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

2017 U.S. DOE Vehicle Technologies Office Annual Merit Review

June 6, 2017 **Project ID: ACS022**

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  - Vitaly Prikhodko, Todd Toops, Sreshtha Majumdar, Charles Finney, Jae-Soon Choi, Bill Partridge, Will Brookshear

- **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

	FY16	FY17
Coordination	$250k	$250k
Analysis	$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 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 Tech Team
- CLEERS Focus Group members
  - 10 engine/vehicle manufacturers
  - 11 component and software suppliers
  - 13 universities
  - 4 national labs
- PNNL, Politecnico di Milano

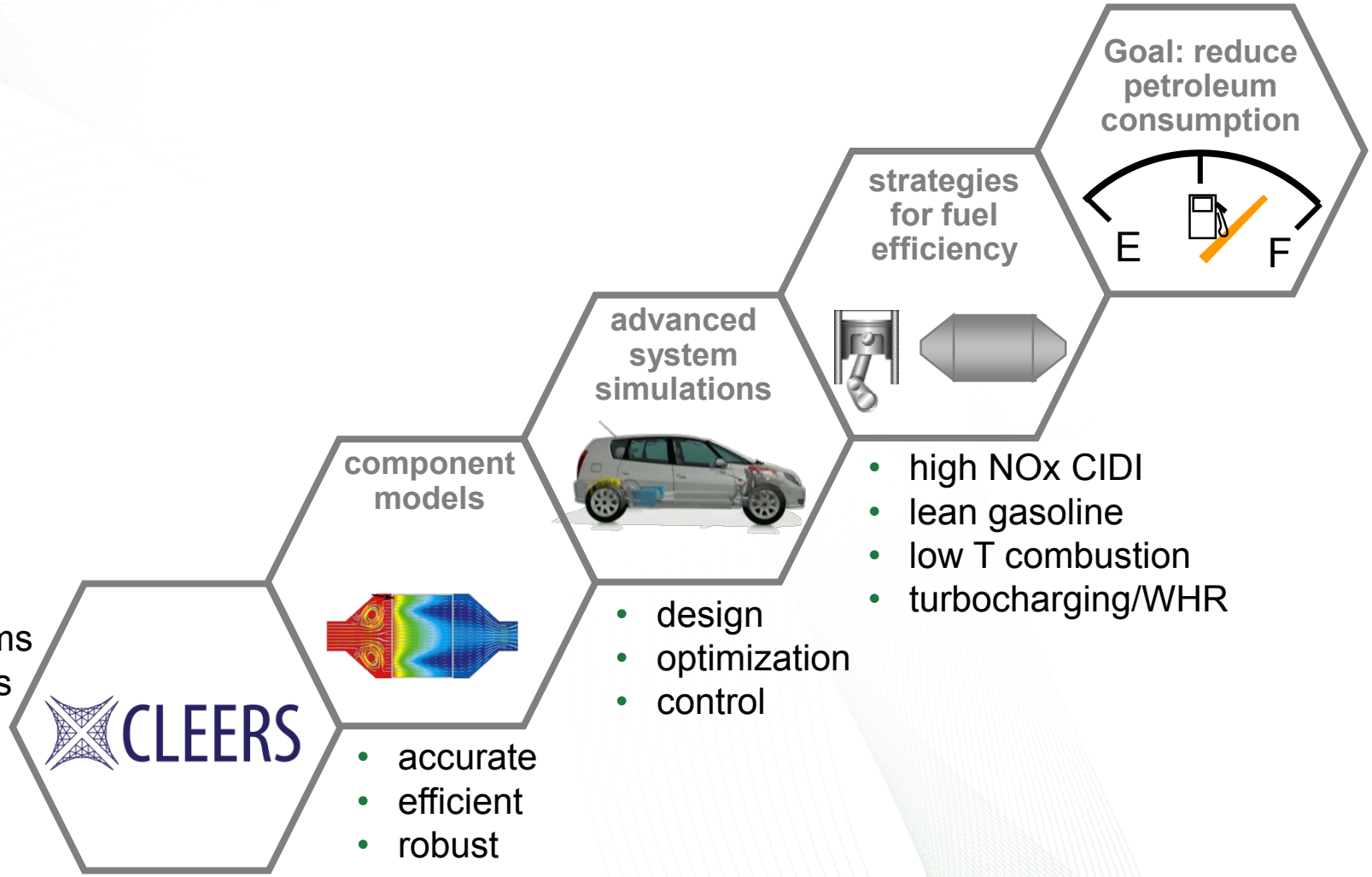
CLEERS enables the DOE VTO goals of improving efficiency while meeting emissions regulations

"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

- 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 high efficiency advanced combustion 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



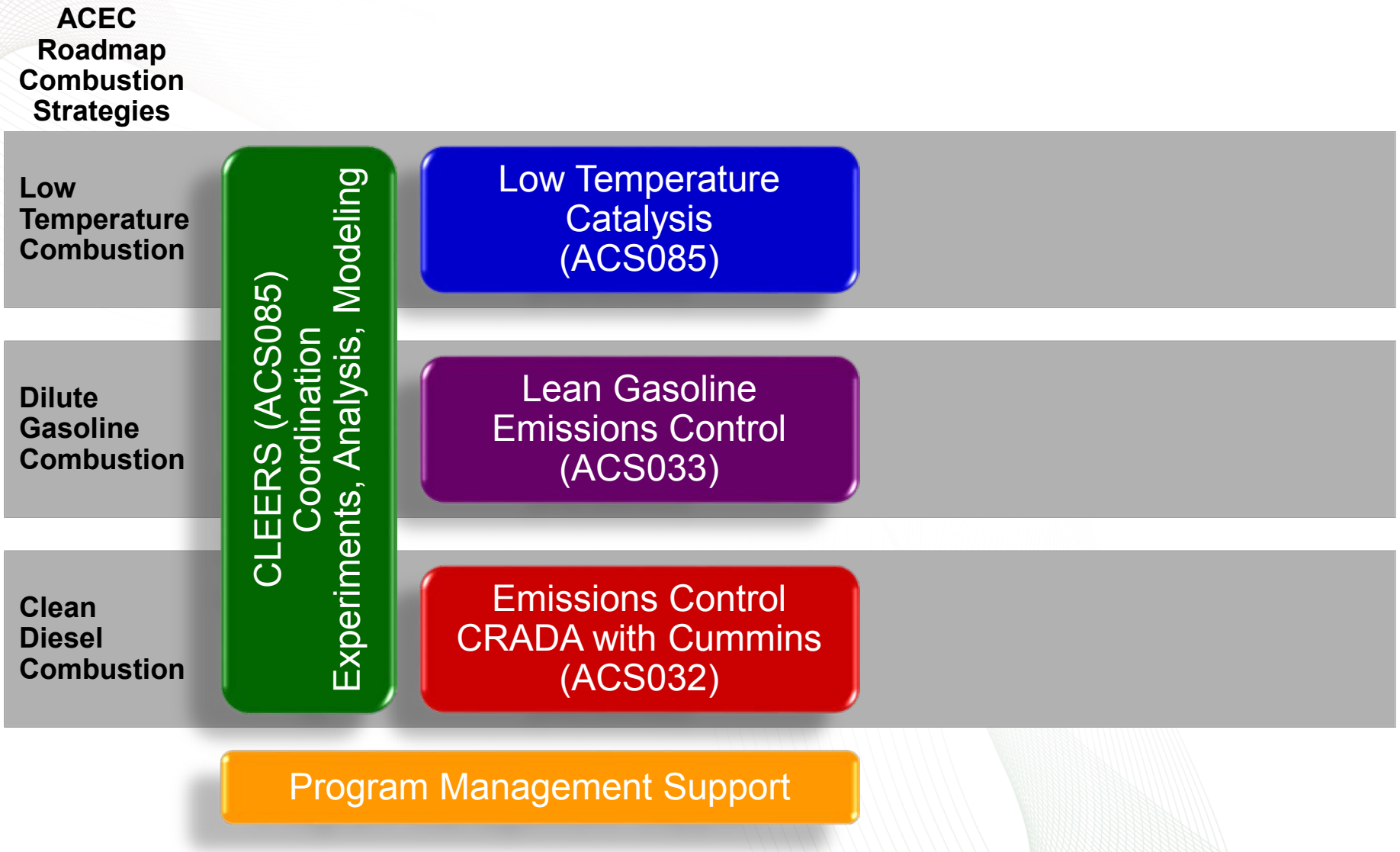
- strategies
- mechanisms
- parameters
- protocols
- data

