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

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**Oak Ridge National Laboratory**
**National Transportation Research Center**


**2018 U.S. DOE Vehicle Technologies Office Annual Merit Review**

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This presentation does not contain any proprietary, confidential, or otherwise restricted information

# Acknowledgements


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  – Ken Howden, Gurpreet Singh, Mike Weismiller
- **Contributions from the ORNL Team:**
  – Vitaly Prikhodko, Todd Toops, Sreshtha Sinha Majumdar, Charles Finney, Jae-Soon Choi, Bill Partridge
- **Catalyst samples & guidance from Johnson Matthey:**
  – Haiying Chen
- **Guidance from CLEERS Advisory Committee members:**
  – Wei Li, Christine Lambert, Craig Dimaggio, Neal Currier, John Kirwan, Balaji Sukumar, Louise Olsson, Mike Harold, Dick Blint, Stuart Daw
- **Collaboration with partners at PNNL:**
  – Mark Stewart, Ken Rappé, Yong Wang, Jamie Holladay

# Overview

## Timeline

**Project start date:** FY2016

**Project end date:** FY2018

- included in ORNL response to 2015 VTO "Lab Call"
- core activity since FY2000
- supports and coordinates emissions control research
- evolves with DOE priorities and industry needs

## Budget

| | FY17 | FY18 |
|---|---|---|
| Coordination | \$250k | \$250k |
| Analysis | \$400k | \$325k |

## Barriers

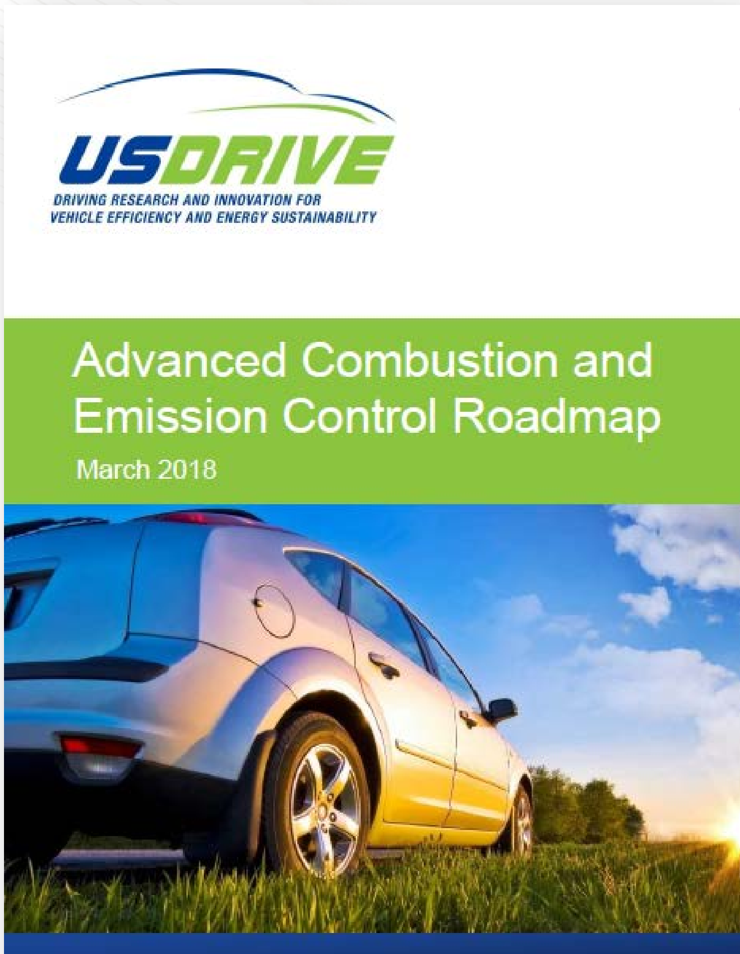
**U.S. DRIVE Advanced Combustion & Emission Control 2018 Roadmap Barriers & Targets:**

- U.S. EPA Tier 3 Bin 30 emission standard
- 90% conversion of criteria pollutants (NOx, CO, HCs) at 150°C for the full useful life of the vehicle
- "Development of models and simulation tools… to predict performance and better understand catalytic processes"

## Partners

- DOE Advanced Engine Crosscut Team
- U.S.DRIVE ACEC Tech Team
- CLEERS Focus Group members
  - 10 engine/vehicle manufacturers
  - 11 component and software suppliers
  - 13 universities
  - 4 national labs
- PNNL, Johnson Matthey

# U.S. DRIVE ACEC Roadmap emphasizes the need for advanced aftertreatment research to ensure emissions compliance for high efficiency combustion engines




"Compliance with exhaust emission regulations will be mandated and requires aftertreatment technologies integrated with the engine combustion approaches."

"The overarching emissions goal for the powertrain technologies shown in Table 3 is the U.S. EPA Tier 3 Bin 30 emission standard…"

"…a principal goal of future low temperature aftertreatment technologies, embraced by the ACEC Technical Team, is to achieve greater than 90% conversion of criteria pollutants (NOx, CO, HCs) at 150°C for the full useful life of the vehicle."

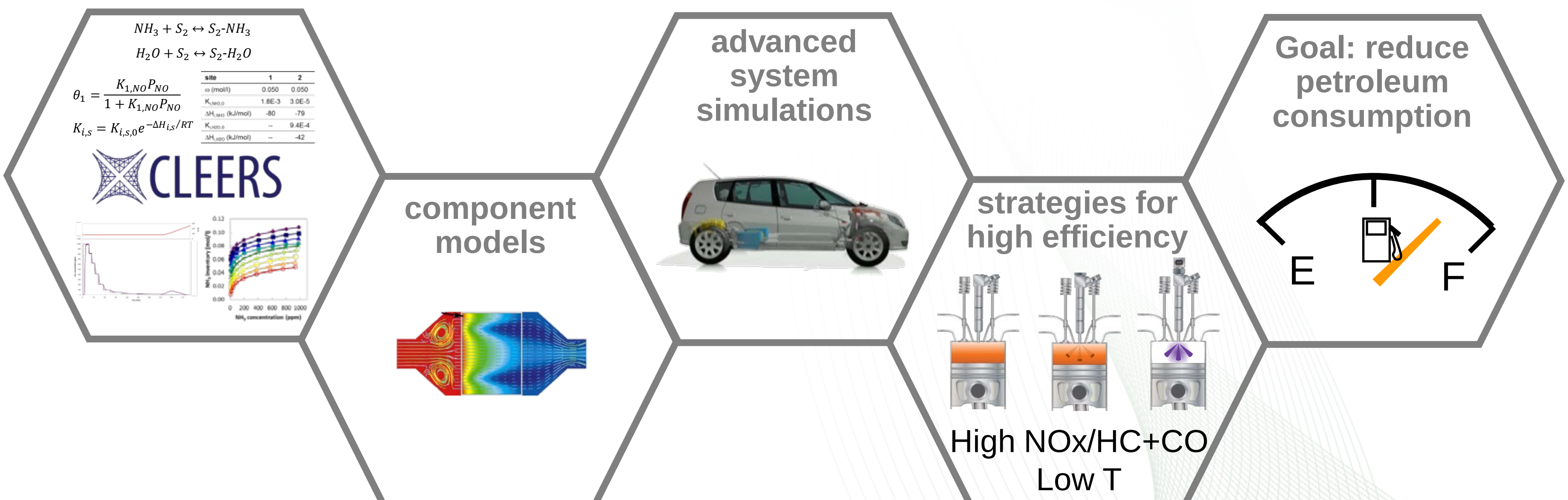
"…development of models and simulation tools ranging from the molecular level to the system level to predict performance and better understand catalytic processes"

"Understand the state of the PNA/HC Trap for shutdown /restart optimize restart/cold start performance"

"Characterize and understand PNA/HC Trap durability"

