CLEERS Coordination

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project ID:
ACE022

Joint Development of Benchmark Kinetics for LNT & SCR

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Bill Partridge, Todd Toops, Stuart Daw

PI: **Stuart Daw**
Presenter: **Josh Pihl**
Oak Ridge National Laboratory

Vehicle Technologies Office Annual Merit Review
May 15, 2013
Arlington, VA

DOE Managers: Ken Howden, Gurpreet Singh

Overview

Timeline

Project start date:

- Coordination: FY2000
- Kinetics: FY2000

Project end date: Ongoing

- core activity supporting & coordinating emissions control research

Budget

	FY12	FY13
Coordination	$200k	$300k
Kinetics	$500k	$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 2 Bin 2 Emissions
- <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
  - 11 component and software suppliers
  - 10 universities
- PNNL, ICT Prague, Politecnico di Milano

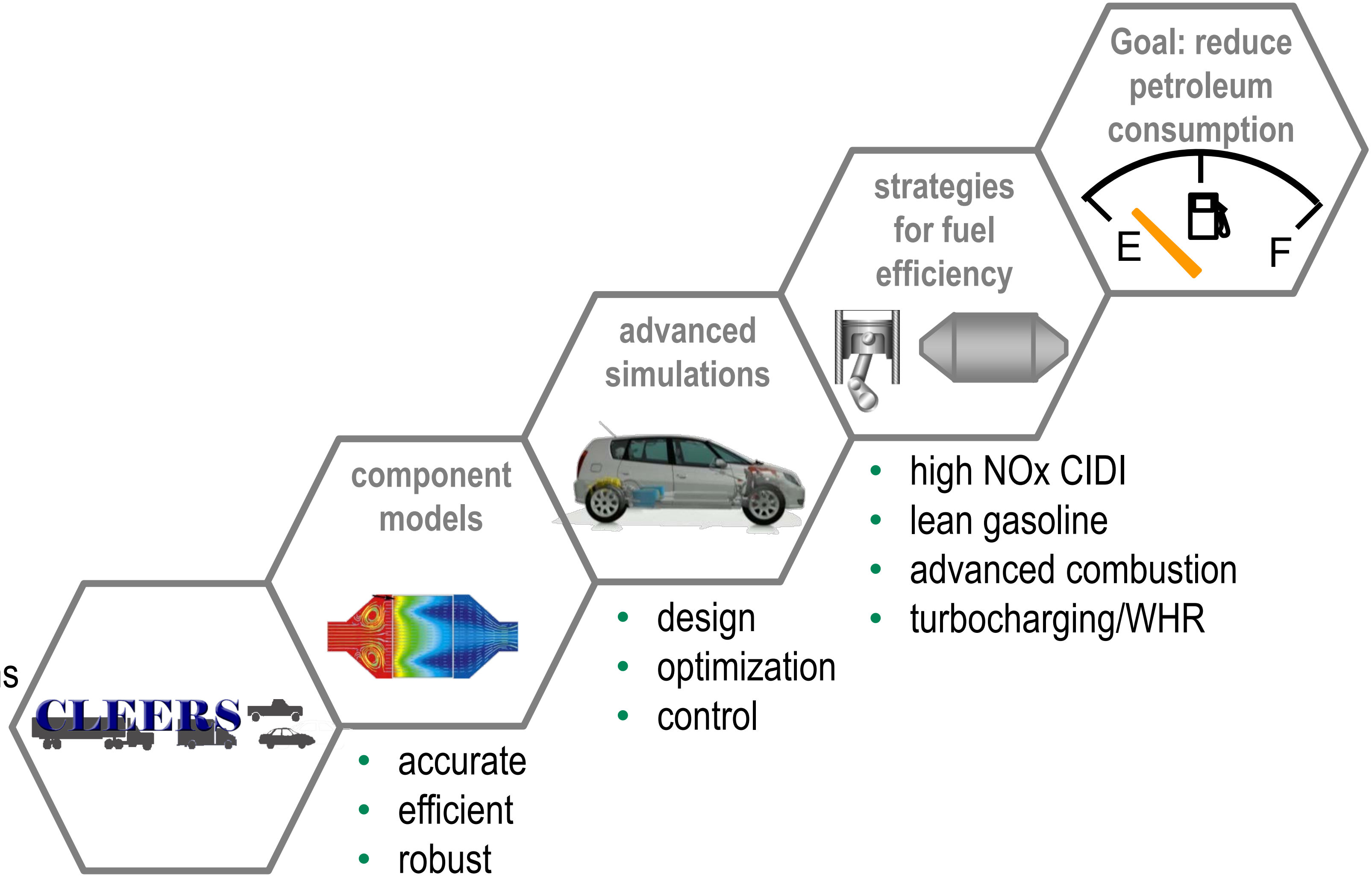
CLEERS supports the VTO goals of improving efficiency while meeting emissions regulations

