Joint Development and Coordination of Emissions Control Data and Models (CLEERS Analysis and Coordination)

project ID: ACE022

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PI: **Stuart Daw**

Presenter: **Josh Pihl**

Oak Ridge National Laboratory

Vehicle Technologies Office Annual Merit Review
June 18, 2014
Washington, DC

DOE Managers:
Ken Howden, Gurpreet Singh, Leo Breton

Overview

Timeline

Project start date: FY2000

Project end date: Ongoing

- core activity supporting & coordinating emissions control research
- evolves with DOE priorities and industry needs

Budget

	FY13	FY14
Coordination	$300k	$250k
Kinetics	$400k	$400k

Barriers

MYPP Challenges and Barriers:

- 2.3.1.B Lack of cost-effective emission control
- 2.3.1.C Lack of modeling capability for...emission control
- 2.3.1.E Durability (of emissions control devices)

MYPP 2015 Technical Targets:

- EPA Tier 3 Emissions (original goal: Tier 2 Bin 2)
- <1% efficiency penalty due to emission control

Partners

- DOE Advanced Engine Crosscut Team
- U.S.DRIVE ACEC Team
- CLEERS Focus Group members
  - 10 engine/vehicle manufacturers
  - 12 component and software suppliers
  - 11 universities
- PNNL, ICT Prague, Politecnico di Milano

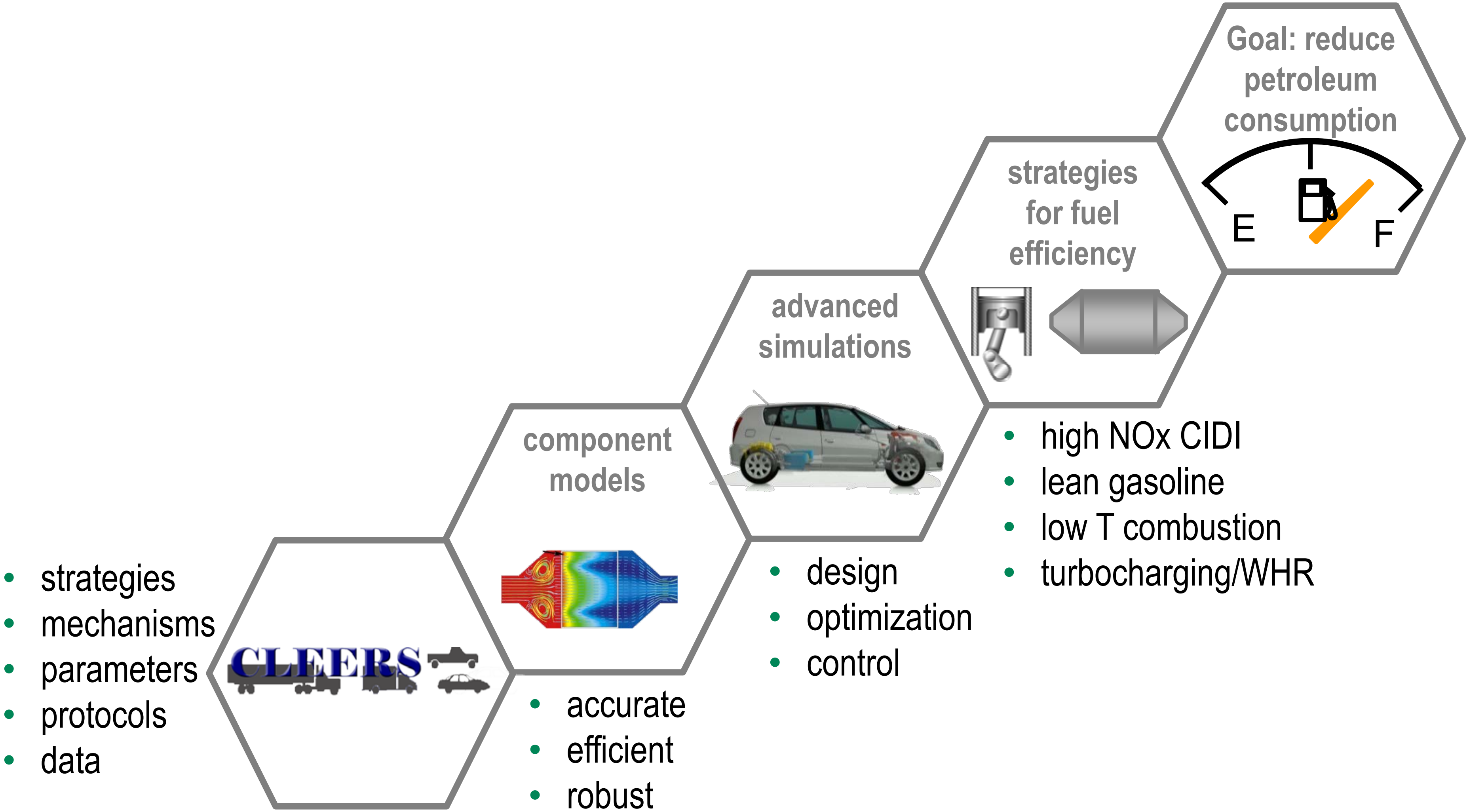
CLEERS enables the VTO goals of improving efficiency while meeting emissions regulations

"The [VTO ACE] R&D approach is to simultaneously improve engine efficiency and meet 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 cost effective aftertreatment technologies to further reduce exhaust emissions with minimal energy penalty."
- Vehicle Technologies Office Multi-Year Program Plan 2011-2015

- CLEERS supports collaborations among industry, university, and national lab partners to develop and disseminate critical pre-proprietary data and improved computational tools for accurately simulating the performance and impact of emissions controls technologies for advanced engines.
- CLEERS provides a mechanism for gathering feedback from industry on critical emissions control research needs and for coordination of DOE National Laboratory research efforts.