- accurate
- efficient
- robust

- design
- optimization
- control

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

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



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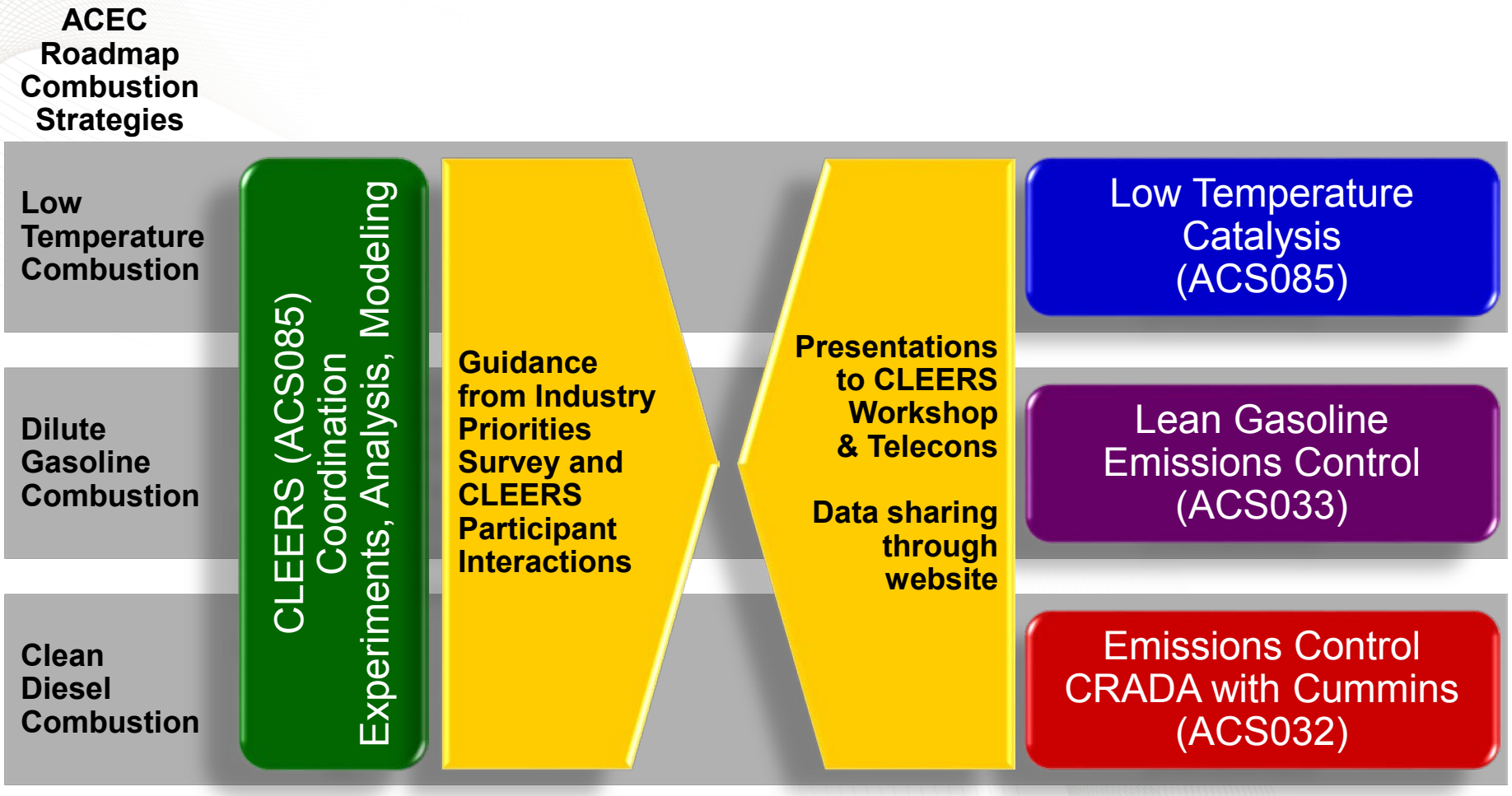

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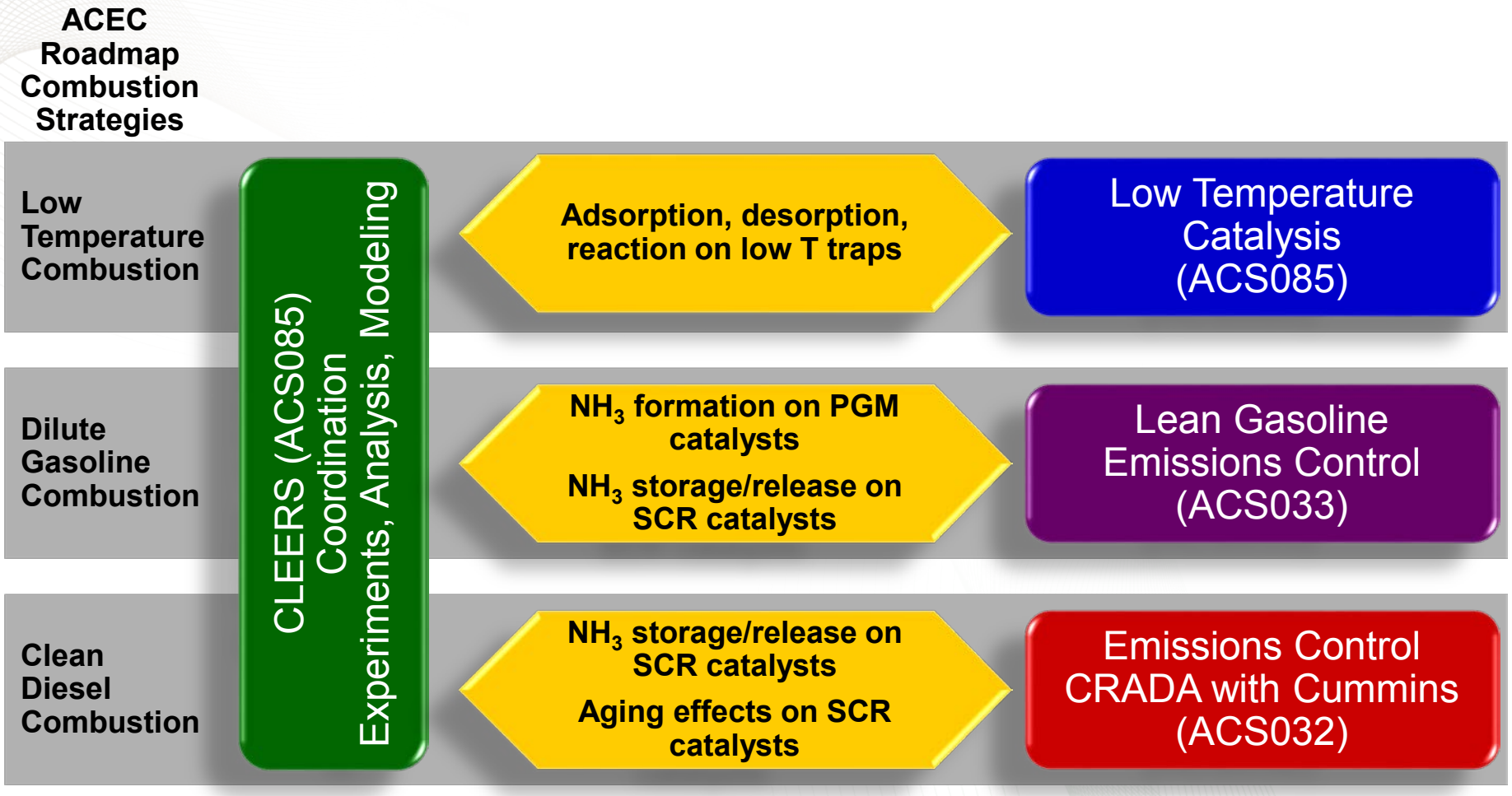

