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

project ID: ACE022

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Presenter: **Josh Pihl**
Oak Ridge National Laboratory

DOE Vehicle Technologies Office
Annual Merit Review & Peer Evaluation Meeting
June 10, 2015
Arlington, VA

DOE Managers:
Ken Howden, Gurpreet Singh, Leo Breton

Overview

Timeline

Project start date: FY2015

Project end date: FY2017

- core activity since FY2000
- supports, coordinates emissions control research
- evolves with DOE priorities and industry needs

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

Budget

	FY14	FY15
Coordination	$250k	$236k
Analysis	$400k	$377k

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, UCT Prague, Politecnico di Milano

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


ENERGY

Vehicle Technologies Program

Multi-Year Program Plan
2011 – 2015

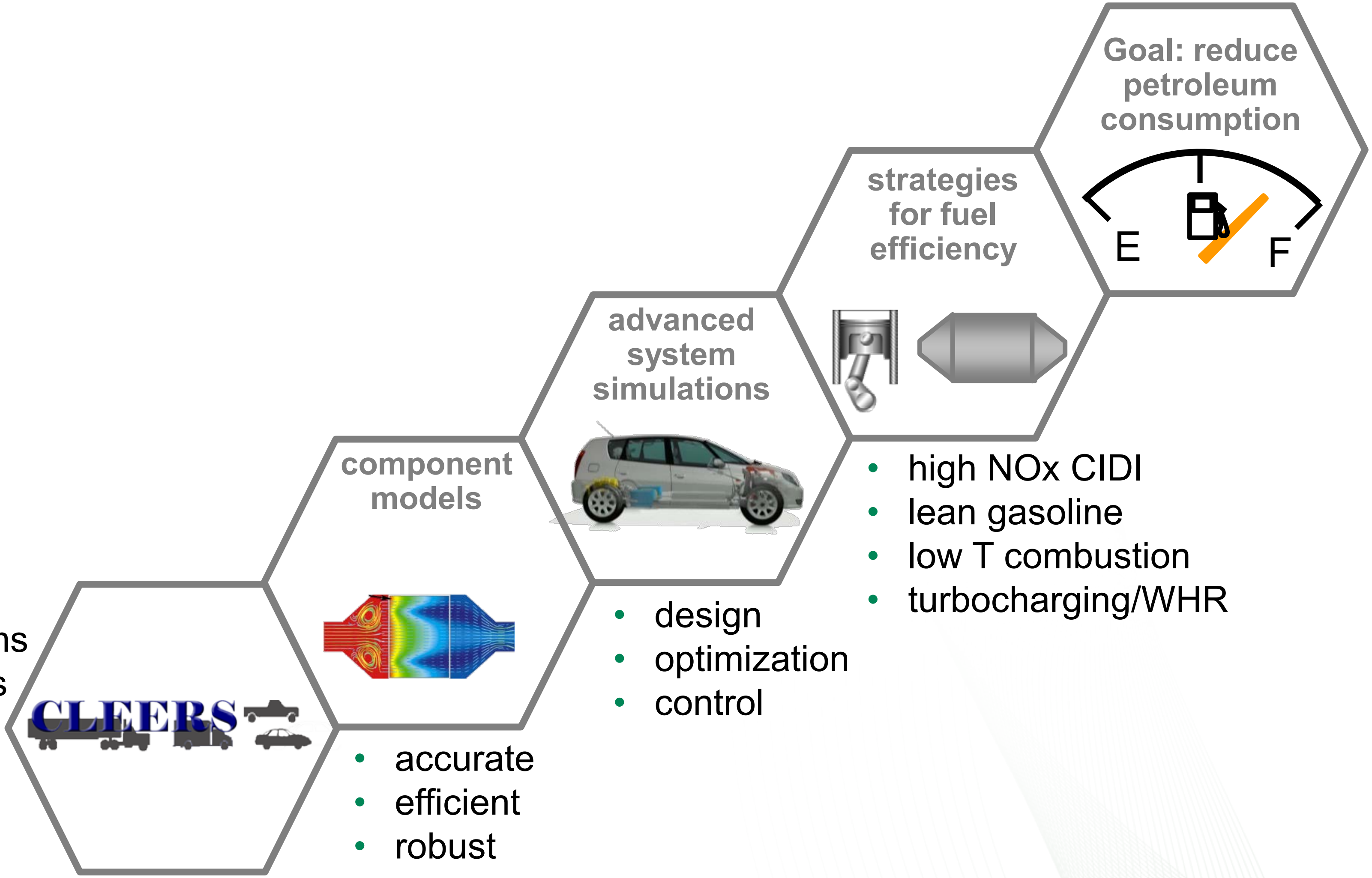
December 2010

"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 = **C**rosscut **L**ean (/**L**ow-temperature) **E**xhaust **E**missions **R**eduction **S**imulations
- CLEERS mission: accelerate the development of emissions control technologies for advanced engines by improving the accuracy of aftertreatment system simulations
- CLEERS objectives:
  – support collaborations among industry, university, national lab partners
  – develop and disseminate pre-competitive data, parameters, and models
  – gather feedback from industry on critical emissions control research needs
  – coordinate DOE National Laboratory research efforts

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



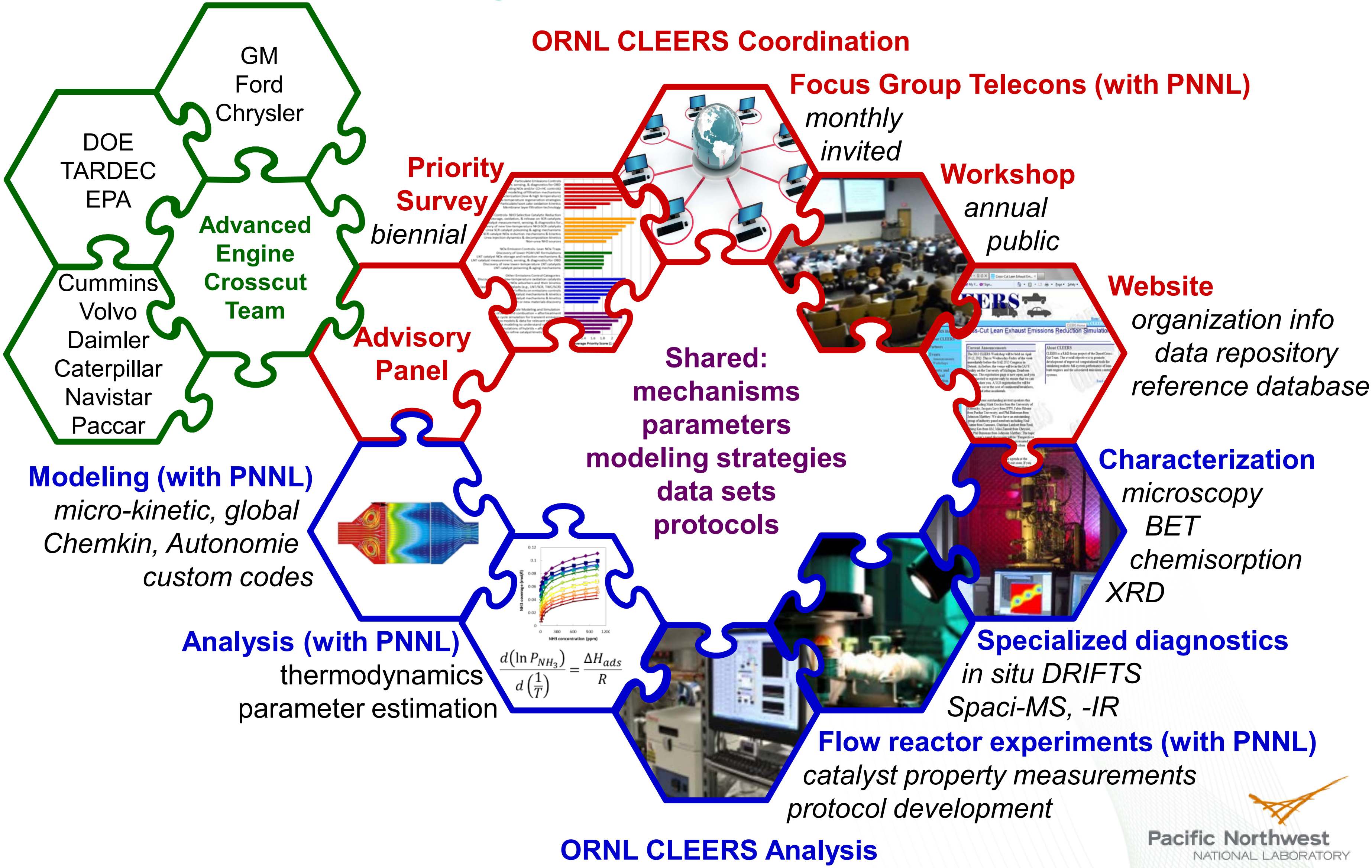
- strategies
- mechanisms
- parameters
- protocols
- data

- accurate
- efficient
- robust

- design
- optimization
- control

- high NOx CIDI
- lean gasoline
- low T combustion
- turbocharging/WHR

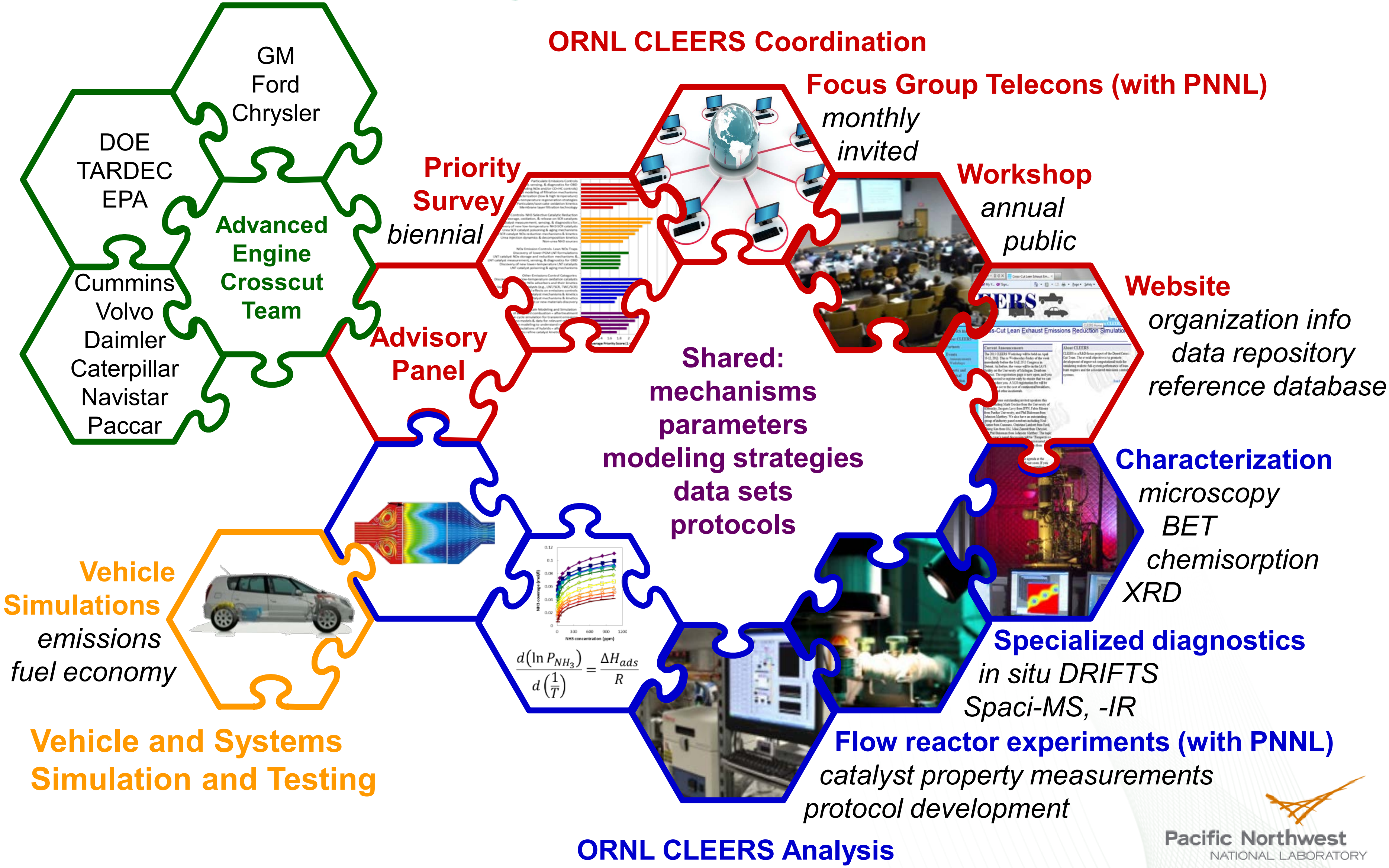
ORNL coordinates CLEERS activities and conducts R&D in support of CLEERS objectives