"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)*

CLEERS provides a key stepping stone on the path to reduced petroleum consumption



Milestones

FY	Qtr	Milestone	Status
2013	4	Expand CLEERS database	complete
2013	4	Measure NOx reduction kinetics and NH_3 storage on a commercial zeolite SCR catalyst under conditions relevant to low temperature exhaust applications	complete
2014	1	Issue final report on the 2013 CLEERS Industry Survey to the DOE Advanced Engine Crosscut Team.	complete
2014	2	Measure NH_3 storage isotherms on a commercial small pore copper zeolite catalyst.	complete
2014	3	Conduct 2014 CLEERS Workshop.	complete
2014	4	Propose a revised mechanism that predicts N_2O formation during regeneration of lean NOx traps.	on schedule

Overall Approach for CLEERS Activities

DOE Advanced Engine Crosscut Team
Chrysler, Ford, General Motors, Caterpillar, Cummins, Detroit Diesel, Navistar, Volvo, DOE-VTO, EPA, TARDEC

CLEERS Website
www.cleers.org
organization info
data sharing

CLEERS Coordination

CLEERS Advisors
Wei Li (GM)
Stuart Daw (ORNL)
Louise Olsson (Chalmers)
Chris Rutland (UW)
Neal Currier (Cummins)
Kevin Sisken (DDC)
John Kirwan (Delphi)

Technology Focus Group
select membership
monthly telecons

Shared:
mechanisms
parameters
models
protocols
data

Vehicle and Systems Simulation and Testing (Lee Slezak)

Modeling & Analysis
modeling strategies
parameter estimation
microkinetic models
global models

Workshop
held annually
near Detroit
open to public

Vehicle Simulations
fuel economy
emissions

VSS048

Experiments
flow reactors
diagnostic tools
characterization

ACE033, ACE085, ACE032

CLEERS Kinetics

Technical Accomplishments (1)

- CLEERS Coordination
  - Organized 17th CLEERS Workshop
  - Coordinated monthly Focus Group teleconferences
  - Provided basic data in support of vehicle systems aftertreatment modeling
  - Established new online database for references relevant to modeling of emissions control devices
  - Analyzed and reported results from 2013 industry priority survey
  - Worked with PNNL to support development of protocols for low temperature catalyst performance evaluation by the ACEC Tech Team Low Temperature Aftertreatment working group

Technical Accomplishments (2)

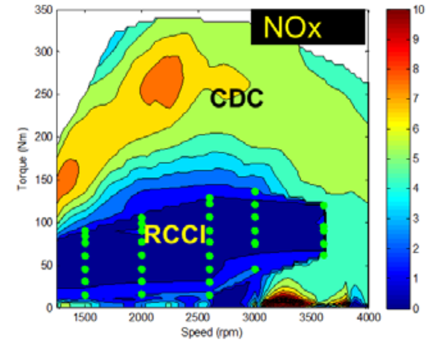
- CLEERS Kinetics: SCR
  - Measured NH_3 storage isotherms on a commercial small pore Cu zeolite
  - Developed and applied analysis techniques for extracting adsorption enthalpies from isotherm data
  - Collaborated with Politecnico di Milano to develop reaction mechanisms for NO oxidation and NO SCR consistent with reaction rate measurements and DRIFTS observations
  - Working with PNNL to update and evaluate CLEERS SCR protocol

- CLEERS Kinetics: LNT
  - Worked with ICT Prague to identify and model mechanisms for N_2O formation

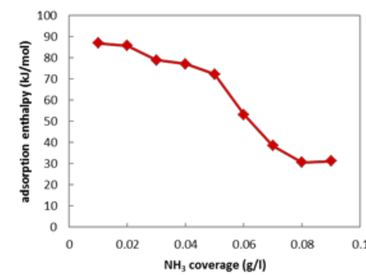
CLEERS Coordination: Approach & Accomplishments

CLEERS is an efficient means for communicating pre-competitive information

- **New web postings:**
  - Steady-state and transient LD engine-out measurements for RCCI
  - Preliminary DOC measurements for RCCI exhaust
  - Lab LNT catalyst kinetics measurements
  - Reference library in Zotero and .ris format on CLEERS website
- **Monthly teleconferences:**
  - Technical presentations of latest results to 20-40 participants
- **Industry priority surveys and scoping**
  - 2013 CLEERS Industry Priorities Survey Final Report to the Crosscut Team
  - Assistance to U.S.DRIVE ACEC Tech Team Low -T Aftertreatment working group
- **Workshop #17, April 29-May 1, 2014, UM Dearborn**
  - 100 attendees: OEMs, component & software suppliers, national labs, universities
  - 39 oral presentations, 12 posters, multiple small group discussions
  - Industry panel on “Expected impacts of advanced combustion regimes and alternate fuels on emissions controls”
- **Collaborations for SCR & LNT catalyst experiments & modeling**
  - Supported collaborations with ICT Prague, Politecnico di Milano, and University of Wisconsin to develop improved kinetic mechanisms



