundamental studies of passive NOx adsorber materials for low temperature applications.
- DPF
  - Participated in cooperative experiments at ORNL to characterize particulates produced by a 2008 BMW 1-series 120i gasoline engine
  - Obtained detailed, micro CT data for advanced high-porosity filter substrate and multi-function SCRFs with various catalyst loadings
  - Developed techniques for converting raw CT data to 3D geometries which match porosities measured by mercury porosimetry
  - Differentiated between catalyst and substrate in 3D data to characterize catalyst location within the filter wall and effects on flow
- LTAT
  - Kinetics experiments were carried out for medium duty and light duty diesel particulate samples
  - Initiating studies of candidate low temperature oxidation catalysts

Technical Accomplishments (SCR task):

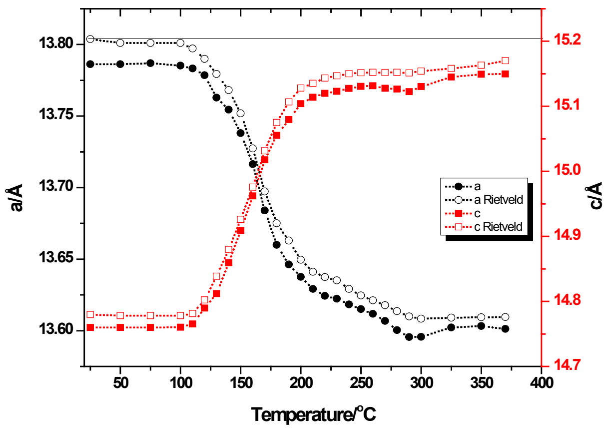
Experimental Studies of State-of-the-art Cu SCR Catalysts

- Cu-SSZ-13, Fe-SSZ-13, and Cu-SAPO-34 catalysts synthesized and studied at PNNL – *these model catalysts allow for fundamental studies of their catalytic and material properties*
  - Cu loaded into SSZ-13 via aqueous ion exchange is straightforward.
  - Fe loading via ion exchange requires low P(O_2) environments.
  - Many methods explored to incorporate Cu into SAPO-34. Very difficult to obtain reproducible model catalysts but significant progress has been made.
- Progress obtained this past year have included:
  - Cu mobility in the presence of water and ammonia evident in a number of state-of-the-art characterization measurements.
  - Cu location as a function of reaction temperature may explain the "seagull"-shaped performance curves.
  - Cu-SAPO-34 catalysts prepared by solid-state ion exchange and 'one-pot' methods display significantly improved properties relation to those prepared by aqueous ion exchange.
  - Part of the team (co-PI) on a newly NSF/DOE-funded university-based project – collaborations initiated and first annual face-to-face meeting on June 13, 2014.
  - Our latest results have been documented this year in 7 publications, as well as 14 presentations (11 invited) at scientific conferences.

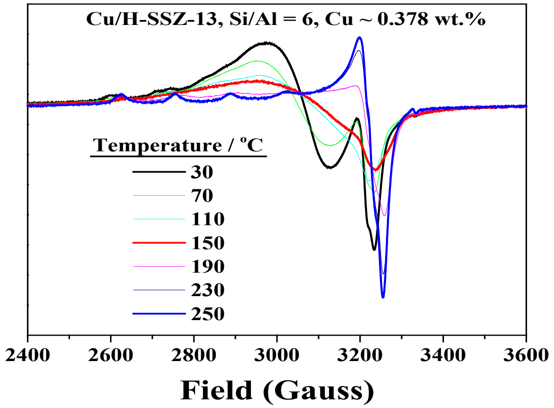
Following the mobility of Cu ions during dehydration



Perturbed T-O-T Vibrations



Unit Cell Parameter Change

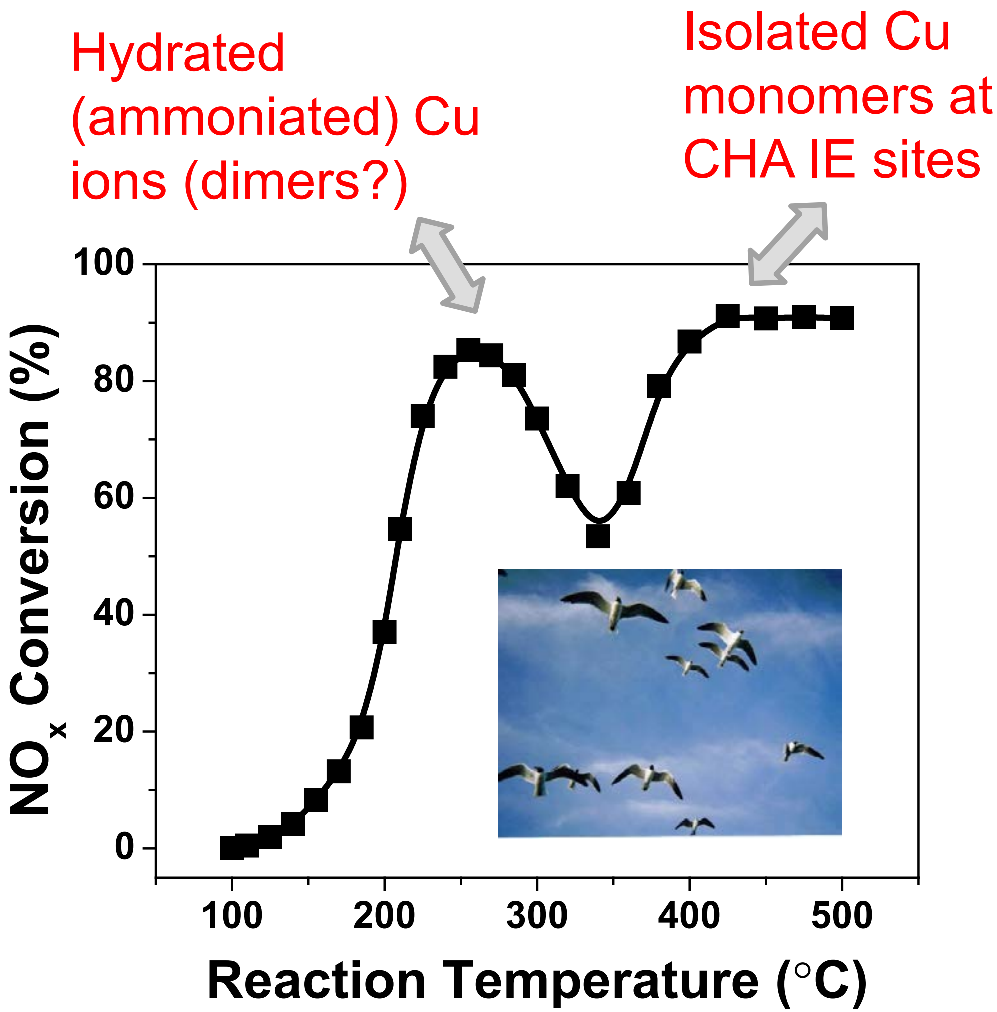


In situ motion of Cu ions

- Cu ion mobility is confirmed from multiple techniques during dehydration.
- Strongly indicates that in the most SCR relevant temperature window (200-300 °C) and in the presence of large amounts of moisture, Cu ions are not localized in 6MR as previously suggested.
- Changing position during dehydration may explain "seagull" shaped performance curves.

JH Kwak, T Varga, CHF Peden, F Gao, JC Hanson and J Szanyi, J. Catal. (2014) in press.

Technical Accomplishments (SCR task):
Results suggest model for active Cu structures – f(temp)

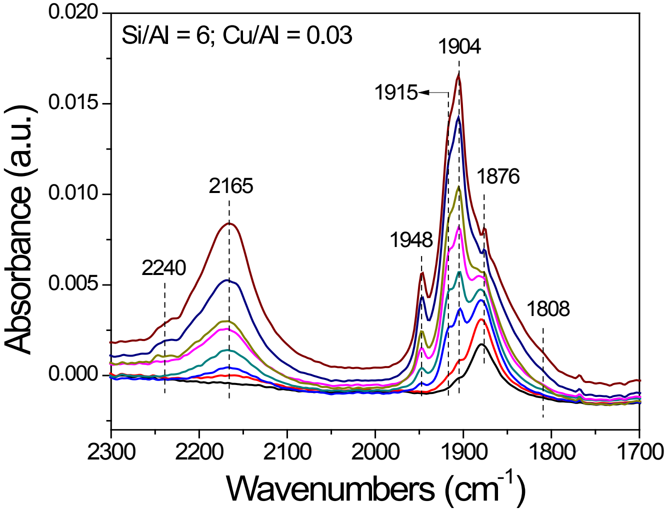


- At temperatures < 250 ºC, water and/or ammonia 'mobilizes' Cu (leads to formation of highly active dimeric species?).
- At higher temperatures, coordinated water and/or ammonia 'desorbs', Cu dimers 'dissociate', and monomeric Cu ion migrate back to zeolitic ion exchange sites.