Pacific Northwest National Laboratory

Oak Ridge National Laboratory

ORNL coordinates CLEERS activities and conducts R&D in support of CLEERS objectives



Pacific Northwest NATIONAL LABORATORY

OAK RIDGE National Laboratory

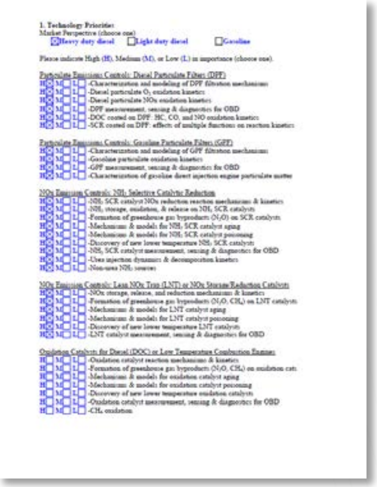
Milestones

FY	Qtr	Milestone	Status
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.	complete
2015	2	Measure impact of catalyst aging on NH_3 storage isotherms and model parameters.	complete
2015	3	Conduct 2015 CLEERS Workshop	complete

Technical Accomplishments (1)

- CLEERS Coordination
  - Coordinated 18th CLEERS Workshop
  - Organized monthly Focus Group teleconferences
  - Expanded online database for emissions control modeling references, including presentations from CLEERS Workshops
  - Updated and distributed 2015 Industry Priority Survey
  - Provided basic data in support of vehicle systems aftertreatment modeling
  - Worked with PNNL to support development of protocols for low T catalyst performance evaluation by the ACEC Tech Team Low Temperature Aftertreatment working group

Kochoff Hall UM Dearborn



1. Technology Priorities
Market Perspective (choose one)
☒Heavy duty diesel ☐Light duty diesel ☐Gasoline

Please indicate High (H), Medium (M), or Low (L) in importance (choose one).

Particulate Emissions Controls: Diesel Particulate Filters (DPF)
- Characterization and modeling of DPF filtration mechanisms
- Diesel particulate O_2 oxidation kinetics
- Diesel particulate NOx oxidation kinetics
- DPF measurement, sensing & diagnostics for OBD
- DOC coated on DPF: HC, CO, and NO oxidation kinetics
- SCR coated on DPF: effects of multiple functions on reaction kinetics

Particulate Emissions Controls: Gasoline Particulate Filters (GPF)
- Characterization and modeling of GPF filtration mechanisms
- Gasoline particulate oxidation kinetics
- GPF measurement, sensing & diagnostics for OBD
- Characterization of gasoline direct injection engine particulate matter

NOx Emission Controls: NH_3 Selective Catalytic Reduction
- NH_3 SCR catalyst NOx reduction reaction mechanisms & kinetics
- NH_3 storage, oxidation, & release on NH_3 SCR catalysts
- Formation of greenhouse gas byproducts (N_2O) on SCR catalysts
- Mechanisms & models for NH_3 SCR catalyst aging
- Mechanisms & models for NH_3 SCR catalyst poisoning
- Discovery of new lower temperature NH_3 SCR catalysts
- NH_3 SCR catalyst measurement, sensing & diagnostics for OBD
- Urea injection dynamics & decomposition kinetics
- Non-urea NH_3 sources

NOx Emission Controls: Lean NOx Trap (LNT) or NOx Storage/Reduction Catalysts
- NOx storage, release, and reduction mechanisms & kinetics
- Formation of greenhouse gas byproducts (N_2O, CH_4) on LNT catalysts
- Mechanisms & models for LNT catalyst aging
- Mechanisms & models for LNT catalyst poisoning
- Discovery of new lower temperature LNT catalysts
- LNT catalyst measurement, sensing & diagnostics for OBD

Oxidation Catalysts for Diesel (DOC) or Low Temperature Combustion Engines
- Oxidation catalyst reaction mechanisms & kinetics
- Formation of greenhouse gas byproducts (N_2O, CH_4) on oxidation cat.
- Mechanisms & models for oxidation catalyst aging
- Mechanisms & models for oxidation catalyst poisoning
- Discovery of new lower temperature oxidation catalysts
- Oxidation catalyst measurement, sensing & diagnostics for OBD
- CH_4 oxidation

Priority Survey

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

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

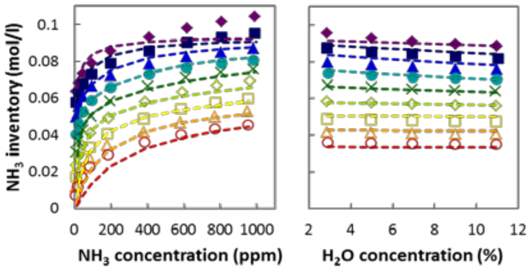
March 2015

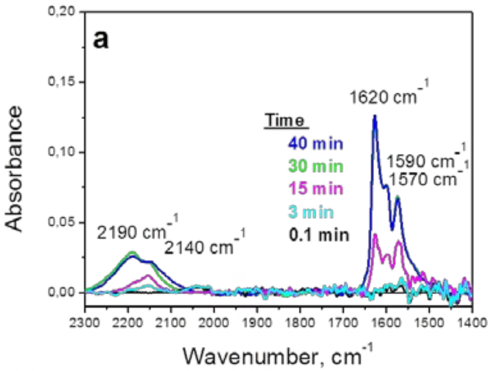
USDRIVE
DRIVING RESEARCH AND INNOVATION FOR VEHICLE EFFICIENCY AND ENERGY SUSTAINABILITY

Low T Protocol

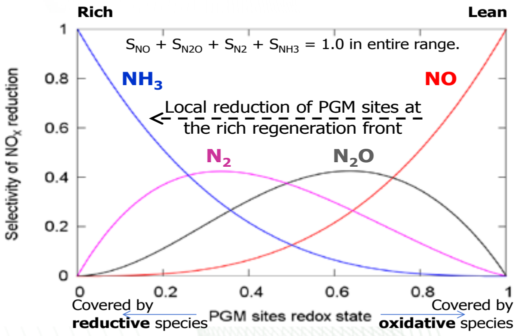
Technical Accomplishments (2)

- CLEERS Analysis: SCR
  - Used equilibrium adsorption/desorption isotherms to measure the effects of oxidation state, humidity, and hydrothermal aging on the NH_3 storage capacity of a commercial Cu-SSZ-13 catalyst
  - Developed an NH_3 storage model that accurately captures the effects of temperature, water competition and hydrothermal aging for a commercial Cu-SSZ-13 catalyst
  - Collaborated with Politecnico di Milano to publish reaction mechanism for NO oxidation over Cu-SSZ-13 consistent with reaction rate measurements and DRIFTS observations
  - Working with PNNL to update and evaluate CLEERS SCR protocol





- CLEERS Analysis: LNT
  - Worked with UCT Prague to refine regeneration mechanisms and models
  - Identified operating guidelines and strategies for minimizing N_2O formation



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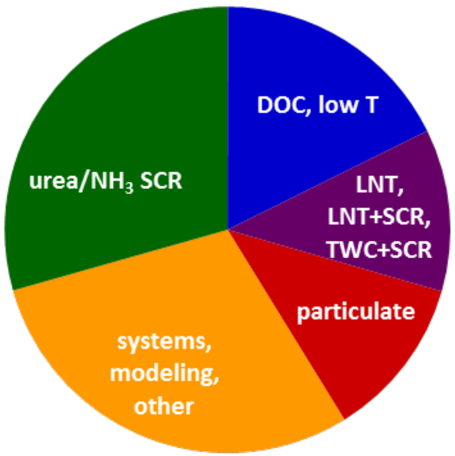
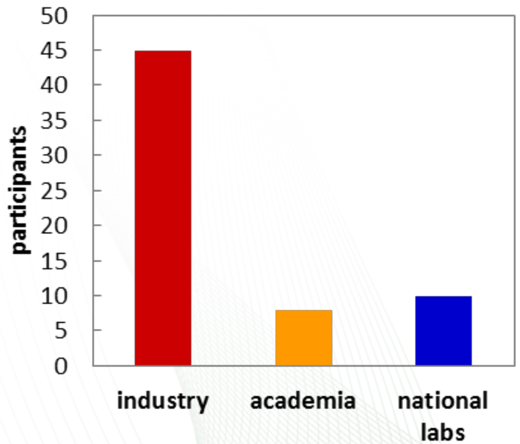
CLEERS is an efficient means for communicating pre-competitive information

- **Workshop #18, April 27-29, 2015, UM Dearborn** ✓(*milestone*)
  - >120 attendees: OEMs, component & software suppliers, national labs, universities
  - 34 presentations, >15 posters, small group discussions
  - Industry panel on “Needs and opportunities for passive adsorber devices for advanced engine emission controls”
- **Monthly teleconferences:**
  - Technical presentations of latest results
  - 20-60 invited participants from around globe
    - typically >50% industry representatives
- **Recent web postings:**
  - NH_3 adsorption isotherm data
  - Past CLEERS Workshop presentations
- **Industry communication and scoping:**
  - 2015 Industry Priorities Survey
  - Assistance to U.S.DRIVE ACEC Tech Team Low Temperature Aftertreatment working group

2015 CLEERS Workshop Presentation Topics



January 2015 Focus Group Teleconference Participants



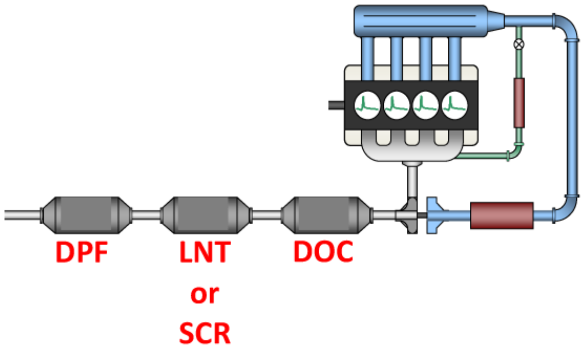
CLEERS is enabling device models for advanced combustion powertrain emissions control simulations

support for VSST (VSS140)