Advanced engine and aftertreatment measurements

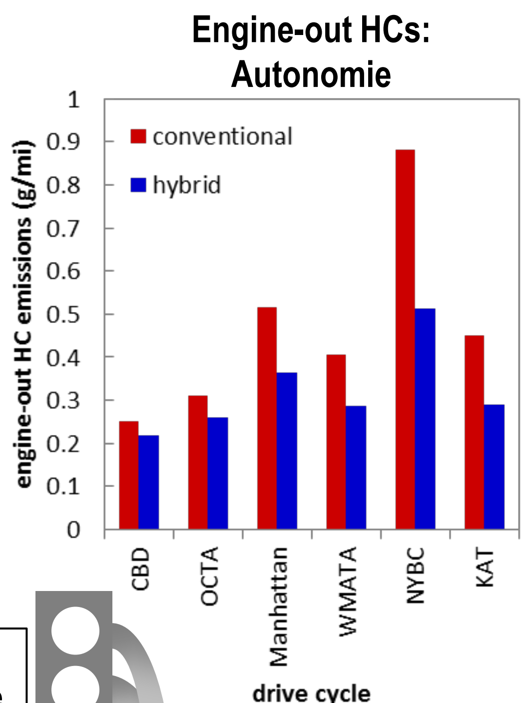


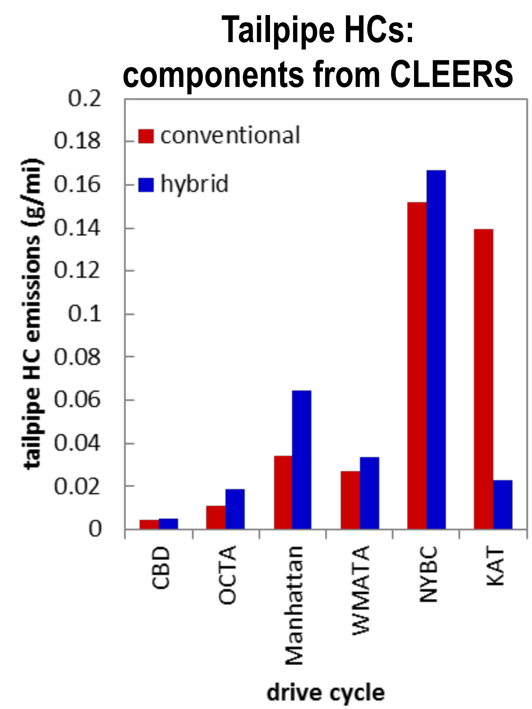
Specialized lab catalyst data

2013 CLEERS Workshop

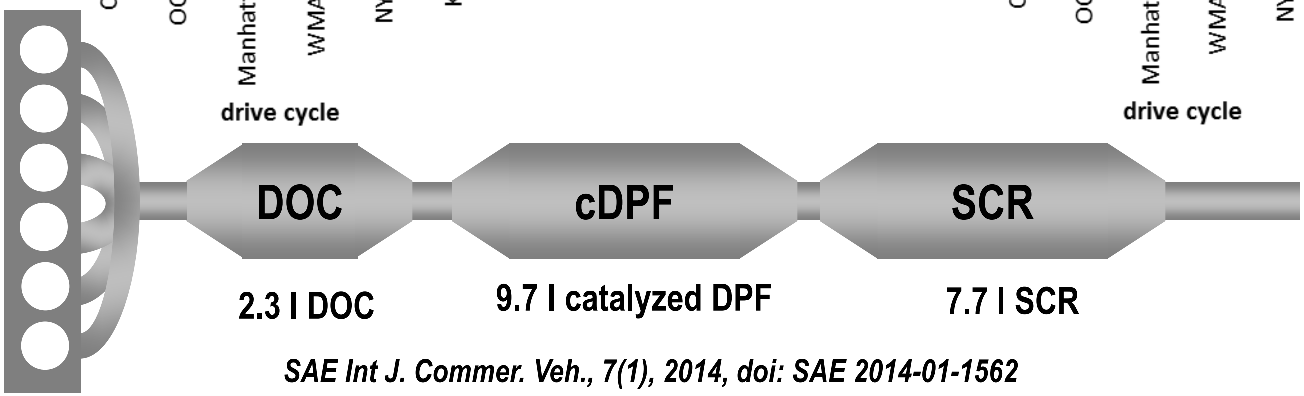
CLEERS is enabling device models for comparing simulated emissions among powertrain options

- Example: Simulations of MD conventional and electric hybrid buses over 6 different drive cycles using CLEERS data and models to relate engine-out and tailpipe emissions





2005 Optima LF-34 bus
Cummins ISB-02 5.9 l diesel engine
5 speed automatic transmission
pre-transmission parallel hybrid
 120 kW motor
 28 Ah battery
 200 kg motor + battery



SAE Int J. Commer. Veh., 7(1), 2014, doi: SAE 2014-01-1562

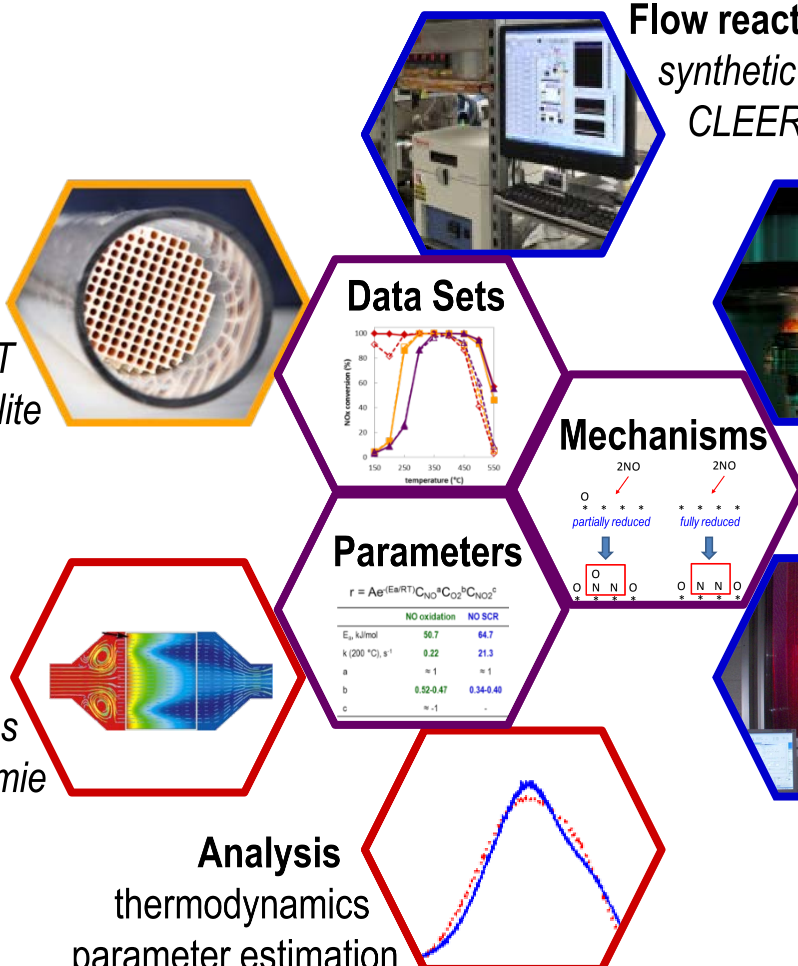
CLEERS Kinetics: Approach & Accomplishments