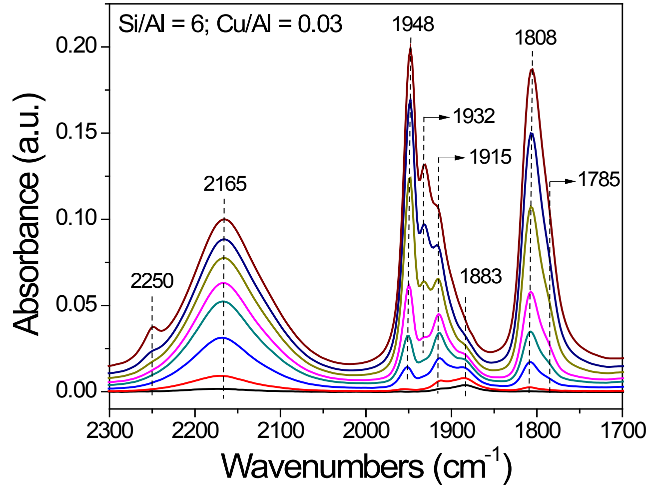
F Gao, ED Walter, M Kollár, Y Wang, J Szanyi, CHF Peden, Journal of Catalysis, submitted.

CO/NO titration FTIR and DFT calculations

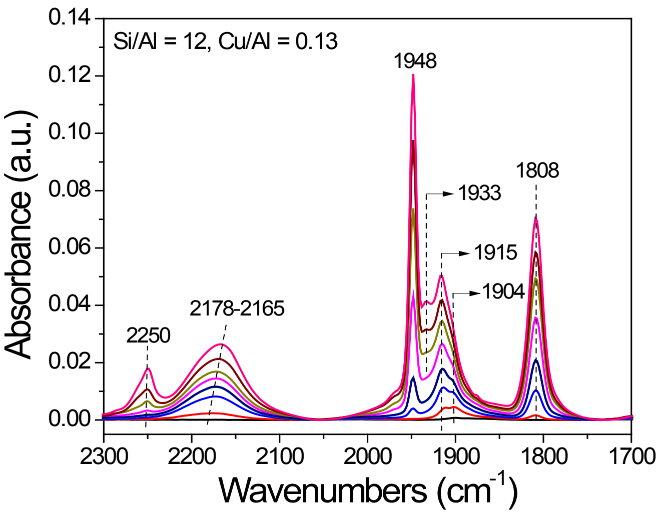
New NSF/DOE-funded program.



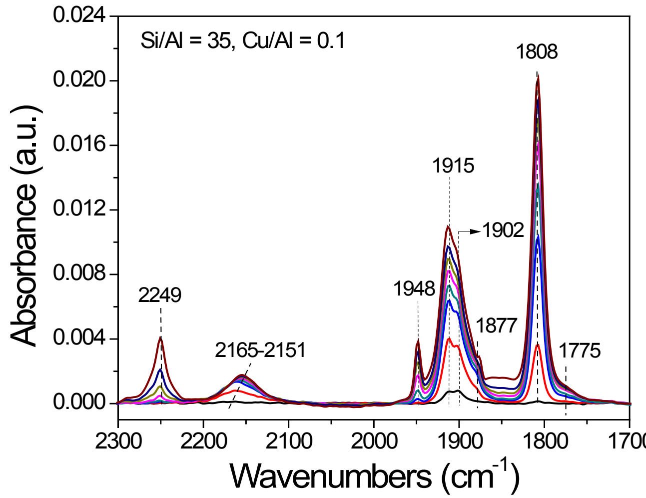
Si/Al = 6, hydrated



Si/Al = 6, dehydrated



Si/Al = 12, dehydrated



Si/Al = 35, dehydrated

- SSZ-13 CHA zeolites with varying Si/Al ratios prepared.
- Although Cu loading levels (Cu/Al ratios) are similar, NO adsorption leads to varying distribution of FTIR peaks.
- These results suggest Cu interactions with the zeolite vary as a function of Si/Al ratios.
- Specific peak assignments being aided by computational studies.

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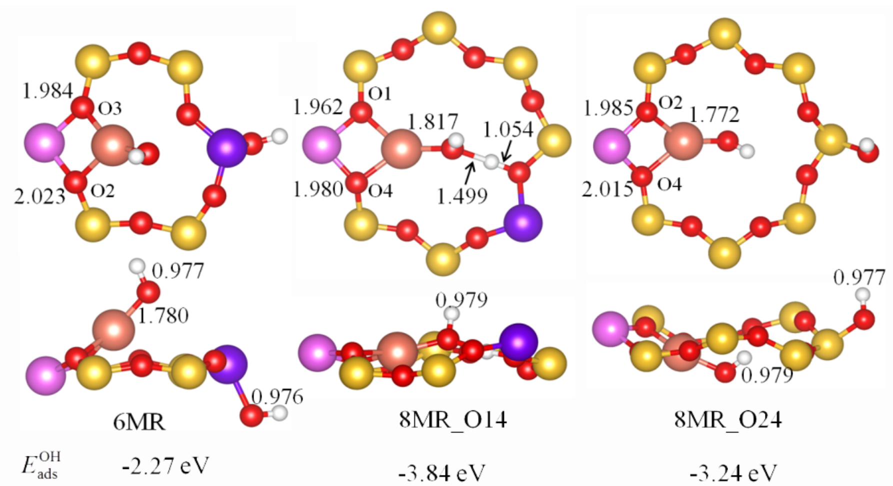
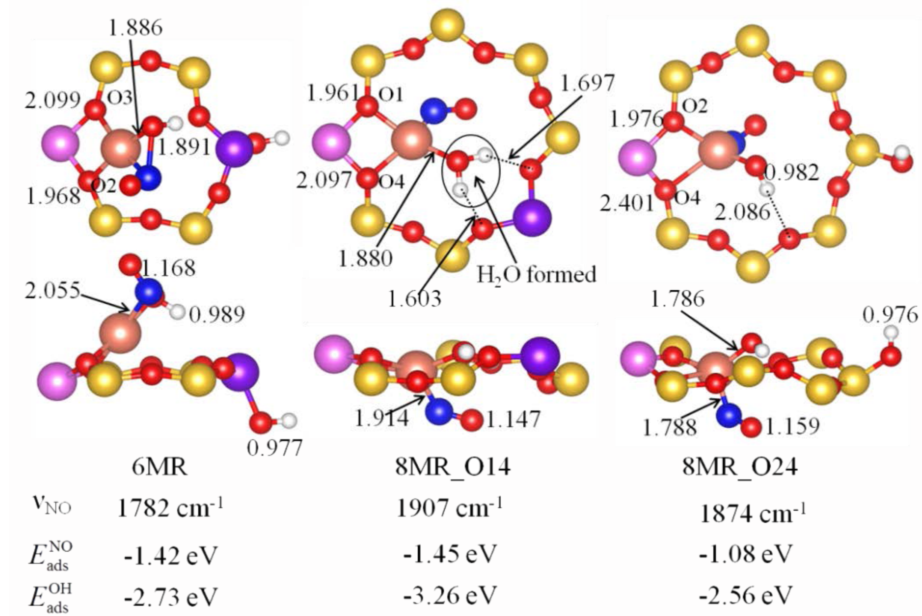
Technical Accomplishments (SCR task):

CO/NO titration FTIR and DFT calculations





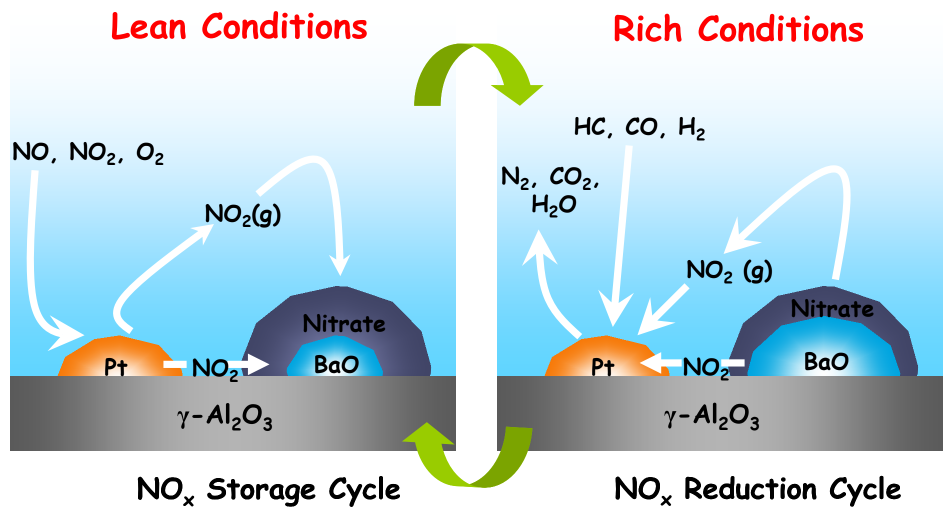
ΔE_2 (eV)	6MR	8MR_O14	8MR_O24
HZ_2Cu	0.00	1.00	0.89
NO_ HZ_2Cu	0.00	-0.07	0.08
OH_ HZ_2Cu	0.00	-0.56	0.02
H_2O_ HZ_2Cu	0.00	-0.18	-0.19
NO+OH_ HZ_2Cu	0.00	-0.60	0.25

- Excellent match between experimental and calculated NO vibrations.
- Significant stabilization of Cu ions in 8-membered rings by various ligands; notably, –OH and H_2O.
- Confirms that Cu ions in 6-membered rings are not the sole active sites.

