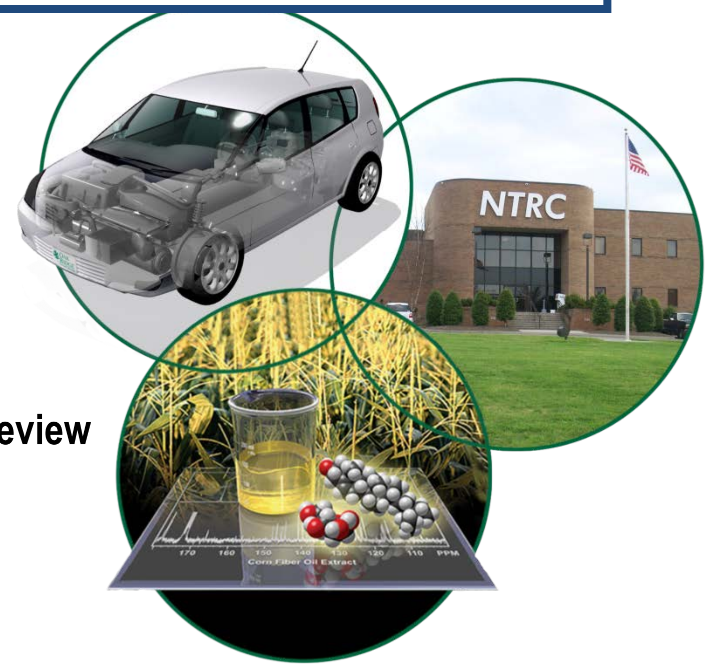
CLEERS Coordination & Joint Development of Benchmark Kinetics for LNT & SCR

CLEERS activities at ORNL are divided into two separate but related projects:

- **Coordination of Cross-Cut Lean Exhaust Emission Reduction Simulation**
  Stuart Daw, Vitaly Prikhodko, Charles Finney
- **Joint Development of Benchmark Kinetics for LNT & SCR**
  Jae-Soon Choi, Josh Pihl, Bill Partridge, Miyoung Kim, Todd Toops
  Michael Lance, Stuart Daw



PI: Stuart Daw

Presenter: Jae-Soon Choi

Oak Ridge National Laboratory

Project ID: ace_022

Vehicle Technologies Program Annual Merit Review
May 16, 2012, Arlington, VA

DOE Managers: Ken Howden, Gurpreet Singh

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Overview

Timeline

- Project start date:
  - CLEERS Coordination FY00
  - CLEERS Kinetics FY00
- Project end date & percent complete:
  - Ongoing (core activity supporting emissions control research and project coordination)

Budget

- Project funding for FY11/FY12
  - CLEERS Coordination: $200K/$200K
  - CLEERS Kinetics : $500K/$500K

Barriers

- Fuel penalty
  - Lightoff, regeneration & desulfation of emission controls consume extra fuel
- Cost
  - High aftertreatment cost inhibits market acceptance of diesel & lean-gasoline

Barriers (continued)

- Durability
  - At present, large built-in margin required
- Low-temperature exhaust
  - High efficiency engines produce exhaust too cool to light-off aftertreatment devices

Partners

- DOE Advanced Engine Crosscut Team
- USDRIVE Advanced Combustion and Emissions Control Team
- CLEERS Focus Group Members
  - 10 engine/vehicle manufacturers
  - 11 component and software suppliers
  - 10 universities
- Sandia and Pacific Northwest National Labs

Relevance

Crosscut Lean Exhaust Emission Reduction Simulation (CLEERS) supports the primary DOE-Vehicle Technology Program (VTP) mission of "developing lower cost, energy efficient, and environmentally friendly engine technologies with reduced petroleum use."[1]

[1] http://www1.eere.energy.gov/vehiclesand fuels/about/fcvt_mission.html

CLEERS is a core Advanced Combustion Engine R&D activity focused "on improving engine efficiency while meeting future federal and state emissions regulations through a combination of combustion and fuels technologies that increase efficiency and minimize in-cylinder formation of emissions, and aftertreatment technologies that further reduce exhaust emissions. "[2]

[2] http://www1.eere.energy.gov/vehiclesandfuels/pdfs/program/vt_mypp_2011-2015.pdf

CLEERS specifically supports collaborations among industry, university, and national lab partners to develop and disseminate critical data and improved computational tools for accurately simulating the performance and impact of emissions controls technology for advanced engines.

- **CLEERS Coordination project supports overall collaboration and information dissemination**
- **CLEERS Kinetics project supports generation of critical data and kinetics models**

As noted recently by the National Academy of Science: "Without aftertreatment constraints in the simulation, the model might allow engine system operation outside the emission-constrained envelope." – NAS study on reducing fuel consumption from MD and HD vehicles (ISBN: 0-309-14983-5)

Milestones

- FY2011 milestones (completed)
  - ✓ Organize 2011 CLEERS public workshop (Coordination)
  - ✓ Develop model for ammonia generation in LNTs (Kinetics)
- FY2012 milestones (completed)
  - ✓ Organize 2012 CLEERS public workshop (Coordination)
  - ✓ Detailed measurements of hydrothermal aging impact on copper zeolite SCR catalyst function (Kinetics)

Approach: Prioritize/Coordinate/Perform Lean Exhaust Emissions Research and Disseminate Results

Coordination

DOE Advanced Engine Cross-Cut Team

Caterpillar, Cummins, Chrysler, Detroit Diesel, DOE-VTP, Ford, General Motors, Navistar, ARDEC, EPA, Volvo

CLEERS Planning Committee

- Wei Li (GM),
- **Stuart Daw (ORNL)**
- Louise Olsson (Chalmers)
- Chris Rutland (UW)
- Kevin Sisken (DDC)
- John Kirwan (Delphi)

Technology Focus Groups

- DPF/DOC, LNT, SCR
- Monthly teleconferences
- Selected membership

Website (www.cleers.org)