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

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



# Enabling Fuel Efficient Engines by Controlling Emissions (ORNL FEERC response to 2015 VTO AOP Lab Call)

**ACEC Roadmap Combustion Strategies**

**Low Temperature Combustion**

**Dilute Gasoline Combustion**

**Clean Diesel Combustion**

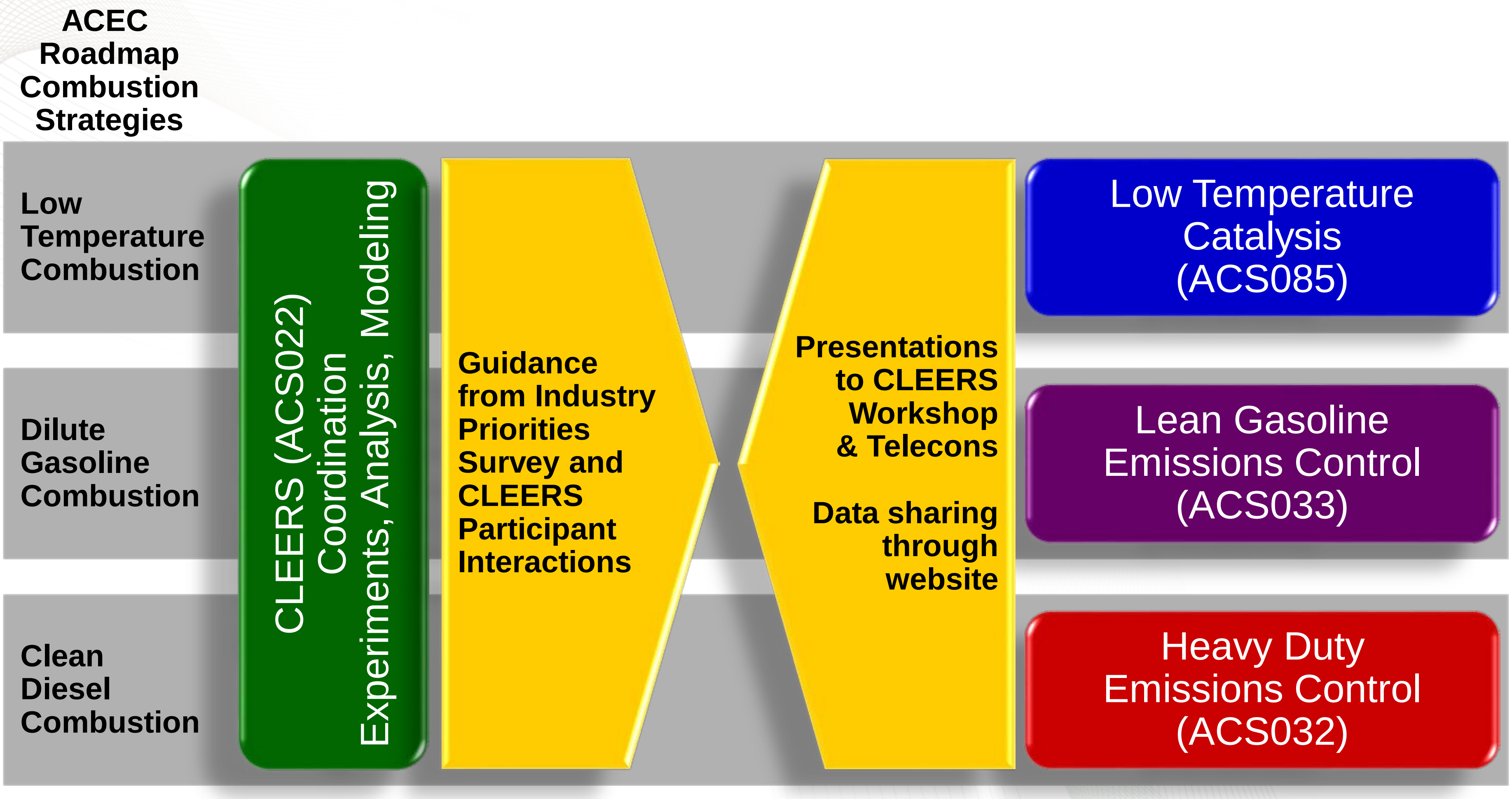
CLEERS (ACS022)
Coordination
Experiments, Analysis, Modeling

Low Temperature Catalysis (ACS085)

Lean Gasoline Emissions Control (ACS033)

Heavy Duty Emissions Control (ACS032)

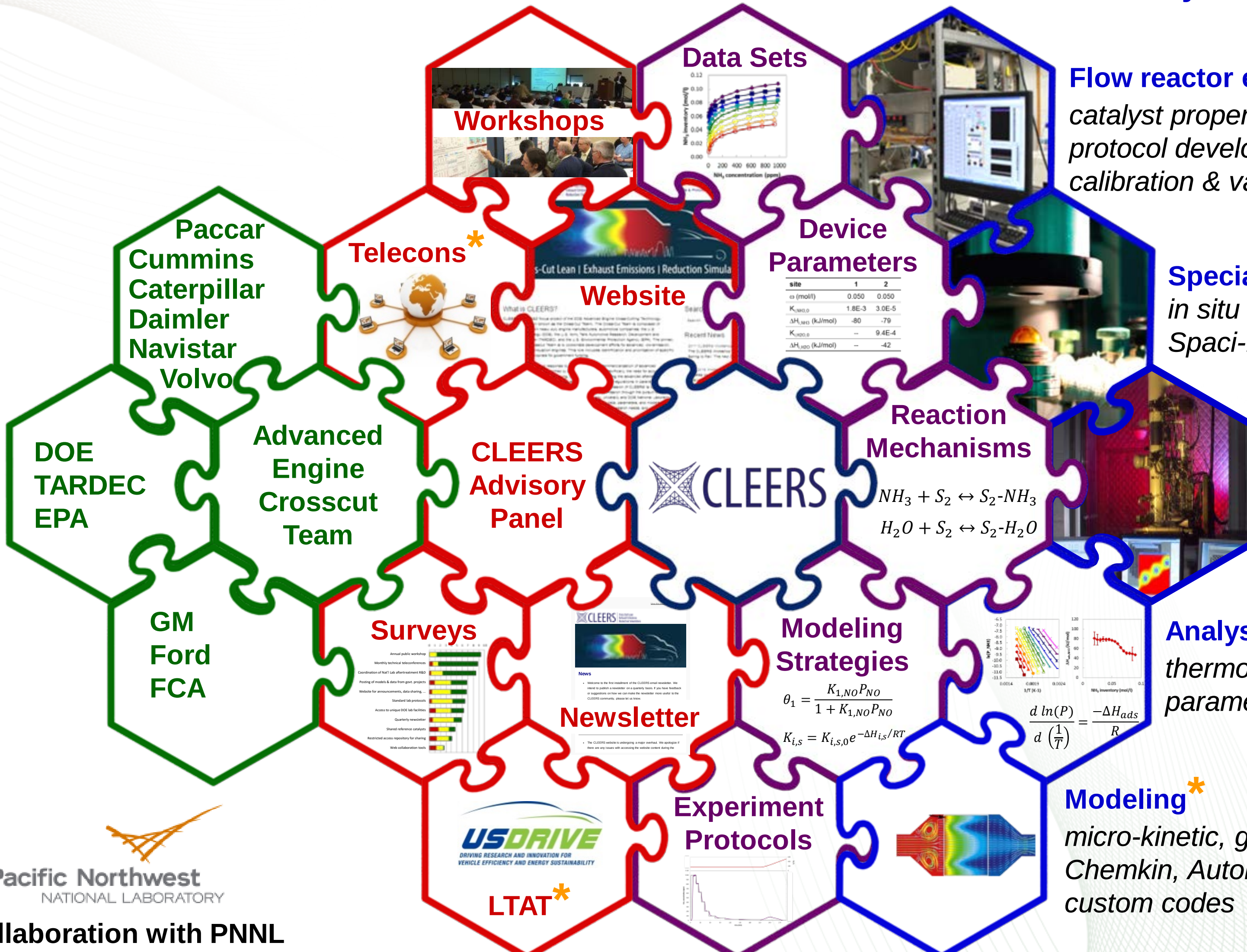
# Enabling Fuel Efficient Engines by Controlling Emissions (ORNL FEERC response to 2015 VTO AOP Lab Call)



# Enabling Fuel Efficient Engines by Controlling Emissions (ORNL FEERC response to 2015 VTO AOP Lab Call)

| ACEC Roadmap Combustion Strategies | | | |
|---|---|---|---|
| **Low Temperature Combustion** | CLEERS (ACS022) Coordination Experiments, Analysis, Modeling | **Adsorption, desorption, reaction on low T traps** | Low Temperature Catalysis (ACS085) |
| **Dilute Gasoline Combustion** | | **$NH_3$ formation on PGM catalysts**<br>**$NH_3$ storage/release on SCR catalysts** | Lean Gasoline Emissions Control (ACS033) |
| **Clean Diesel Combustion** | | **$NH_3$ storage/release on SCR catalysts**<br>**Aging effects on SCR catalysts** | Heavy Duty Emissions Control (ACS032) |

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




**Flow reactor experiments***
*catalyst property measurements*
*protocol development*
*calibration & validation data sets*

**Specialized diagnostics**
*in situ DRIFTS*
*Spaci-MS, Spaci-IR*

**Characterization**
*microscopy*
*XRD*
*BET*
*chemisorption*

**Analysis***
*thermodynamics*
*parameter estimation*

**Modeling***
*micro-kinetic, global*
*Chemkin, Autonomie*
*custom codes*

Pacific Northwest NATIONAL LABORATORY

*= collaboration with PNNL

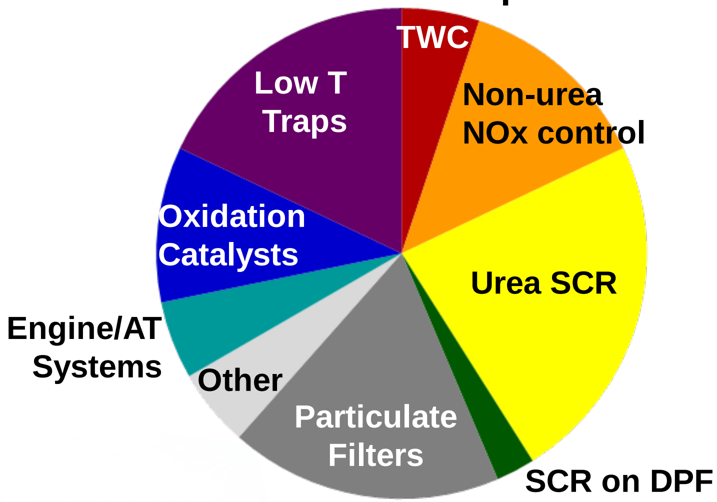
# Milestones

| FY | Qtr | Milestone | Status |
|---|---|---|---|
| 2017 | 4 | Organize 2017 CLEERS Workshop | complete |
| 2018 | 4 | Organize 2018 CLEERS Workshop | on schedule |

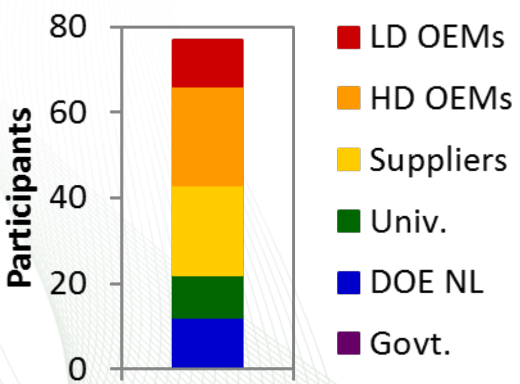
# CLEERS is an efficient means for communicating pre-competitive information