R Zhang, J-S McEwen, M Kollár, F Gao, Y Wang, J Szanyi, CHF Peden, JPCC (2014) submitted.

Completed Activities on High Temp NSR Tasks

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



- PNNL/Cummins/JMI CRADA has focused on degradation of possible materials for next-generation high temperature NSRs.
- A relatively small effort in our CLEERS program has been addressing more fundamental issues of these potential new NSR materials related to composition, morphology, and chemical reaction kinetics and mechanisms.
- Studies this next year will focus on studies of NO (rather than NO_2) storage for low-temperature applications.

Focus on NO for Low Temperature Aftertreatment

Low temperature NSR storage likely limited by the light-off temperatures of DOCs for NO oxidation.

Comparison: Pt-Mg/Al_2O_3 vs. Pt-Ba/Al_2O_3

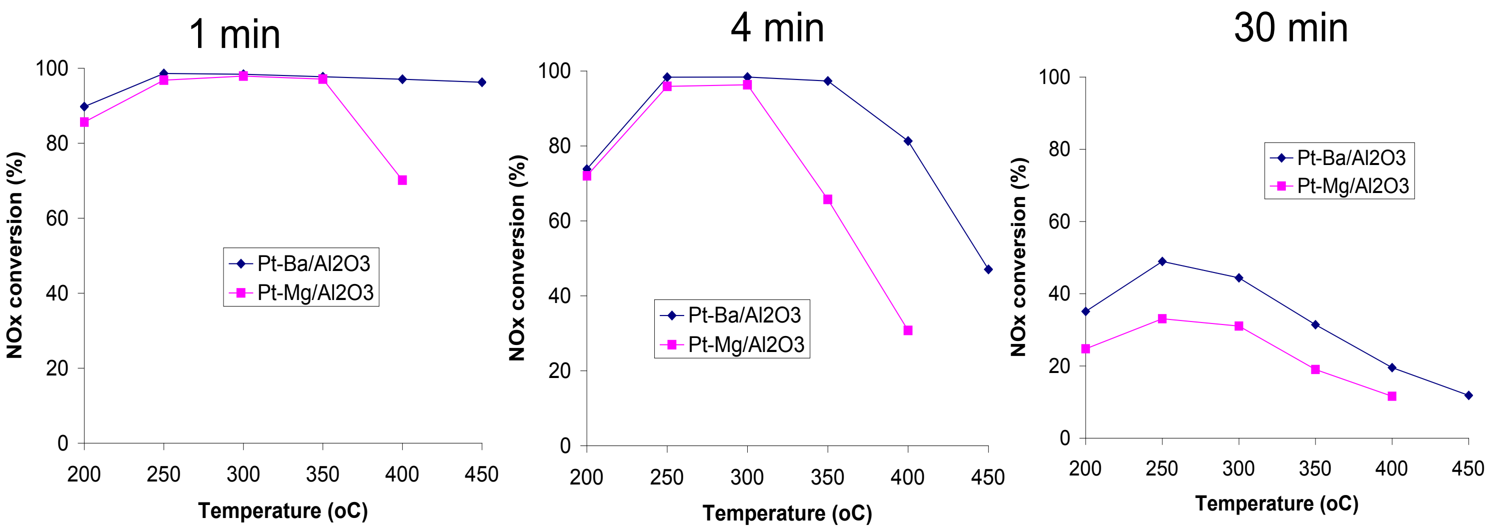


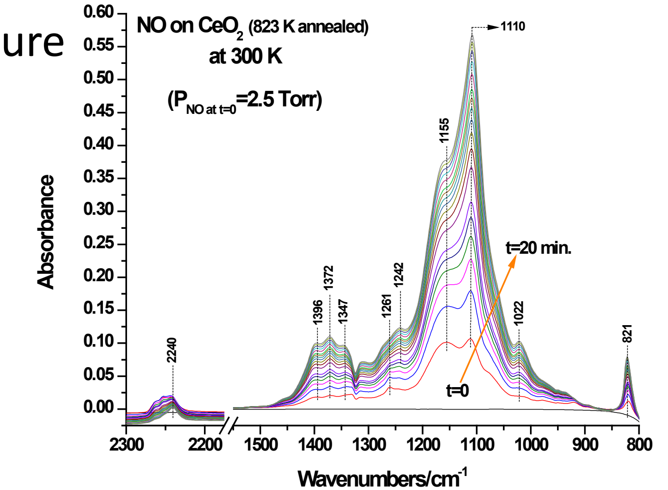
Figure 3

DH Kim, JH Kwak, J Szanyi and CHF Peden - unpublished

Technical Accomplishments (NSR/LNT task):

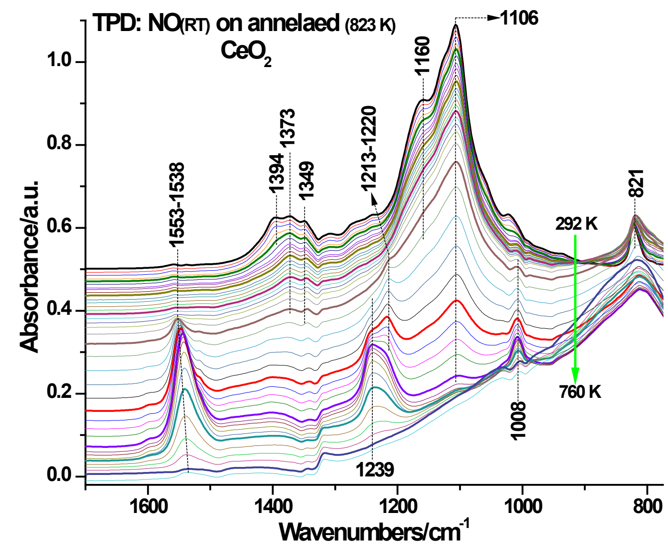
Preliminary studies of low-temp NO adsorption

Studies include FTIR during, and FTIR and TPD after NO exposure



Results obtained this year have included:

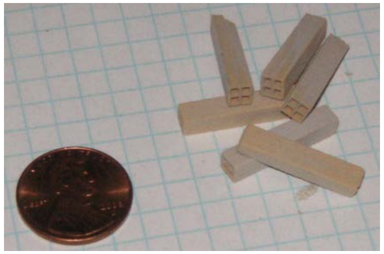
- 'Passive', low temperature NOx storage may require NO rather than NO_2 adsorption (i.e., lack of catalytic NO oxidation at these temperatures).
- Unlike LNT oxides such BaO, NO adsorbs readily on ceria surfaces leading largely to the formation of nitrite species.
- TPD and FTIR show that these nitrite species mostly desorb at modest temperatures.
- Mechanisms for this low-temperature 'storage', and sensitivity to aging and S poisoning are under study.



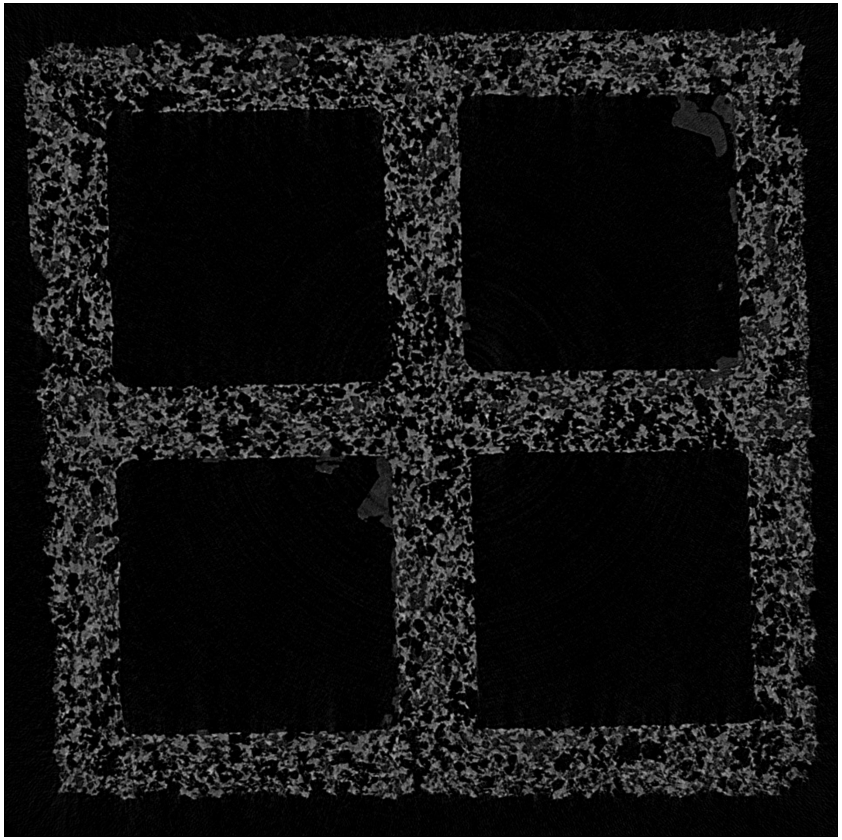
J Szanyi and CHF Peden - unpublished

Technical Accomplishments (DPF task):