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

"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



- strategies
- mechanisms
- parameters
- protocols
- data

- accurate
- efficient
- robust

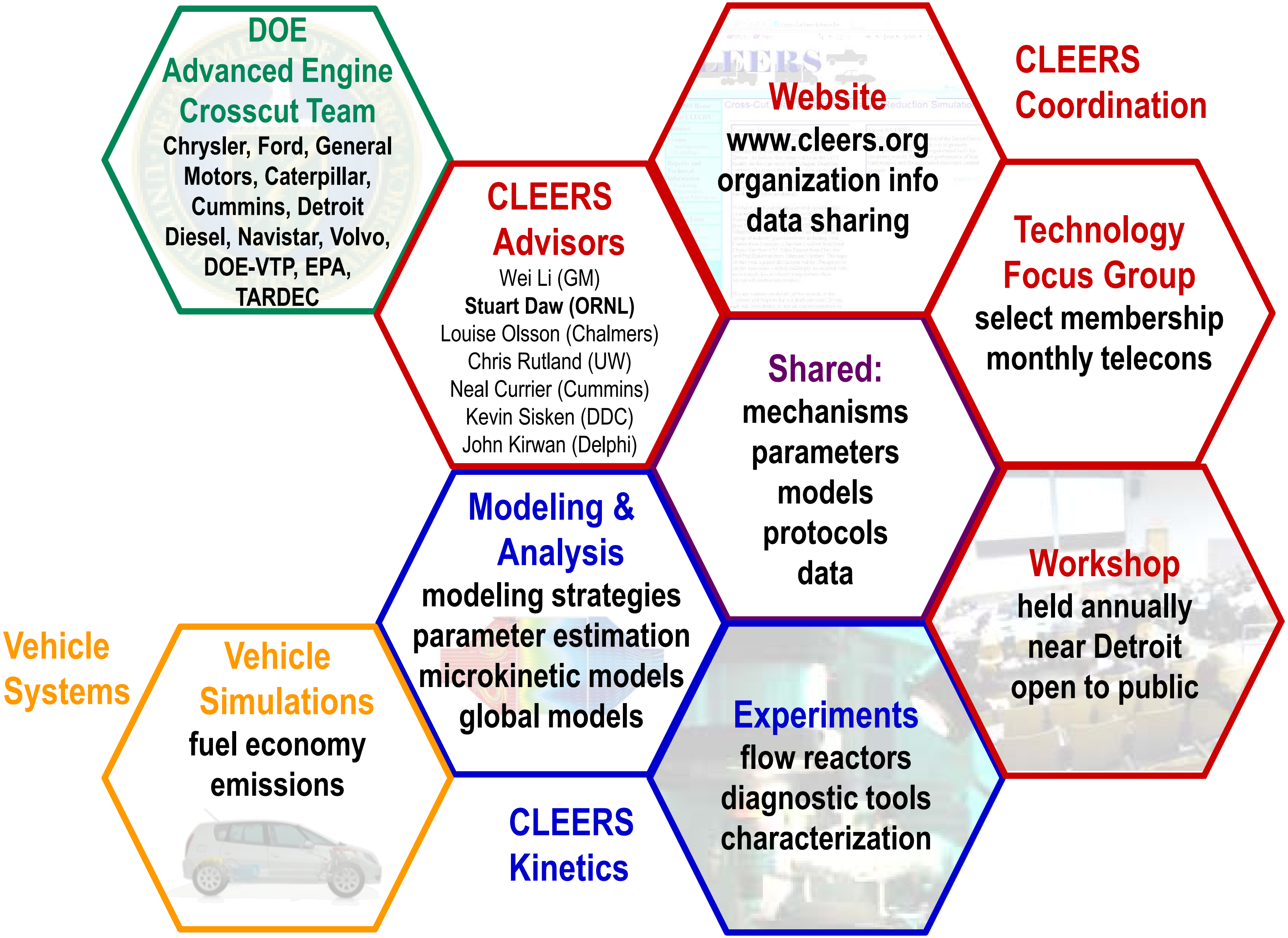
- design
- optimization
- control

- high NOx CIDI
- lean gasoline
- advanced combustion
- turbocharging/WHR

Milestones

FY	Project	Milestone	Status
2012	Coordination	Organize 2012 CLEERS public workshop	complete
2012	Kinetics	Measure hydrothermal aging impact on copper zeolite SCR catalyst function	complete
2013	Coordination	Expand CLEERS database	on schedule
2013	Kinetics	Measure NOx reduction kinetics and NH_3 storage on a commercial zeolite SCR catalyst under conditions relevant to low temperature exhaust applications	complete

Overall Approach for CLEERS Activities



Technical Accomplishments (1)

- CLEERS Coordination
  - Organized 16th CLEERS Workshop
  - Coordinated monthly Focus Group teleconferences
  - Provided basic data in support of vehicle systems aftertreatment modeling
  - Expanded engine-out, kinetics, and aftertreatment model data sharing
  - Assisted U.S.DRIVE low-temperature workshop and dissemination of results
  - Coordinated 2013 industry priority survey
- CLEERS Kinetics: SCR
  - Characterized storage capacity and stability of NH_3 on a commercial small pore Cu zeolite as a function of temperature, pretreatment, feed composition, and aging
  - Developed strategies for estimating NH_3 storage model parameters
  - Worked with PNNL to quantify changes in global SCR model parameters with hydrothermal aging
  - Collaborated with Politecnico di Milano to develop reaction mechanisms that account for observed differences between NO oxidation and NO SCR reactivity