- General information
- Meeting announcements
- Shared data

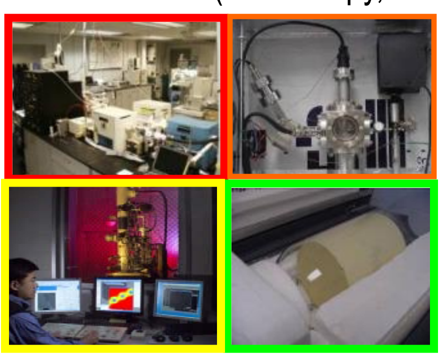
Workshops

- Public
- Annual in Detroit area
- Presentations on website

R&D

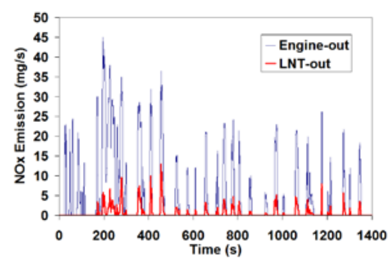
Experiments

- Bench/micro/DRIFTS reactors
- Specialized diagnostics (SpaciMS)
- Characterization (Microscopy, TPR)



Modeling/Simulation

- Microkinetic-based model
- Global model



New insights, data & models relevant to development of robust, energy-efficient, & cost-effective emission controls

Collaboration w/ PNNL, SNL, ICT Prague, Chalmers, UKY, UH, MTU, TU Milan, UTK, USC

Technical Accomplishments

- **CLEERS coordination (*addresses fuel penalty, cost, and durability barriers*)**
  - Organized 15th (2012) CLEERS Workshop
  - Coordinated monthly Focus Group teleconferences
  - Leveraged ORNL, PNNL, SNL unique capabilities
  - Updated website and addressed accessibility issues
  - Initiated expansion of engine out, kinetics, and aftertreatment model data sharing
- **SCR research (*addresses durability barrier*)**
  - Quantified impact of hydrothermal aging on commercial small pore Cu zeolite catalyst
  - Suggested modeling strategy for incorporating aging impact on NH_3 storage
  - Identified properties sensitive to aging for potential diagnostics
  - Working with PNNL to quantify changes in model parameters with aging

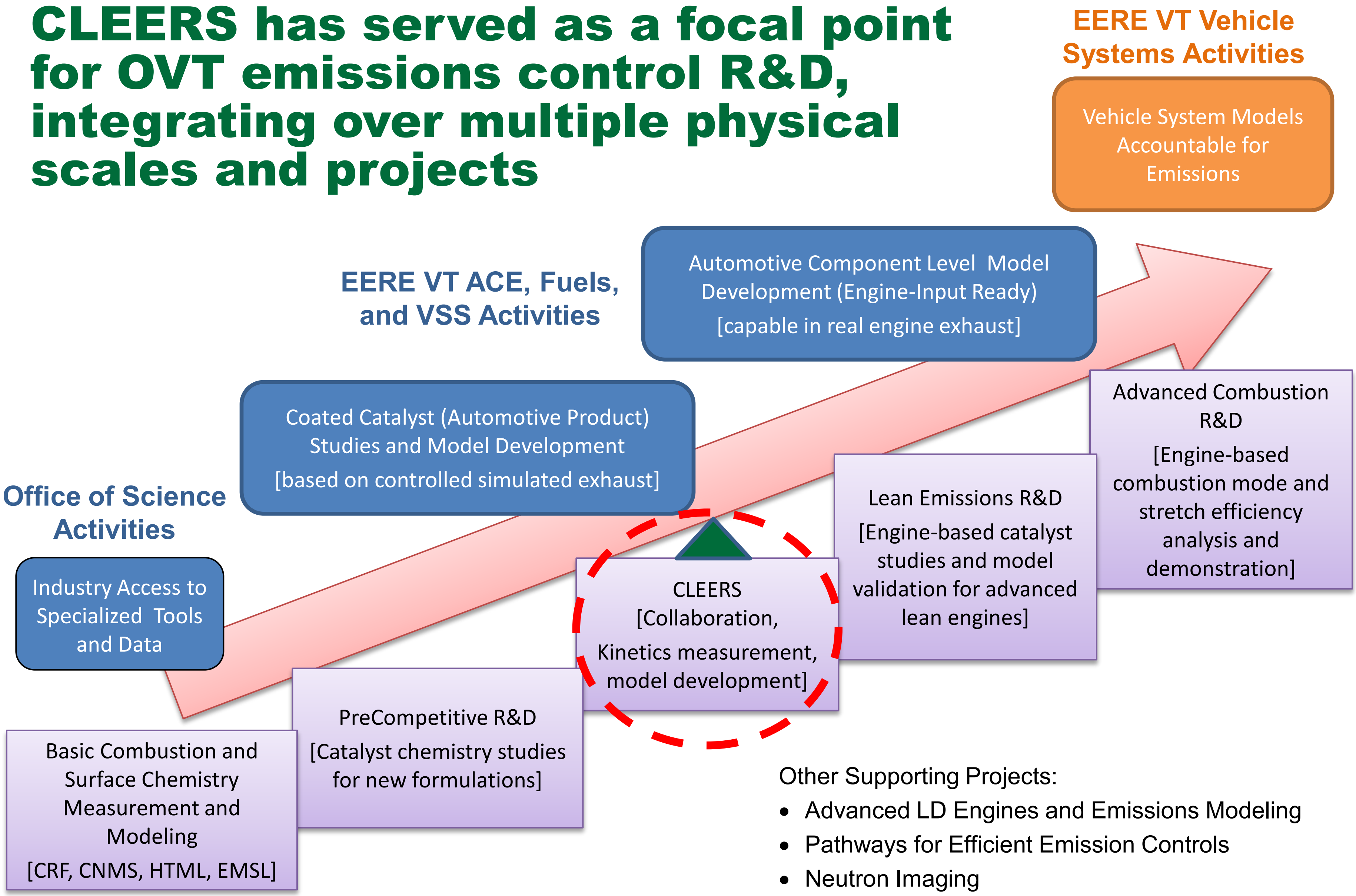
Technical Accomplishments (cont'd)