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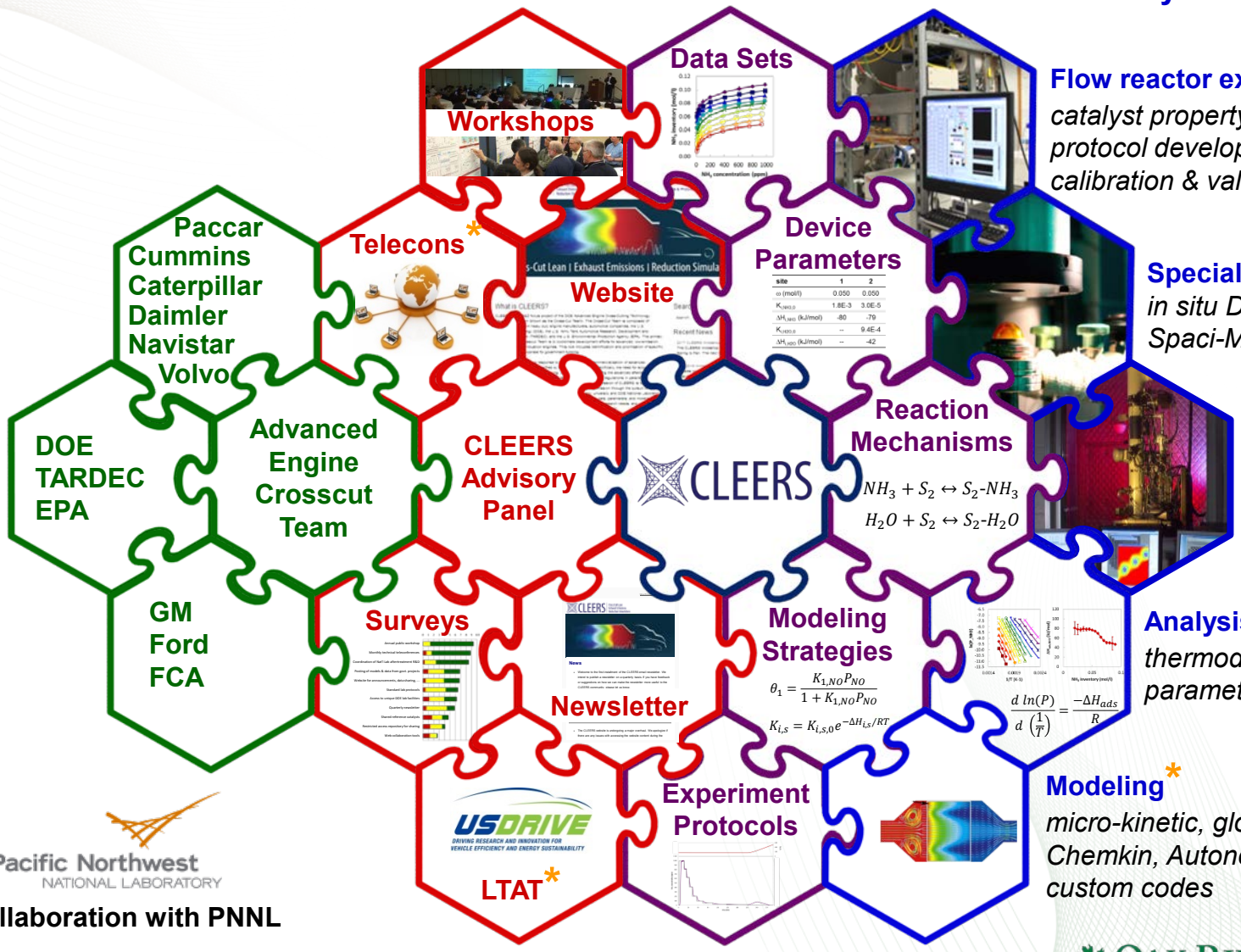
ORNL coordinates CLEERS activities and conducts focused R&D in support of CLEERS objectives

ORNL CLEERS Coordination

ORNL CLEERS Analysis



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

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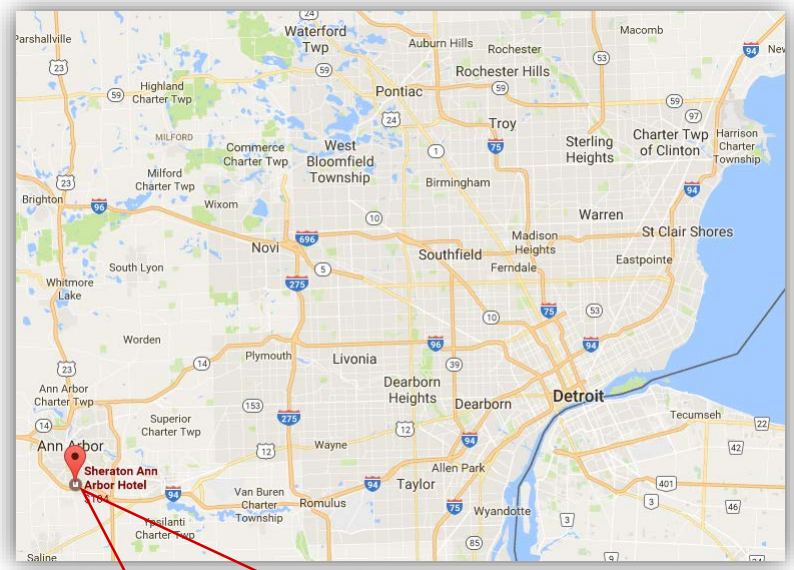
Milestones

FY	Qtr	Milestone	Status
2016	3	Host 2016 CLEERS Workshop	complete
2016	4	Complete characterization of NH_3 storage on two primary commercial SCR catalysts (Cu-SSZ-13 & Cu-SAPO-34), publish findings, and post NH_3 isotherm data on the CLEERS website	complete
2017	4	Organize 2017 CLEERS Workshop	on schedule

2017 CLEERS Workshop has been moved to the fall based on participant feedback and scheduling conflicts

- Dates: Tue. Oct. 3 –Thu. Oct. 5
  - Moved from spring based on CLEERS Advisory Committee and AMR feedback
  - Avoids SAE WCX, DOE FOA process
- Location: Sheraton Ann Arbor
  - 3200 Boardwalk Street, Ann Arbor, MI
  - www.sheratonannarbor.com
- Agenda: currently under development
  - similar to 2016 Workshop
    - 3 full days
    - ~5 invited speakers
    - panel discussion
    - poster session
  - contributed abstract submissions through CLEERS website



http://www.sheratonannarbor.com/en/gallery

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Proceedings of the 2016 CLEERS Workshop were published in a special issue of ECS&T

Springer Link | Search

Emission Control Science and Technology
All Volumes & Issues

Volume 3, Issue 1, March 2017

2016 CLEERS

Issue Editors: Todd Toops, Josh A. Pihl, Vitaly Y. Prikhodko

ISSN: 2199-3629 (Print) 2199-3637 (Online)

In this issue (10 articles)

Special Issue: 2016 CLEERS April 6-8, Ann Arbor, MI, USA

A Review of the Annual US-DOE CLEERS Conference: Trends in Real Driving Emissions, Novel Catalyst Technologies, and NOx Reduction

John Hoard

» Download PDF (242KB) » View Article Pages 1-4

Special Issue: 2016 CLEERS April 6-8, Ann Arbor, MI, USA

Coupled Heterogeneous and Homogeneous Hydrocarbon Oxidation Reactions in Model Diesel Oxidation Catalysts

Melanie J. Hazlett, William S. Epling

» Download PDF (2195KB) » View Article Pages 5-17

Special Issue: 2016 CLEERS April 6-8, Ann Arbor, MI, USA

Understanding low temperature oxidation activity of nanoarray-based monolithic catalysts: from performance observation to structural and chemical insights

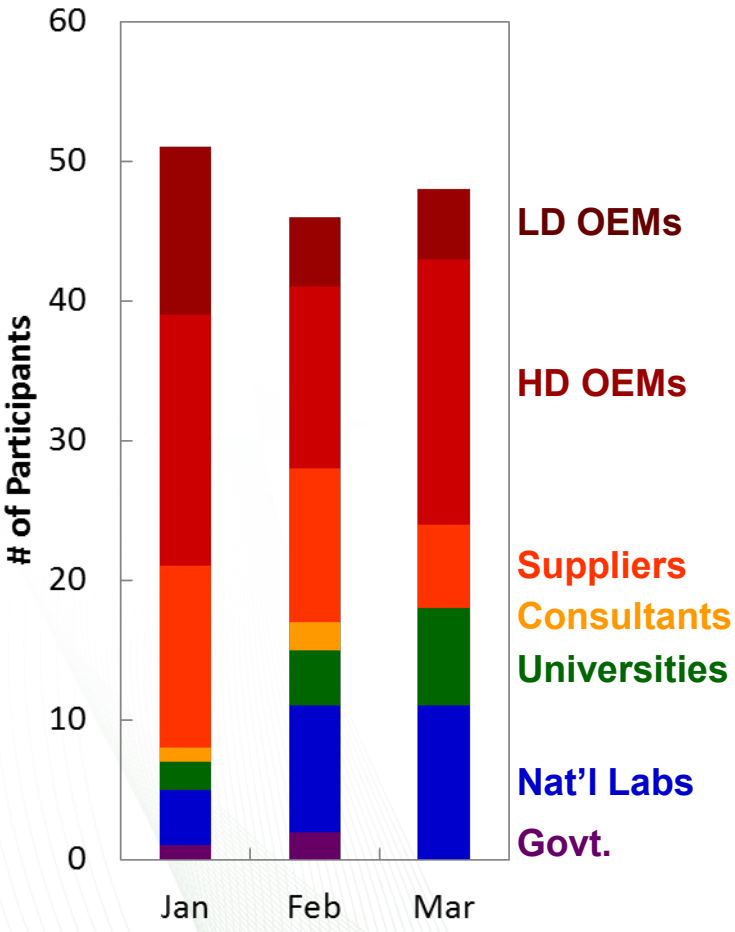
Shoucheng Du, Wenxiang Tang, Yanbing Guo...