Technical Accomplishments (2)

- CLEERS Kinetics: LNT
  - Conducted detailed flow reactor characterization of BMW lean GDI LNT catalyst
    - revised CLEERS LNT protocol based on feedback from modeling partners
  - Collaborated with Gamma Technologies to improve kinetic parameter estimates
  - Worked with ICT Prague to model N_2O and NH_3 generation mechanisms, with particular emphasis on impact of PGM redox states
- CLEERS Kinetics: Oxidation catalyst
  - Demonstrated durability and facile desulfation of oxidation catalysts based on metal oxide coated supports

CLEERS Coordination: Approach & Accomplishments

CLEERS is an efficient means for communicating pre-competitive information

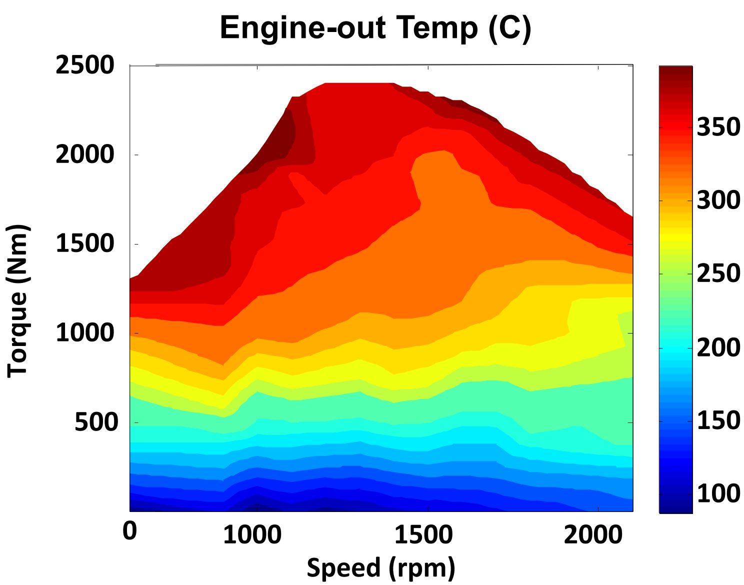
- **Website posts:**
  - additional transient LD and HD engine-out measurements
  - updated LNT and SCR catalyst characterization protocols and data
  - reference inputs for models
- **Monthly teleconferences:**
  - technical presentations of latest results to 20-40 participants
- **Industry priority surveys and scoping**
  - 2013 CLEERS Industry Priorities Survey Final Report to the Crosscut Team
  - Assistance to U.S.DRIVE Low-temperature Workshop
- **Workshop #16, April 10-12, 2013, UM Dearborn**
  - ~90 representatives of OEMs, suppliers, software developers, national labs, universities
  - 30 oral presentations, 10 posters, small group discussions
  - industry panel on low temperature emissions control challenges
- **Collaborations for SCR & LNT catalyst experiments & modeling**
  - supported collaborations with ICT Prague, Politecnico di Milano, and Gamma Technologies to develop improved kinetic mechanisms

BMW engine and aftertreatment chassis dynamometer measurements

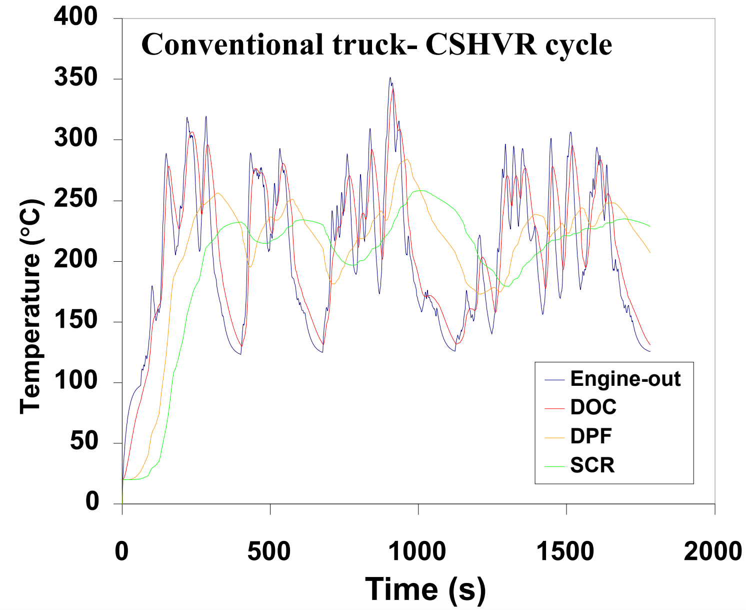
2012 CLEERS Workshop

CLEERS provides a mechanism for sharing measured & simulated engine + aftertreatment results