- **LNT research (*addresses durability and fuel penalty barriers*)**
  - Initiated experimental characterization of a new generation lean GDI LNT
    - Bench reactor evaluation according to the CLEERS Protocol
  - Enhanced LNT kinetic model with respect to N_2O and NH_3 selectivites
    - Good simulation-experiment agreement over a broader range of conditions
    - Clarified and integrated selectivity dependence on PGM redox states
- **Oxidation catalyst research (*addresses low-temperature and durability barriers*)**
  - Explored surface modification method to enhance Pt dispersion and durability
    - Leveraged surface science capabilities for catalyst design

Technical Highlights

CLEERS Coordination

CLEERS has served as a focal point for OVT emissions control R&D, integrating over multiple physical scales and projects



Other Supporting Projects:

- Advanced LD Engines and Emissions Modeling
- Pathways for Efficient Emission Controls
- Neutron Imaging
- NPBF Fuels Program

CLEERS supported technical interactions among lab, industry, and university partners in multiple ways

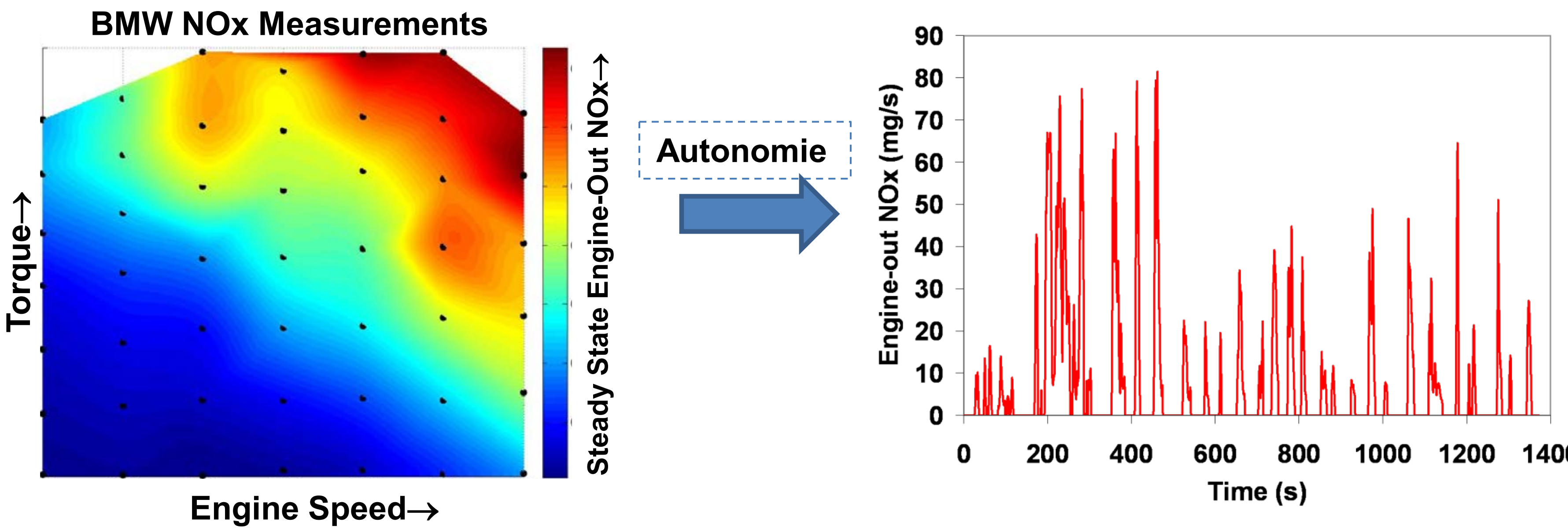
- Website
  - Recently improved security and expanded data bases
- Monthly teleconferences
  - Continued group technical telecon presentations of very recent results (20-40 domestic + int'l participants)
- Industry priority surveys and discussions
  - 2011 CLEERS Industry Priorities Survey Final Report Analysis, Summary, and Recommendations, 9/27/2011, Report to the AEC Team
  - CLEERS Telecon by Mike Zammit, "ACEC Future Aftertreatment Strategy Report To The Advanced Powertrain Leadership Council," Jan. 10, 2012
- Workshop #15, April 30-May 2, 2012, UM Dearborn
  - Circa 90 attendees (OEMs, suppliers, software companies, national labs, universities), 32 oral technical presentations, 10 poster presentations, extended informal small group discussions, industry panel on emission controls vs. fuel efficiency
- SCR catalyst characterization
  - Translated protocol data to device model for vehicle studies
- LNT catalyst modeling
  - Completed SNL kinetics model, interfaced with Prague and Gamma in kinetics refinement, distributed BMW vehicle and LNT catalyst data

2011 CLEERS Workshop

CLEERS has provided an important path for sharing engine and aftertreatment data

<u>Trial dissemination of BMW lean GDI vehicle data has helped establish future approach for data sharing</u>

- **Engine out emissions for both steady-state and transient conditions**
- **Simultaneous measurements of TWC and LNT inlet/outlet species and temperatures**
- **Matched to lab characterizations of LNT catalyst kinetic properties**
- **Combined data are used to develop improved GDI drive cycle simulations**



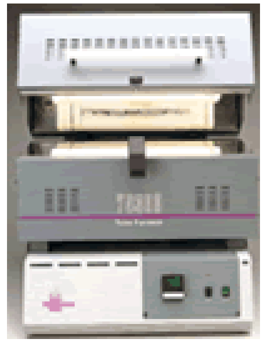
Technical Highlights

SCR

Quantifying the impact of hydrothermal aging on SCR catalyst properties and model parameters

PNNL obtains commercial small pore Cu zeolite catalyst from supplier

PNNL work will be presented in ACE023



ORNL ages cores in tube furnace under conditions from other PNNL investigations

1. no aging ('fresh')
2. 700ºC 4 h ('degreened')
3. 800ºC 6 hr
4. 800ºC 16 hr (approximates 135k mile vehicle aging)

ORNL conducts CLEERS transient SCR protocol flow reactor experiments

PNNL develops and calibrates SCR model

$$r_{ads,s2} = A_{ads,s2} c_{g,NH_3} (1 - \theta_{NH_3,s2})$$

$$r_{des,s2} = A_{des,s2} e^{\frac{-E_{des,s2}}{RT}} \theta_{NH_3,s2}$$

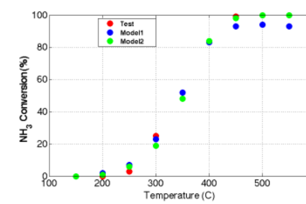
$$r_{ads,s1} = A_{ads,s1} c_{g,NH_3} (1 - \theta_{NH_3,s1})$$