- Emission Control Science & Technology Vol. 3, Iss. 1
  - published March 2017
- Issue edited by Todd Toops, Vitaly Prikhodko, Josh Pihl
- Contents:
  - Overview by John Hoard
  - 9 articles contributed by CLEERS Workshop participants
- Journal Editor-in-Chief (Mansour Masoudi) shared positive feedback received at SAE WCX

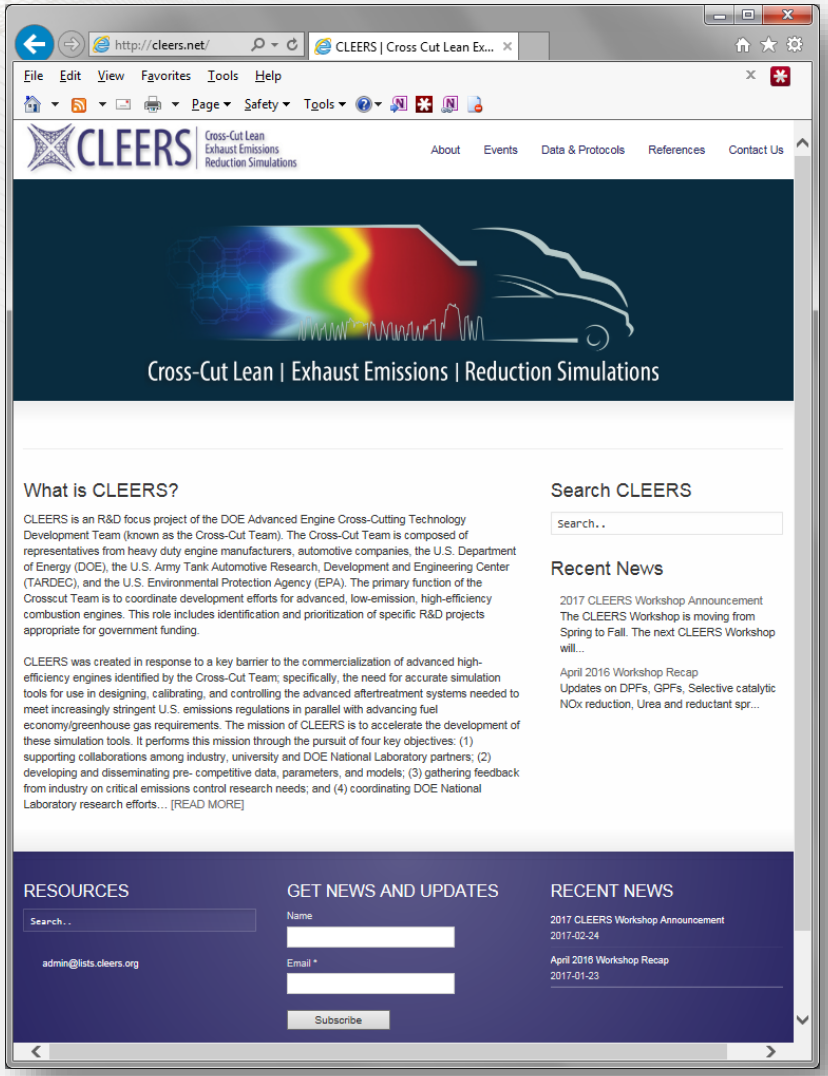
CLEERS Focus Group Teleconferences continue to draw high levels of interest, particularly from industry

- First three teleconferences of 2017 drew an average of 48 participants
  - participation limited to Crosscut Team members and their nominees
  - 60-80% of participants from industry
- Broad mix of speakers and topics scheduled for 2017:

Month	Speaker	Org.	Topic
Jan	Rasto Brezny	MECA	Emission Standards
Feb	John Farrell	NREL	Co-Optima emissions
Mar	Boopathi Mahadevan	MTU	Soot permeability
May	Hee Je Song	ANL	Ash in GPFs
Jun	Balaji Sukumar	J-M	TBD
TBD	Subir Roychoudhury	PCI	Low PGM TWCs



CLEERS Website (www.cleers.org) has been completely overhauled

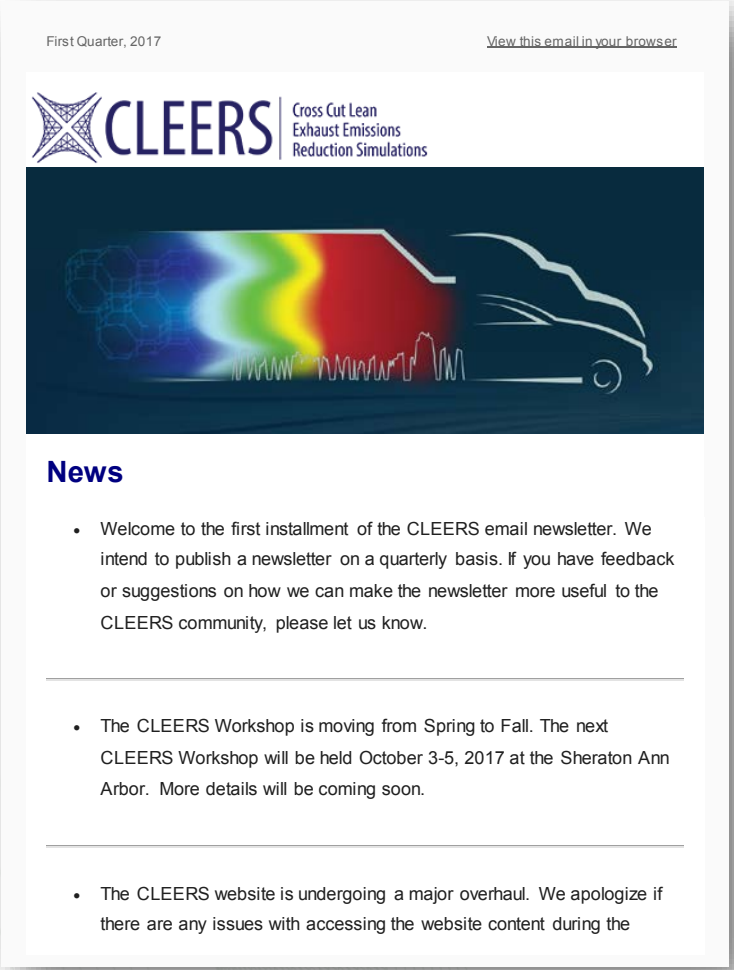


- Modernized user interface
- Updated content
  - About: general CLEERS info
  - Events
    - Workshop info, abstracts, registration
    - ***teleconference schedule***
    - ***calendar of events***
  - Data & Protocols
    - ***data repository***
    - experimental protocols
  - References
    - Workshop presentations
    - priorities survey reports
    - bibliography
    - ***dissertations***

New quarterly CLEERS Newsletter provides another mode of communication with CLEERS participants

Newsletter objectives:

- Provide timely updates on CLEERS activities
  - Upcoming Teleconferences
  - News about the CLEERS Workshop
  - Other upcoming events
- Drive traffic to CLEERS website by highlighting new content
  - Recently posted data sets
  - New reports
- Create a forum to further engage the CLEERS community
  - Invited column intended to spark reflection, discussion
    - Q1: Tim Johnson
    - Q2: Ed Bissett



First Quarter, 2017 View this email in your browser

CLEERS Cross Cut Lean Exhaust Emissions Reduction Simulations

News

- Welcome to the first installment of the CLEERS email newsletter. We intend to publish a newsletter on a quarterly basis. If you have feedback or suggestions on how we can make the newsletter more useful to the CLEERS community, please let us know.

- The CLEERS Workshop is moving from Spring to Fall. The next CLEERS Workshop will be held October 3-5, 2017 at the Sheraton Ann Arbor. More details will be coming soon.

- The CLEERS website is undergoing a major overhaul. We apologize if there are any issues with accessing the website content during the

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 Ming Yang
PNNL	Ken Rappe Mark Stewart
ORNL	Jim Parks Josh Pihl
UM	Galen Fisher
DOE	Ken Howden

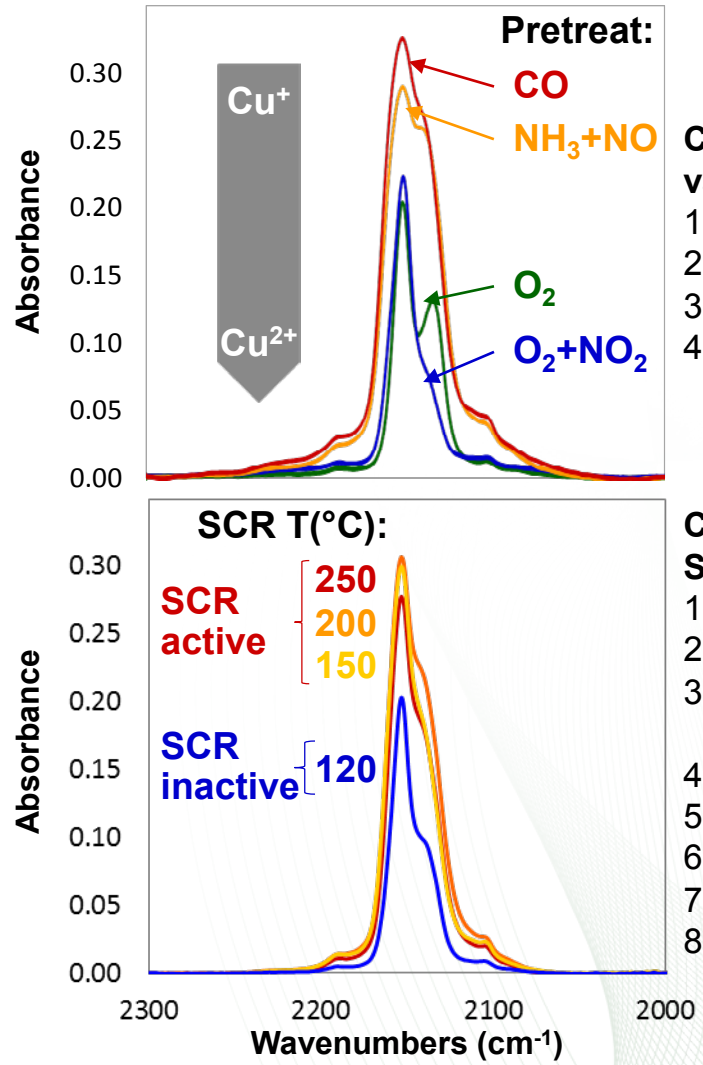
- Supported development of screening protocols for low T oxidation catalysts (2014-15), storage catalysts (2015-16), and TWCs (2016-17)
- Hosting protocols on CLEERS website