- Workshop #20, Oct 3-5, 2017, Ann Arbor, MI
  - 162 attendees representing OEMs, component & software suppliers, national labs, universities, government agencies
  - 39 presentations (4 invited), 23 posters
  - Panel discussion on emerging low temperature aftertreatment modeling needs
- Focus Group teleconferences:
  - Technical presentations of latest results
  - 40-80 invited participants from around globe
  - Typically >50% industry representatives
- 2017 Industry Priorities Survey:
  - Industry guidance on CLEERS activities and R&D priorities
  - Results presented to DOE Advanced Engine Crosscut Team
  - Report posted to CLEERS Website

**2017 CLEERS Workshop Presentation Topics**



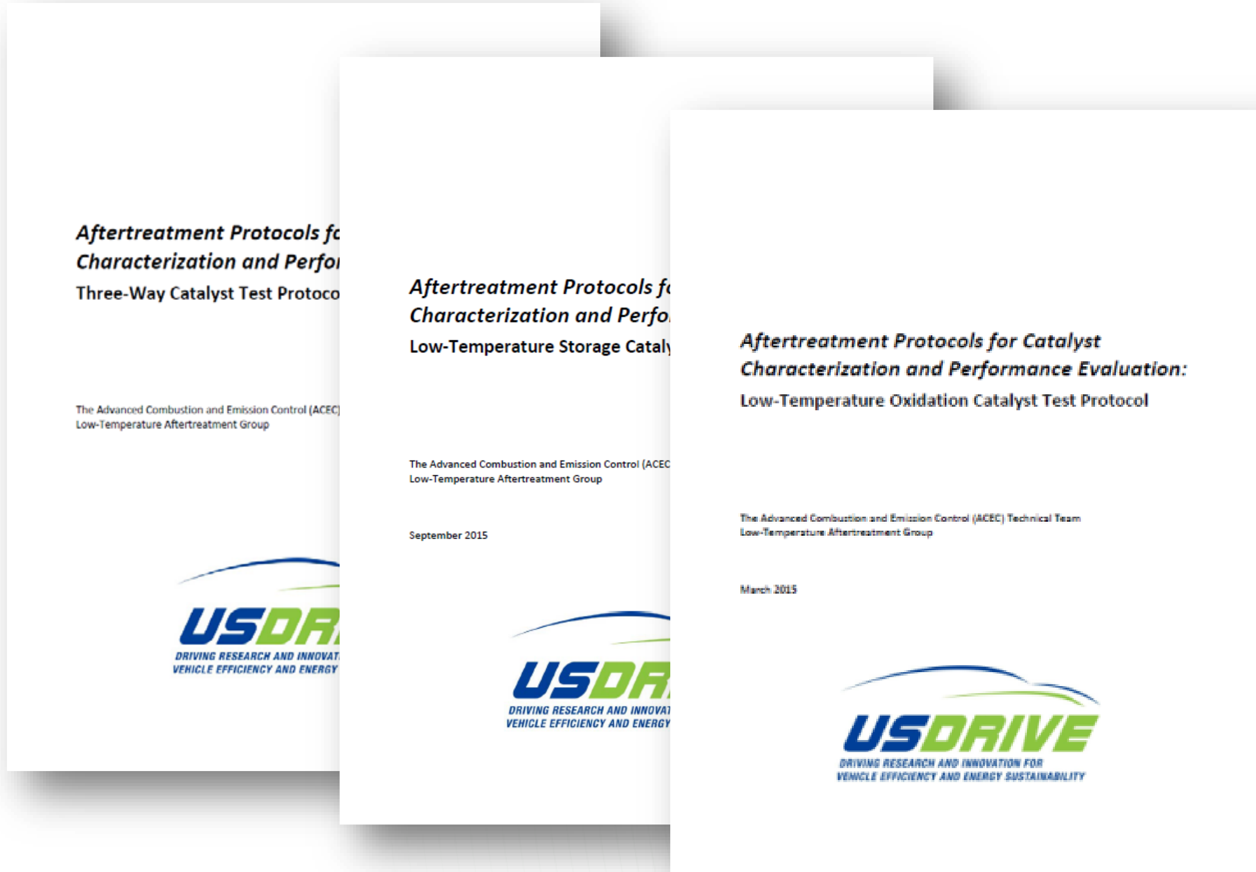

**Feb. 2018 CLEERS Focus Group Teleconference Participation**



# Supported the U.S.DRIVE ACEC LTAT team in developing and testing experimental protocols for low T catalysts

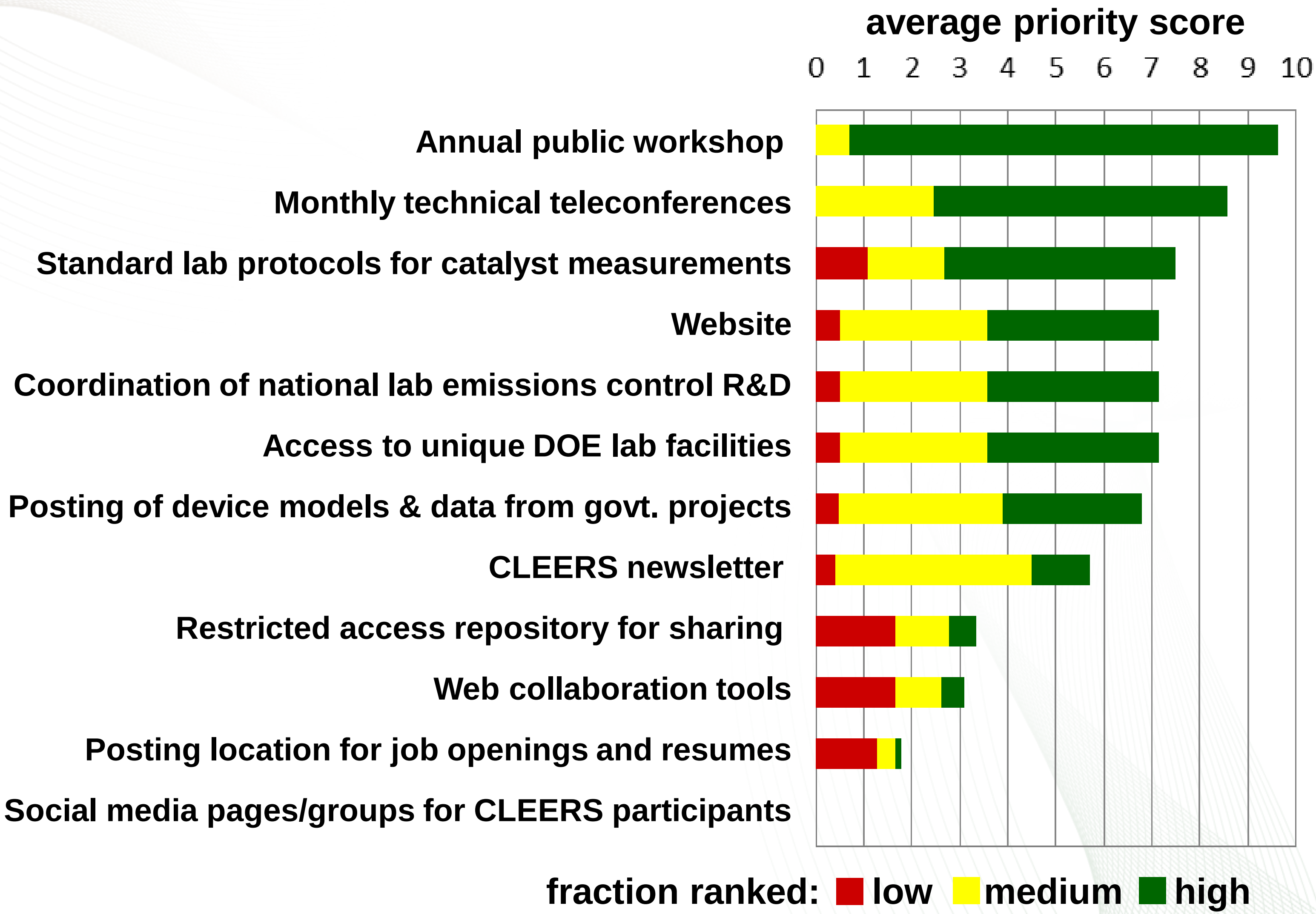
**U.S.DRIVE**
**ACEC Tech Team**
**Low Temperature**
**Aftertreatment**
**Working Group**

| Org. | Representatives |
|---|---|
| **FCA** | Craig DiMaggio |
| **Ford** | Joe Theis |
| **GM** | Se Oh<br>Ming Yang |
| **PNNL** | Ken Rappe<br>Mark Stewart |
| **ORNL** | Jim Parks<br>Josh Pihl |
| **UM** | Galen Fisher |
| **DOE** | Ken Howden |