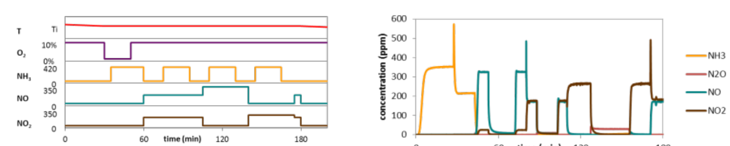
$$r_{des,s1} = A_{des,s1} e^{\frac{-E_{des,s1}(1-\gamma\theta_{NH_3,s1})}{RT}} \theta_{NH_3,s1}$$

$$\frac{\partial c_{g,NH_3}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NH_3}}{\partial x} + \frac{\Omega_1}{\varepsilon}(r_{des,s1} - r_{ads,s1}) + \frac{\Omega_2}{\varepsilon}(r_{des,s2} - r_{ads,s2})$$

$$\frac{d\theta_{NH_3,s1}}{dt} = r_{ads,s1} - r_{des,s1}$$

$$\frac{d\theta_{NH_3,s2}}{dt} = r_{ads,s2} - r_{des,s2}$$





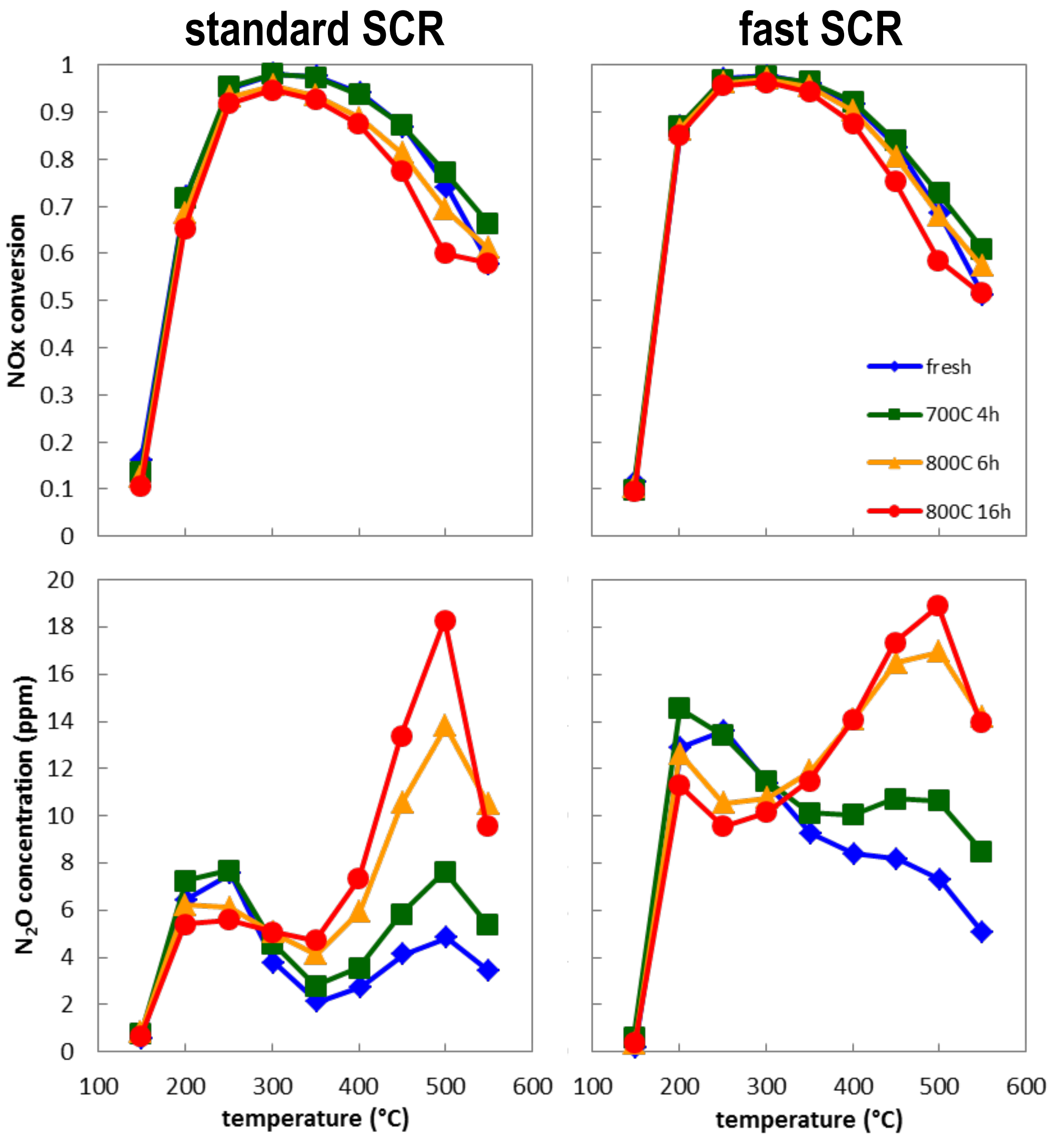
ORNL and PNNL collaborate on experiment design, data analysis, modeling strategies