Method for measuring Cu oxidation state supports NO SCR reaction mechanism development for Cu-SSZ-13

Collaboration with Politecnico di Milano

- Developed method for probing Cu oxidation state in Cu-SSZ-13 through DRIFT spectra of adsorbed CO
  - Oxidation of Cu^{+} to Cu^{2+} reduces intensity of CO peaks (2100-2200 cm^{-1})
- Used method to probe Cu oxidation state after running SCR reaction
  - Cu remains in reduced state at Ts with even moderate SCR activity
  - Cu re-oxidized at 120 °C, where SCR is inactive

Cu oxidation state probe will support mechanism development efforts



Cu oxidation state after various pretreatments:

1. Pretreat 500°C
2. Cool to 40°C (Ar)
3. Expose to CO
4. Purge (Ar)

Cu oxidation state after SCR at various Ts:

1. Reduce 500°C (NH_3+NO)
2. Cool to 120-250°C (Ar)
3. Run NO SCR mixture ($NO+NH_3+O_2+H_2O$)
4. Purge (Ar)
5. Flash heat to 250°C (Ar)
6. Cool to 40°C (Ar)
7. Expose to CO
8. Purge (Ar)

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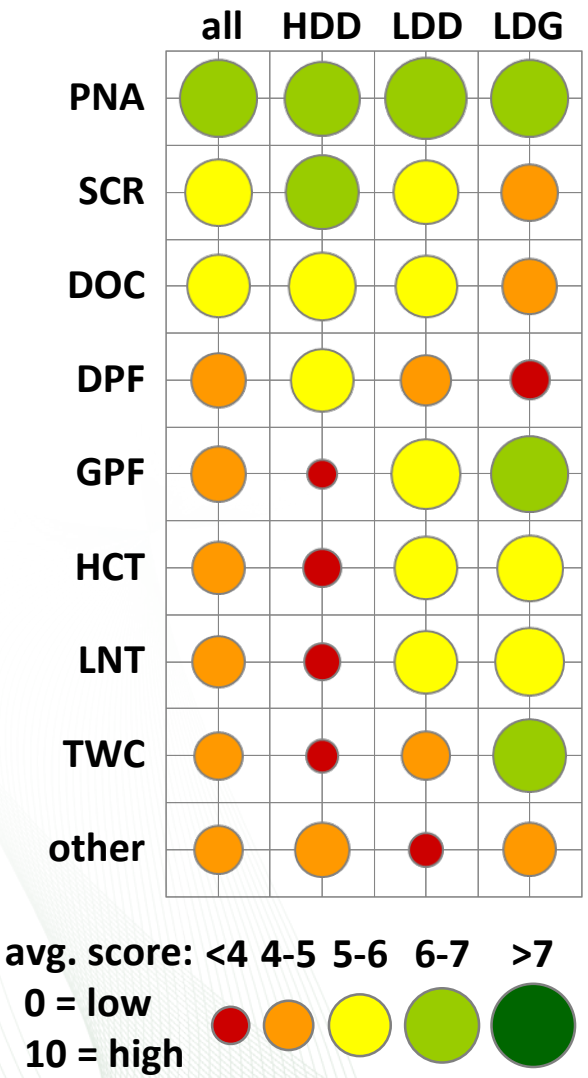
PNAs are a top R&D priority for industry

- What is a PNA?
  - Passive NOx Adsorber
  - Traps NO at low Ts
  - Releases NO at higher Ts when downstream NOx conversion catalysts are active
- Why are we investigating PNAs?
  - Highest interest ranking of all technology areas in 2015 CLEERS Industry Priorities Survey
  - Merit review comments
- Why are PNAs so important?
  - Higher engine efficiency = lower exhaust T
    - longer cold starts
    - low steady state exhaust Ts at low loads for advanced combustion engines
  - Current NOx control catalysts (urea SCR, LNT, TWC) do not work effectively below 200 °C



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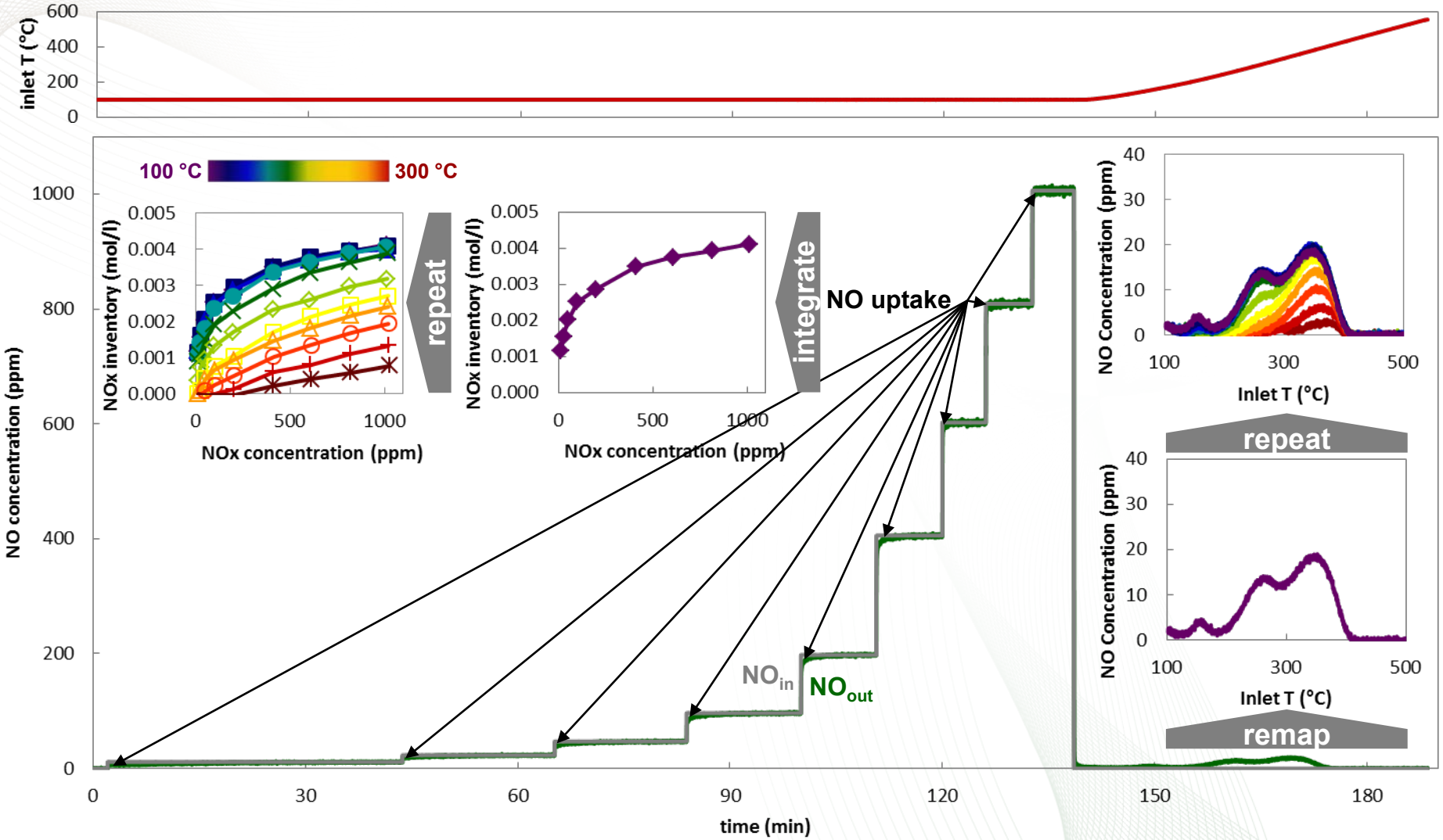
Experimental method designed to measure both NO adsorption isotherms and TPDs on PNA materials