- Example: 2010 certified HD diesel engine-out data is being disseminated via CLEERS in a similar manner to the previous BMW LD GDI data
  - measured engine-out emissions and temperature at steady state and under transients
  - CLEERS kinetics data and low-order device models used to simulate DOC, SCR, and DPF inlet/outlet compositions and temperatures
  - combined data/models allow improved HD drive cycle simulations

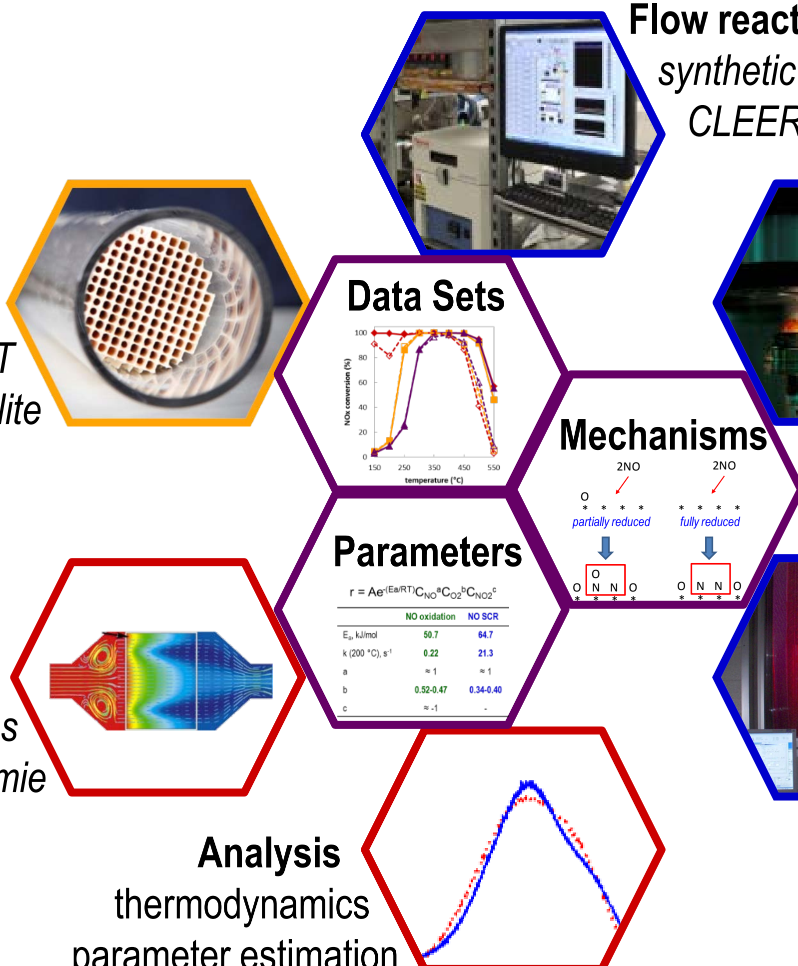


Autonomie



CLEERS Kinetics: Approach & Accomplishments

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



$r = Ae^{-(Ea/RT)} C_{NO}^{a} C_{O2}^{b} C_{NO2}^{c}$

	NO oxidation	NO SCR
E_a, kJ/mol	50.7	64.7
k (200 °C), s^{-1}	0.22	21.3
a	≈ 1	≈ 1
b	0.52-0.47	0.34-0.40
c	≈ -1	-

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

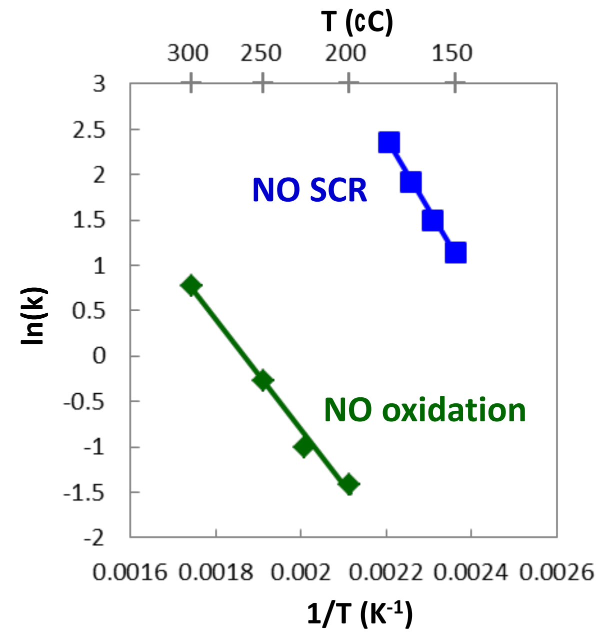
SCR of NO does not appear to proceed through NO oxidation to NO_2 over small pore Cu zeolites

collaboration with Politecnico di Milano

- Commonly assumed NO SCR mechanism:

NO oxidation:	$NO + \frac{1}{2} O_2 \rightarrow NO_2$	(rds)
+		
fast SCR:	$2 NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$	
NO SCR:	$2 NH_3 + 2NO + \frac{1}{2} O_2 \rightarrow 2N_2 + 3H_2O$	