 Managed by UT-Battelle for the U.S. Department of Energy

Hydrothermal aging does not have much of an impact on SCR performance…

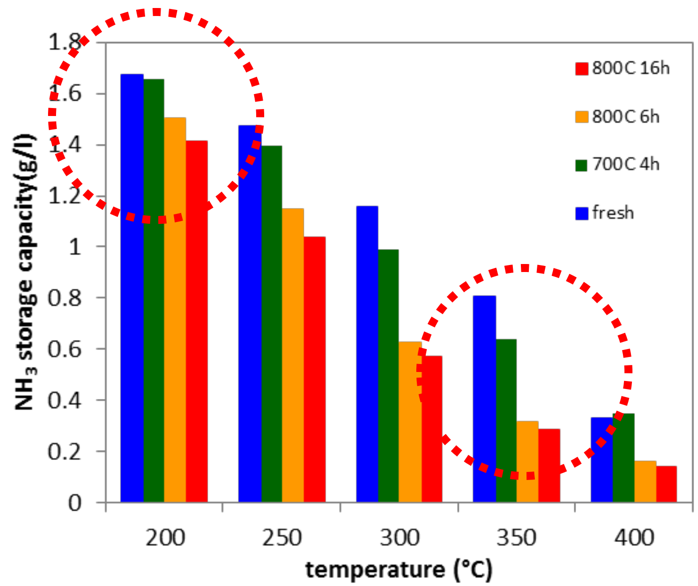
- Impact of 800°C aging on steady state NOx conversion:
  - Low to moderate T:
    - slight drop for standard SCR
    - no impact on fast SCR
  - High T:
    - more significant decrease for both standard and fast SCR
    - NH_3 conversion 100%; higher dosing might recover performance

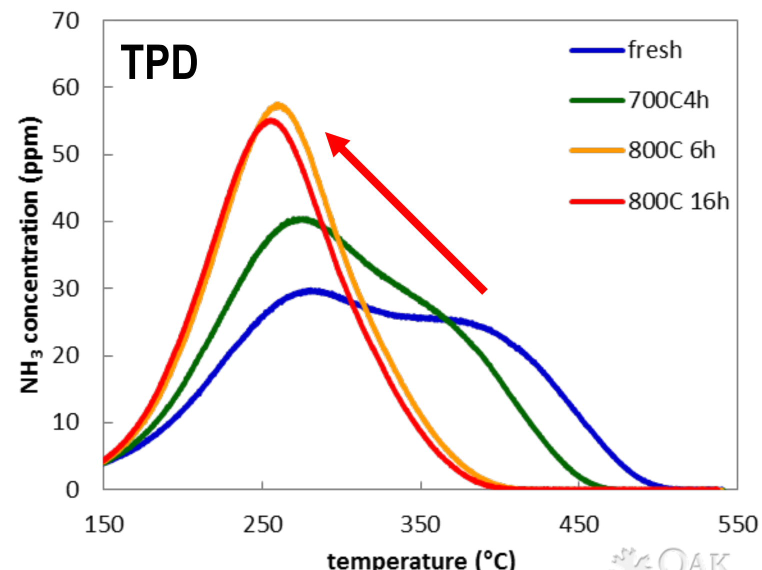
- Aging shifts N_2O selectivity of SCR reactions



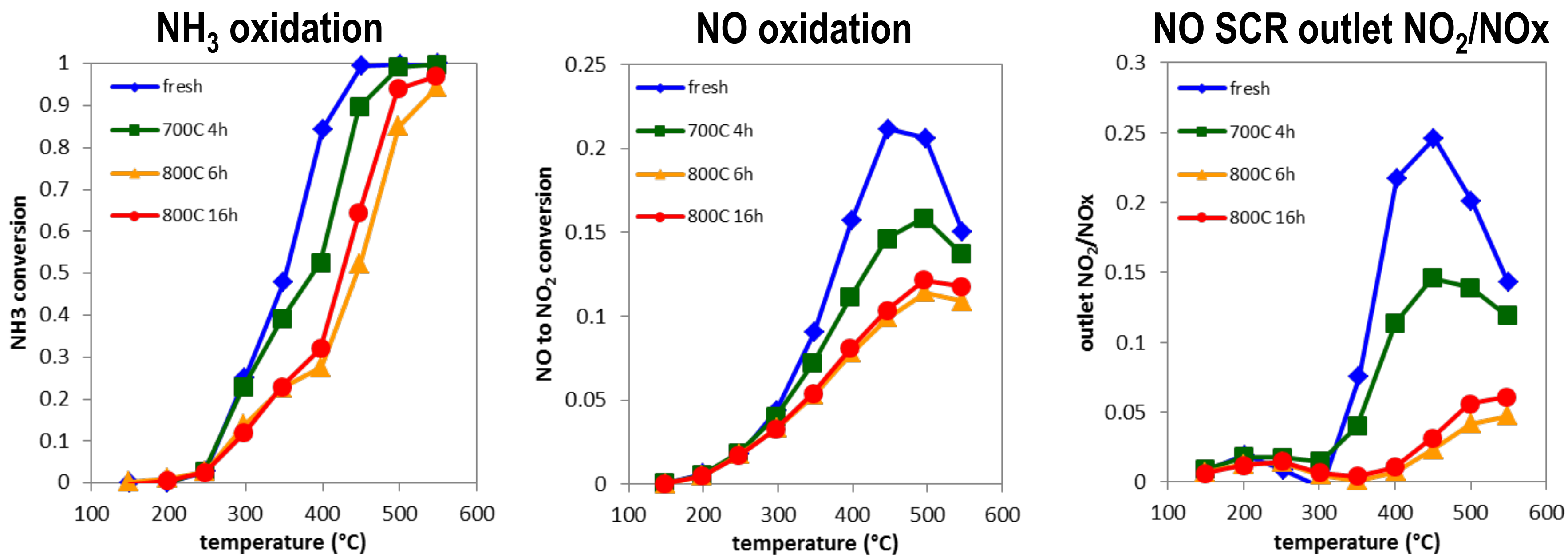
...but it does significantly alter NH_3 storage properties

- Impacts of aging on isothermal NH_3 storage capacity:
  - small loss at low T
  - much more significant drop at higher T
  - NH_3 inventory under standard SCR conditions shows similar trends
- NH_3 TPD experiments provide insights into stability of stored NH_3:
  - small drop in total capacity, but significant decrease in stability of stored NH_3
  - two distinct sites in fresh catalyst
  - aging converts high stability sites into lower stability sites
- Interconversion of sites provides possible mechanism for incorporating aging impacts on NH_3 storage into models





Hydrothermal aging degrades SCR catalyst oxidation functionality



- Aging significantly reduces steady state rates of both NO and NH_3 oxidation
  - also apparent in NO_2/NOx outlet composition under standard SCR conditions
- Lack of aging impact on SCR NOx conversion raises questions about role of oxidation sites in SCR mechanism
- Decrease in oxidation rates could provide sensitive diagnostic for aging