ORNL conducts experiments and analysis aimed at improving models for NOx control catalysts

Flow reactor experiments
synthetic exhaust mixtures
CLEERS protocol development

Specialized diagnostics
in situ DRIFTS
SpaciMS
SpaciIR

Commercial catalysts
BMW Lean GDI LNT
GM small pore Cu zeolite



Characterization
microscopy
BET, chemisorption
XRD

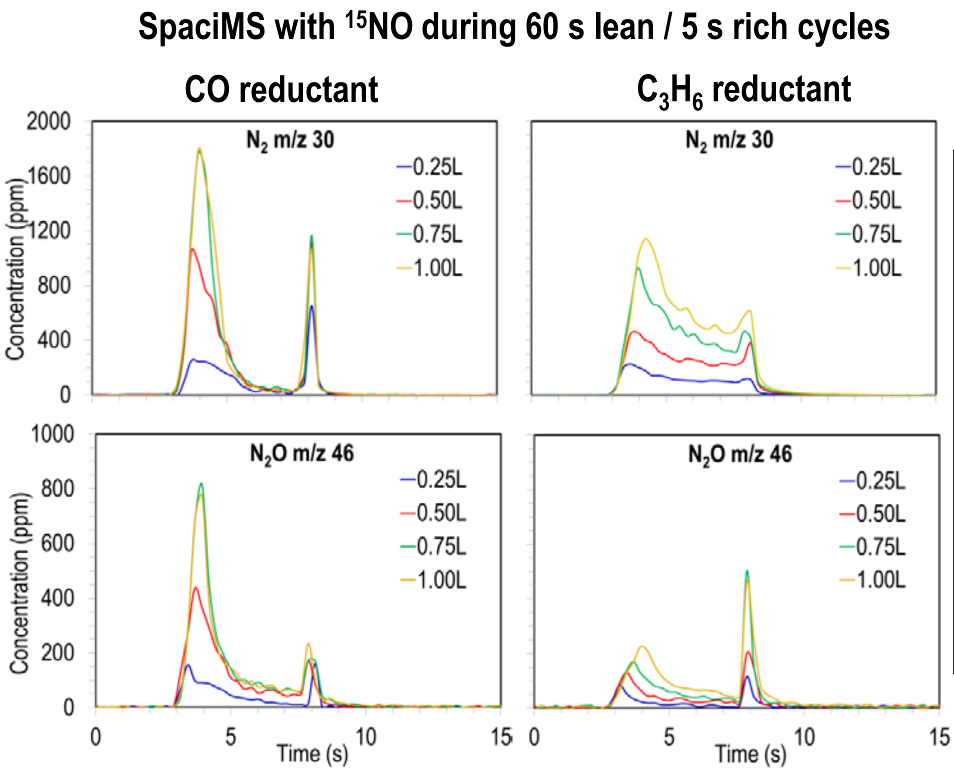
Modeling
custom codes
Chemkin, Autonomie

Analysis
thermodynamics
parameter estimation

Spatially & temporally resolving LNT regeneration chemistry clarifies N_2O formation mechanisms

collaboration with ICT Prague

- Priority survey: LNT mechanisms ranked medium or high priority by majority of LD diesel respondents
- Hosted David Mráček (student) and Dr. Petr Kočí from ICT Prague
- (FY 13) Primary N_2O peak at regen. start from reduction of stored NO_x over poorly reduced PGM sites at regen. front
- Secondary N_2O peak at rich to lean switch from reaction between residual NO_x and reductants on LNT surface (NH_3, CO, HC)