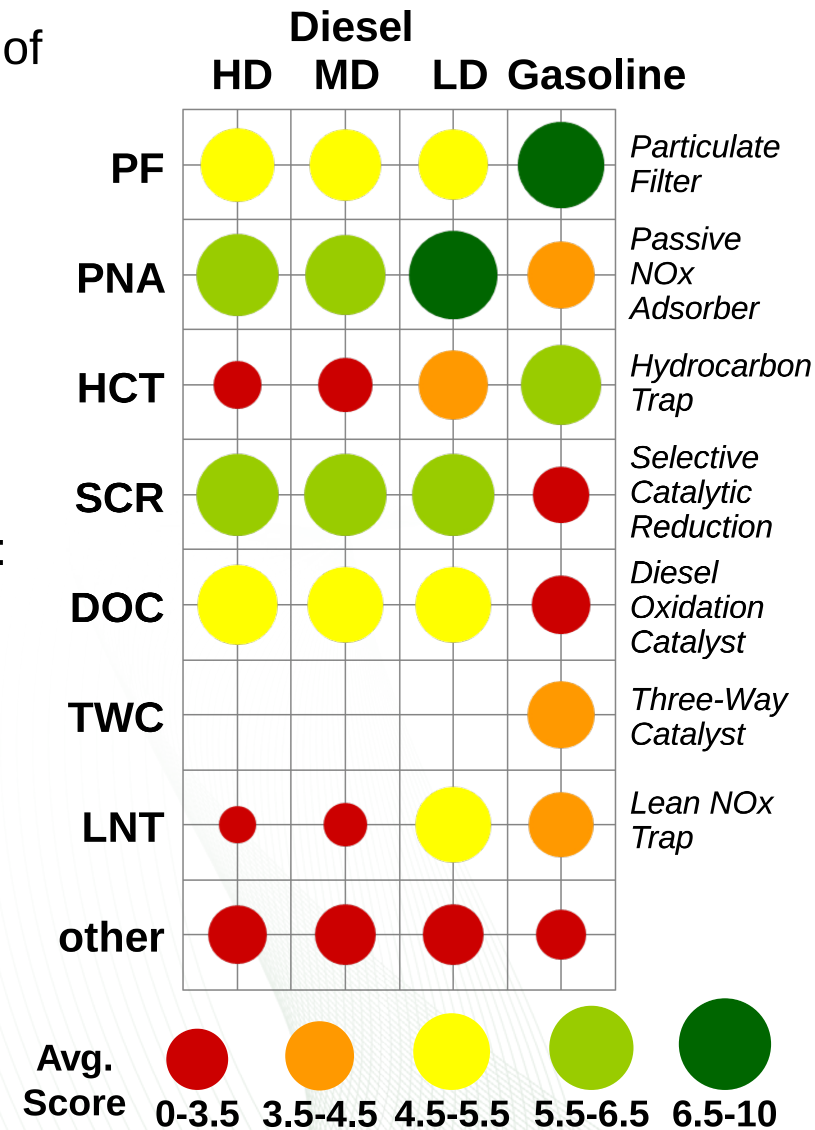

- Supported development of low T catalyst screening protocols for oxidation (2014-15), NOx+HC storage (2015-18), TWCs (2016-17), and $NH_3$ SCR (2018)
- Hosting protocols on CLEERS website

# Core CLEERS organizational activities remain high priorities for industry participants



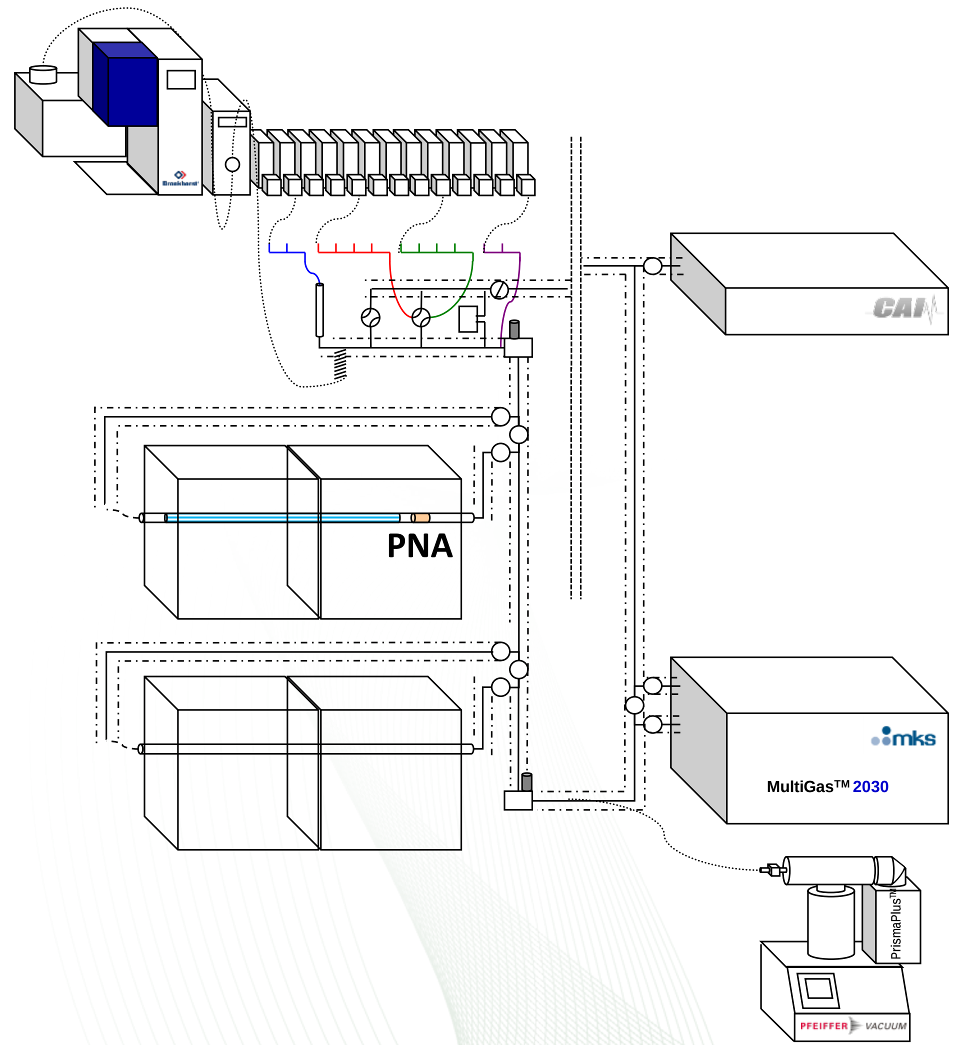
# 2017 CLEERS Industry Priorities Survey showed continuing interest in low temperature strategies

- As in the past, the survey revealed a diversity of opinions in industry
- Several R&D topics received high priority rankings across multiple technologies:
  - low temperature formulations
  - aging mechanisms
  - multifunctional filters
- Top ranked technologies varied by application:
  - gasoline: GPFs, HC traps
  - diesel: PNAs, urea SCR
- ORNL's CLEERS R&D activities are currently focused on understanding and modeling the operation and aging of:
  - passive NOx adsorbers (PNA)
  - hydrocarbon traps (HCT)

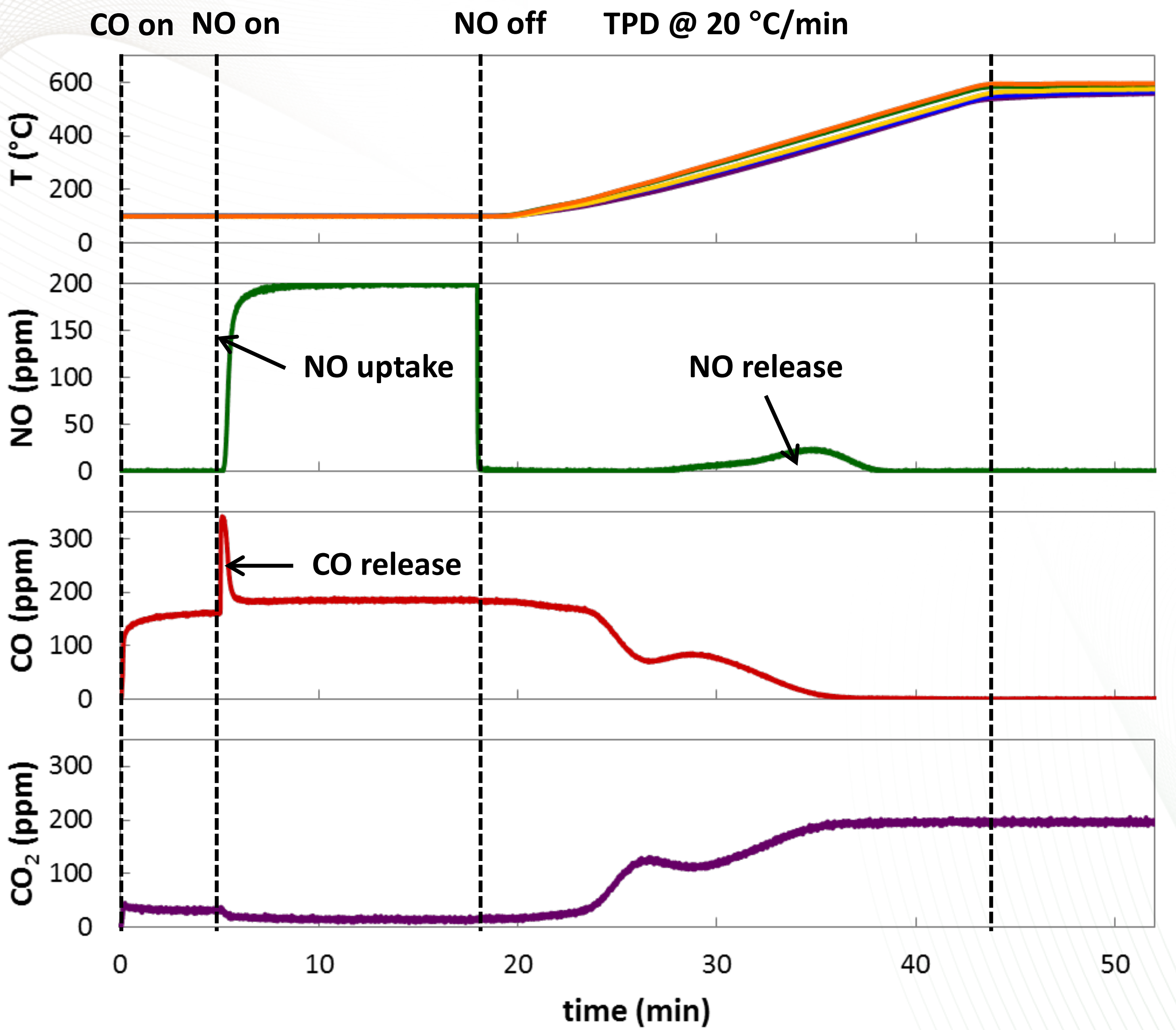


# Synthetic exhaust flow reactor experiments starting to reveal the chemistry underlying NO adsorption on a PNA

- Obtained catalyst core sample from Johnson Matthey
  - model dCSC™ component
  - Pd-exchanged ZSM-5
    - Pd loading: 50 g/ft$^3$ (1.8 g/l)
  - washcoated on a 400 cells/in$^2$ cordierite monolith
- Loaded in automated synthetic exhaust flow reactor
- Degreened at 600 °C for 4 h under 10% $O_2$/7% $H_2O$/$N_2$
- Ran NO storage/release experiments:
  - isothermal NO adsorption
  - TPD
  - varied gas composition, storage T