Technical Highlights

LNT

Lab experiments continue to be directed at enhancing LNT kinetic models

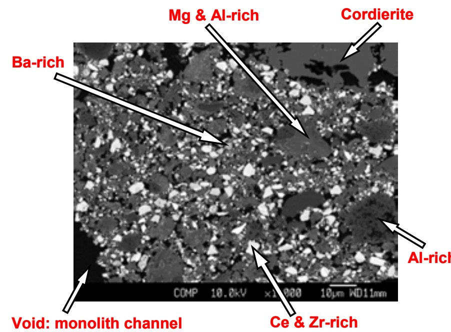
Experiments

- **Bench reactor evaluation**
  CLEERS protocol
- **Specialized measurements**
  SpaciMS, transient response
  Microscopy, DRIFTS

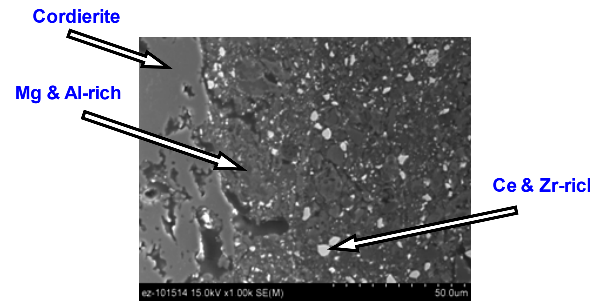
Automated bench reactor

New insights into lean GDI LNTs & models

CLEERS reference
2004, Umicore

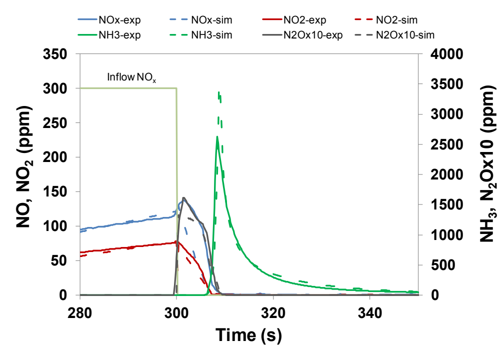


New LNT
2009, from BMW 120i



Simulation

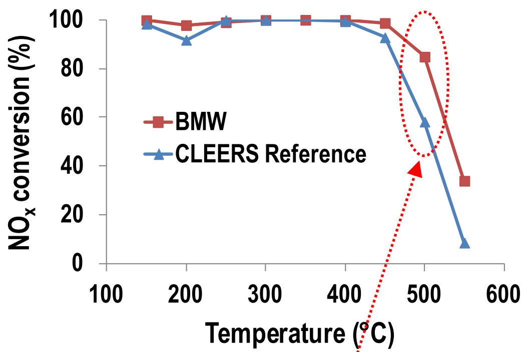
- **Incorporate new findings**
- **Extend reaction kinetics model**
  NH_3 & N_2O selectivities
  PGM redox state

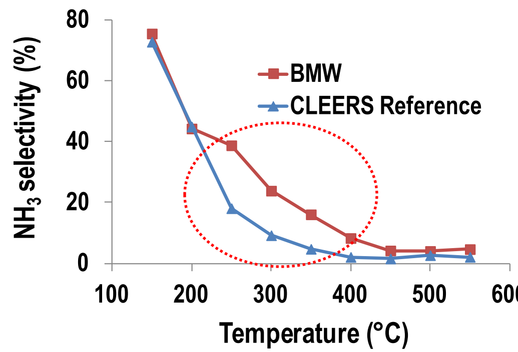


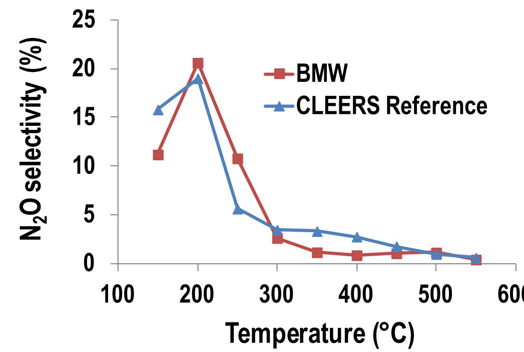
LNT example results 1: Benchmarking of a new generation GDI LNT initiated

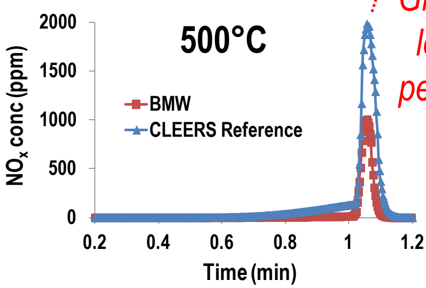
- **Comparison of BMW catalyst (2009) with CLEERS reference (Umicore, 2004)**
  - To maintain relevance of CLEERS research by migrating into a new generation LNT of similar formulation
  - CLEERS protocol; reductant & temperature sweep experiments

Lean (60 s): 300ppm NO + 10% O_2 / Rich (5 s): 3.4% H_2 (common: 5% H_2O + 5% CO_2 + N_2 bal)









Greater stability of nitrates leads to superior high-T performance of BMW LNT

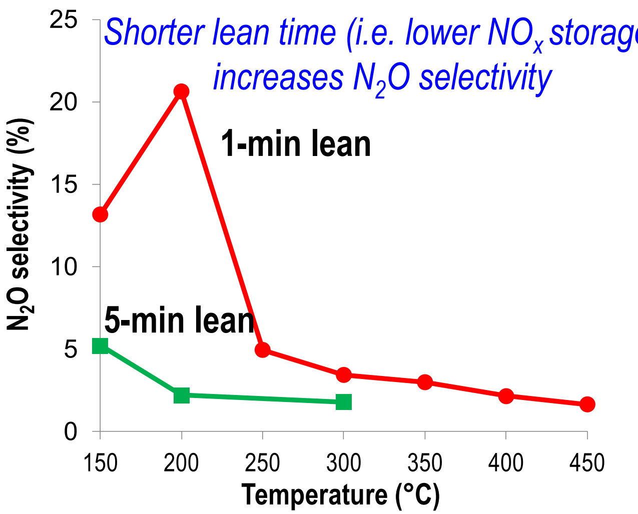
- **Initial observations on BMW LNT**
  - Improved high temperature conversion due to greater nitrate stability
  - Higher NH_3 selectivity at mid temperatures
  - Otherwise, overall similar performance trends
  - Existing knowledge & models on CLEERS reference LNT relevant to new generation LNTs