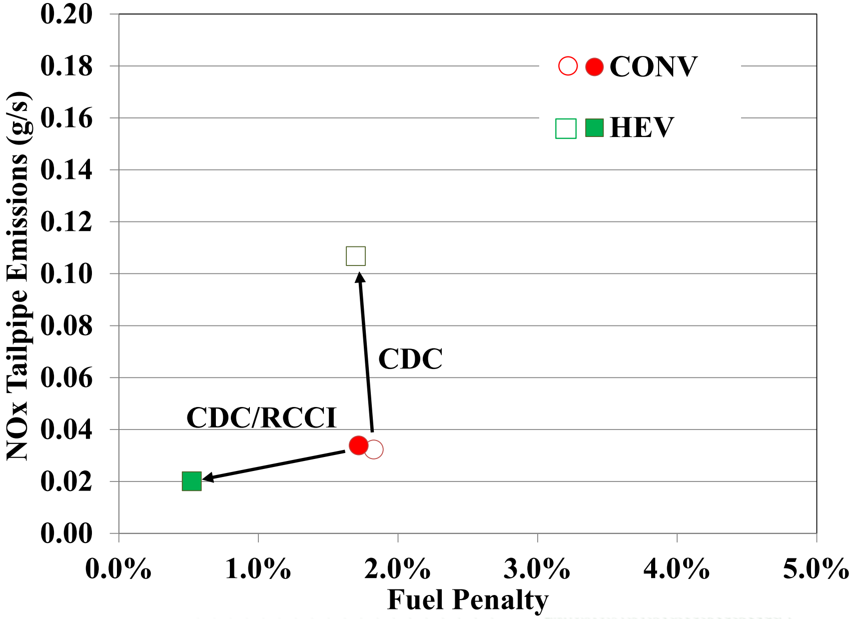
- Simulated tailpipe emissions and fuel penalty of multiple advanced engine drivetrain + aftertreatment configurations
  - simulated FTP75 with cold start
  - engine: CDC or CDC/RCCI
  - drivetrain: conventional or hybrid electric
  - emissions control system:
    - DOC/LNT/DPF
    - DOC/SCR/DPF
- Results indicate engine capable of advanced combustion operation could reduce emissions and fuel penalty in HEV drivetrains
  - points to new area for investigation

CLEERS component models and data sets are supporting vehicle simulations of advanced engines & aftertreatment

Example emissions control system configuration



Simulated tailpipe NOx and LNT fuel penalty for different advanced drivetrain options



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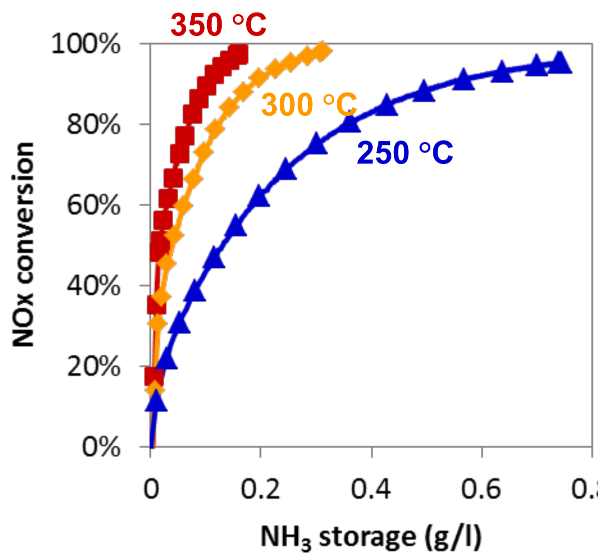
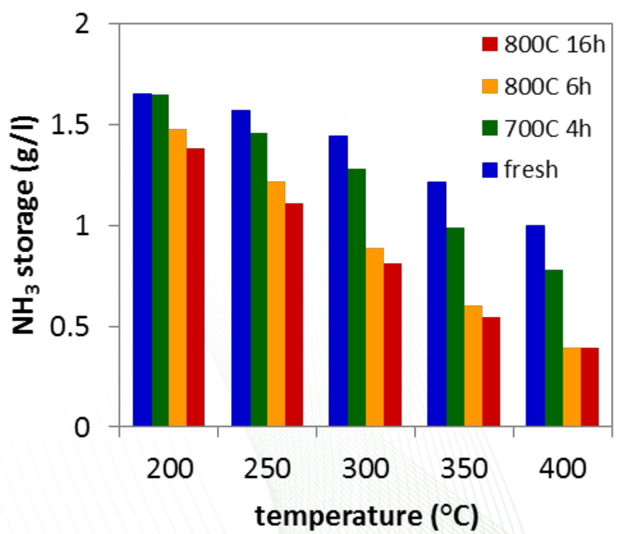
Accurate models of NH_3 storage needed to develop high NOx conversion SCR systems

collaboration with PNNL (ACE023)

- Survey: NH_3 storage, oxidation, and release ranked as a high priority topic
  - #1 of 7 urea SCR topics
  - #1 of 12 NOx control topics
  - #3 of all 32 survey topics
- NH_3 inventory must be managed to maximize NOx conversion, minimize NH_3 slip, efficiently utilize urea
  - high NH_3 coverages required for high NOx conversion
  - critical for 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
  - high T capacity drops by half over vehicle life
  - models must capture these dependencies



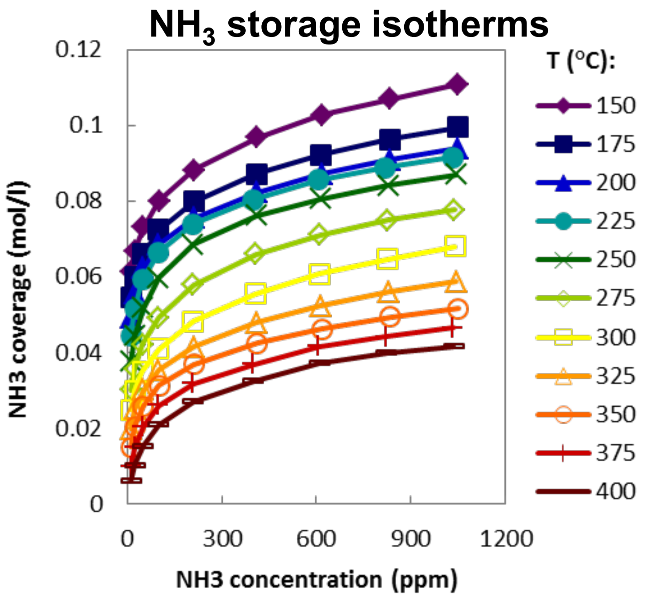


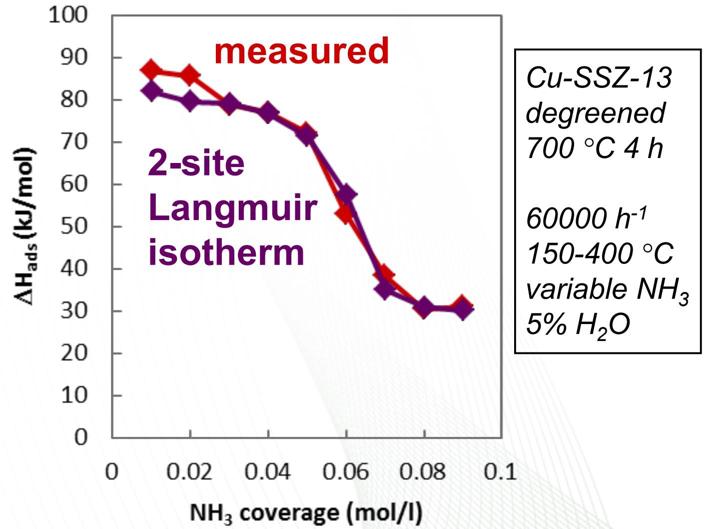
Steady state isotherms and thermodynamic analysis isolate SCR NH_3 adsorption energetics, guide model development

- Challenges in current measurements & modeling:
  - model structures uncertain (site multiplicity, etc.)
  - data sets confound thermodynamics, kinetics, mass transport
  - resulting parameters neither global nor universal
- New approach: measure storage isotherms to isolate energetics of adsorption under steady state conditions
  - eliminate transport and kinetic effects
  - extract adsorption enthalpies with standard thermodynamic relation (Clausius-Clapeyron)

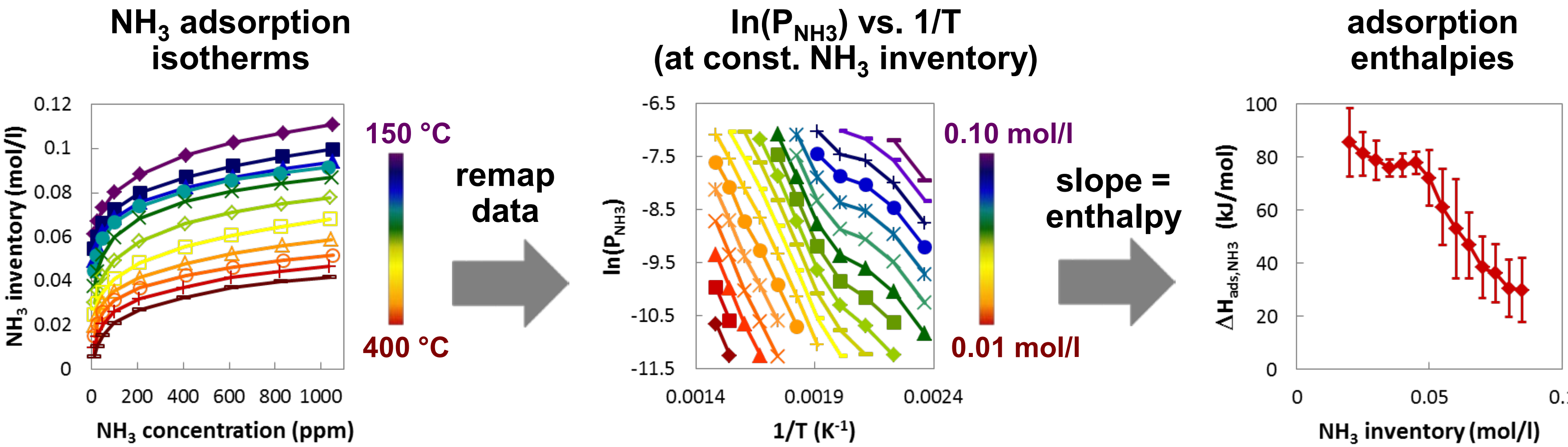
$$\frac{d\ln(P)}{d\left(\frac{1}{T}\right)} = \frac{-\Delta H_{ads}}{R}$$

- Use ΔH_{ads} vs. NH_3 coverage to characterize storage sites and identify modeling strategies:
  - multiplicity and abundance of sites
  - energetics of adsorption at each site





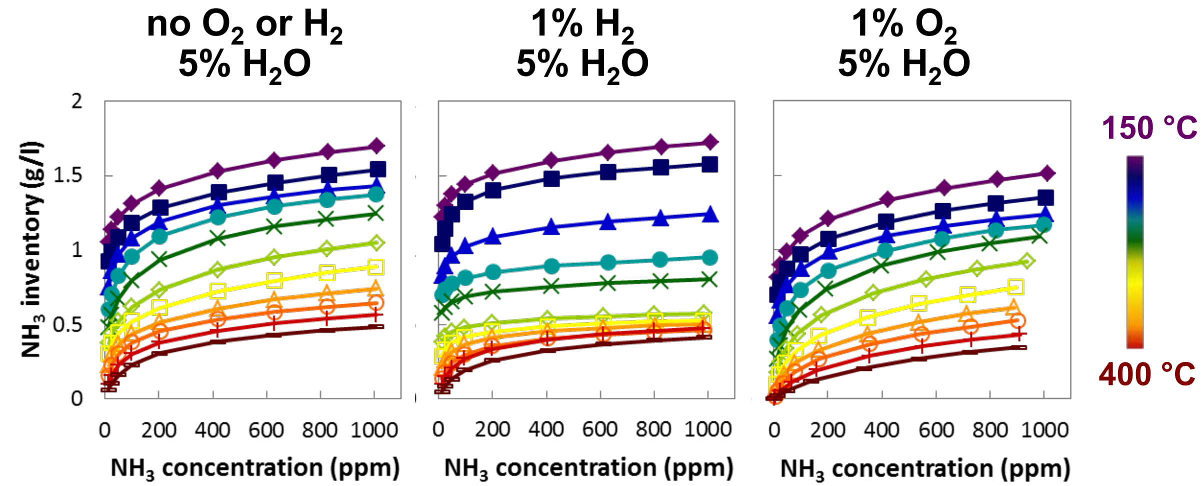
Estimation of uncertainty in calculated adsorption enthalpy highlights need for improvements in experimental protocol