# PNA isothermal storage/TPD experiments enable reproducible measurements of capacity and stability

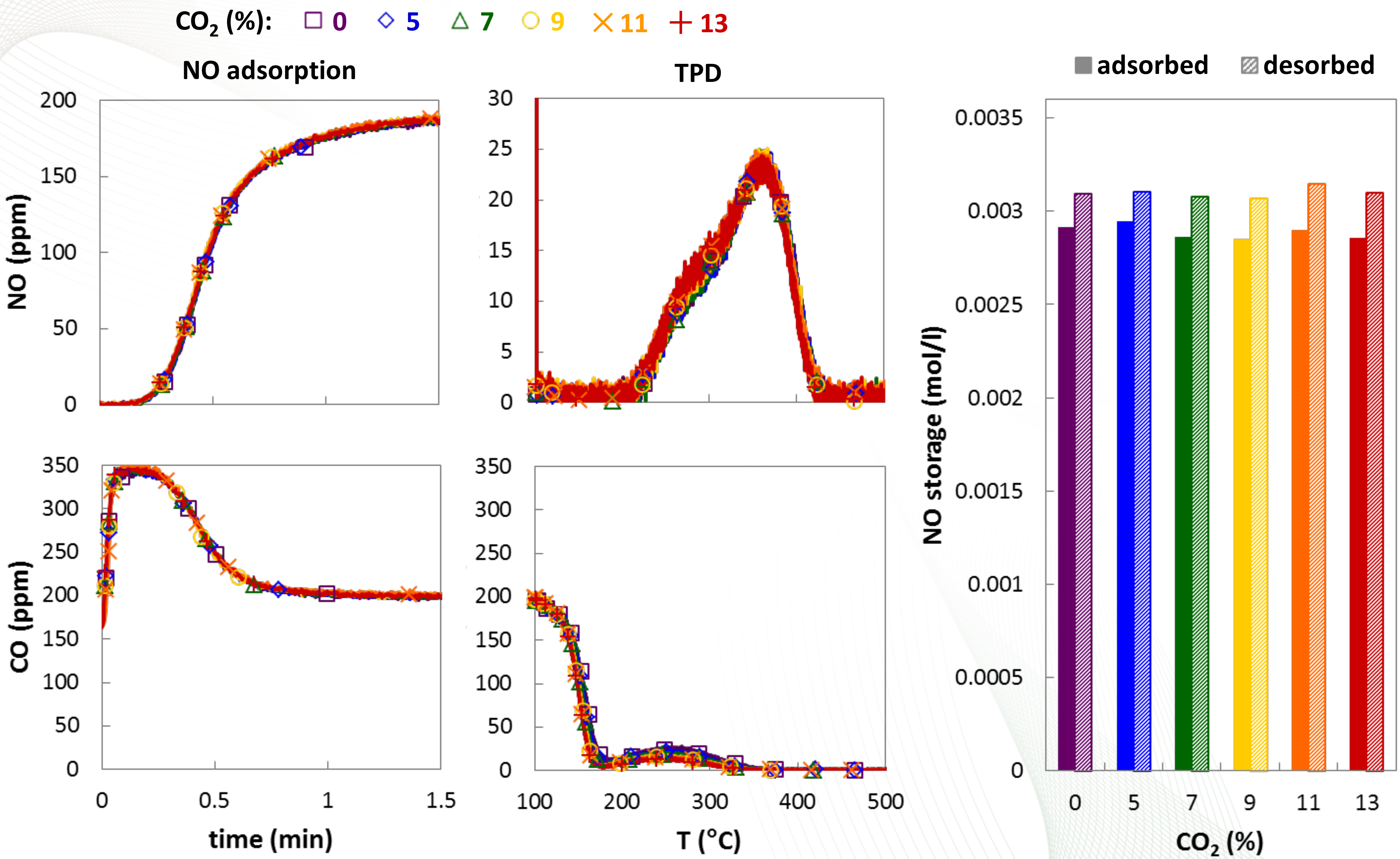



| pretreat, cool conditions | |
|---|---|
| $O_2$ | 10% |
| $H_2O$ | 7% |
| T | 600-100°C |
| SV | 30000 $h^{-1}$ |

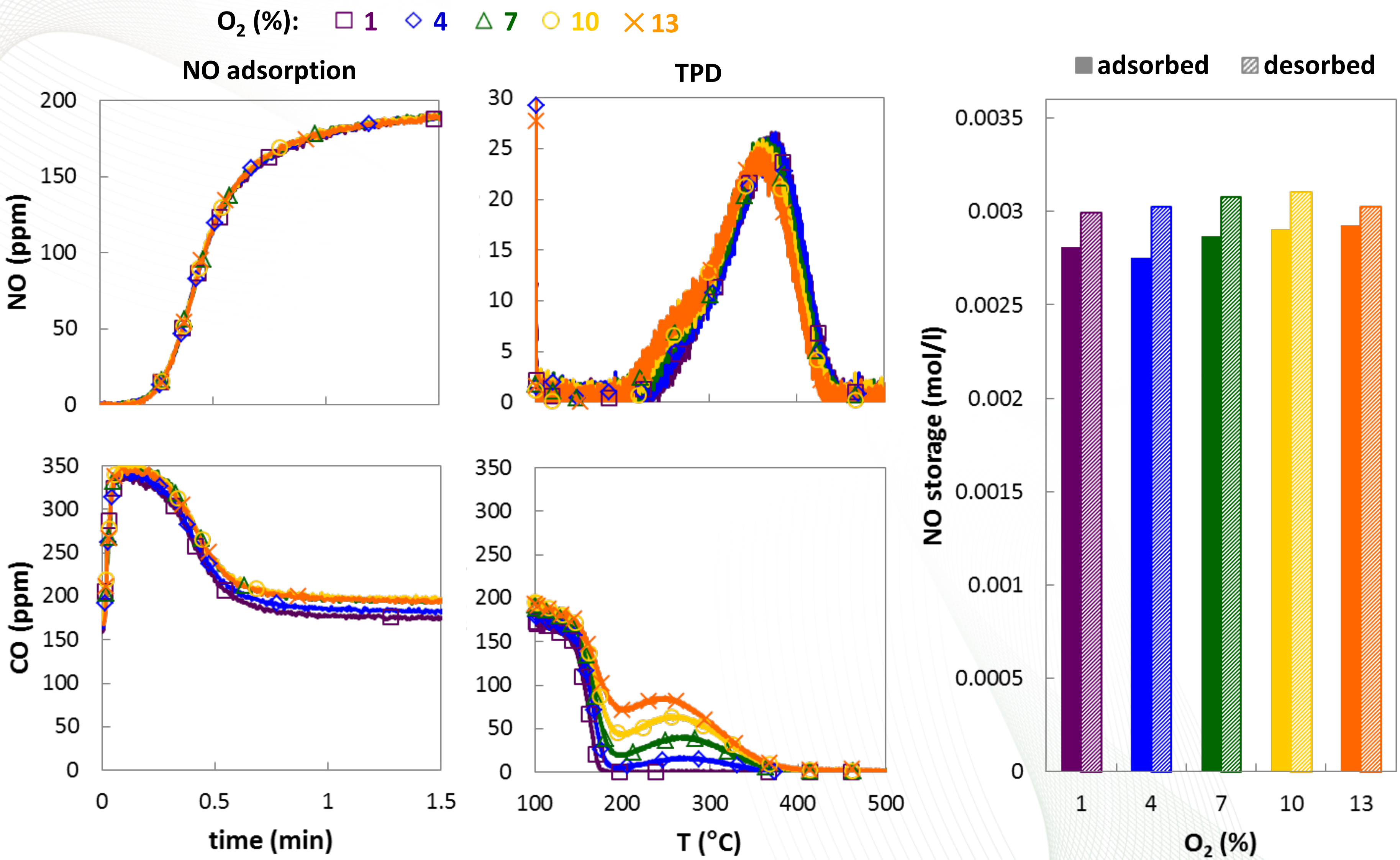
| NO exposure conditions | | |
|---|---|---|
| NO | 200 ppm | (25-1600) |
| CO | 200 ppm | (50-800) |
| $O_2$ | 10% | (1-13) |
| $H_2O$ | 7% | (5-13) |
| $CO_2$ | 0% | (0-13) |
| T | 100°C | (75-225) |
| SV | 30000 $h^{-1}$ | |