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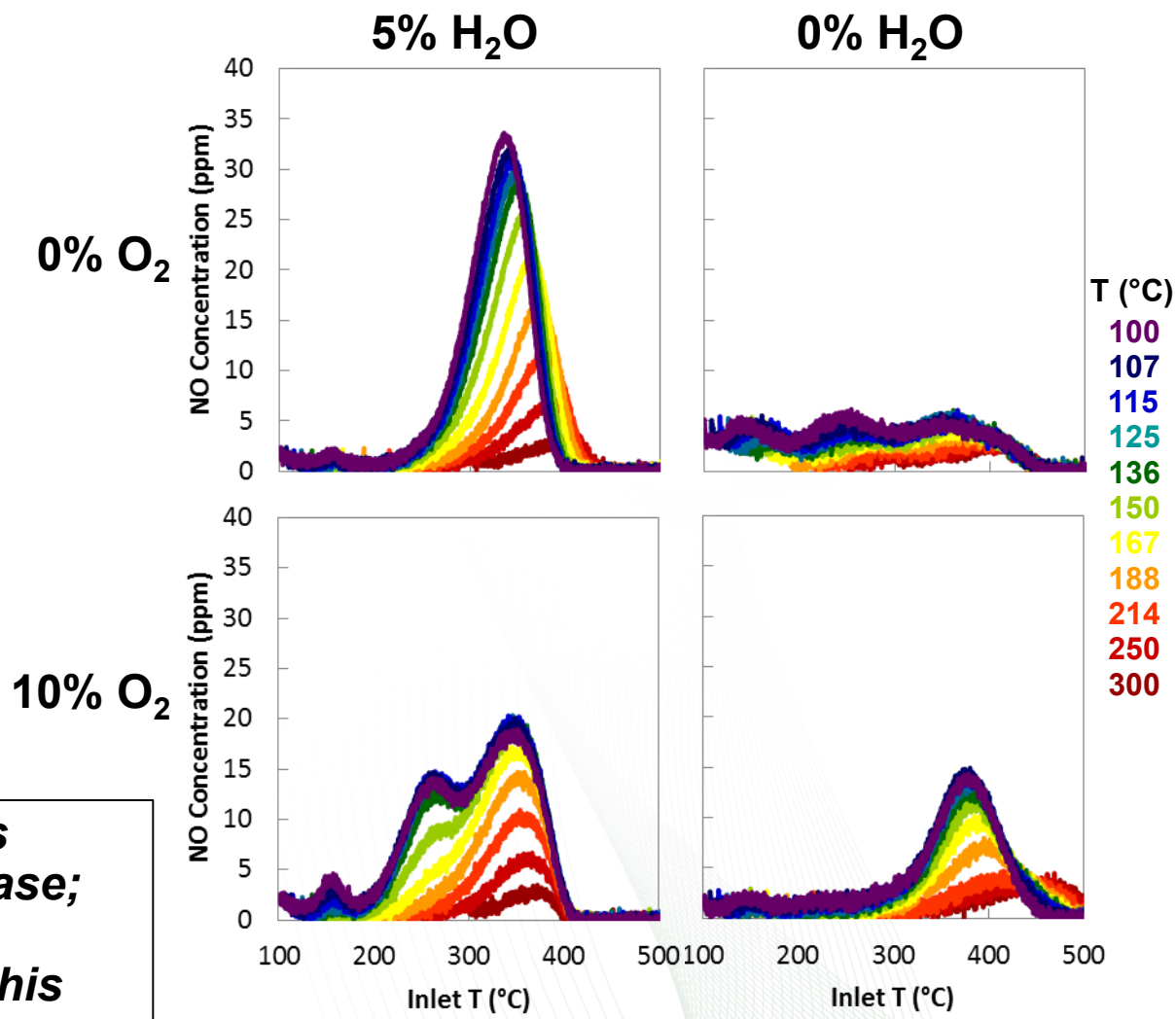
PNA TPDs illustrate effects of gas composition on NO storage and release

- Inclusion of O_2 in feed gas:
  - increases total NO storage capacity
  - results in NO release at lower temperatures
- Removal of H_2O from feed gas:
  - significantly decreases NO storage capacity
  - does not yield insights into adsorption behavior



Other exhaust constituents impact PNA storage & release; dry measurements of NO storage are not useful for this type of PNA

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Preliminary analysis shows NO storage behavior can be captured with simple Langmuir isotherms

- Used adsorption isotherms to estimate parameters for two simple NO storage models:
  - one or two sites

    $$I_{NO} = \omega_1 \theta_1$$

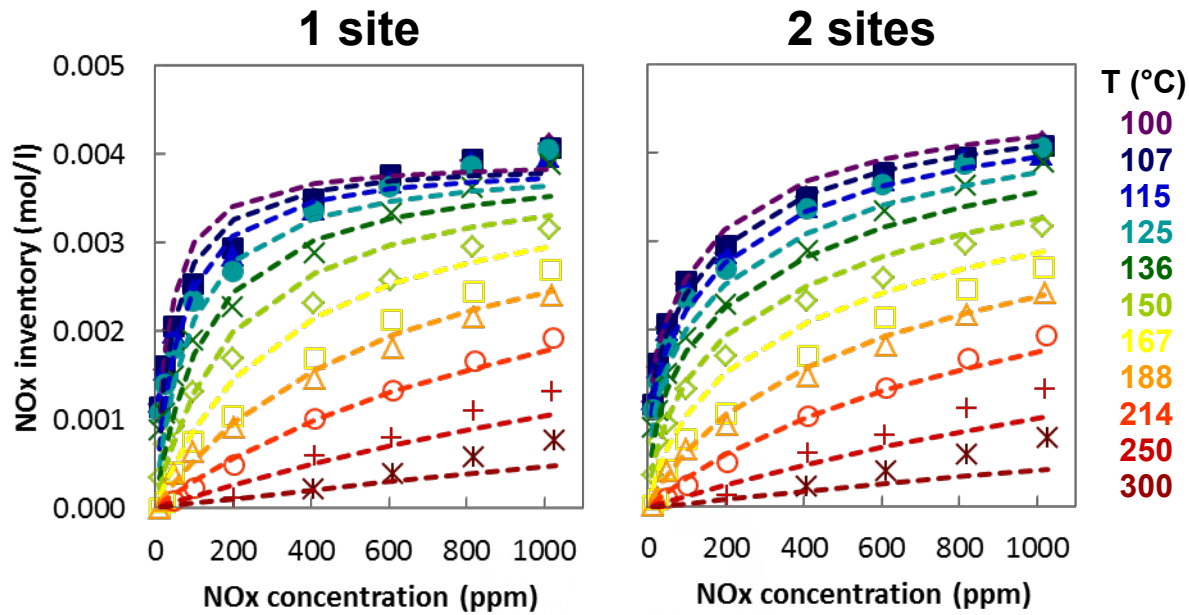
    $$I_{NO} = \omega_1 \theta_1 + \omega_2 \theta_2$$

  - Langmuir isotherm with no inhibition

    $$\theta_i = \frac{K_{i,NO} P_{NO}}{1 + K_{i,NO} P_{NO}}$$

  - constant ΔH_{ads}

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



site	1	1	2
ω (mol/l)	0.0039	0.0016	0.0031
$K_{i,NO,0}$	4.8E-3	8.7E-5	3.7E-2
$\Delta H_{i,NO}$ (kJ/mol)	-49	-68	-37

Simple Langmuir isotherms adequately represent NO adsorption behavior for this PNA; 2 site model is more consistent with adsorption and TPD data

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Collaborations

CLEERS Technology Focus Group

Adv. Eng. Crosscut

ACEC TT

DOE VTO

LD OEMs:
FCA
Ford
GM

HD OEMs:
Caterpillar
Cummins
Daimler
Navistar
Paccar
Volvo

EPA
TARDEC

Suppliers:
BASF
Johnson-Matthey
Umicore
Corning
Delphi
Haldor Topsoe

CLEERS Industry Survey Recipients

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.
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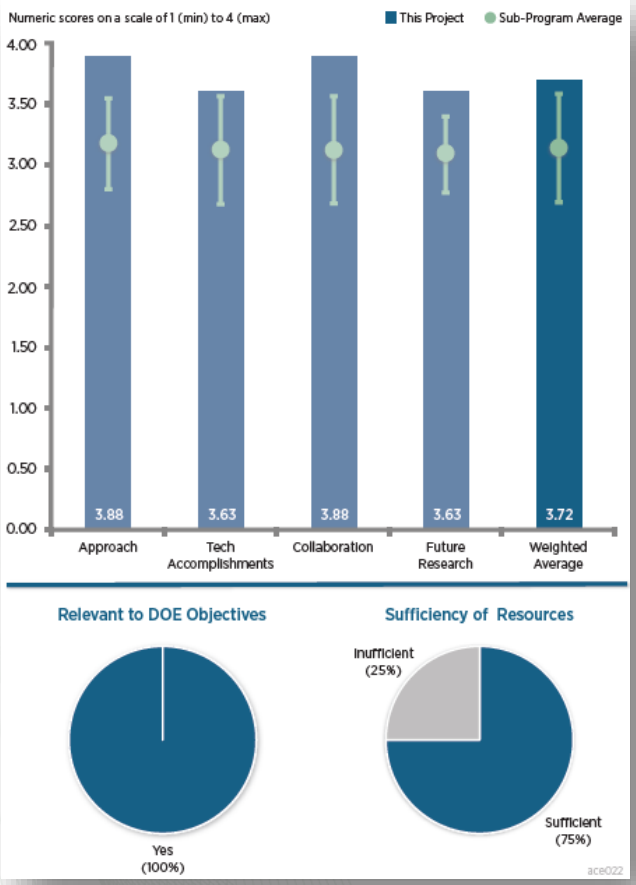
Michigan State Univ.
Ohio State Univ.
Queens Univ. Belfast
Seoul National Univ.