- **Next steps**
  - Simulations and results comparison
  - Additional experiments to further understand and improve kinetic models if necessary

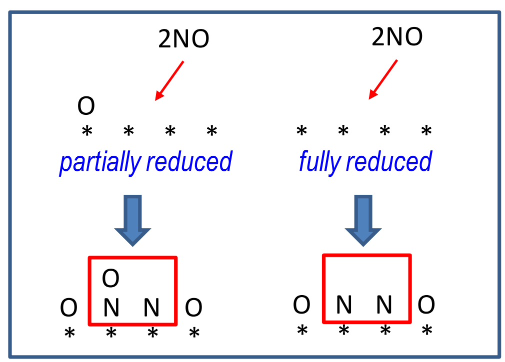
LNT example results 2: N_2O selectivity dependence on PGM redox state clarified

- N_2O: an important area (greenhouse gas) requiring model improvements
- Our previous study clarified the role of NH_3 intermediate in N_2O formation
  - NH_3 reaction with nitrates (N_2O) vs. reaction with oxygen storage capacity (no N_2O)
- Proposed mechanism (NH_3+nitrates > N_2O+N_2) showed limitations
  - Unable to explain the increased N_2O with hydrocarbon addition
  - Unable to explain low-T discrepancy between two different cycle times (short vs long cycles)

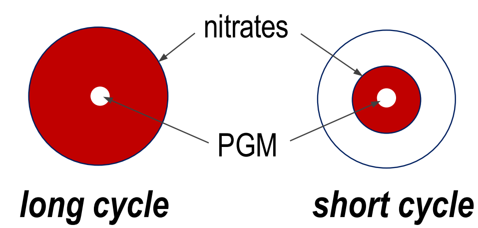
Shorter lean time (i.e. lower NO_x storage) increases N_2O selectivity



N_2O mainly on partially reduced PGM (e.g., early regen times)



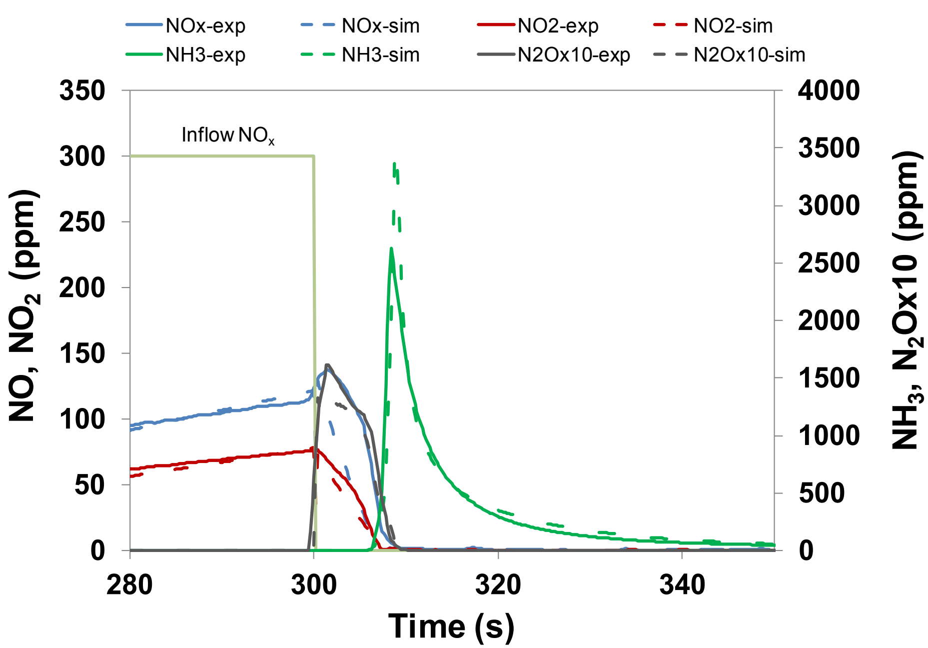
During long cycles, higher percentage of local nitrates reduced over fully reduced PGM



- Observation suggests the importance of accounting for
  - Redox states of PGM surface
  - Spatial distribution of nitrates
  - Light-off properties of reductants (i.e., relative speed of H_2, NH_3, HCs "fronts")

LNT example results 3: Mechanistic insights on selectivity led to enhanced model

- Global model extended with respect to NO_x reduction selectivity
  - Selectivity factor depends on the local redox state of PGM surfaces
  - Collaboration with ICT Prague (Dr. Kočí, Prof. Marek)



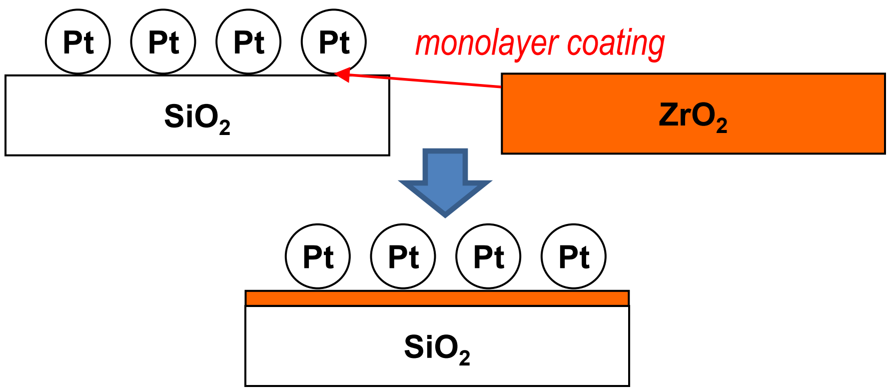
CLEERS reference LNT

- *Lean (300 s): 300 ppm NO + 10% O_2*
- *Rich (300 s): 3.4% H_2*
- *Common: 5% H_2O + 5% CO_2 + N_2 bal*
- *Temperature: 300°C*