*Note: procedure focuses on reaction mechanism identification and model parameter estimation, and therefore differs from the ACEC LTAT protocol for storage catalyst performance evaluation*

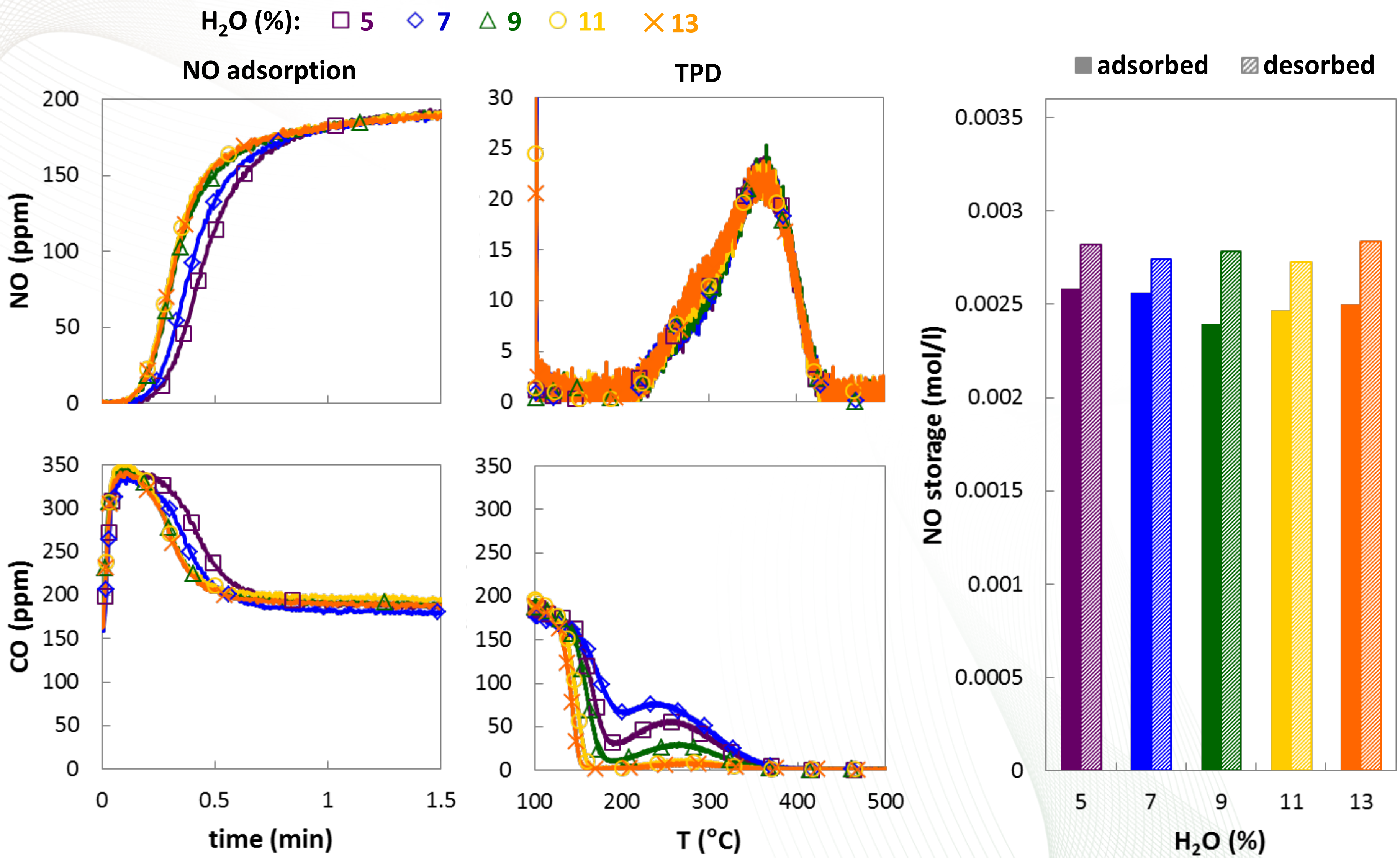
# $CO_2$ has no effect on PNA NO uptake/release or CO oxidation