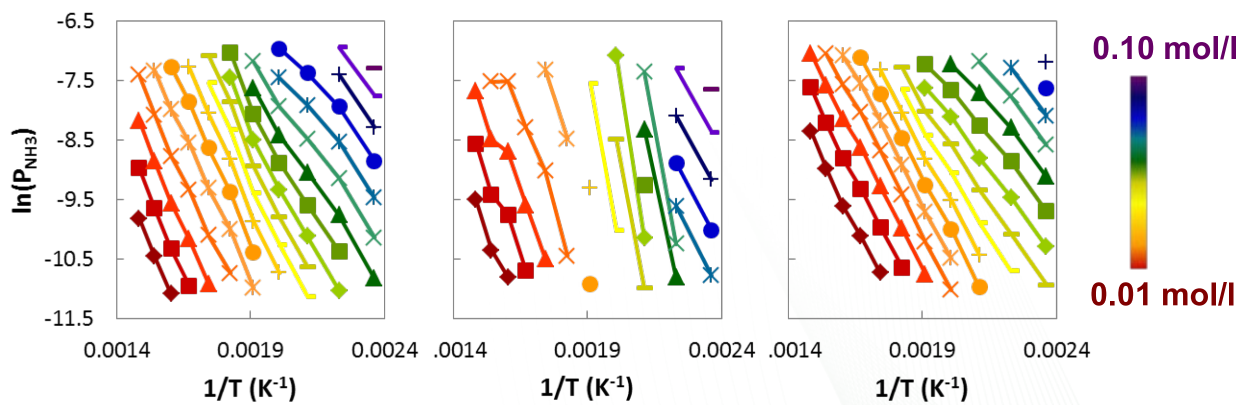
- Adsorption enthalpy calculated from slope of ln(P_{NH3}) vs. 1/T
- 95% confidence intervals estimated from error on linear regression slope
  - nonlinearity increases uncertainty in estimated enthalpies & modeling approach
  - note: simple isotherms predict straight lines
- Potential sources of nonlinearity/uncertainty:
  - changes in catalyst oxidation state
  - H_2O competitive adsorption

Controlling catalyst oxidation state is critical in quantifying NH_3 adsorption properties

- NH_3 adsorption controlled by complex interactions between redox environment and humidification
  - see backup slides for more details
- Reducing conditions result in very different NH_3 adsorption behavior
  - potential implications for LNT or TWC + SCR
  - simple isotherm analysis breaks down
- Oxidizing conditions yield expected linear behavior for $\ln(P_{NH3})$ vs. 1/T
  - most relevant conditions for urea SCR
  - used for subsequent investigations



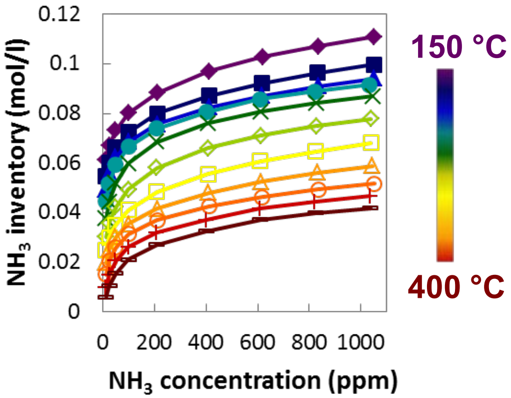
Redox environment & humidity both affect NH_3 storage



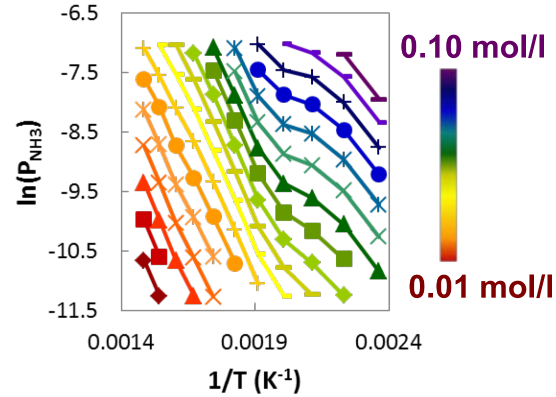
Holding catalyst in oxidized state leads to more consistent NH_3 storage behavior

Controlling catalyst oxidation state increases confidence in adsorption enthalpy estimates & modeling approach

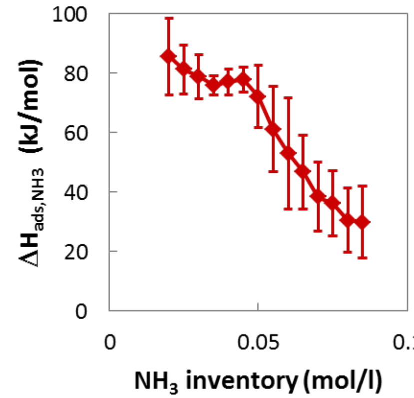
NH_3 adsorption isotherms



$\ln(P_{NH3})$ vs. 1/T (at const. NH_3 inventory)



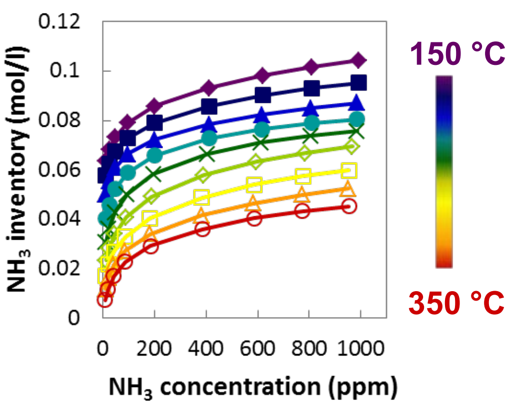
adsorption enthalpies

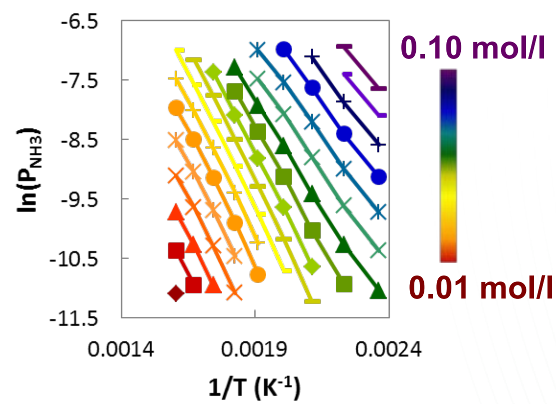


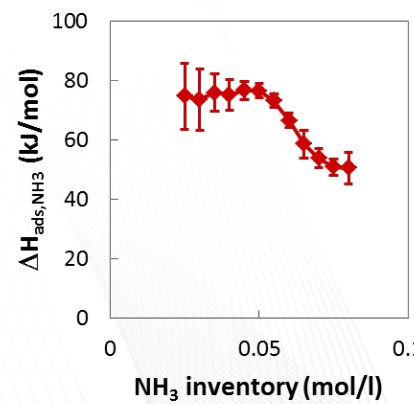
include 0.2% O_2

eliminates slope discontinuities

reduces uncertainty

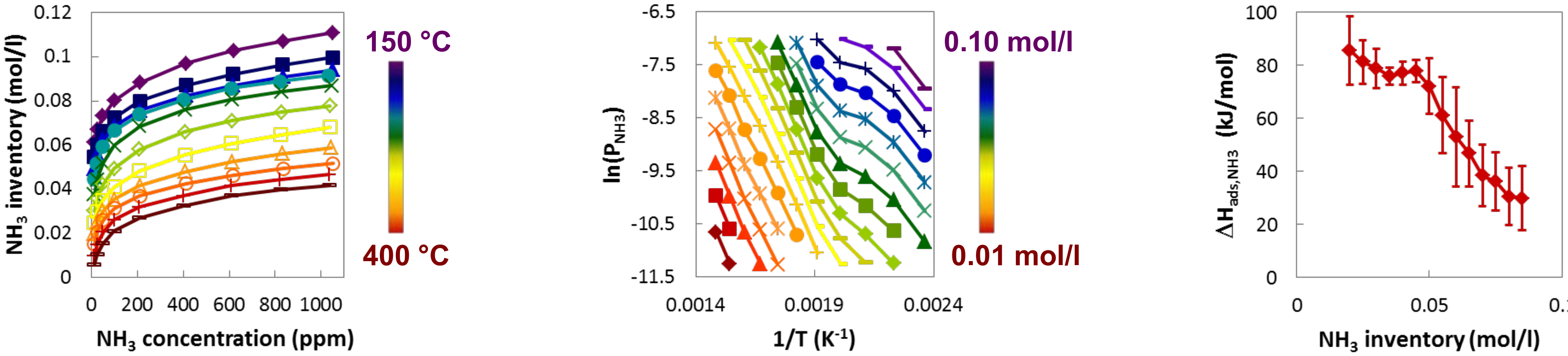




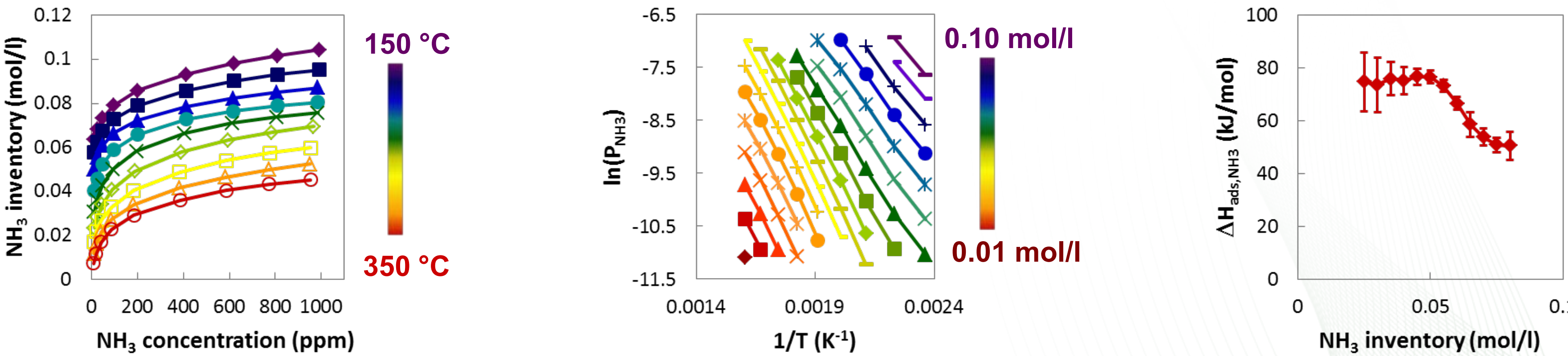


Controlling catalyst oxidation state increases confidence in adsorption enthalpy estimates & modeling approach

NH_3 adsorption isotherms | $\ln(P_{NH3})$ vs. 1/T (at const. NH_3 inventory) | adsorption enthalpies

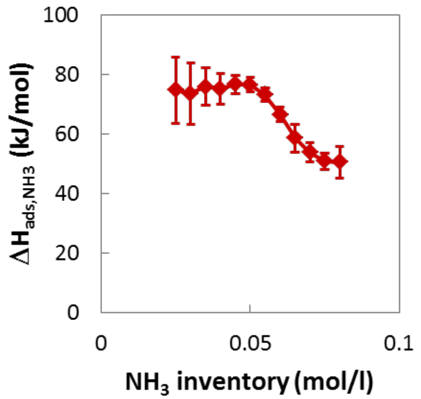


We now know how to accurately and repeatably measure NH_3 adsorption energetics; what can we do with this information?