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

CLEERS Participants

Responses to Reviewer Comments

Reviewer Comments:	Responses:
• Workshop should definitely be continued, perhaps moved to late summer or fall	• Next CLEERS Workshop will be held Oct. 3-5, 2017
• Start emphasizing PNAs, HC traps, and low T catalysts	• Based on reviewer feedback and survey results, work on PNAs has been moved up in priority and timing, and work on both PNAs and HC traps is now underway.
• Aging effects on SCR performance is also of value for industry • Resources may not be sufficient to continue the NH_3 storage modeling while adding work on PNAs, HC traps	• The reviewers were correct in their assessment that resources are getting stretched • SCR NH_3 storage, aging, and mechanism investigations have continued, but at a reduced level of effort and slower pace, and leveraged through collaborations where possible



Remaining Challenges & Barriers/Future Work

Remaining Challenges:	Future Work:
• Decreasing exhaust temperatures from higher efficiency engines and advanced combustion modes.	• Passive NOx Adsorbers: - Improve methods for measuring NO adsorption - Develop model(s) for NO adsorption and estimate associated parameters from data • Hydrocarbon traps: - Measure adsorption isotherms for single HCs (ethanol, toluene, iso-octane, decane...) - Develop preliminary model(s) for HC adsorption
• Improved NH_3 SCR models needed for design and control of aftertreatment systems with higher NOx conversion efficiencies over full vehicle life.	• Collaborate with PoliMi in using DRIFTS to develop reaction mechanisms and identify rate-limiting steps for NO SCR over Cu-SSZ-13 • Measure NH_3 storage isotherms on model Cu-SSZ-13 materials to develop more fundamental understanding of storage sites and aging effects
• Ongoing need for coordination and collaboration in developing simulation tools for next generation emissions control devices.	• Continue coordinating CLEERS activities: workshops, teleconferences, website, surveys

Any proposed future work is subject to change based on funding levels

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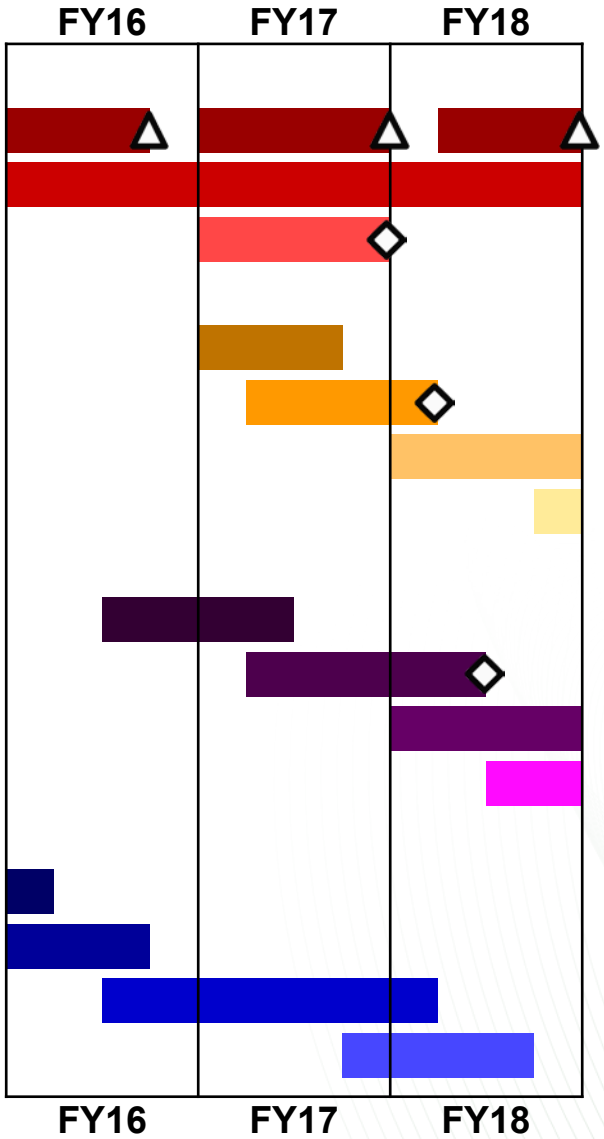
Proposed schedule for ORNL CLEERS activities shifts focus to adsorbers for low T applications

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



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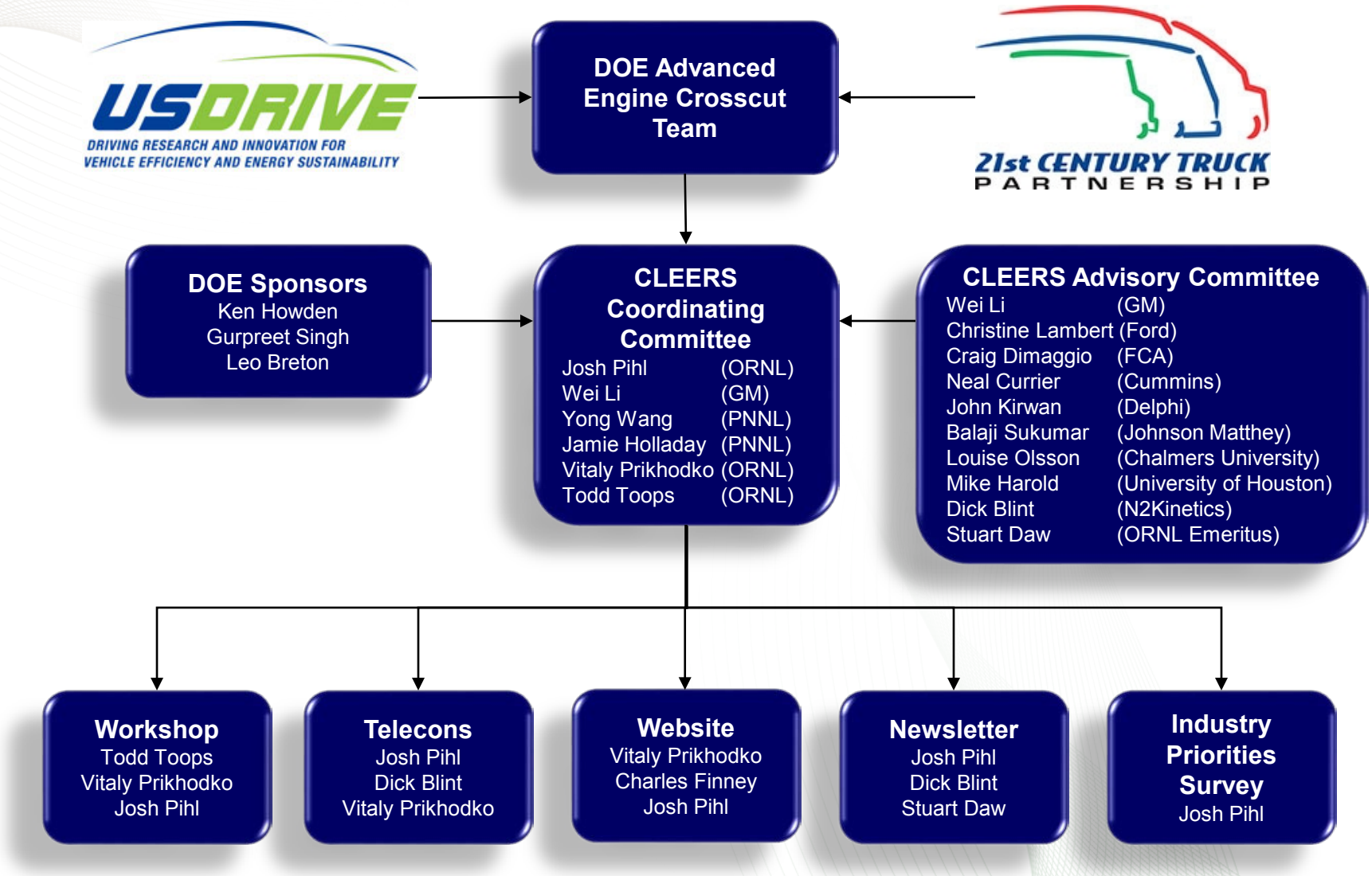
Summary