- Measured NO oxidation and NO SCR reaction rates are inconsistent with assumed mechanism:
  - overall activity
  - apparent activation energy
  - dependence on O_2
  - inhibition by H_2O
- Currently using DRIFTS and flow reactor observations to develop more consistent mechanisms
- More accurate mechanisms will improve SCR model predictions, particularly at low temperatures



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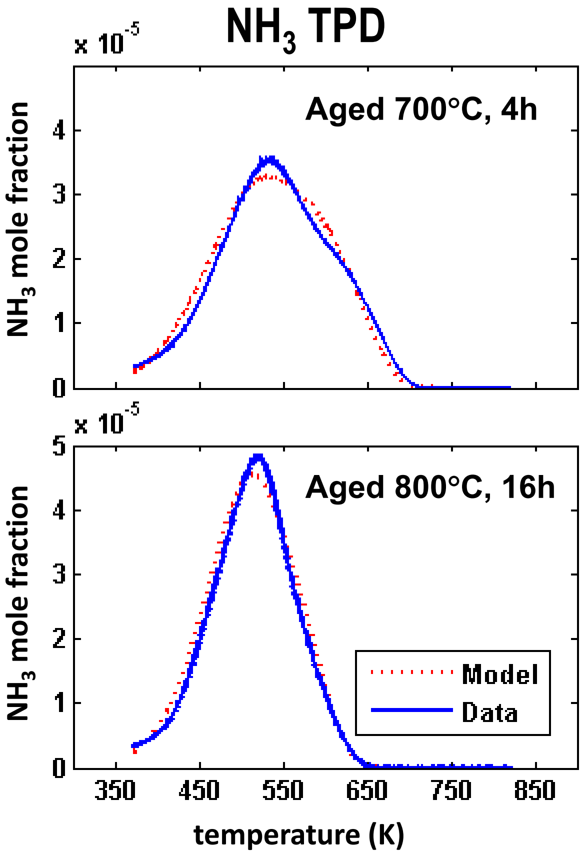
SCR NH_3 storage modeling requires richer data sets to improve parameter estimates

collaboration with PNNL (ACE023)

- Aging significantly reduces stability of NH_3 stored on small pore Cu zeolite SCR catalyst (FY12)
- Catalyst hydration and oxidation states also impact NH_3 storage capacity and stability
- Equilibrium isotherms (Temkin, 2-site Langmuir) generate reasonable fits to adsorption/TPD data
  - parameters vary with initial values & fit strategy
- Generating consistent, physically relevant parameters will require different experiments
  - direct measurement of isotherms
- Better predictions of NH_3 storage enable control strategies with higher NOx conversion and lower reductant consumption for urea SCR and combined (TWC+SCR, LNT+SCR) architectures
- Modeling and estimation strategies will be applied to low T adsorber materials in future



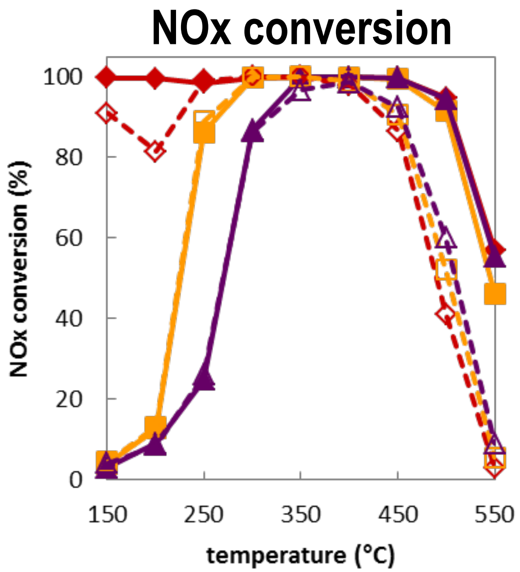
GM Cu zeolite
30000 hr^{-1}
aging:
  20% O_2
  10% H_2O
pretreat: 550°C
  10% O_2
  5% H_2O
adsorption: 150ÁC
  350 ppm NH_3
  5% H_2O
desorption: 150ÁC
  5% H_2O
TPD: 2°C /min
  5% H_2O

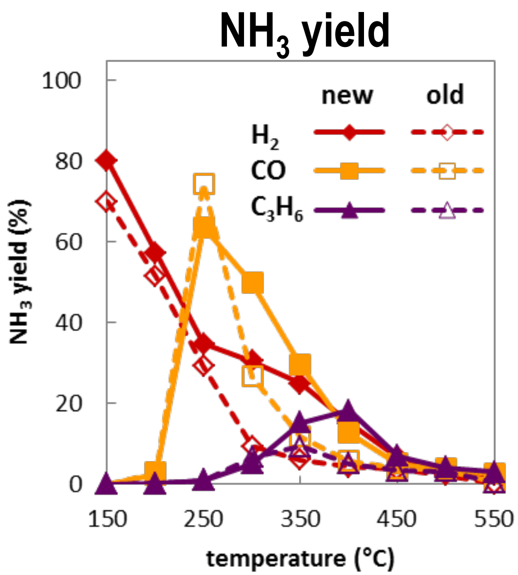
	700C 4h	800C 16h
capacity (mol/l)	0.48	0.45
ads. enthalpy (kJ/mol)	46	48
coverage factor	0.89	3.05