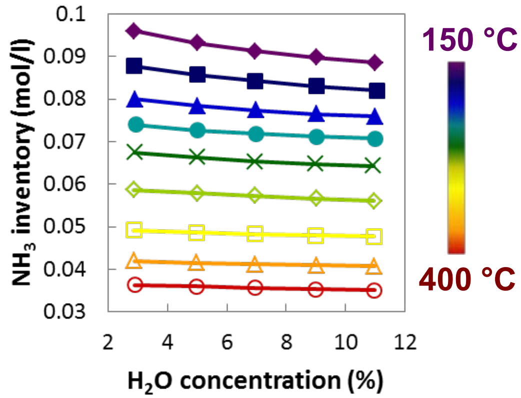


NH_3 storage model structure selected based on adsorption enthalpy trends, H_2O competition measurements

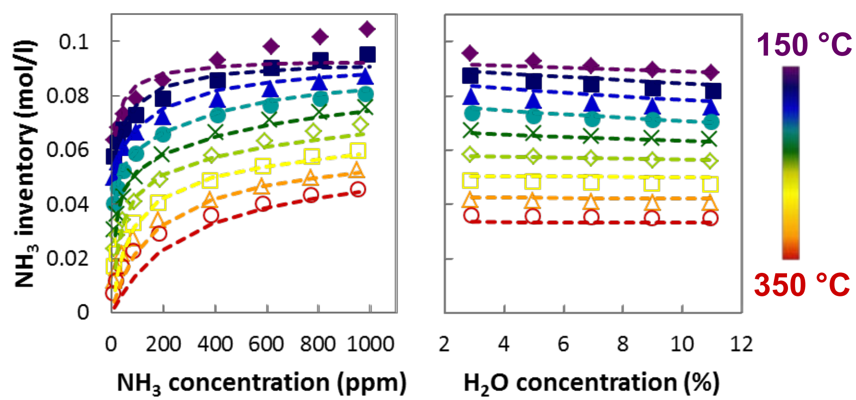
NH_3 adsorption enthalpy vs. inventory



H_2O competition with NH_3 (measured)



full NH_3 adsorption data set (points)



model structure:
- 2 sites
- Langmuir isotherms

H_2O competition:
- low energy site only

parameter estimation:
- fit model (dashed lines) to data
- initial guesses from enthalpy curve

$$I_{NH_3} = \omega_1 \theta_{1,NH_3} + \omega_2 \theta_{2,NH_3}$$

$$\theta_{1,NH3} = \frac{K_{1,NH_3} P_{NH_3}}{1 + K_{1,NH_3} P_{NH_3}}$$

$$\theta_{2,NH3} = \frac{K_{2,NH_3} P_{NH_3}}{1 + K_{2,NH_3} P_{NH_3} \boxed{+ K_{2,H_2O} P_{H_2O}}}$$

$$K_{i,a} = K_{i,a,0} e^{-\Delta H_{i,a}/RT}$$

NH_3 storage model incorporates:
- ***temperature***
- ***NH_3 concentration***
- ***H_2O concentration***
- ***aging?***

site	1	2
ω (mol/l)	0.054	0.039
$K_{i,NH3,0}$	3.1E-3	5.2E-6
$\Delta H_{i,NH3}$ (kJ/mol)	-84	-85
$K_{i,H2O,0}$	--	2.9E-4
$\Delta H_{i,H2O}$ (kJ/mol)	--	-44

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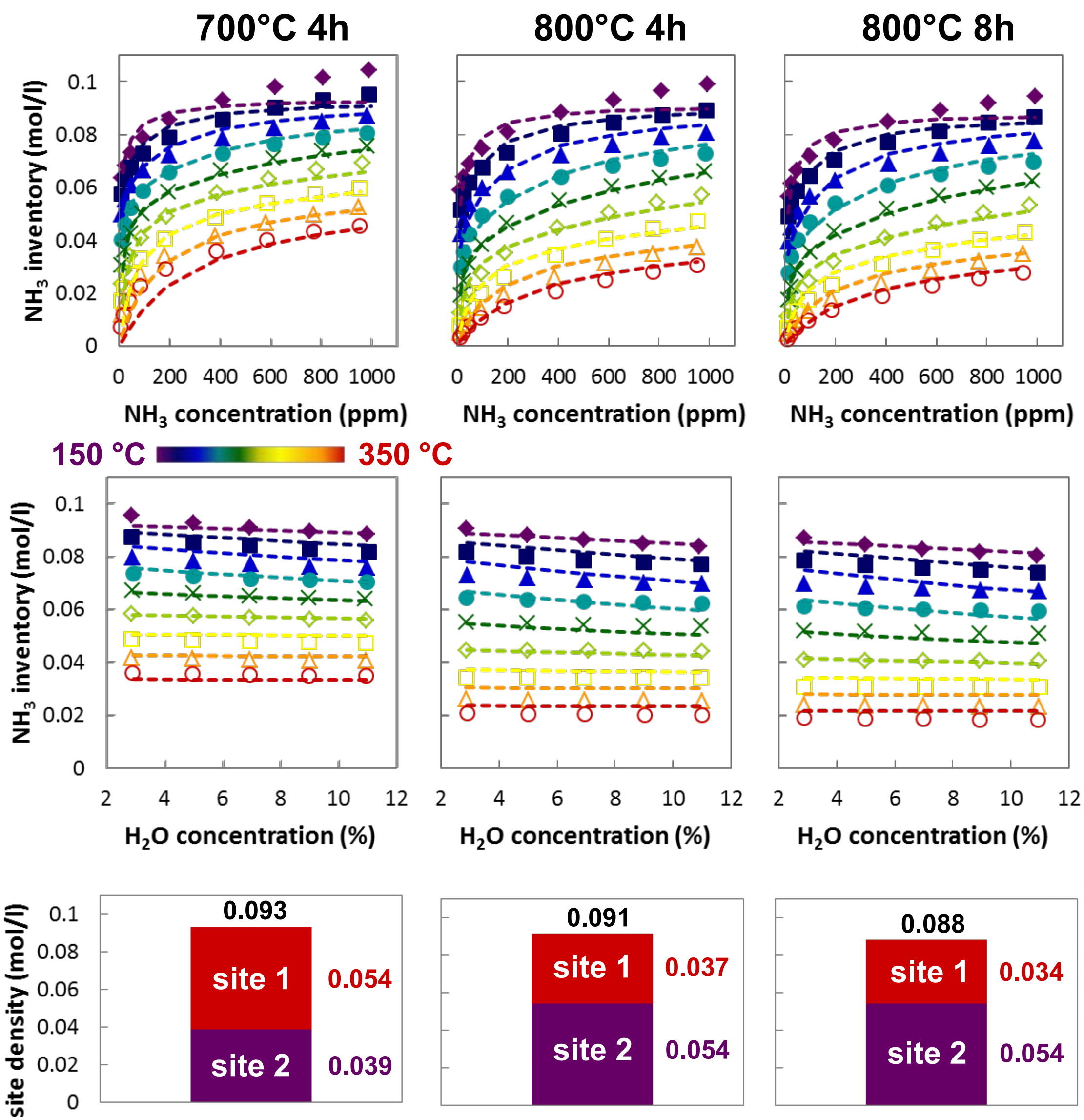
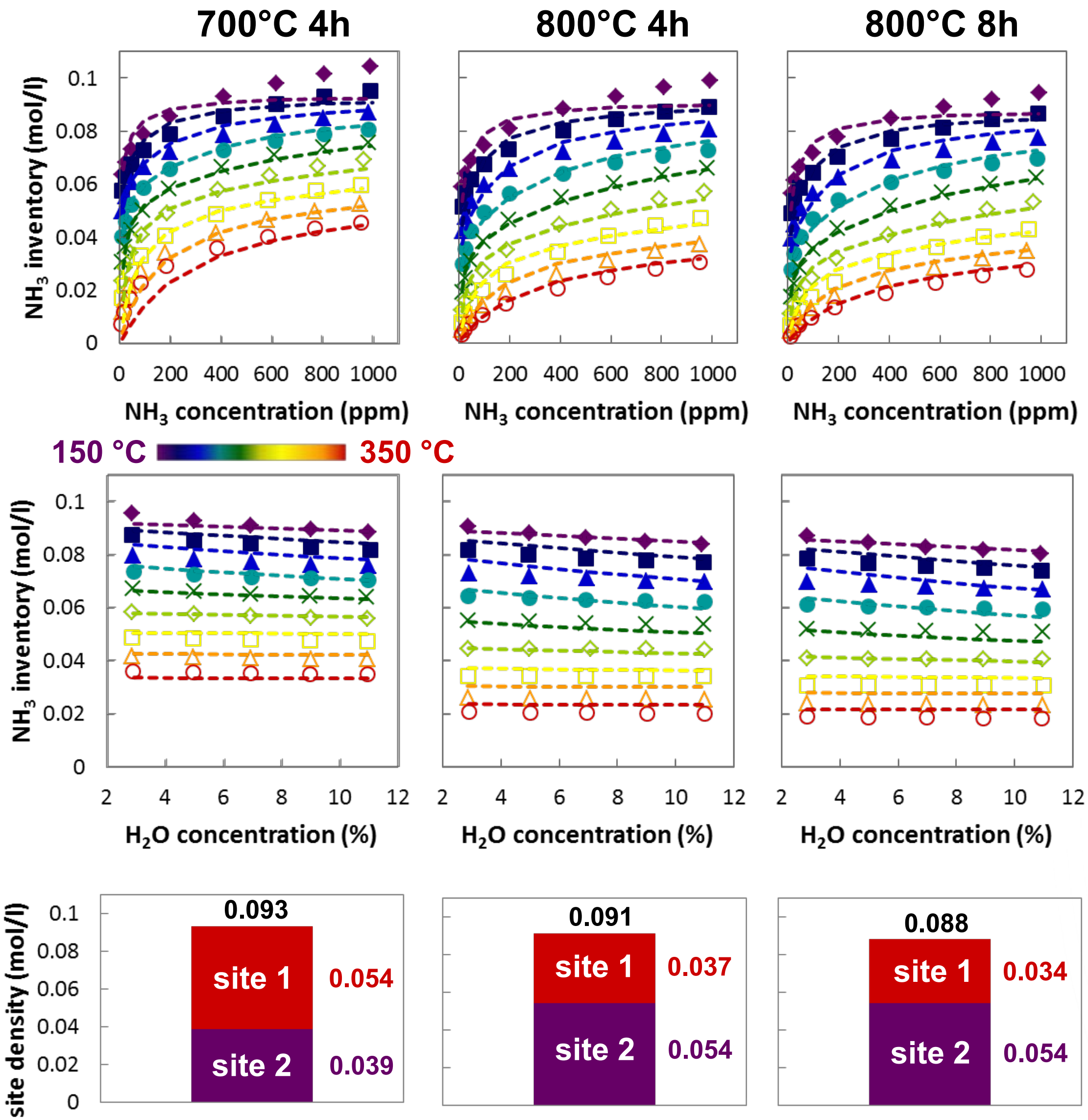
Impact of hydrothermal aging captured by changing site densities while holding other parameters fixed



- Re-measured NH_3 isotherms after stepwise 800 °C hydrothermal aging
- Model calibration strategy:
  - fit model to all data points
  - vary site densities w/ aging
  - hold other parameters fixed
- Changes in site density:
  - site 1: decreases
  - site 2: increases
  - total sites: ~constant

site	1	2
ω (mol/l)	f(age)	f(age)
$K_{i,NH3,0}$	3.1E-3	5.2E-6
$\Delta H_{i,NH3}$ (kJ/mol)	-84	-85
$K_{i,H2O,0}$	--	2.9E-4
$\Delta H_{i,H2O}$ (kJ/mol)	--	-44

Impact of hydrothermal aging captured by changing site densities while holding other parameters fixed