Micro X-Ray CT data of multi-function filters



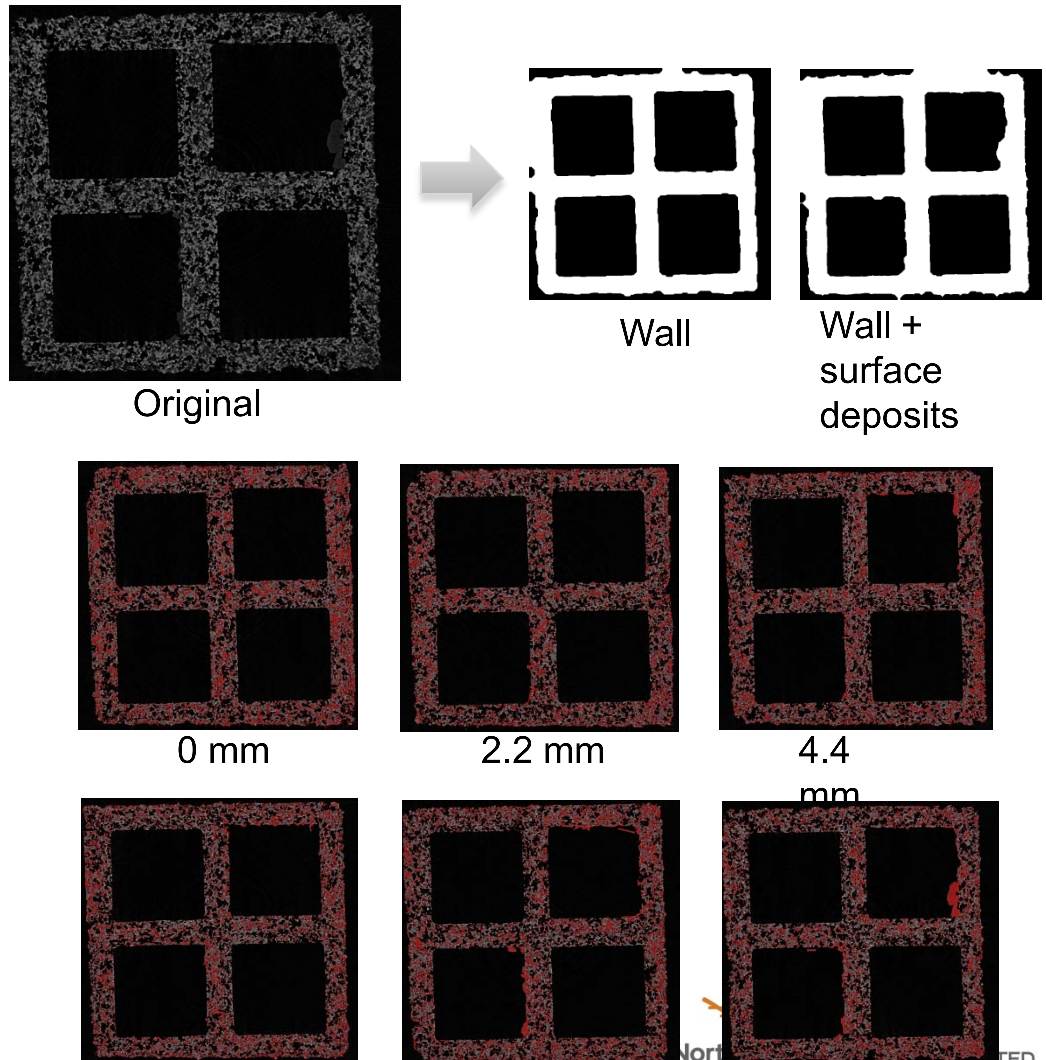
- High resolution X-Ray CT data obtained for four samples:
  - bare high porosity substrate
  - three different loading levels of state-of-the-art SCR catalyst coated by a major catalyst company
- Catalyst can be distinguished from void volume and cordierite substrate
- Irregular lumps and flakes of catalyst were apparent at some locations along the channels
- Total porosity and pore size distribution were measured for the four samples by Hg porosimetry



Technical Accomplishments (DPF task):

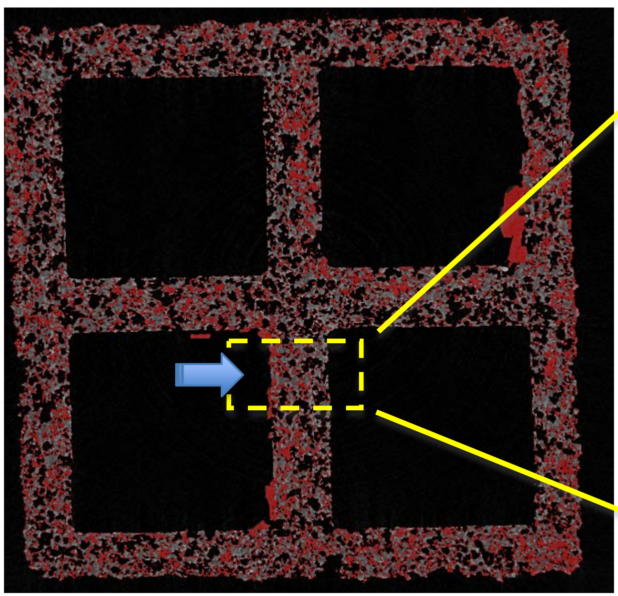
Differentiating catalyst from substrate

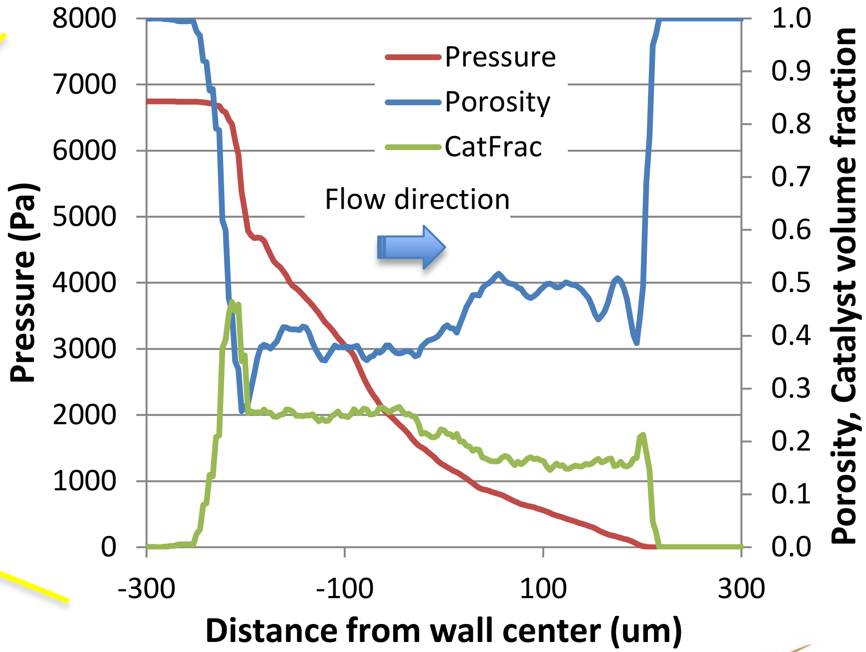
- Filtering and morphological functions in MATLAB® image processing tool box were used to generate masking arrays which approximated the substrate bare substrate wall volume and wall + surface deposits
- Two grayscale thresholds were chosen to match total porosity of the coated sample and porosity of the bare substrate measured by Hg porosimetry
- This allowed identification of catalyst voxels and assignment to volume inside or outside wall
- The monolith was coated primarily from one side, but the catalyst penetrates all the way through the wall
- Large lumps and flakes only appear on one side of the filter walls
- 93% of the total catalyst volume is inside the wall



Distribution of catalyst in filter wall

- A small section of one wall was examined for catalyst distribution and pressure drop (using the lattice-Boltzmann method
- Catalyst further restricts pore mouths at the wall surface
- There is a bias in the catalyst loading within the wall
- The catalyst has a big impact on pressure drop through local porosity