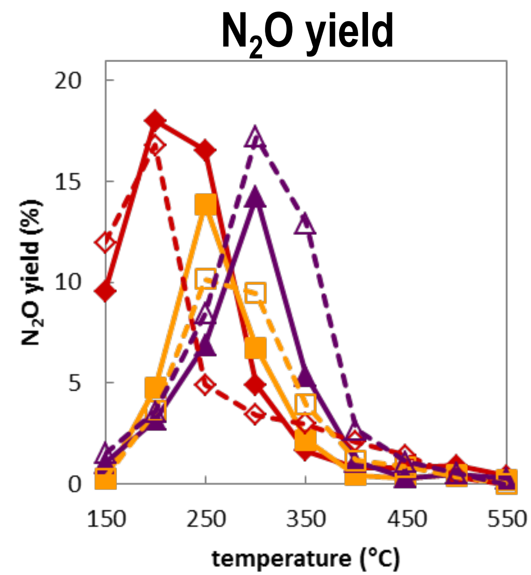
Newer BMW LNT shows similar performance and selectivity trends to prior CLEERS formulation

collaboration with Gamma Technologies

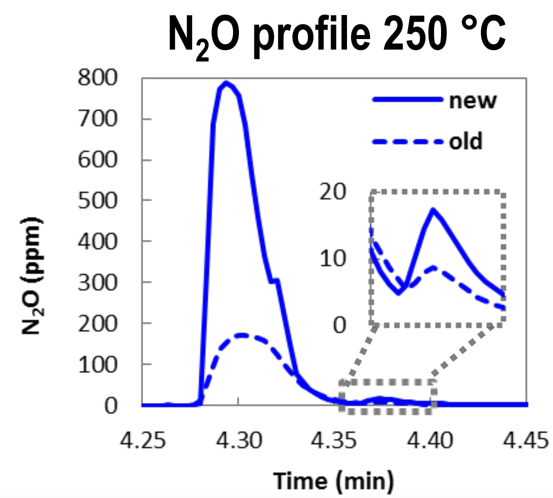
old: from Umicore
new: from BMW 120i
30000 hr^{-1}
60 s lean:
  300 ppm NO
  10% O_2
5 s rich:
  3.4% H_2
  or 3.4% CO
  or 0.38% C_3H_6
both:
  5% H_2O
  5% CO_2







- Conducted CLEERS LNT protocol, other characterization experiments
- Performance and selectivity trends similar; newer BMW LNT has:
  - better high T conversion for all reductant types
  - higher NH_3 yield at mid-range T (lower OSC?)
- Comparison of model parameter estimates underway
  - test robustness of models, mechanisms to change in formulation
  - provide data and parameters on updated formulation to CLEERS

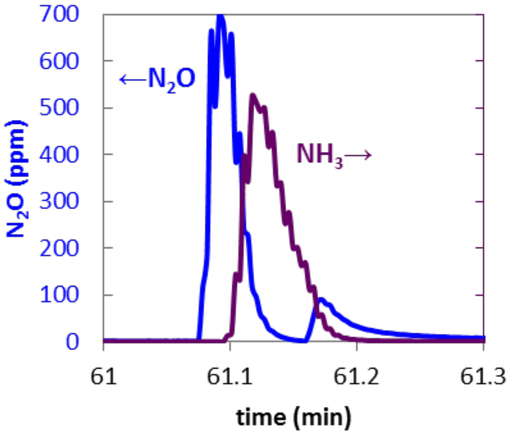


Secondary N_2O formation due to oxidation of N- & C-containing intermediates

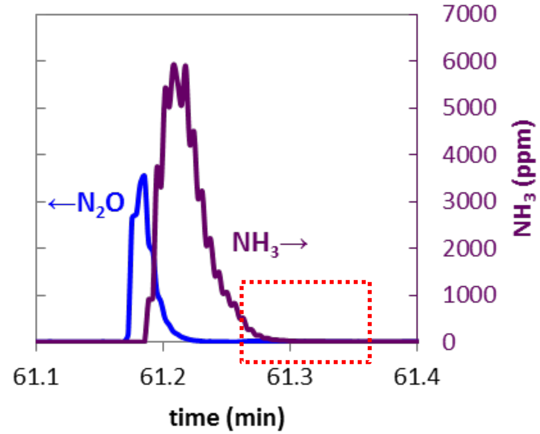
collaboration with ICT Prague

BMW LNT
150°C
30000 hr^{-1}
60 s lean:
  300 ppm NO
  10% O_2
5 s rich
  3.4% H_2
both:
  5% H_2O
  0 or 5% CO_2