- Re-measured NH_3 isotherms after stepwise 800 °C hydrothermal aging
- Model calibration strategy:
  - fit model to all data points
  - vary site densities w/ aging
  - hold other parameters fixed
- Changes in site density:
  - site 1: decreases
  - site 2: increases
  - total sites: ~constant
  - conceptual model:

site 1 (high energy) → **site 2** (low energy)

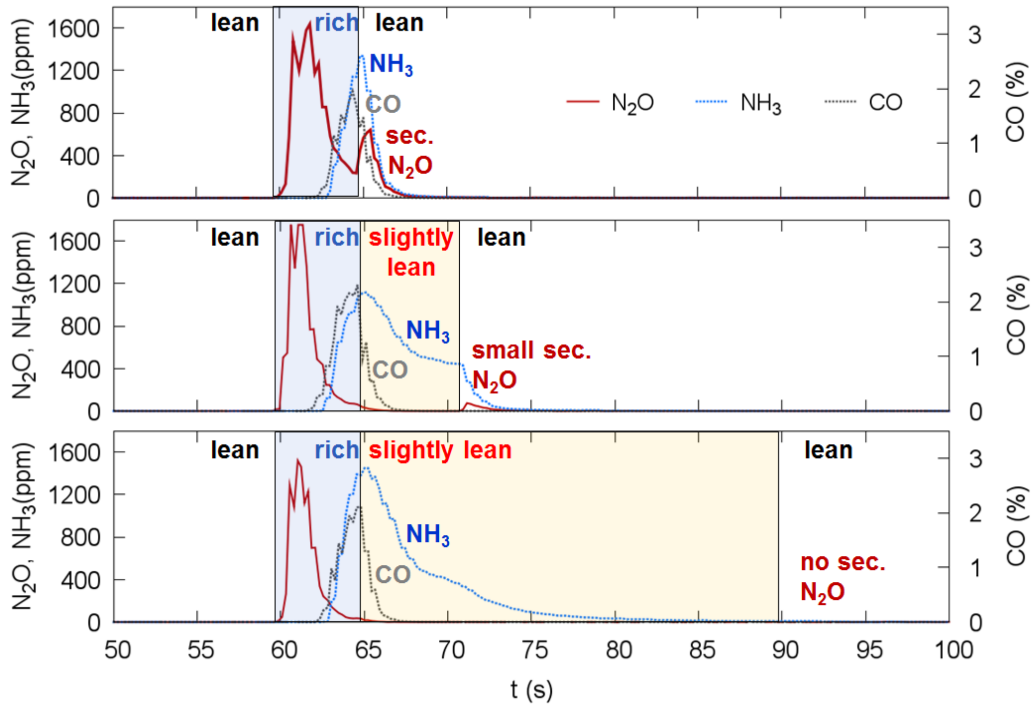
NH_3 storage model accounts for hydrothermal aging through adjustment of site densities ✓(milestone)

LNT research led to fundamental mechanistic insights relevant to technology implementation

collaboration with UCT Prague

- Priority survey: LNT mechanisms ranked medium or high priority by majority of LD diesel respondents
- Hosted UCT Prague's Dr. Koci and grad student David Mracek at ORNL
- Prior work on LNT selectivity:
  - resolved spatial and temporal distributions of N species
  - refined LNT regen model
- Simulations & experiments identified conditions minimizing N_2O:
  - longer regeneration duration
  - higher temperatures
  - more reactive reductant
  - lambda control after regen

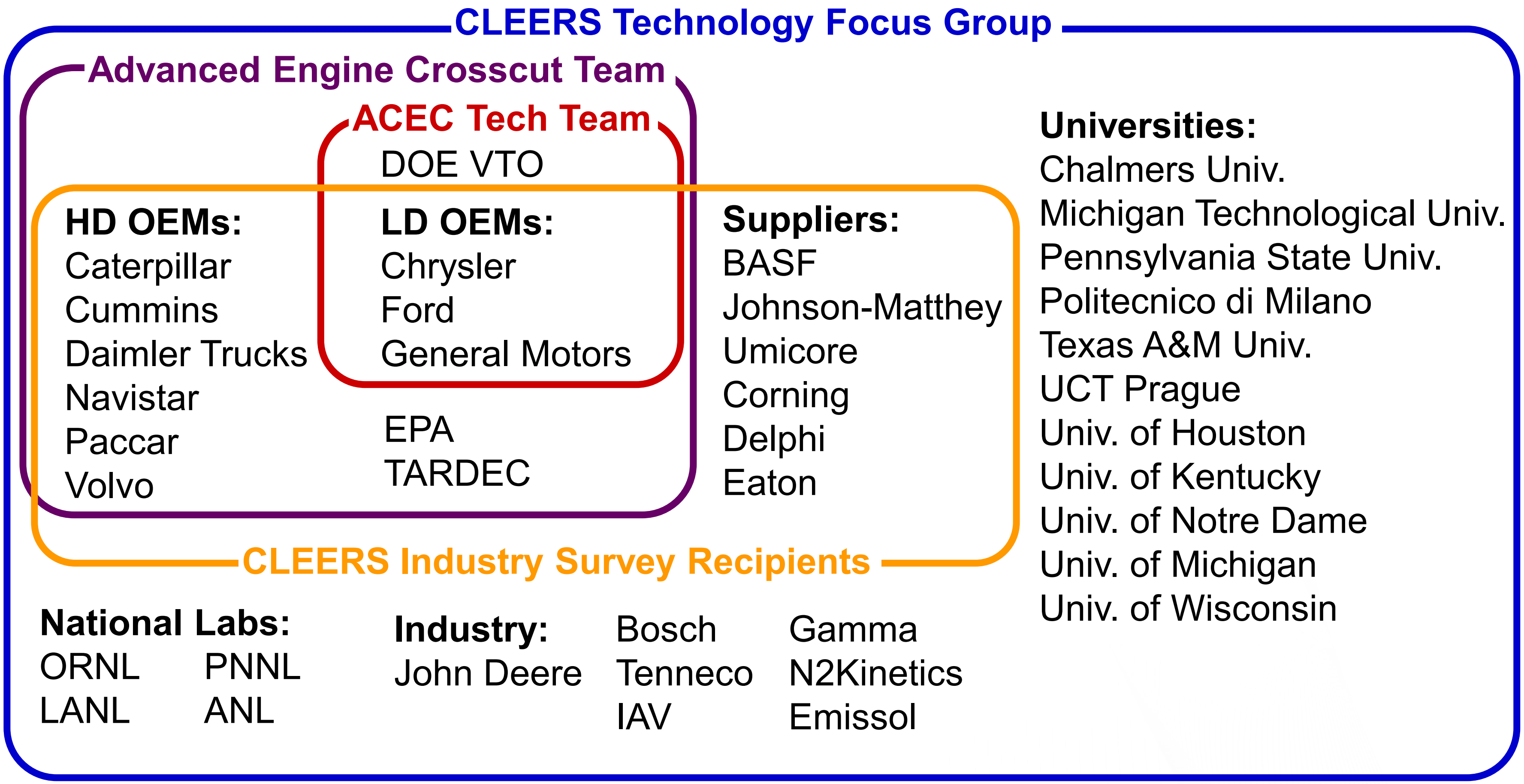
Lambda control impact on secondary peak selectivity



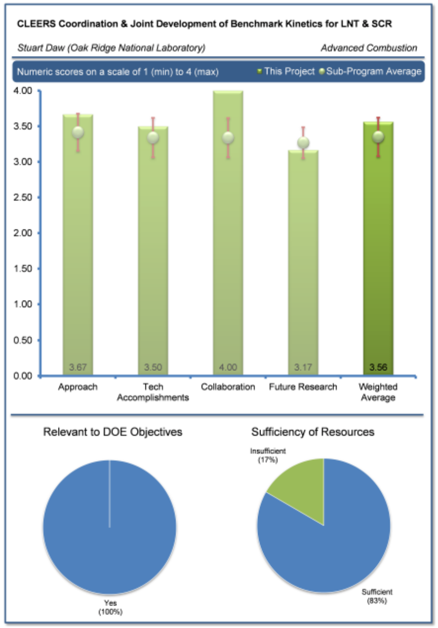
BMW LNT (225 °C, 30000 hr^{-1})
All: 300 ppm NO, 5% H_2O, inert balance
Lean (60 s): 10% O_2 | Rich (5 s): 3.4% CO | Slightly lean (6 or 25 s): 0.5% CO, 0.28% O_2

More accurate LNT model enabled development of control strategies that minimize production of N_2O, a potent greenhouse gas included in emissions regulations

Collaborations



Responses to Reviewer Comments



- **"...more specific and measurable deliverables for next year in the future plan"; "...more specific action plans for low temperature catalyst work..."**

  We have added a schedule of topics and deliverables for the next three fiscal years which includes a major focus on developing models for low temperature adsorbers (HC traps, passive NOx adsorbers).

- **"...it is not clear how ORNL will approach competing with or implementing homegrown models with other models being used in industry."**

  ORNL focuses on generating data sets, catalyst property measurements, modeling strategies, and kinetic parameters that can be implemented in any software package by modelers in industry and academia. We also collaborate with developers of models used by industry (both Gamma Technologies and UCT Prague on LNT kinetics, for example) to increase the likelihood that our work will have an impact.

- **"interaction with combustion groups working on the advanced combustion area is relatively low"**

  We work closely with PIs on advanced combustion and emissions characterization both at ORNL and elsewhere to make sure we utilize accurate exhaust compositions. These connections are already supporting the performance evaluation protocol development activities of the ACEC Low Temperature Aftertreatment Working Group, and will play a key role in development of experimental protocols aimed at model calibration for low temperature adsorber materials.

- **"... the one weakness ... is the need to leverage outside partners who are working on the project under their own funding ... the ability ... to reach their stated goals is dependent on the willingness of the partners"**

  While we have historically collaborated with outside groups to maximize the impact of DOE's investment and engage world leaders in aftertreatment modeling, ORNL maintains the core competencies and resources needed to meet our goals without the support of outside groups, although the scope of the project may decrease a bit in the absence of leveraged resources.

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 HC adsorber protocol and begin experimental characterization
• Requirements for higher NOx conversion efficiencies coupled with limited accuracy of available NH_3 SCR device models, particularly for predictions of NH_3 inventories.	• Refine simple, accurate NH_3 storage modeling and parameter estimation strategies based on adsorption isotherms • Expand NH_3 storage measurements and modeling to other catalyst formulations
• 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 activities

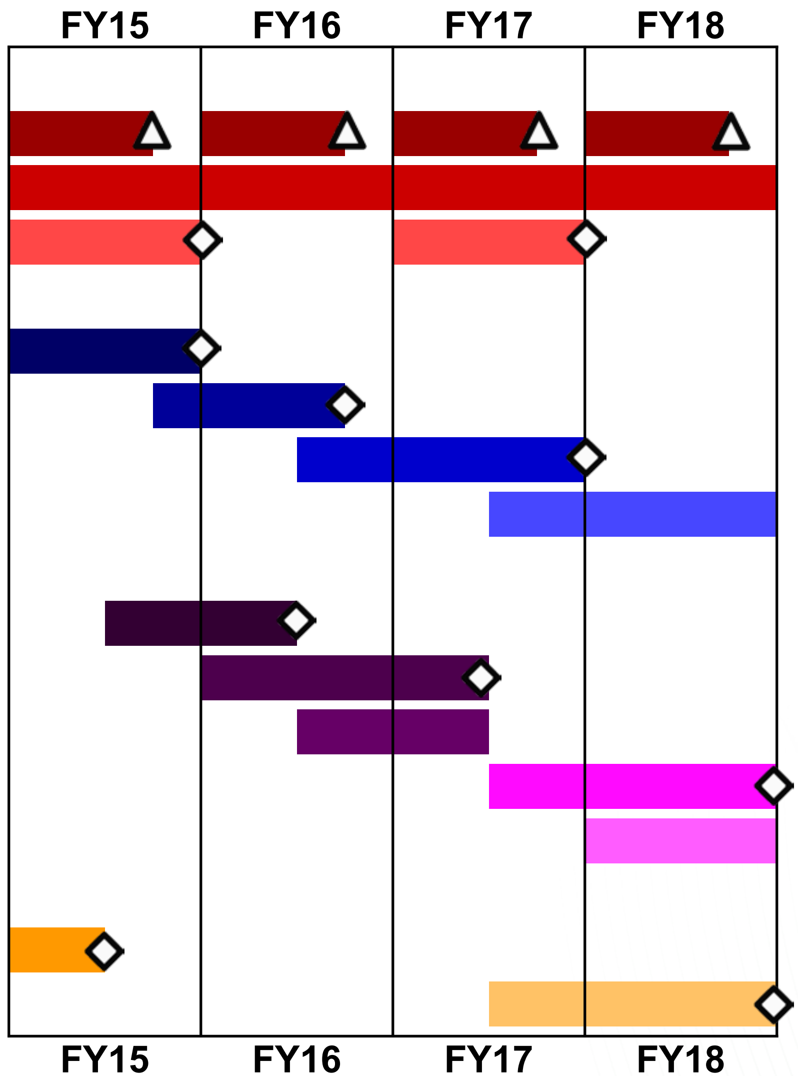
Proposed schedule for ORNL CLEERS activities includes an increasing emphasis on adsorbers for low T applications