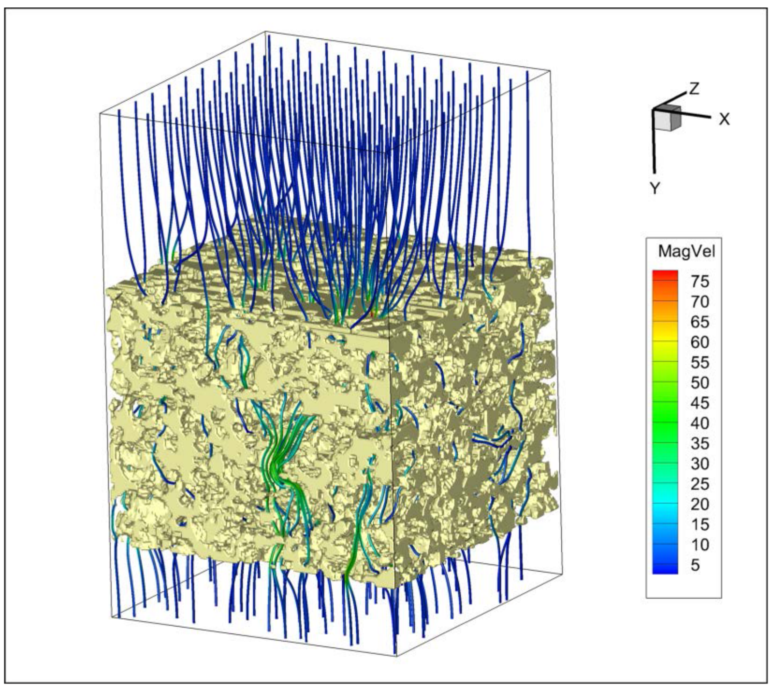




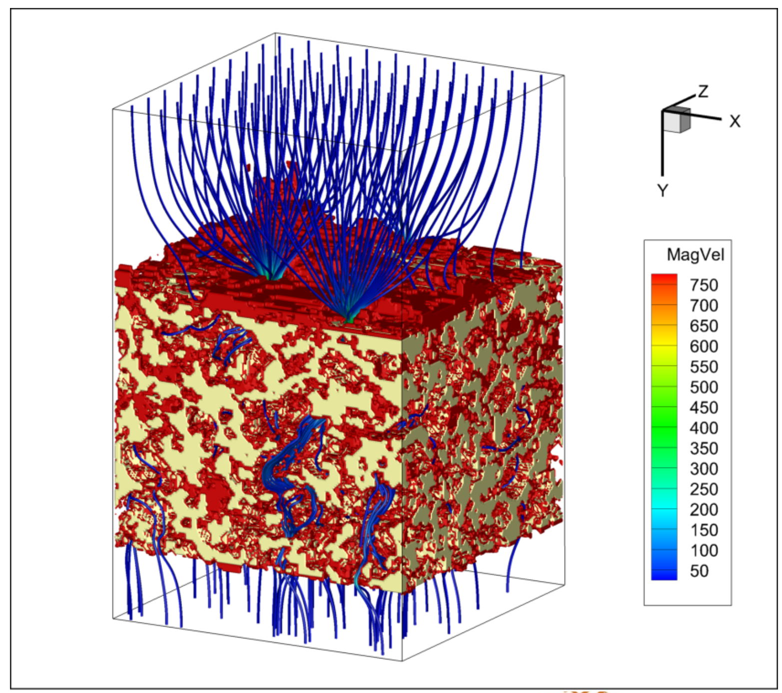
Technical Accomplishments (DPF task):

Effect of catalyst on flow through filter wall

- Effect of catalyst on flow is dependent on position along the channels because of the inhomogeneity of surface deposits
- Where significant surface coatings are present, many of the pore mouths in the substrate are blocked
- Pores are also restricted by catalyst within the walls



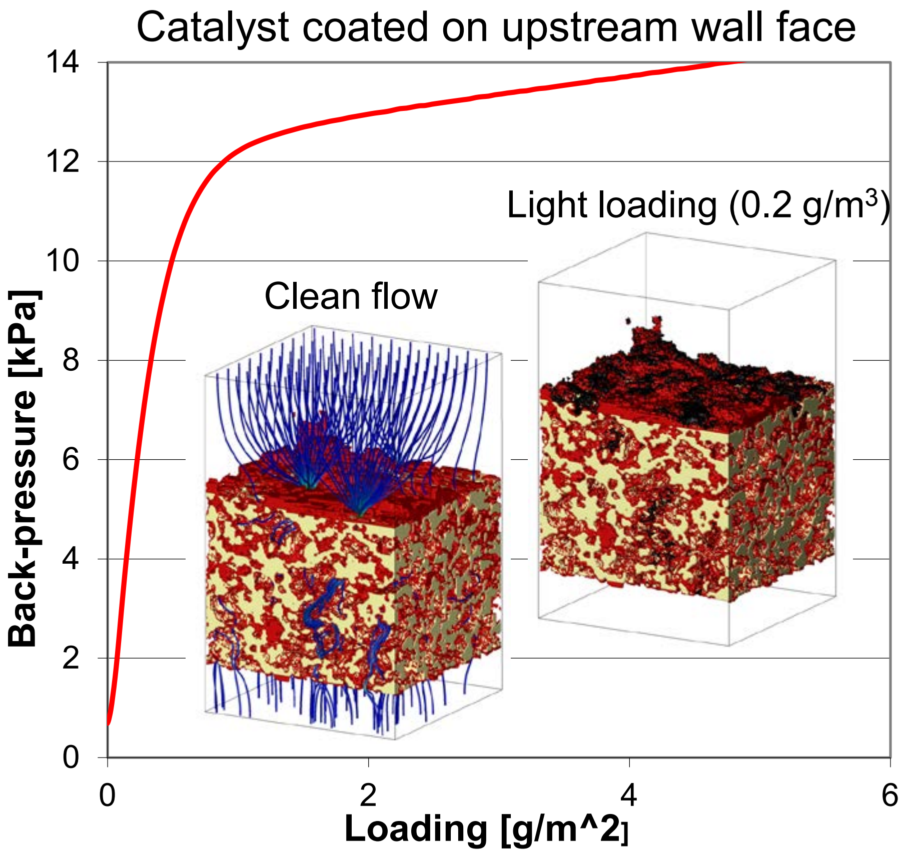
Catalyst digitally removed



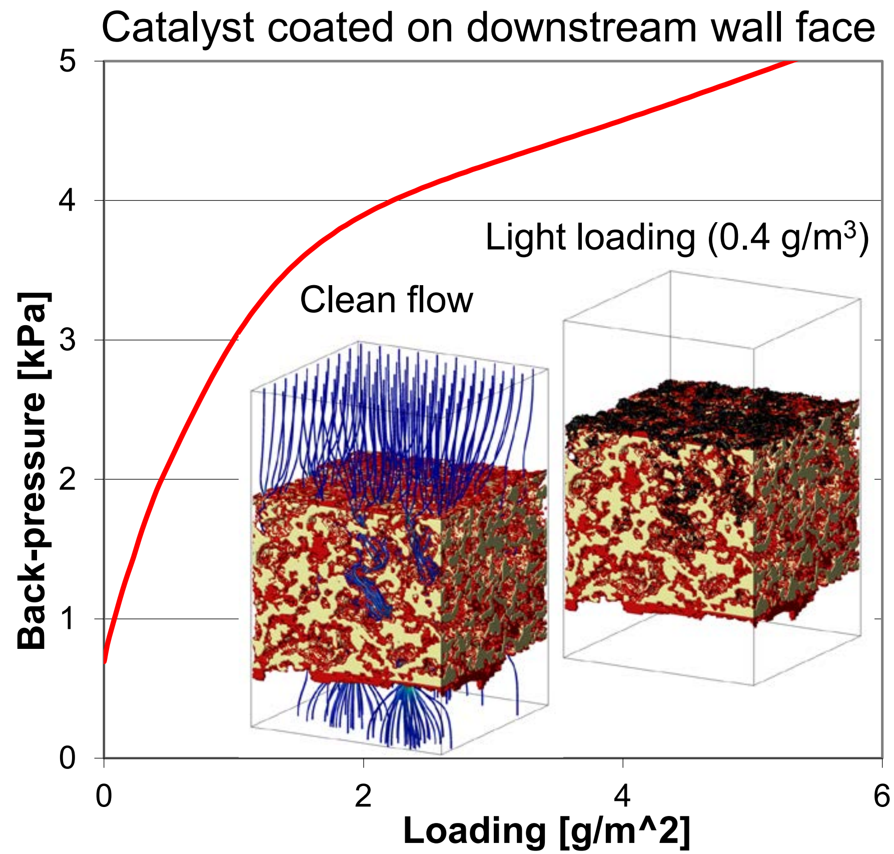
With catalyst: 10-fold increase in maximum local velocity and pressure drop