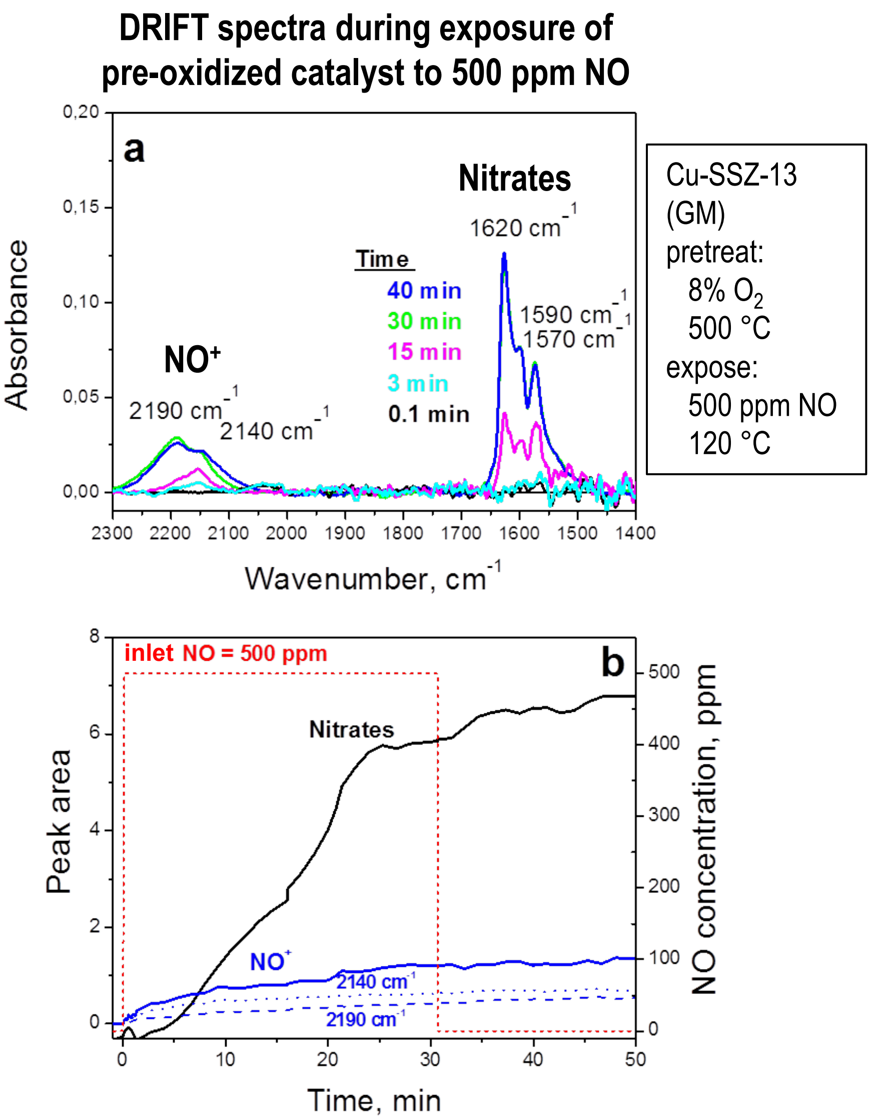
BMW LNT
250 °C
30000 hr^{-1}
60 s lean:
300 ppm NO
10% O_2
5 s rich
3.4% CO
or
0.38% C_3H_6
both:
5% H_2O
5% CO_2

  - N_2O minimized by more complete regeneration: more effective reductant (H_2 > CO > C_3H_6), higher temperature, longer regeneration duration
- **Models that accurately predict N_2O formation will enable development of control strategies that minimize production of N_2O, a potent greenhouse gas included in emissions regulations**

Developing experimentally consistent NO SCR reaction mechanism to improve low T accuracy

collaboration with Politecnico di Milano

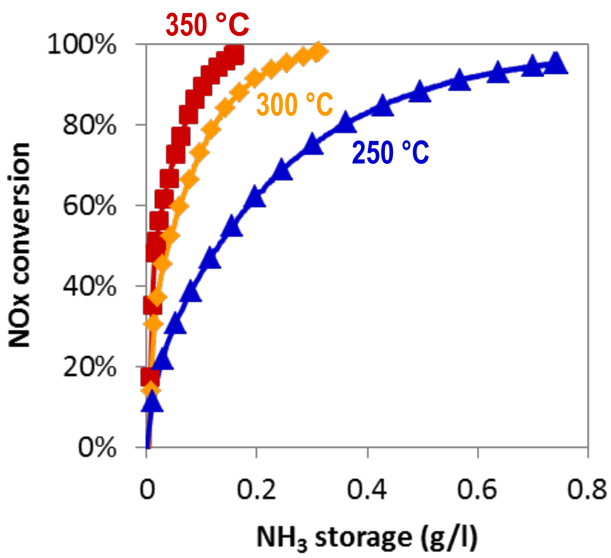
- Priority survey: NH_3 SCR mechanisms ranked medium or high priority by majority of respondents
- Hosted PoliMi graduate student Maria Pia Ruggeri
- (FY13) Concluded NO oxidation to NO_2 is not a key step in NO SCR based on reaction rates
- Conducted DRIFTS investigations, revealing:
  - Cu site redox activity: NO oxidized by Cu^{2+} in absence of O_2
  - potential NO^+ intermediate
- Proposed new mechanism for NO oxidation
  - submitted journal manuscript
- Working on related NO SCR mechanism
- **More accurate mechanisms will improve SCR model predictions, particularly at low T**

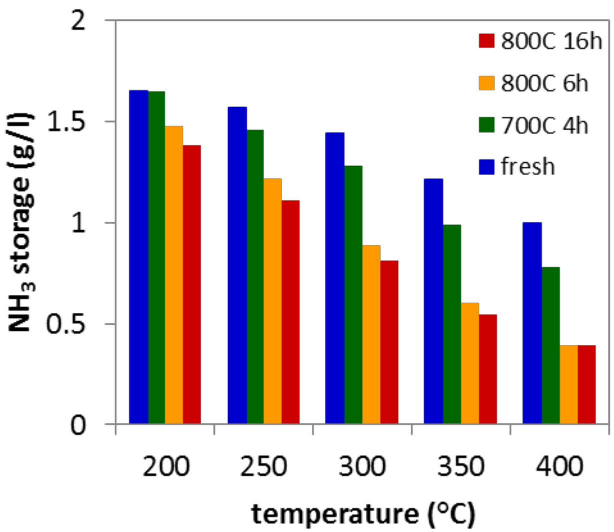


Accurate models of NH_3 storage needed to develop high NOx conversion SCR systems

collaboration with PNNL (ACE023)