1. Coordination
- 1.a. Workshop
- 1.b. Telecons, website
- 1.c. Priority Survey

2. NH_3 storage/release on SCR
- 2.a. commercial Cu-SSZ-13
- 2.b. commercial Cu-SAPO-34
- 2.c. model SSZ-13
- 2.d. other SCR catalysts

3. HC storage/release on traps
- 3.a. Protocol & instrumentation
- 3.b. Single HCs (BEA)
- 3.c. HC mixes (BEA)
- 3.d. metal ion exchange
- 3.e. zeolite structure, acid sites

4. NOx storage
- 4.a. N_2O from LNT
- 4.b. PNA adsorption/desorption



- Common theme: adsorption/desorption
- Critical process in:
  - NH_3 SCR
  - HC traps
  - PNAs
- Models needed for:
  - system design
  - optimization
  - control
- Vision: apply methods & modeling strategies across multiple technologies
- Potential for CLEERS to make broad impact

Note: schedule contingent on funding availability, DOE program needs, industry feedback

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

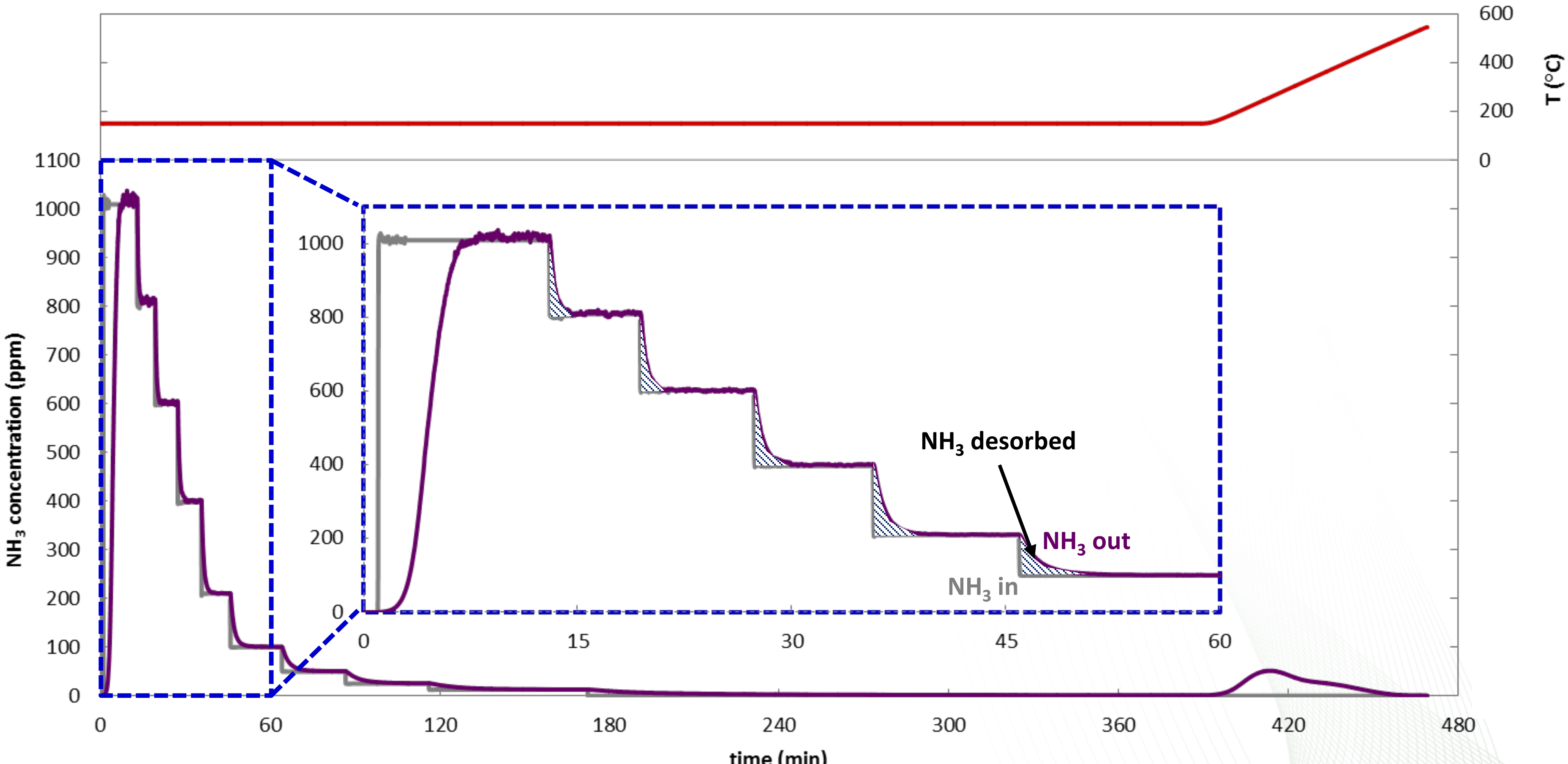
- **Approach**
  - Organized technical exchanges based on:
    - annual public Workshops
    - Focus Group teleconferences
    - industry priority surveys (alternating years)
    - Crosscut team updates
    - website for posting data & models
  - Multi-scale experiments and modeling on commercial catalysts under relevant conditions
    - focus: adsorption/desorption phenomena
- **Collaborations**
  - PNNL; UCT Prague; Politecnico di Milano
  - Collaborations through CLEERS structure:
    - 21 industrial entities
    - 11 universities
    - 3 national labs

- **Technical Accomplishments**
  - Hosted 2015 CLEERS Workshop
    - demand > capacity for speakers, attendees
  - Coordinated teleconferences
    - dozens of participants, most from industry
  - Served as source for data, models, and info for parallel DOE projects, industry partners
  - Identified lambda control strategy for minimizing N_2O formation during LNT regen
  - Developed SCR catalyst NH_3 storage model that accurately captures effects of gas composition, temperature, and aging
- **Future Work**
  - Continue coordination activities
  - Extend NH_3 storage model to other formulations
  - Initiate protocol development, characterization of hydrocarbon traps

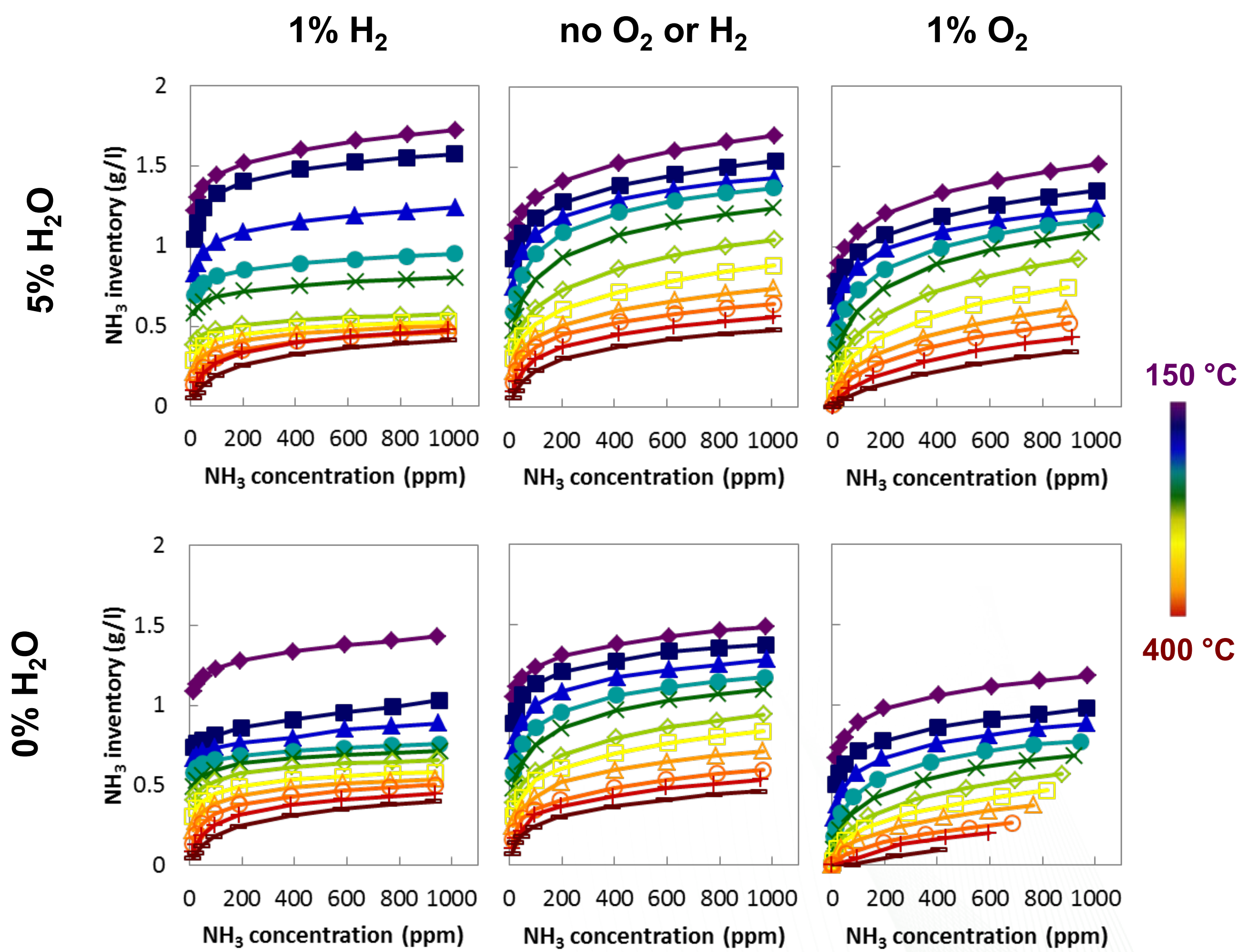
Technical Back-Up Slides

Experiment to measure equilibrium NH_3 storage isotherms

- Measure NH_3 released during isothermal stepwise desorption
  - eliminates kinetic and transport effects during storage measurements
  - note: kinetic information still available from transients between steps
- Repeat at multiple temperatures to generate family of isotherms



Both humidification and redox environment impact NH_3 adsorption processes through complex interactions