Effect of wall orientation

- Filtration experiments had shown much higher loaded pressure drop when the more heavily coated side of the filter wall was oriented toward the exhaust inlet
- Simulations show that soot is forced into the throats of major flow pathways when the coated wall surfaces are on the upstream side



Soot packed into primary flow restrictions



Soot more evenly distributed on wall face

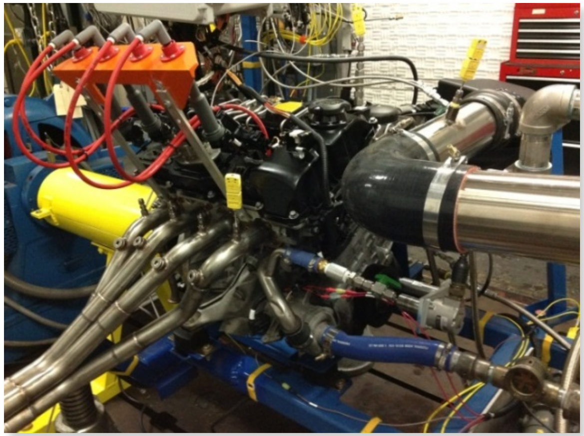
Technical Accomplishments (DPF task):

Lean-Burn GDI Particulate Characterization

- Advanced aerosol analysis – PNNL/ORNL tests
  - characterize particulates from a 2.0L lean-burn GDI engine
  - lean homogeneous, lean stratified, stoich., and fuel rich
  - Tested under 20+ operating conditions
  - Measured PM number concentrations, size distributions, vacuum aerodynamic size, mass, composition, and effective density of individual exhaust particles
  - Calculated fractal dimension, average diameter of primary spherules and number of spherules, void fraction, and dynamic shape factors as function of particle size
- Explored differences between PM emitted by GDI in three operating modes: lean stratified, lean homogeneous, stoichiometric
- Lean stratified operation yielded the most diesel-like size distributions
- Stoichiometric operation resulted in PM number concentrations an order of magnitude lower than those emitted under lean stratified operation
- Stoichiometric PM contains a higher fraction of Ca-dominated non-fractal particles
- Lean homogeneous PM contains a high fraction of Ca-dominated and organic particles

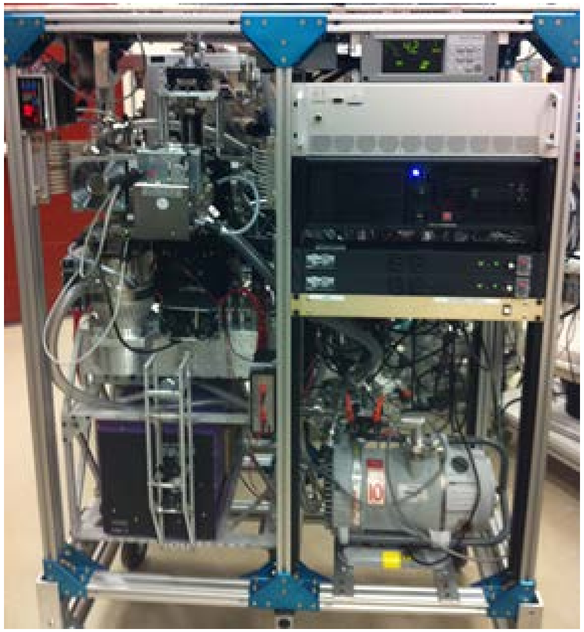
PNNL: Alla Zelenyuk, Jacqueline Wilson, Mark Stewart

ORNL: John Storey, Vitaly Prikhodko, Samuel Lewis, Mary Eibl



GDI engine (ORNL)

miniSPLAT (PNNL



Response to Previous Reviewer Comments

- Nearly all the comments from the reviewers last year were very supportive and complementary.

- The only significant feedback was in regards to the LNT subtask. These comments included:
  - LNT subtask was not very lined up with the CRADA portfolio
  - …did not emphasize NOx storage catalyst-based technologies and the challenges those face with low temperature aftertreatment
  - LNT work did not seem to have made as good progress
  - Planned work on LNT was not clear

- PNNL response:
  - We entirely agree with all the reviewer comments on the LNT/NSC activities
  - Last year the LNT/NSC task was a very small activity comprising only approx. $15k out of a total of $750k project. As such, it was primarily an activity carried over from the prior year to finish work on a specific high temperature durability issue.
  - This year we have closed out those previous studies and have completely revisited this subtask.
  - We are investigating low temperature adsorption activities consistent with the guidance provided by the prior year's reviewers.
  - Although our efforts in this area are still rather small we are ramping up this work considerably in support of the general low temperature aftertreatment thrust.

Collaboration and Coordination with Other Institutions

- Collaborators/Coordination
  - DOE Advanced Engine Crosscut Team (this group is the primary sponsor and oversight of all activities)
  - CLEERS Focus Group
  - 21CTP partners
  - USCAR/USDRIVE ACEC team
  - Oak Ridge National LabNSF/DOE-funded program with partners at Purdue, Notre Dame, WSU, Cummins and ANL

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

Future Work

- SCR
  - Experimentally address the continuing fundamental issues being identified in modeling studies.
  - Continue studies of the reaction mechanism for Cu-CHA relative to Fe-CHA catalysts:
    - Why differences in NO oxidation, low- and high-temperature performance, and sensitivity to NO/NO_2 ratios?
    - Are there differences in the structure and location of these metal cations?
  - In collaboration with collaborators on new NSF/DOE-funded program, probe the nature and stability of the active Cu species in the CHA-based catalysts, especially for SAPO-34 zeolite-based catalysts.
  - Cooperate with ORNL to improve SCR characterization protocols and experiments with fresh and aged samples for model development
  - Recalibrate two-site SCR model with updated high temperature data and publish results
- NSR
  - Focus will be on low-temperature NO adsorption. Reducible oxides such as ceria and titania appear to be useful for this but likely prone to aging and sulfur poisoning.
  - Studies this next year will probe mechanisms of NO adsorption and desorption.
- DPF
  - Extend analysis of X-ray CT data to samples with intermediate catalyst loadings to clarify the effect of catalyst loading on catalyst location and back-pressure

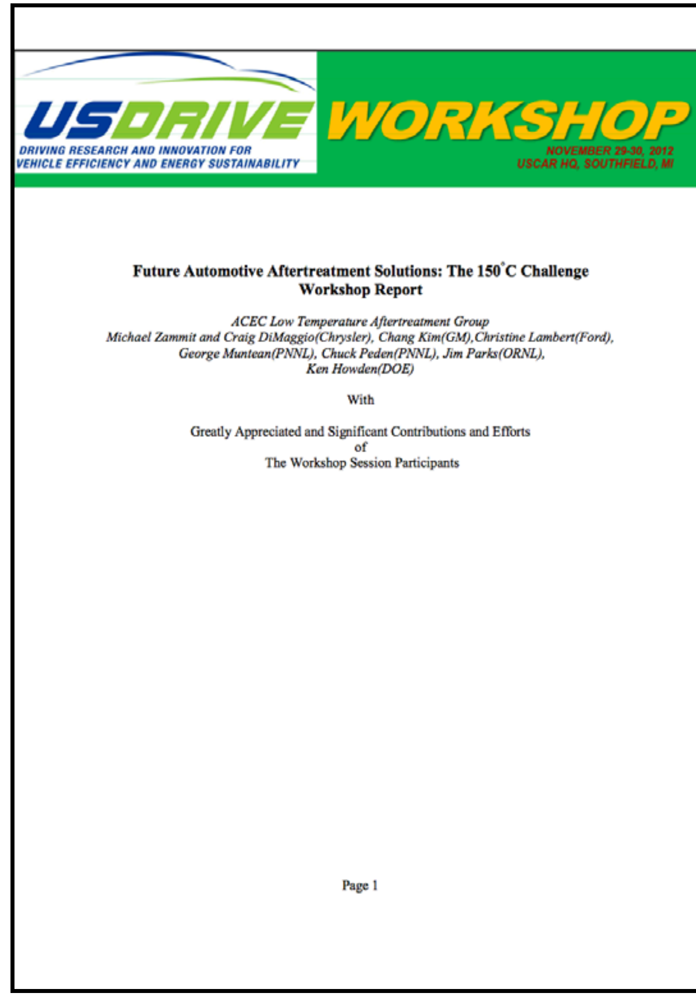
Summary and Remaining Challenges

- SCR
  - The nature and location of the active Cu species in Cu-CHA SCR catalysts is changing during operation. This likely explains the "seagull"-shaped performance curves observed for these catalysts.
  - Combined FTIR vibrational spectroscopy/DFT calculations are providing additional insights into the structure of these various active Cu species.
- NSR
  - Unlike Ba-based NSRs, K-based NSR catalysts on all support materials (Al_2O_3, $MgAl_2O_4$, TiO_2) studied to date are seriously degraded during hydrothermal aging. While promising high-temperature performance is achieved, efforts to stabilize K via the use of TiO_2 and $K_2Ti_6O_{13}$ supports were unsuccessful.
  - Current studies are addressing the materials properties of low-temperature NO adsorption materials, and mechanisms for NOx adsorption/desorption.
- DPF
  - SCR catalyst can be differentiated from the cordierite substrate in X-Ray CT data from commercially coated SCRF samples
  - Most of the SCR catalyst resides within the porous cordierite walls, but at high loadings some is present as lumps and flakes on one wall surface
  - The SCR catalyst has a major impact on flow and pressure drop through the filter walls, but flow paths remain open through the filter wall, even in heavily loaded regions
  - Heavily coated SCRF filters must be oriented properly to avoid filling constricted pore mouths on catalyzed wall surfaces with soot, resulting in very high back-pressure