- Good agreement between experiments and simulations
  - Conversion & selectivity over a wider range of temperature and H_2 concentration
- Next step: account for light-off properties of reductants (e.g., hydrocarbons)

Oxycat example results: novel design shows potential for durable low-T catalysts

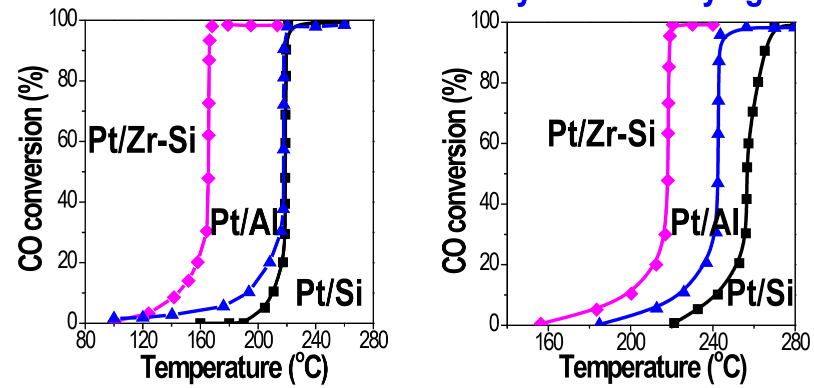
- **Exploratory research demonstrates the potential of surface modification approach**



Support property	SiO_2	ZrO_2	ZrO_2-SiO_2
Surface area	High (+)	Low (-)	High (+)
Sulfur tolerance	High (+)	High (+)	High (+)
Interaction with Pt	Low (-)	High (+)	High (+)
Hydrothermal stability	Low (-)	High (+)	High (+)

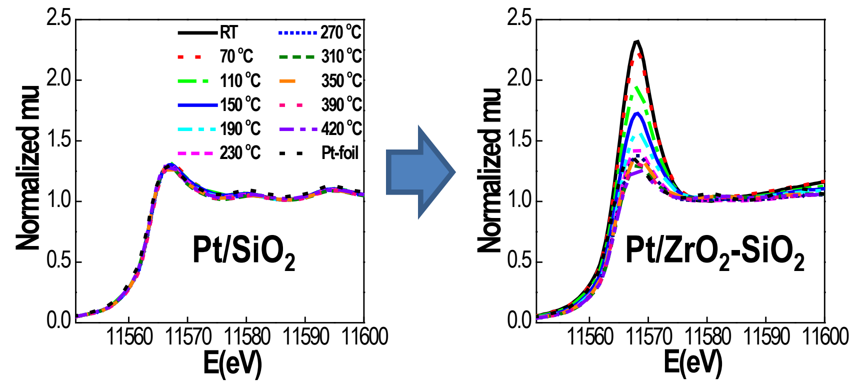
- **Leveraged BES & university capabilities**
  - Center for Nanophase Materials Sciences, ORNL
  - Advanced Photon Sources, ANL
  - Chonbuk Nat'l University, Korea

CO oxidation



- **Superior performance of ZrO_2-modifed catalyst**
  - In fresh, sulfated, desulfated & HT-aged states

Pt LIII-edge XANES spectra during TPR



- **Dramatically increased redox capacity of Pt atoms**
  - Favorable property for oxidation reactions

Collaborations

- **Partners**
  - National laboratories: ORNL (HTML, CNMS), PNNL, SNL
  - Universities: Kentucky, Houston, ICT Prague (Dr. Kočí), Chalmers (Prof. Olsson), Milan (Prof. Nova), Michigan Tech (Prof. Johnson), Tennessee (Prof. Nguyen), South Carolina (Prof. Amiridis)
  - Industry: CLEERS Focus Groups, DOE Advanced Engine Crosscut Team, and Advanced Combustion and Emissions Control Team (includes Caterpillar, Cummins, Navistar, Ford, GM, Chrysler, Daimler, Volvo, Umicore, BASF, Delphi)
- **Technology Transfer**
  - 17 publications & presentations: SAE, NAM, int'l journals, CLEERS Workshop
  - Lab protocols and data posted on the website
  - Dyno and vehicle data posted on the website
  - Lab and dyno measurements utilized in CRADAs
  - Student/faculty exchanges with universities

Future Work

- CLEERS coordination
  - Continue Planning, Focus Group, Workshop & website activities
  - Continue synchronizing ORNL-PNNL-SNL R&D
  - Expand leveraging with other DOE-OVT and DOE-OS projects
  - Expand data and modeling tool exchange (response to last industry survey)
    - RIDES (Repository for Information and Data on Emissions Simulation)
- Small pore SCR catalyst characterization
  - Hydrothermal aging
  - Mechanism and active site identification
  - Kinetic parameter estimation (especially at low temperatures)
- BMW (GDI) LNT catalyst characterization
  - Hydrocarbon impact on regeneration chemistry
  - Kinetic parameter estimation (especially at low temperatures)
- Exploratory study of low-temperature technologies
  - Surface modification of oxidation catalysts
  - Passive adsorber characterization (modeling based on literature data)

Summary

- **Relevance**
  - Assist DOE in coordinating & conducting R&D enabling development of energy & cost effective lean emissions control technologies
- **Approach**
  - Coordination of collaborations, Focus Groups, website, Workshops, industry surveys, Crosscut updates, data & model exchanges
  - Multi-scale experiments and modeling of commercial & model LNT & urea-SCR catalysts under relevant conditions
- **Technical Accomplishments**
  - Focus meetings, website, 2012 Workshop, Crosscut reports, systems implementation of CLEERS data & models
  - Fundamental understanding and modeling of practically relevant urea-SCR & LNT catalysts
- **Collaborations**
  - Non-proprietary collaborations among industry, national labs, universities, & foreign institutions through CLEERS organizational structure
  - Continued publications/presentations in major conferences, journals
- **Plans for Remainder of Current and Next Fiscal Years**
  - Continue current coordination activities, expand data and modeling exchanges
  - Lab measurements of small pore Cu zeolite catalyst aging, mechanisms, kinetics
  - Lab measurements of BMW LNT catalyst chemistry and kinetics