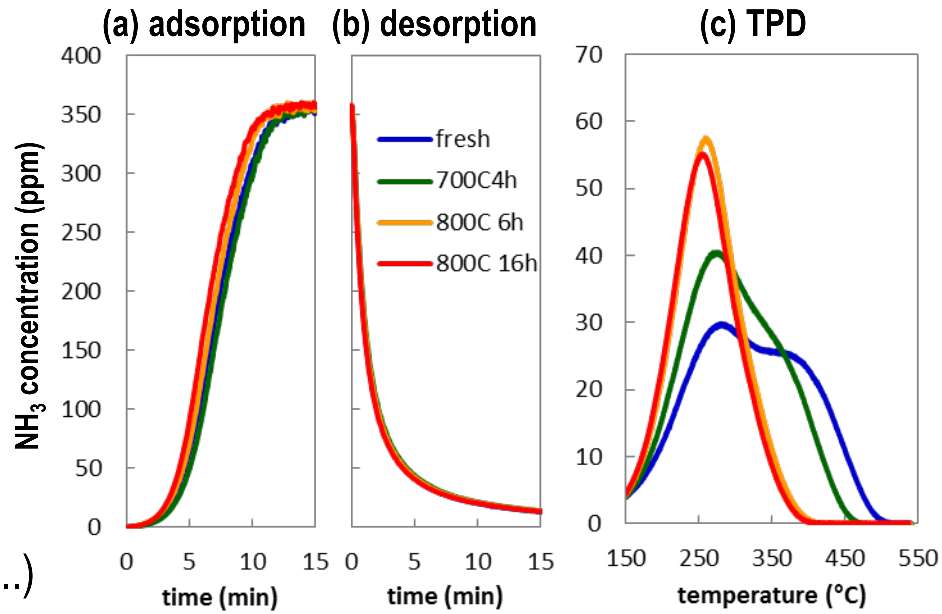
- Priority survey: NH_3 storage, oxidation, and release ranked as a high priority topic
  - #1 of 7 urea SCR topics
  - #1 of 12 NOx emission control topics
  - #3 of all 32 survey topics
- NH_3 inventory must be managed to maximize NOx conversion, minimize NH_3 slip, and efficiently utilize urea
  - high NH_3 coverages required for high NOx conversion
  - especially critical for non-urea approaches based on NH_3 production/consumption cycles (passive SCR, LNT-SCR)
  - dosing strategies often built with simulation tools
- NH_3 storage capacity varies significantly with temperature, gas composition, and catalyst age
  - models must capture these dependencies
  - high T capacity drops by half over vehicle life



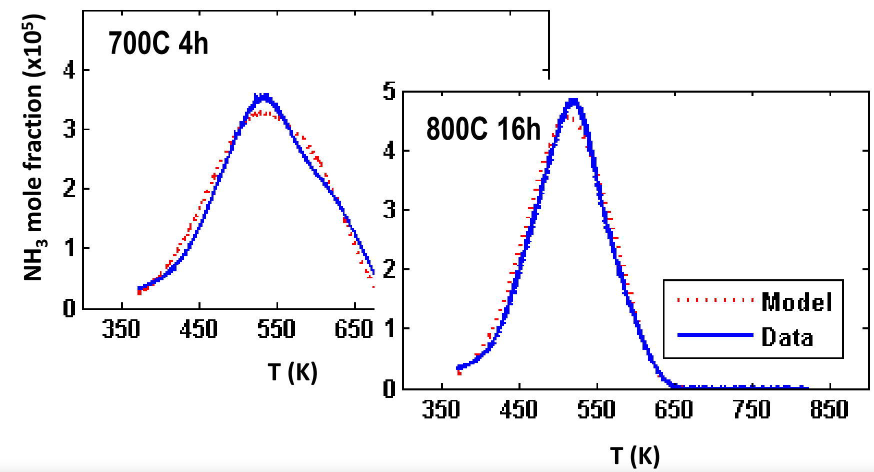


Current strategies for measuring and modeling NH_3 are insufficient

- Commonly used experimental protocols rely on transient operating conditions that confound:
  - transport (diffusion limitations)
  - kinetics (reaction rates)
  - thermodynamics (energies, capacities)
- No agreement on model strategies in literature
  - number of NH_3 storage sites
  - energetics of adsorption (Temkin, Langmuir,...)
- Complicated data sets and uncertain model structures make parameter estimation challenging
  - easy to generate "reasonable" fits to data
  - resulting parameters neither unique nor globally valid
- **We are working with PNNL to develop better measurement and modeling strategies**