Technical Back-Up Slides

Activity Background on LTAT Protocol Project

- Low temperature aftertreatment (LTAT) research needs highlighted by the ACEC group under USDRIVE
- Topical workshop held in November 2012, report issued
- DOE solicitations on topic issued
- Initial projects have been initiated
- Protocol & base lining activities identified as early needs



Future Automotive Aftertreatment Solutions: The 150˚C Challenge
Workshop Report

ACEC Low Temperature Aftertreatment Group
Michael Zammit and Craig DiMaggio(Chrysler), Chang Kim(GM), Christine Lambert(Ford), George Muntean(PNNL), Chuck Peden(PNNL), Jim Parks(ORNL), Ken Howden(DOE)

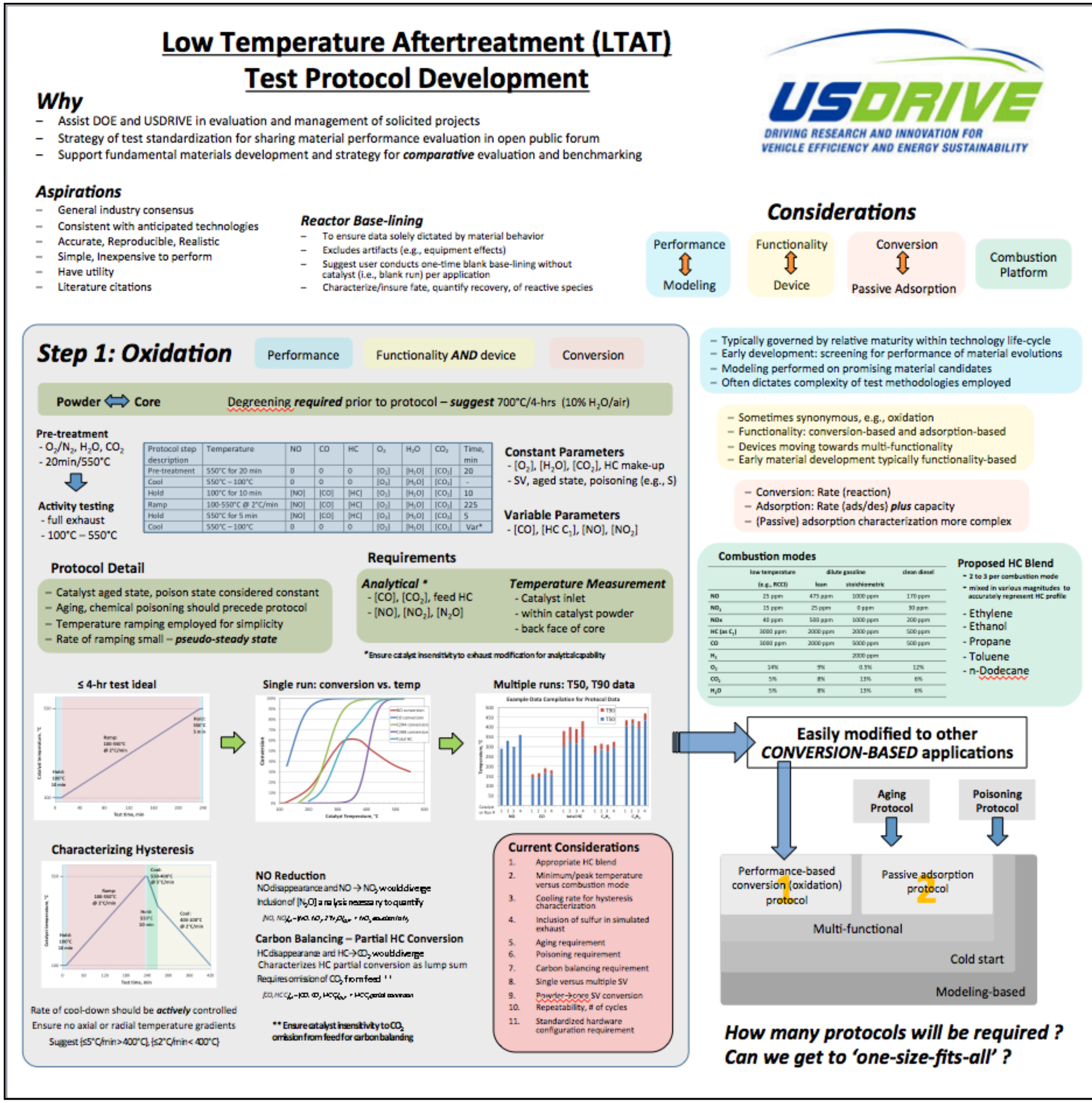
With

Greatly Appreciated and Significant Contributions and Efforts of The Workshop Session Participants

Page 1

Reference:
http://www.pnnl.gov/main/publications/external/technical_Reports/PNNL-22815.pdf

First Attempt at a LTAT Oxidation Protocol – described in poster at CLEERS Workshop



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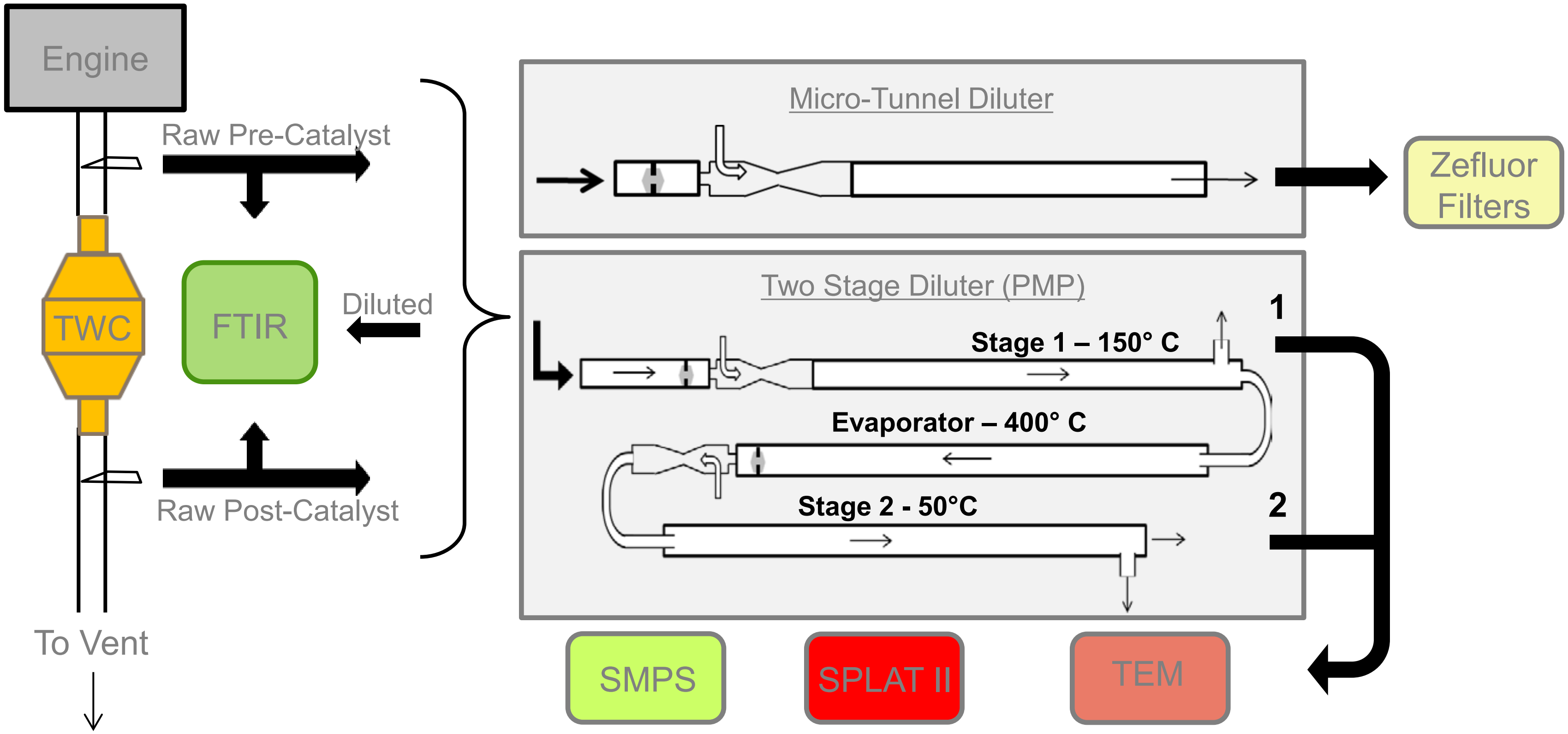
Sampling Setup – Particulate Characterization