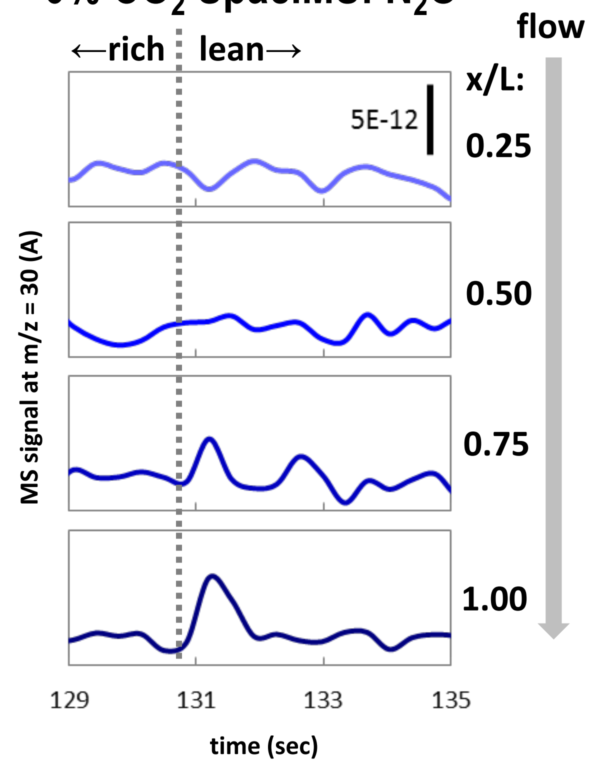
5% CO_2



0% CO_2



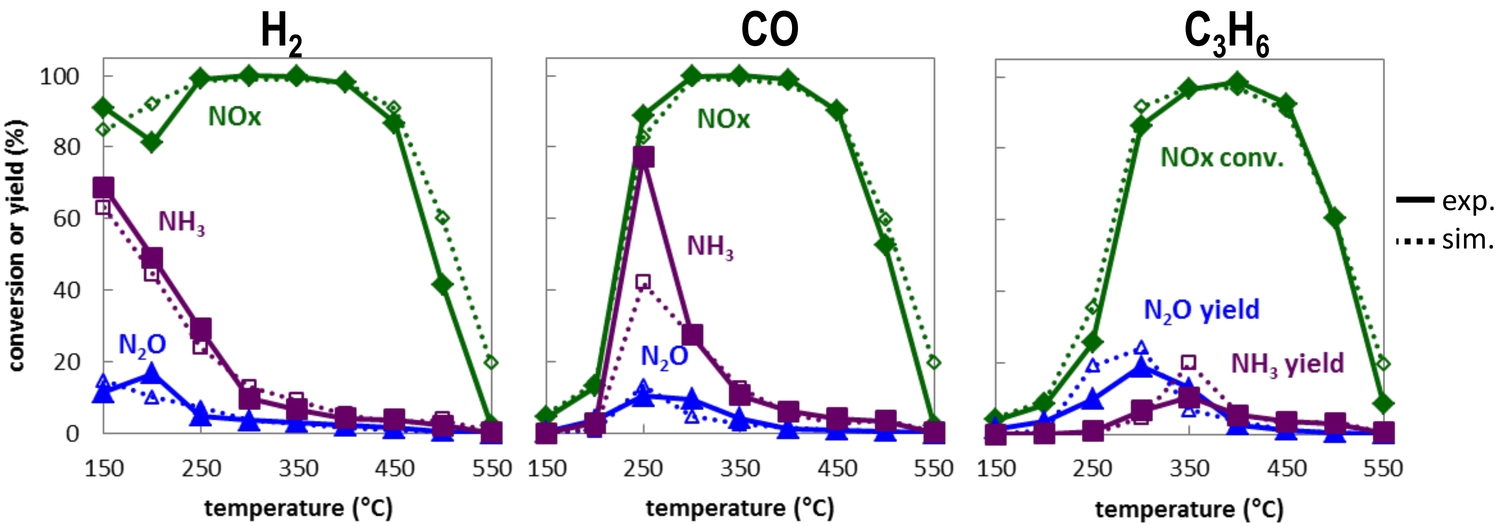
0% CO_2 SpaciMS: N_2O



- Second N_2O peak observed upon switch from rich to lean:
  - requires C source (rules out NH_3 oxidation mechanism)
  - forms in rear half of catalyst where no NOx stored
- Proposed mechanism:
  - rich: regeneration forms N- & C-containing intermediates that adsorb downstream
  - lean: oxidation of intermediates by O_2 forms N_2O
  - DRIFTS identification of intermediates underway
- Accurate mechanisms lead to better model predictions of N_2O (regulated as a greenhouse gas)