TPD simulations

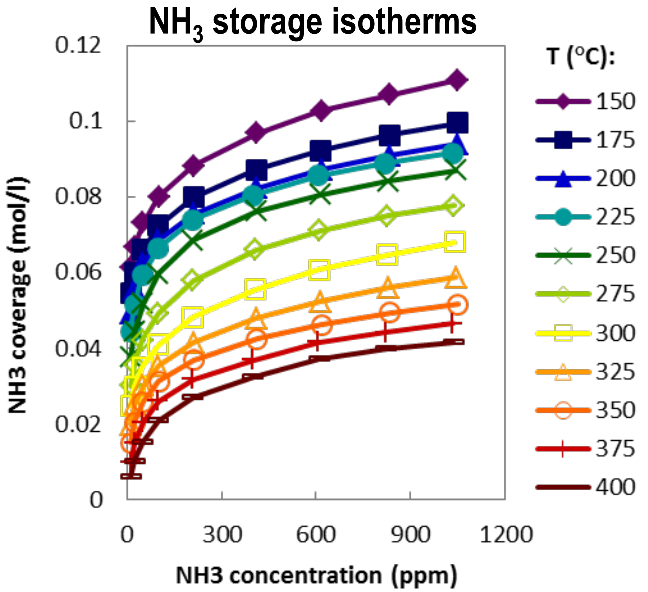


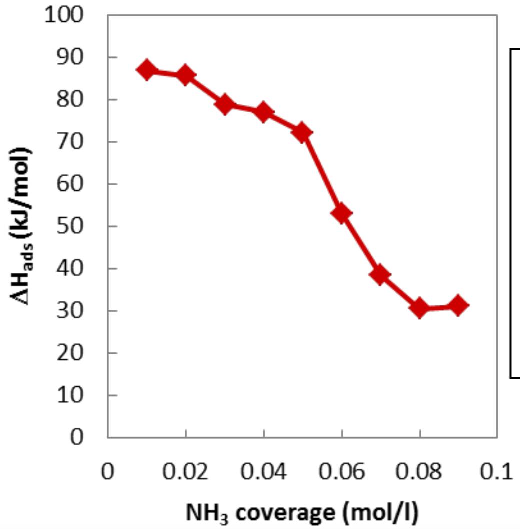
New approach: use steady state isotherms and thermodynamic analysis to isolate energetics

- Measure equilibrated NH_3 storage under steady state operating conditions
  - eliminates transport and kinetic effects
  - time consuming (requires automated reactor)
- Extract adsorption enthalpies with thermodynamic relation (Clausius-Clapeyron equation):

$$\frac{d\left(\ln P_{NH_3}\right)}{d\left(\frac{1}{T}\right)} = \frac{\Delta H_{ads}}{R}$$

- Use ΔH_{ads} vs. NH_3 coverage plots to characterize storage sites and identify modeling strategies:
  - number and relative abundance of sites
  - energetics of adsorption at each site
- Note: ΔH_{ads} vs. NH_3 coverage curve could be used directly in a map-based modeling strategy



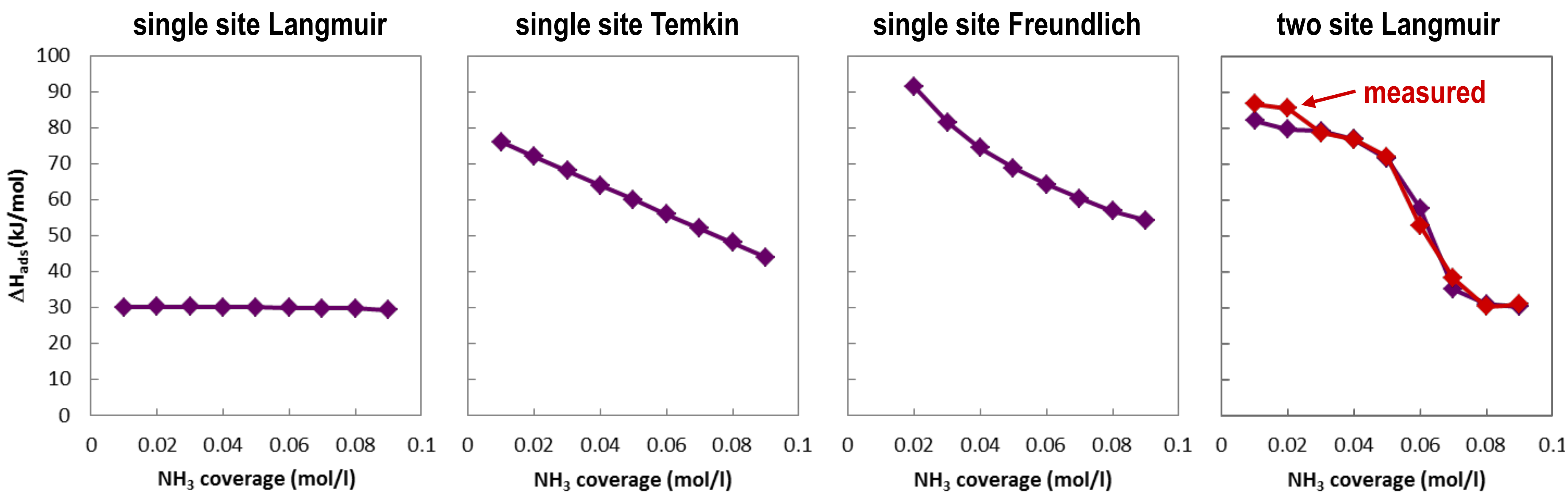


Cu-SSZ-13 degreened 700 °C 4 h

60000 h^{-1}
150-400 °C
variable NH_3
5% H_2O

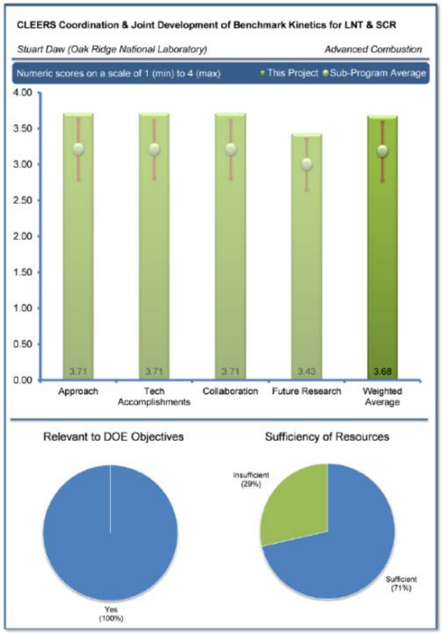
relevance approach **accomplishments** collaborations future work

NH_3 adsorption enthalpy trends elucidate catalyst properties and appropriate modeling strategies



- Comparison of calculated ΔH_{ads} vs. NH_3 coverage with model isotherms reveals key catalyst properties and informs selection of appropriate model structure:
  - roughly equal populations of two distinct NH_3 storage sites that follow Langmuir isotherm behavior with (constant) adsorption enthalpies of -30 and -85 kJ/mol
- Currently studying impacts of H_2O inhibition and hydrothermal aging on NH_3 adsorption energetics
- Findings have been shared with PNNL for incorporation in their global SCR model
- **We will apply a similar approach to hydrocarbon traps for low T combustion in late FY14**

Responses to Reviewer Comments



- **"External publication seemed to be light compared to the amount of work they had done, although there were many oral presentations.**

  This is a side effect of the cyclical nature of research; we already have one manuscript published, one submitted, and one in preparation for FY14.