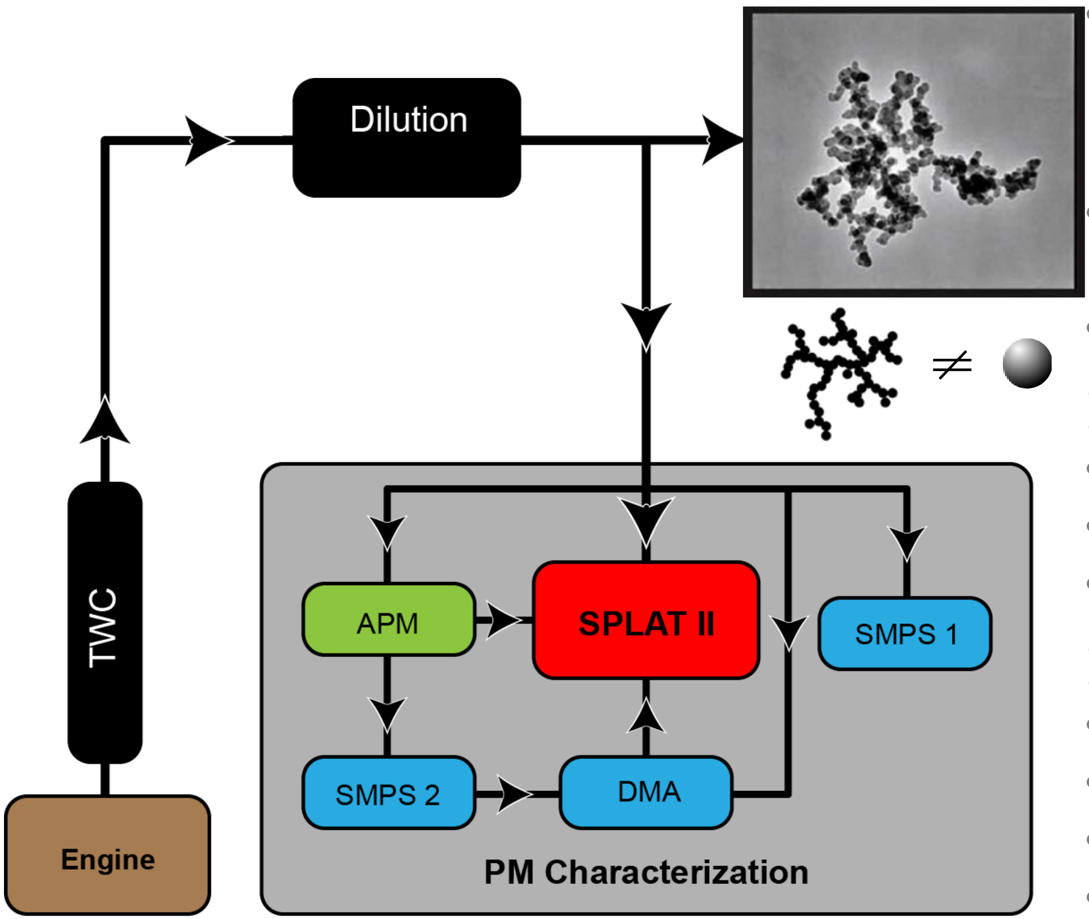


- 2008 BMW 1-series 120i, 87 AKI Gasoline, 2.0 L, naturally aspirated
- Three-Way Catalyst (TWC)
- Fuel EEE Cert (low S) 97 RON, 89 MON
- FTIR on raw exhaust
- Single stage dilution for filters

- DR 1st stage: 12-15; 2nd stage: 140-160
- Engine Points (PM measured with and w/o TWC):
  - 2000 rpm @ 2, 4, & 8 bar;
    1000 rpm @ 1 & 2.5 bar
  - lean stratified, lean homogeneous, stoichiometric, and rich

Advanced Particulate Characterization Setup

Real-time, *in-situ,* highly detailed particulate matter (PM) characterization:



➢ **SMPS:**
- size distributions (mobility diameters, d_m)

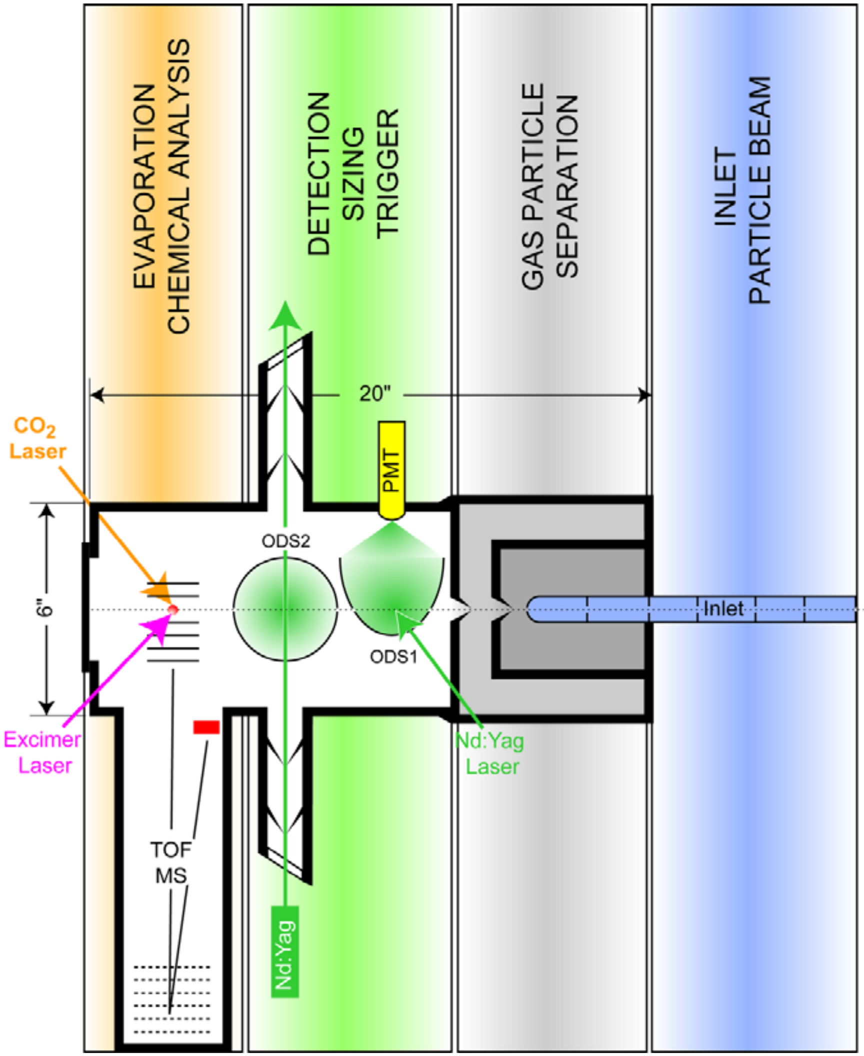
➢ **SPLAT II:**
- single particle size (vacuum aerodynamic diameter, d_{va})
- single particle composition, *MS*

➢ **DMA/SPLAT II:**
- effective density, ρ_{eff}
- fractal dimension, D_{fa}
- primary spherule diameter, d_p

➢ **APM/DMA/SPLAT II:**
- particle mass, m_p
- fractal dimensions, D_{fm}, D_{pr}
- primary spherule diameter, d_p
- number of spherules, N_p
- void fraction, Φ
- shape (χ_t , χ_v)

Zelenyuk et al. **(2014)** Combustion and Flame, doi:10.1016/j.combustflame.2014.01.011.

SPLAT II
Single-Particle Mass-Spectrometer,



- Characterizes particles with sizes from 50 nm to 3 µm (50% cut-off at 85 nm)
- Sizes up to 5,000 particles/sec
- Sizes particles with 0.5% precision
- Measures the composition of 20-100 particles/sec
- Uses IR/UV ion formation mode to yield quantitative particle composition, material density, morphology
- Characterizes mobility or/and mass selected particles to yield information on particle effective density, mass, fractal dimension, dynamic shape factors, average primary spherule diameter, number of spherules, void fraction

Zelenyuk et al. **(2014)** Combustion and Flame, doi:10.1016/j.combustflame.2014.01.011

Zelenyuk, A., Yang, J., Imre, D. and Choi, E. **(2009)**. *Aerosol Science and Technology,* 43:5,411-424.

Zelenyuk, A., and Imre **(2009)**. *International Reviews in Physical Chemistry,* 28(2):309-358.