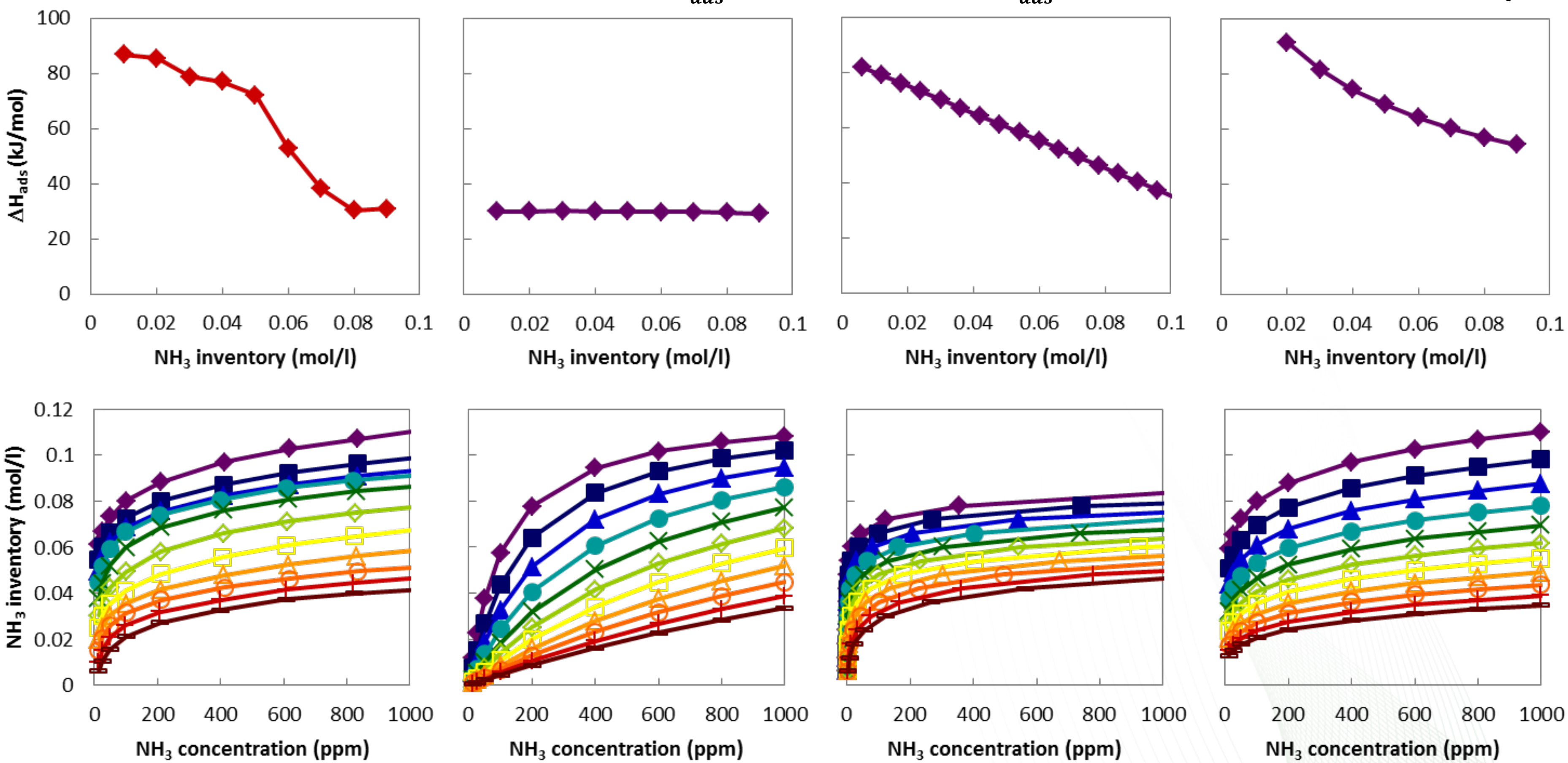


relevance approach **accomplishments** collaborations future work

Oak Ridge National Laboratory

ΔH_{ads} vs. coverage trends for simple (single site) isotherms guide selection of modeling strategy

Measured	Langmuir	Temkin	Freundlich
	$K_0 e^{(-\Delta H^0{}_{ads}/RT)} P = \frac{\theta}{(1-\theta)}$	$K_0 e^{(-\Delta H^0{}_{ads}(1-\alpha\theta)/RT)} P = \frac{\theta}{(1-\theta)}$	$K_0 e^{(-\alpha RT/\Delta H^0{}_{ads})} P^{(RT/\Delta H^0{}_{ads})} = \theta$
$\Delta H_{ads} = f(\theta)$	$\Delta H_{ads} = \Delta H^0{}_{ads}$	$\Delta H_{ads} = \Delta H^0{}_{ads}(1-\alpha\theta)$	$\Delta H_{ads} = \Delta H^0{}_{ads} \ln\frac{\theta}{K_0}$

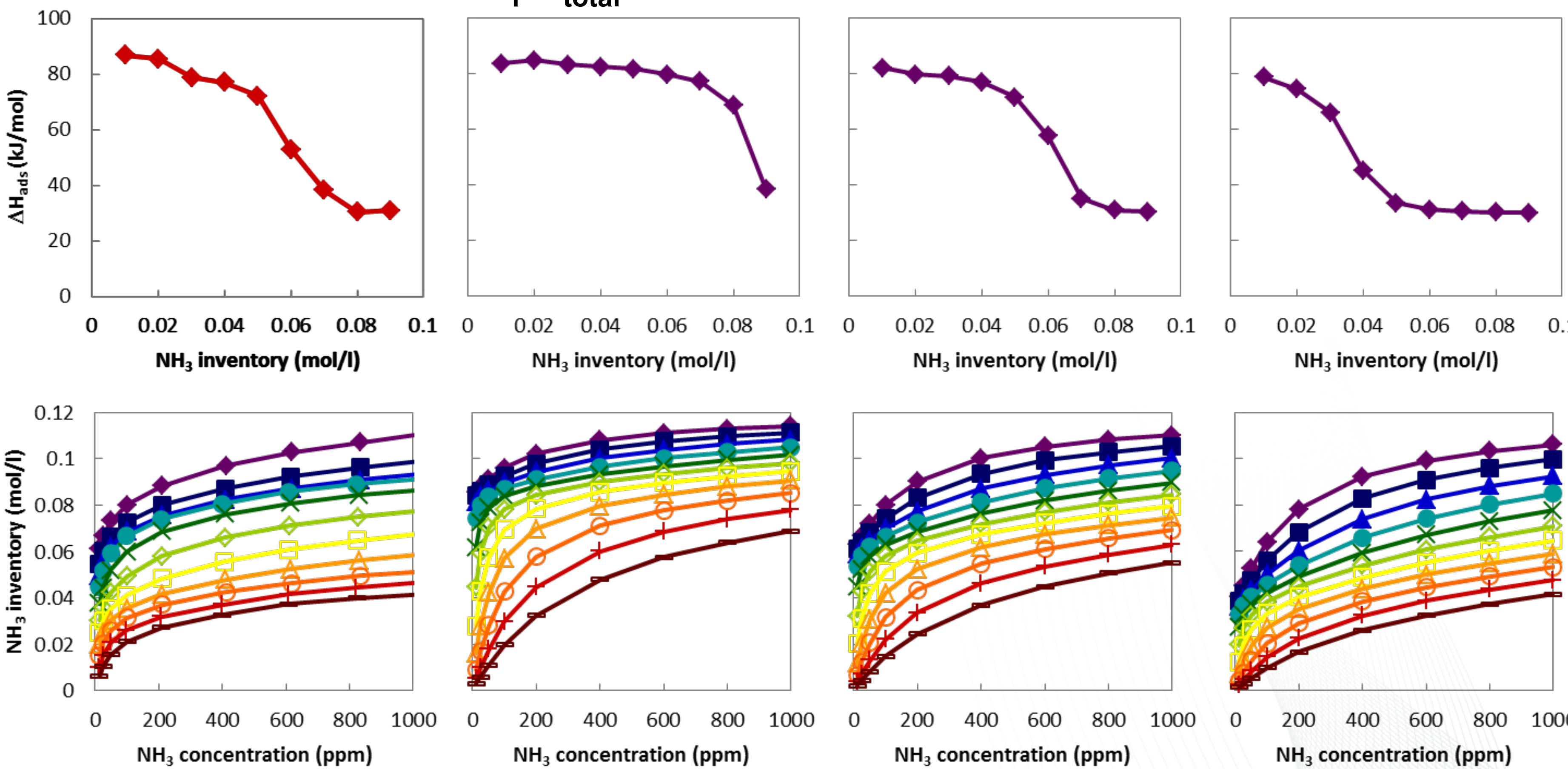


ΔH_{ads} vs. coverage trends for simple (two site) isotherms guide selection of modeling strategy

Measured | **2 site Langmuir isotherms**

$\Delta H_{ads,1}$ = -85 kJ/mol; $\Delta H_{ads,2}$ = -30 kJ/mol

N_1/N_{total}: 0.7 | 0.5 | 0.3



Mapping of equilibrium adsorption model parameters to reaction rate expressions for a transient model

Equilibrium model equations

$$\theta_{1,NH3} = \frac{K_{1,NH_3}P_{NH_3}}{1 + K_{1,NH_3}P_{NH_3}}$$

$$K_{1,NH3} = K_{1,NH3,0}e^{-\Delta H_{1,NH3}/RT}$$

$$\theta_{2,NH3} = \frac{K_{2,NH_3}P_{NH_3}}{1 + K_{2,NH_3}P_{NH_3} + K_{2,H_2O}P_{H_2O}}$$

$$K_{2,NH3} = K_{2,NH3,0}e^{-\Delta H_{2,NH3}/RT}$$

$$K_{2,H2O} = K_{2,H2O,0}e^{-\Delta H_{2,H2O}/RT}$$

Transient model rate equations

$NH_3 + S_1 \leftrightarrow S_1\text{-}NH_3$ $\quad r_{1,f} = k_{1,f}P_{NH3}\theta_{1,v}$ $\quad k_{1,f} = K_{1,NH3,0}A_{1,b}$

$r_{1,b} = k_{1,b}\theta_{1,NH3}$ $\quad k_{1,b} = A_{1,b}e^{-\Delta H_{1,NH3}/RT}$

$NH_3 + S_2 \leftrightarrow S_2\text{-}NH_3$ $\quad r_{2,f} = k_{2,f}P_{NH3}\theta_{2,v}$ $\quad k_{2,f} = K_{2,NH3,0}A_{2,b}$

$r_{2,b} = k_{2,b}\theta_{2,NH3}$ $\quad k_{2,b} = A_{2,b}e^{-\Delta H_{2,NH3}/RT}$

$H_2O + S_2 \leftrightarrow S_2\text{-}H_2O$ $\quad r_{3,f} = k_{3,f}P_{H2O}\theta_{2,v}$ $\quad k_{3,f} = K_{2,H2O,0}A_{3,b}$

$r_{3,b} = k_{3,b}\theta_{2,H2O}$ $\quad k_{3,b} = A_{3,b}e^{-\Delta H_{2,H2O}/RT}$

Derivation of transient rate expressions for site 1

at equilibrium: $r_{1,f} = r_{1,b}$

$$\frac{k_{1,f}}{k_{1,b}} = \frac{\theta_{1,NH3}}{P_{NH3}\theta_{1,v}} = K_{1,NH3}$$

$$\frac{A_{1,f}e^{-E_{a,1,f}/RT}}{A_{1,b}e^{-E_{a,1,b}/RT}} = K_{1,NH3,0}e^{-\Delta H_{1,NH3}/RT}$$

$$\frac{A_{1,f}}{A_{1,b}} = K_{1,NH3,0} \qquad -E_{a,1,f} + E_{a,1,b} = -\Delta H_{1,NH3}$$

assuming non-activated adsorption: $E_{a,1,b} = -\Delta H_{1,NH3}$

- 6 of the 9 parameters in the transient model rate equations can be calculated directly from the equilibrium storage model parameters
- The remaining 3 parameters ($A_{1,b}$, $A_{2,b}$, $A_{,3,b}$) must be fit to transient data, such as the NH_3 concentration profiles between steps of the isotherm experiments