- **"...most OEMs already had models for commercial catalyst system..."**

  Industry partners tell us they need better models, parameters, and data sets to design next generation systems and control strategies; DOE does not have access to OEM device models, but needs accurate system simulations for scoping and goal setting

- **Mention "some of the other partners' contributions... " and "involvement of the DOE Advanced Engine Crosscut Team, the U.S. DRIVE ACEC Team, and the CLEERS Focus Group members."; "...show a brief rationale connected to the industry partners and other users when setting priorities..."**

  We have tried to more explicitly address the roles of research collaborators and CLEERS participants, and to motivate each activity based on survey feedback in this presentation.

- **"add a CLEERS use/feedback survey, ...to gauge industry/researcher interest and value, and to provide feedback."**

  The CLEERS Industry Priorities Survey includes questions on the importance of various CLEERS activities.

- **"...like to see the PM work integrated into the ORNL program."**

  There aren't enough resources in this project to investigate PM without eliminating other topics, particularly since generating PM samples requires engine experiments; there are projects at ORNL and other labs focused directly on PM that utilize tools and techniques developed under CLEERS

- **"...one concern would be the mechanism between ORNL and international partners; collaboration often requires balanced contributions and face-to-face interaction to facilitate scientific discussions.... With the given travel restrictions, it would be more difficult."**

  We appreciate your concerns regarding travel restrictions. We host foreign graduate students in our labs, and our partners graciously come to visit us or meet with us at conferences held in the U.S.

Collaborations

CLEERS Technology Focus Group

Advanced Engine Crosscut Team

ACEC Tech Team

DOE VTO

Heavy Duty:
Caterpillar
Cummins
Daimler Trucks
Navistar
Volvo

Light Duty:
Chrysler
Ford
General Motors

EPA TARDEC

Suppliers:
BASF
Johnson-Matthey
Umicore
Corning
Delphi
Eaton

CLEERS Industry Survey Recipients

National Labs:
ORNL PNNL
SNL ANL

Industry:
Paccar
John Deere
Bosch
Tenneco
IAV
Gamma
N2Kinetics
Emissol

Universities:
Chalmers Univ.
ICT Prague
Michigan Technological Univ.
Pennsylvania State Univ.
Politecnico di Milano
Texas A&M Univ.
Univ. of Houston
Univ. of Kentucky
Univ. of Notre Dame
Univ. of Michigan
Univ. of Wisconsin

- **Technology Transfer:**
  - CLEERS website postings: lab protocols; flow reactor, engine, and vehicle data sets
  - Publications and presentations: journals, SAE, NAM, ICEC, ICC, CAPoC, CLEERS
  - Student/faculty exchanges

Remaining Challenges & Barriers/Future Work

Remaining Challenges:	Future Work:
• Decreasing exhaust temperatures from higher efficiency engines and advanced combustion modes.	• Continue emphasizing low T emissions control priorities in CLEERS activities and plans • Identify modeling strategies and key parameters for passive adsorber devices • Develop a CLEERS adsorber protocol and begin experimental characterization
• Requirements for higher NOx conversion efficiencies coupled with limited accuracy of available NH_3 SCR device models, particularly at low temperatures and for predictions of NH_3 inventories.	• Propose mechanisms for NO oxidation and NO SCR, emphasizing low T chemistry • Refine simple, accurate NH_3 storage modeling and parameter estimation strategies based on adsorption isotherms
• N_2O formation during LNT regeneration combined with inclusion of N_2O in greenhouse gas regulations.	• Develop more accurate LNT models that will enable design of operating strategies that minimize N_2O formation
• Ongoing need for coordination and collaboration in developing simulation tools for next generation emissions control devices.	• Continue planning, focus group, workshop, website, and DOE lab coordination

Summary

- **Relevance**
  - CLEERS supports the development of accurate and robust simulation tools that can be used to design, optimize, and control next generation emissions control technologies, which reduce fuel use by enabling higher efficiency engine operation and advanced combustion concepts
- **Approach**
  - Organized technical exchanges based on Focus Groups, Workshops, industry surveys, Crosscut updates, pre-competitive data & models
  - Multi-scale experiments and modeling of commercial catalysts under relevant conditions
- **Technical Accomplishments**
  - Well-attended teleconferences and public Workshop; Crosscut Team reports; shared data and protocols; source for data and models for parallel DOE projects and CRADAs
  - More accurate mechanisms for N_2O formation in LNTs and NO SCR and oxidation over Cu-SSZ-13
  - Improved strategies for measurement, analysis, and modeling of NH_3 storage on SCR catalysts
- **Collaborations**
  - PNNL; ICT Prague; Politecnico di Milano
  - Collaborations among industry, national labs, and universities through CLEERS organizational structure
- **Future Work**
  - Continue coordination activities: workshop, telecons, website, priorities survey
  - Continue mechanistic investigations into small pore Cu zeolite and BMW LNT materials, with emphasis on low temperature operating conditions
  - Initiate characterization of passive adsorber materials and protocol development