# Increasing $O_2$ has no effect on NO uptake, slightly decreases release T, inhibits CO oxidation



# Increasing $H_2O$ decreases NO uptake, increases CO oxidation



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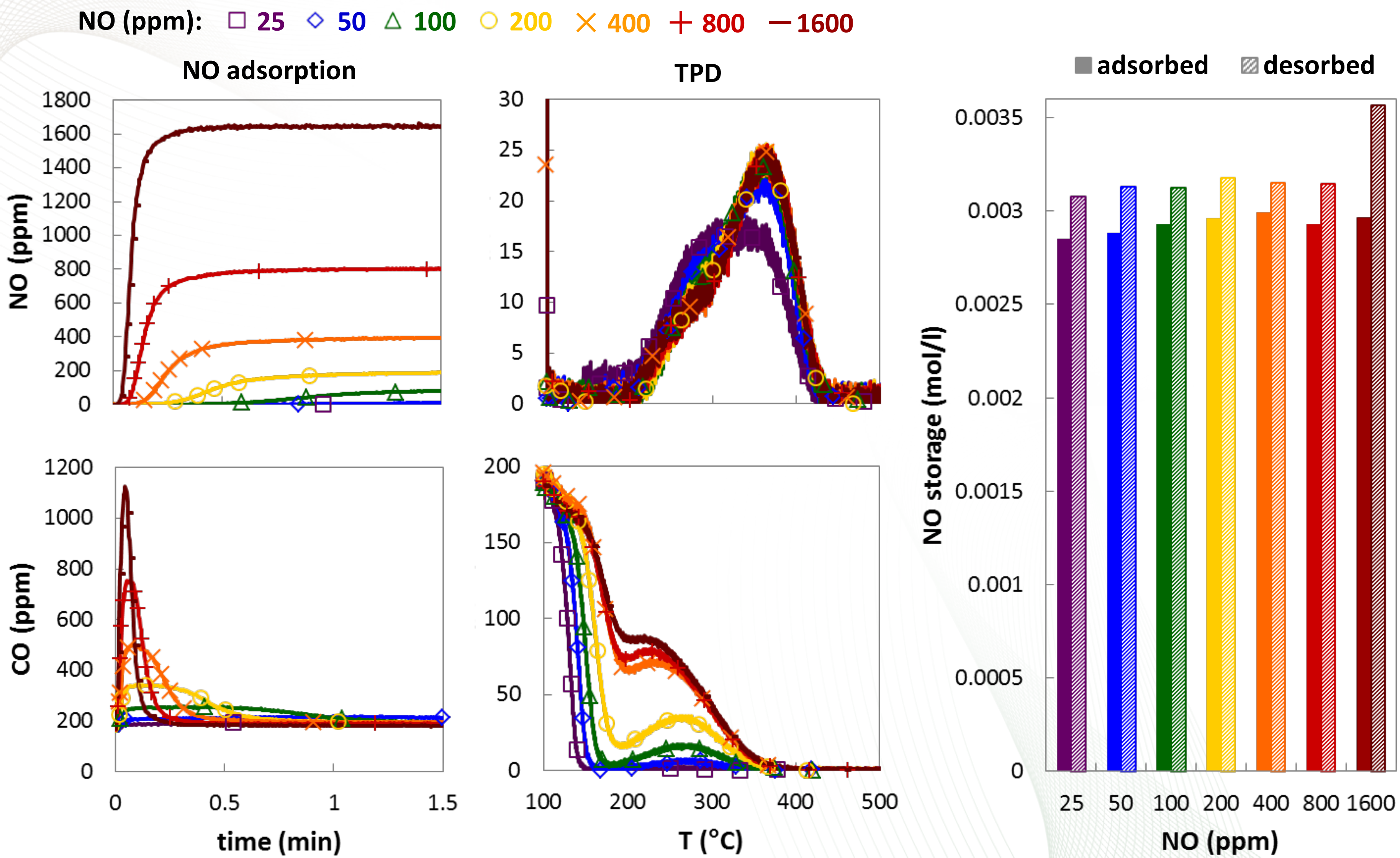
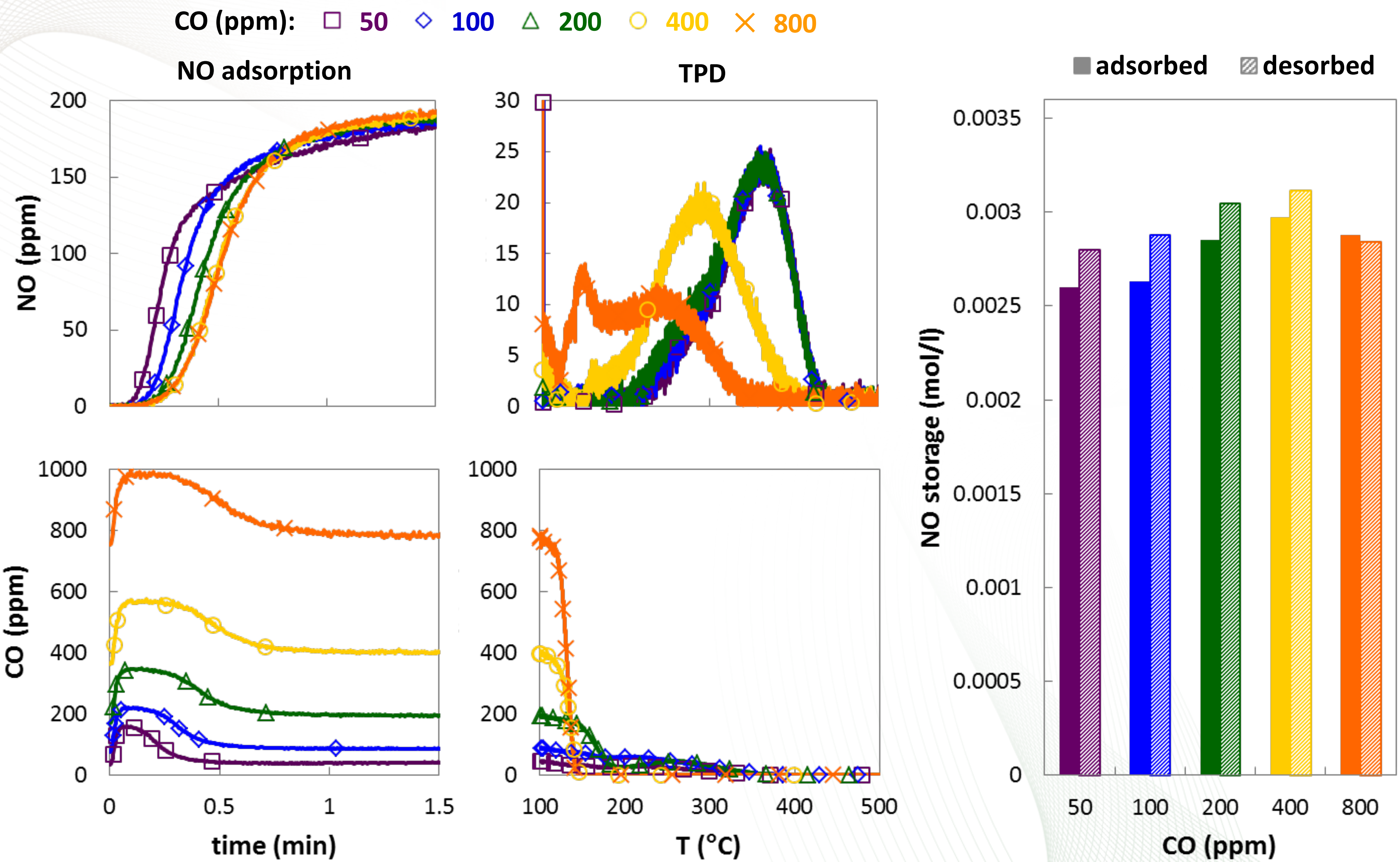
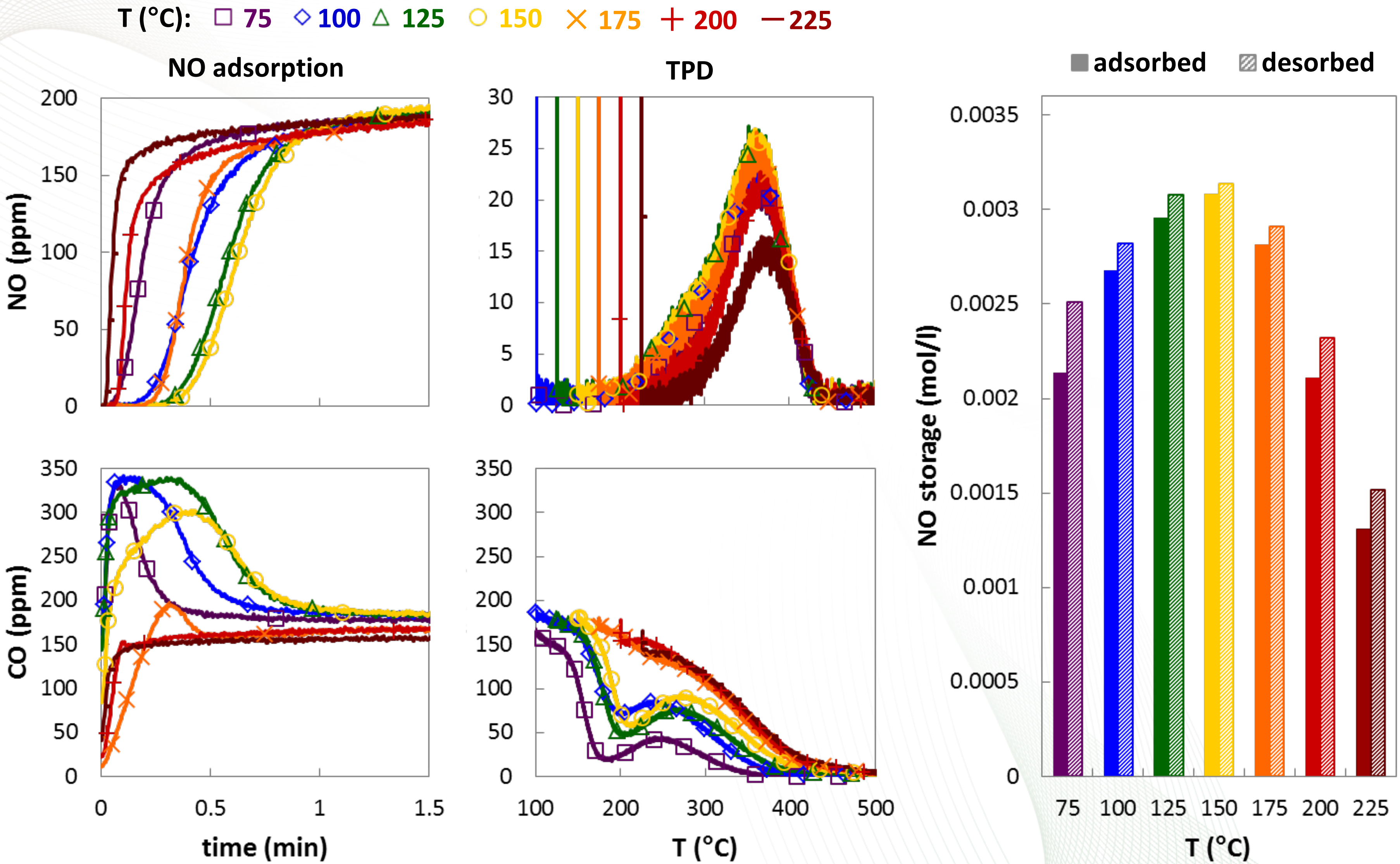
# Increasing NO increases rate of uptake (but not capacity) and inhibits CO oxidation



# Increasing CO increases NO uptake, decreases release temperature, and increases CO oxidation activity



# NO uptake first increases, then decreases with increasing temperature, resulting in a "sweet spot" at 150 °C



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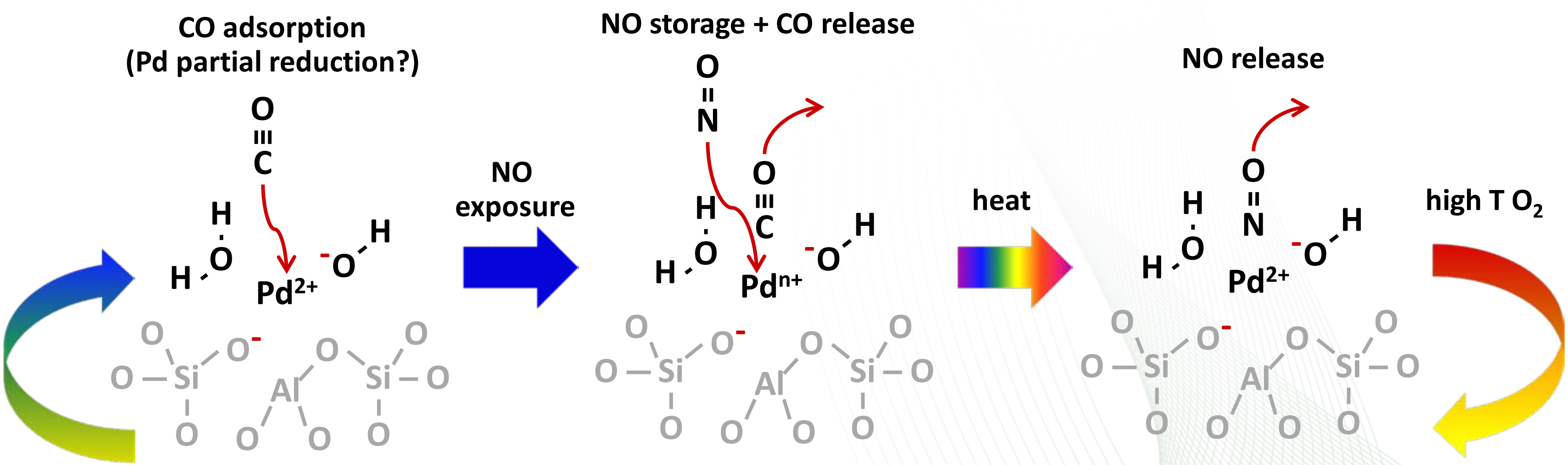
# Experiments are starting to shed light on PNA chemistry, modeling approaches

| | Storage Impact | Release Impact | Notes |
|---|---|---|---|
| $CO_2$ | none | none | *can remove $CO_2$ from experiments* |
| $O_2$ | none | none | *high T $O_2$ required to recover capacity* |
| $H_2O$ | small decrease[3] | none | *possible competition for surface sites* |
| NO | none | lower T @ low NO | *not simple equil. adsorption/desorption* |
| CO | increase[2] | lower T | *partial Pd reduction required for NO storage?* |
| T | increase, decrease[1] | -- | *$H_2O$ inhibition giving way to NO desorption?* |

*Literature with similar observations: [1]Chen et al., Catal Lett 2016 146, 1706 (JM); [2]Vu et al., Catal Lett 2017 147, 745 (UVA); [3]Zheng et al., J. Phys. Chem. C 2017, 121, 15793 (PNNL)*