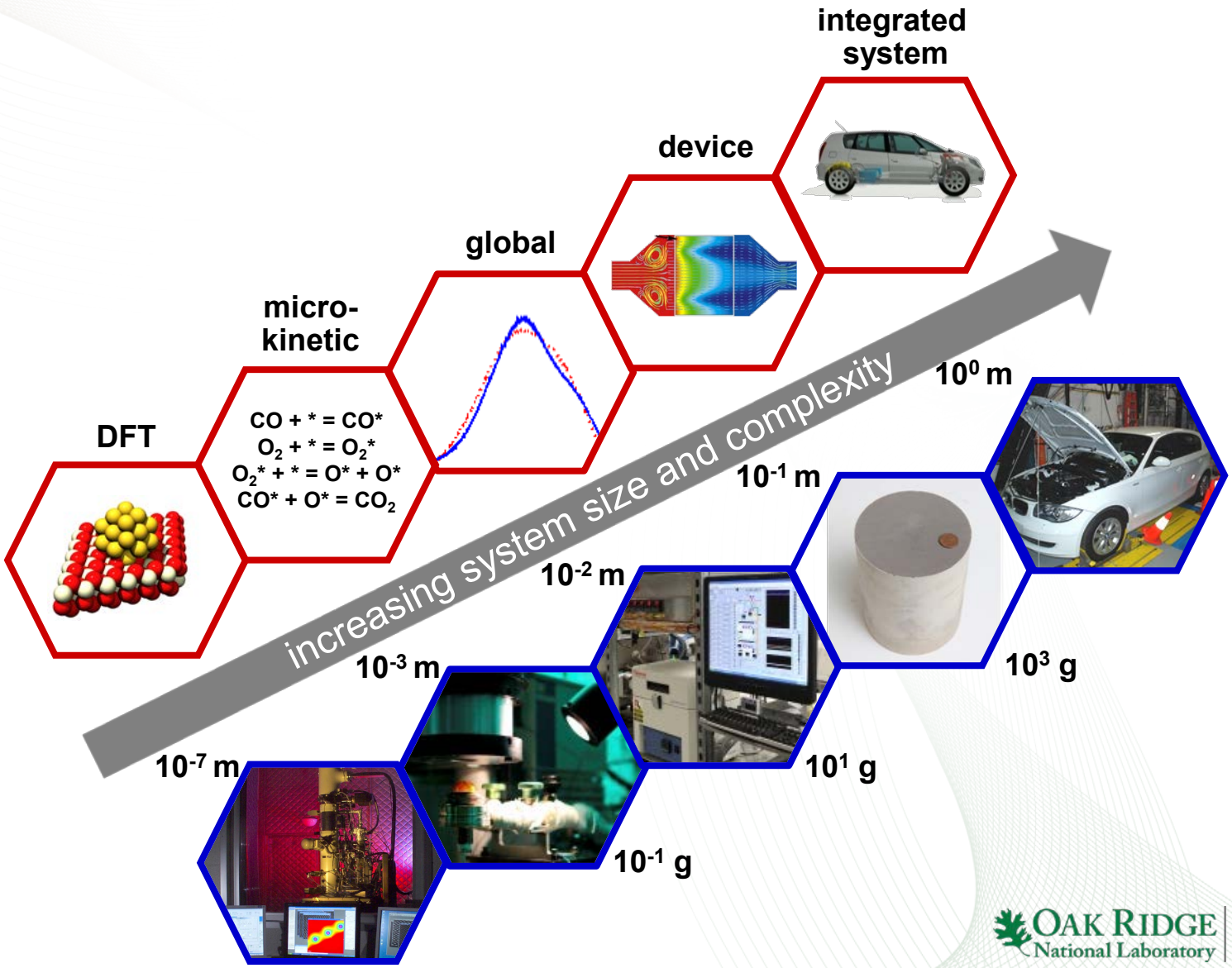
- **Relevance**
  - CLEERS supports the development of simulation tools for the design, optimization, and control of next generation advanced combustion engine/aftertreatment systems that maximize efficiency while still meeting emissions standards
- **Approach**
  - Promote sharing of precompetitive information among the emissions control community through workshops, teleconferences, website, newsletters, 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
  - Measured and began modeling NO adsorption isotherms on a PNA catalyst
- **Collaborations**
  - PNNL; Politecnico di Milano
  - 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 National Labs provide unique capabilities in multi-scale integration, ability to share precompetitive information across entire emission control community



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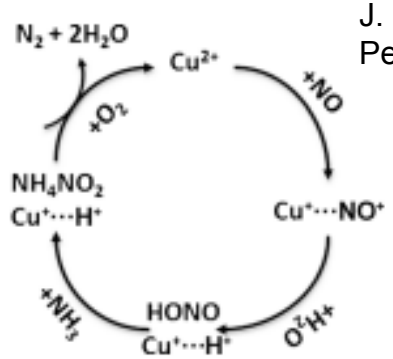
Many mechanisms have been proposed for NO SCR

Reaction
$NH_3 + S1 \overset{r1}{\Leftrightarrow} S1 - NH_3$
$NH_3 + S2 \overset{r2}{\Leftrightarrow} S2 - NH_3$
$NH_3 + S3 \overset{r3}{\Leftrightarrow} S3 - NH_3$
$2S1 - NH_3 + 1.5O_2 \overset{r4}{\Rightarrow} N_2 + 3H_2O + 2S1$
$2S2 - NH_3 + 1.5O_2 \overset{r5}{\Rightarrow} N_2 + 3H_2O + 2S2$
$4S1 - NH_3 + 4NO + O_2 \overset{r6}{\Rightarrow} 4N_2 + 6H_2O + 4S1$
$4S2 - NH_3 + 4NO + O_2 \overset{r7}{\Rightarrow} 4N_2 + 6H_2O + 4S2$
$S2 - NH_3 + NO \overset{r8}{\Leftrightarrow} S2 - NH_3 - NO$
$2S2 - NH_3 - NO + O_2 \overset{r9}{\Rightarrow} N_2O + N_2 + 3H_2O + 2S2$
$2S2 - NH_3 + 2NO + O_2 \overset{r10}{\Rightarrow} N_2O + N_2 + 3H_2O + 2S2$

L. Olsson et al. / Applied Catalysis B: Environmental 174–175 (2015) 212–224



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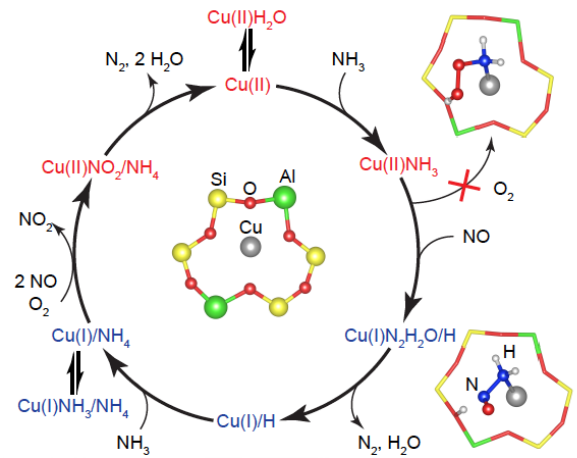

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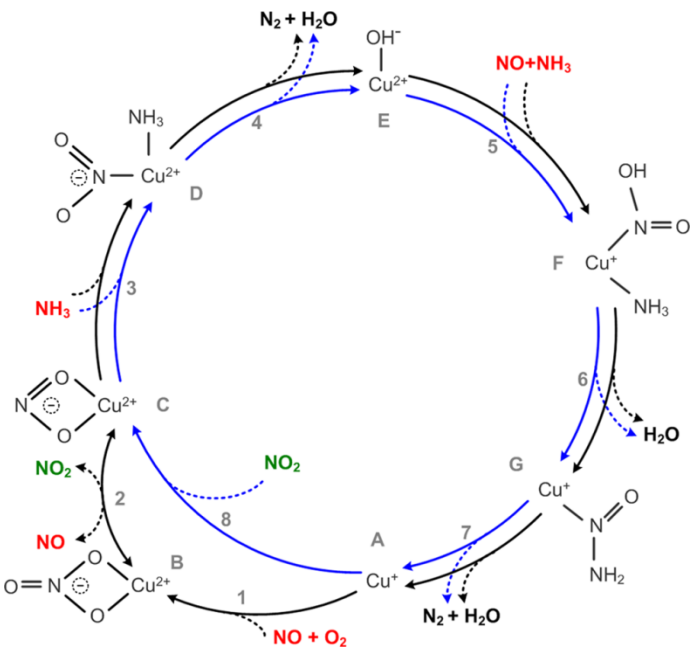

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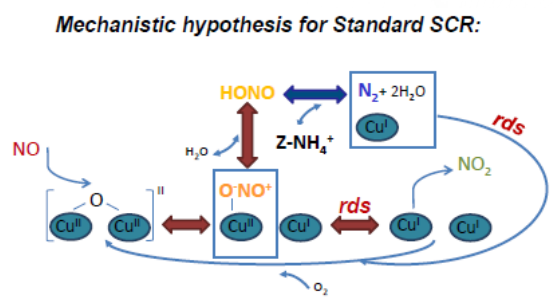

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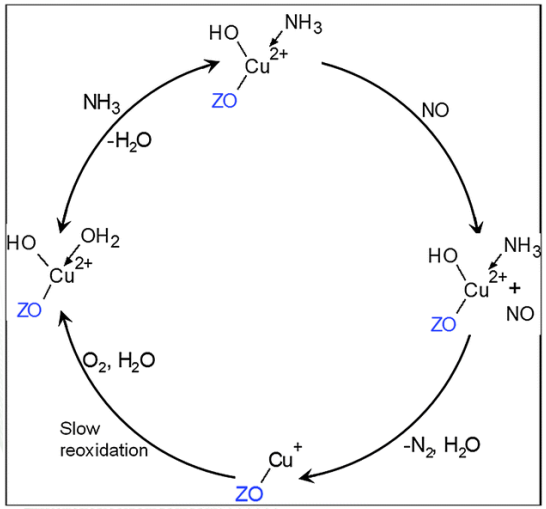

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