# Collaborations: 36 Industry, 27 Academic, 9 Natl. Labs/Govt.

## CLEERS Participants

### CLEERS Technology Focus Group

#### Adv. Eng. Crosscut

##### ACEC TT

DOE VTO

#### CLEERS Industry Survey Recipients

**LD OEMs:**
FCA
Ford
GM

EPA
TARDEC

**HD OEMs:**
Caterpillar
Cummins
Daimler
Navistar
Paccar
Volvo

**Suppliers:**
BASF
Johnson-Matthey
Umicore
Corning
Delphi
Haldor Topsoe

**Industry:**
John Deere
Bosch
Tenneco
IAV
N2Kinetics
Emissol

**Nat'l Labs:**
ORNL
PNNL
ANL
LANL

**Universities:**
Chalmers Univ.
Michigan Tech. Univ.
Pennsylvania State Univ.
Politecnico di Milano
Purdue Univ.
Texas A&M Univ.
UCT Prague
Univ. of Houston
Univ. of Kentucky
Univ. of Notre Dame
Univ. of Michigan
Univ. of Virginia
Univ. of Wisconsin

Denso
Eaton
GE
Hyundai
Hino
NGK
Toyota

Aramco
AVL
CD Adapco
Converge
Exothermia
Gamma
Ricardo

SwRI
NRCan
NREL
CPERI/CERTH
PSI
TNO

Hannam Univ.
Karlsruhe Inst. of Tech.
Mass. Inst. of Tech.
Michigan State Univ.
Ohio State Univ.
Queens Univ. Belfast
Seoul National Univ.

Univ. of Connecticut
Univ. of Kansas
Univ. of New Mexico
Univ. Pierre & Marie Curie
Univ. of Tennessee
West Virginia Univ.
Wayne State Univ.

# Responses to Comments from Reviewers (4)

| Reviewer Comments: | Responses: |
| --- | --- |
| • *"…project could be outstanding with a simple survey of participants for strengths, weaknesses, and solutions"* | • We conduct the CLEERS Priorities Survey every 2 years |
| • *"Continued research in the area of SCR characterization and performance prediction is very desirable from an OEM standpoint… the embracing of LT catalyst formulations is critical to helping enable future powertrains…"* | • Our focus is guided by results of the Industry Priorities Survey as well as Merit Review comments |
| • *"…not clear how CLEERS is contributing to the lack of cost-effective emission control because it seems to be studying the same technologies as everyone else"*<br>• *"…continuing to provide understanding of the functionality and chemical state of copper (Cu) in SCR formulations is of value to the OEM community"*<br>• *"…reviewer was very tired of hearing about Cu/chabazite"* | • We are developing models for PNA, HC Trap, and SCR catalysts because they have been identified as high priority technologies by survey participants and most reviewers |
| • *"…more activities addressing catalyst aging/deactivation mechanisms"* | • Ongoing $NH_3$ SCR work has emphasized aging effects<br>• Aging will be included in future PNA, HC Trap efforts |

# CLEERS data sets, parameters, and modeling strategies are put to use by industry partners

- Reviewer comments:
  - *"The reviewer questioned next steps once CLEERS has data and models."*
  - *"The reviewer noted that there is no proof that the CLEERS mission of accelerating development of emission control technologies is being fulfilled. Rather, the development is led by suppliers and OEMs that do not share competitive information."*
- One example of industry applying CLEERS data for model development:
  - ECS&T paper led by Gamma Technologies (makers of GT-POWER)
  - Development of LNT model
  - Based on ORNL CLEERS data

SpringerLink

Emission Control Science and Technology
March 2017, Volume 3, Issue 1, pp 73–92 | Cite as

Development of a Global Kinetic Model for a Commercial Lean $NO_x$ Trap Automotive Catalyst Based on Laboratory Measurements

Authors | Authors and affiliations

Mahsa Rafigh, Ryan Dudgeon, Josh Pihl, Stuart Daw, Richard Blint, Syed Wahiduzzaman

Special Issue: 2016 CLEERS April 6-8, Ann Arbor, MI, USA
First Online: 19 October 2016

630 Downloads | 1 Citations

Abstract

We summarize a global kinetic model for a commercial automotive Lean $NO_x$ Trap (LNT) catalyst derived from laboratory flow reactor measurements at Oak Ridge National Laboratory (ORNL). The experimental measurements were made according to a modified version of a publicly shared protocol developed for characterizing the dynamic responses of LNT catalysts over a temperature range of 150–550 °C under lean-rich cycling with CO, $H_2$, and $C_3H_6$ as the reductants. The resulting model includes three $NO_x$ storage sites. The present model also includes reactions for oxygen storage, water gas shift, steam reforming, $NO_x$ reduction, and $N_2O$ and $NH_3$ generation. When implemented in 1D integral reactor simulations of long-period cycling, the model was found to accurately predict the observed outlet concentrations of CO, $H_2$, $C_3H_6$, NO, $NO_2$, $NH_3$, and $N_2O$.

Keywords

Emission regulation | Lean $NO_x$ Trap | Oxygen storage capacity | $NO_x$ storage reduction

*M .Rafigh, R. Dudgeon, J. Pihl, S. Daw, R. Blint, S. Wahiduzzaman, Emission Control Science and Technology 3 (1), 73-92, 2017*

# Remaining Challenges & Barriers/Future Work

| **Remaining Challenges:** | **Future Work:** *(subject to change based on funding)* |
|---|---|
| • Ongoing need for coordination and collaboration in developing simulation tools for next generation emissions control devices. | • Continue coordinating CLEERS activities: workshops, teleconferences, website, surveys |
| • Better $NH_3$ SCR models needed for design and control of aftertreatment systems with higher NOx conversion efficiencies over full vehicle life to meet Tier 3 regulations and beyond. | • Finish incorporating 2 site $NH_3$ storage model with aging adaptation into full SCR device model<br>• Measure $NH_3$ storage isotherms on model Cu-SSZ-13 materials to develop fundamental understanding of storage sites and aging effects |
| • Decreasing exhaust temperatures from higher efficiency engines and advanced combustion modes.<br>• 90% conversion of NOx and HCs at 150 °C | • Passive NOx Adsorbers:<br>- Develop model(s) for NO adsorption and estimate associated parameters from data<br>- Evaluate effectiveness of models for other PNA formulations<br>• Hydrocarbon traps:<br>- Measure adsorption isotherms for single HCs (ethanol, toluene, iso-octane, decane...)<br>- Develop preliminary model(s) for HC adsorption/desorption |

# Summary

- **Relevance**
  - CLEERS supports the development of simulation tools for the design, optimization, and control of next generation advanced combustion engine/aftertreatment systems that maximize efficiency while still meeting emissions standards
- **Approach**
  - Promote sharing of precompetitive information among the emissions control community through workshops, teleconferences, website, and surveys
  - Develop modeling strategies, reaction mechanisms, parameter estimates, experimental protocols, and data sets to support development of aftertreatment simulation tools, with a particular focus on catalysts for low temperature exhaust
- **Technical Accomplishments**
  - Maintained high levels of participation in CLEERS activities
  - Conducted detailed measurements of gas composition impacts on NO uptake on a PNA catalyst; began to develop conceptual model of NO adsorption/desorption
- **Collaborations**
  - PNNL; Johnson Matthey
  - Advanced Engine Crosscut Team, U.S.DRIVE ACEC Tech Team, CLEERS Participants
- **Future Work** *(subject to change based on funding levels)*
  - Continue coordination of CLEERS activities
  - Measure & model adsorption/desorption phenomena on PNAs and HC Traps

# Technical Back-Up Slides

# CLEERS is a team effort involving contributions from many people and organizations

### DOE Advanced Engine Crosscut Team

### DOE Sponsors
Ken Howden
Gurpreet Singh
Leo Breton

### CLEERS Coordinating Committee

| | |
|---|---|
| Josh Pihl | (ORNL) |
| Wei Li | (GM) |
| Yong Wang | (PNNL) |
| Jamie Holladay | (PNNL) |
| Vitaly Prikhodko | (ORNL) |
| Todd Toops | (ORNL) |

### CLEERS Advisory Committee

| | |
|---|---|
| Wei Li | (GM) |
| Christine Lambert | (Ford) |
| Craig Dimaggio | (FCA) |
| Neal Currier | (Cummins) |
| John Kirwan | (Delphi) |
| Balaji Sukumar | (Johnson Matthey) |
| Louise Olsson | (Chalmers University) |
| Mike Harold | (University of Houston) |
| Dick Blint | (N2Kinetics) |
| Stuart Daw | (ORNL Emeritus) |

### Workshop
Todd Toops
Vitaly Prikhodko
Josh Pihl

### Telecons
Josh Pihl
Dick Blint
Vitaly Prikhodko

### Website
Vitaly Prikhodko
Charles Finney
Josh Pihl

### Newsletter
Josh Pihl
Dick Blint
Stuart Daw

### Industry Priorities Survey
Josh Pihl

# Proposed schedule for ORNL CLEERS activities shifts focus to adsorbers for low T applications

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

**2. NOx storage/release on PNAs**
- 2.a. Protocol development
- 2.b. NO adsorption/desorption
- 2.c. Co-adsorption/inhibition
- 2.d. PNA formulation effects

**3. HC storage/release on traps**
- 3.a. Instrumentation & protocols
- 3.b. Single HCs
- 3.c. HC mixes
- 3.d. Trap formulation effects

**4. $NH_3$ storage/release on SCR**
- 4.a. commercial Cu-SSZ-13 aging
- 4.b. commercial Cu-SAPO-34
- 4.c. reaction & aging mechanisms
- 4.d. model SSZ-13