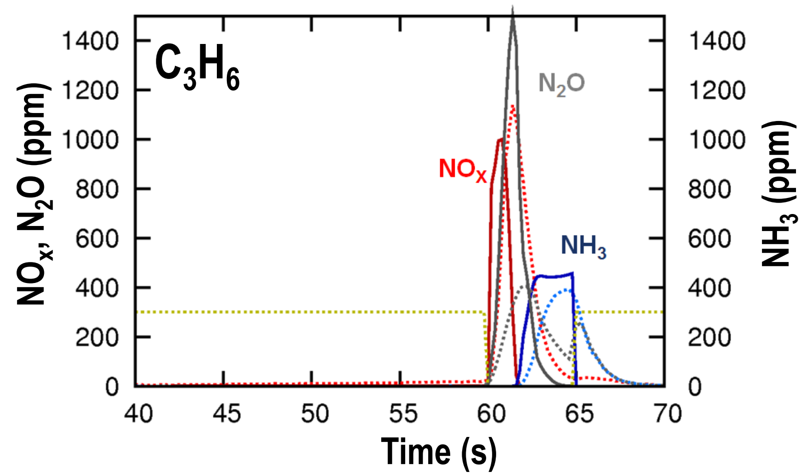
Improved regeneration mechanism improved LNT model predictions of NH_3 and N_2O formation

collaboration with ICT Prague



BMW LNT
30000 hr^{-1}
60 s lean:
300 ppm NO
10% O_2
5 s rich
3.4% H_2
or 3.4% CO
or 0.38% C_3H_6
both:
5% H_2O
5% CO_2

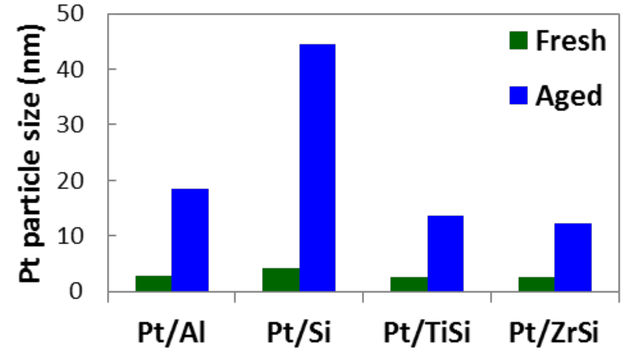
- Extended global LNT model to include:
  - impact of reductant type on Pt redox state
  - role of adsorbed species in secondary N_2O
- New mechanistic features yield improved agreement between predicted and measured N_2O and NH_3 production, both of which are key to meeting emissions regulations

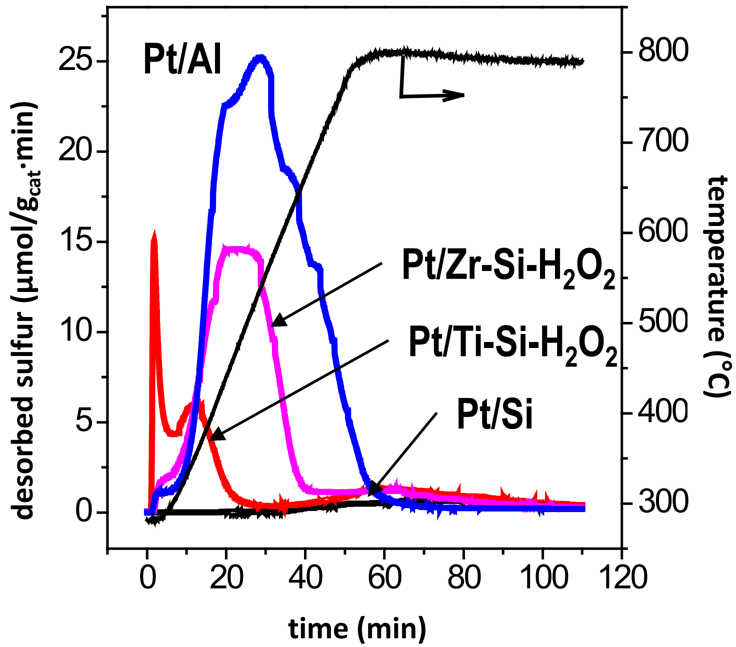


Oxide coated support improves oxidation catalyst performance and durability

collaboration with ORNL CNMS, ANL APS, Chonbuk National University

- Exploratory research in collaboration with DOE-BES and university partners
  - response to industry interest in low T emissions control (within existing projects)
  - transitioning to new project (ACE085)
- Novel approach for improved light-off performance, durability, sulfur tolerance
  - sol-gel coating of high surface area SiO_2 with metal oxides (TiO_2, ZrO_2)
  - coating enhances dispersion, durability, and redox properties of Pt
  - TiO_2-SiO_2 and ZrO_2-SiO_2 much easier to desulfate than Pt/Al_2O_3





Collaborations

- **Partners:**
  - National Laboratories: PNNL, SNL, ORNL (HTML, CNMS)
  - Universities: ICT Prague, Politecnico di Milano, University of Kentucky, University of Houston, Michigan Technological University, University of Tennessee, University of South Carolina, Chalmers University
  - Industry:
    - Gamma Technologies
    - DOE Advanced Engine Crosscut Team
    - Advanced Combustion and Emissions Control Tech Team
    - CLEERS Focus Group participants
- **Technology Transfer:**
  - CLEERS website postings: revised lab protocols; data sets from flow reactor, engine, and vehicle experiments
  - Publications and presentations: peer-reviewed journals, DEER, SAE, ICEC, ICC, CAPoC, CLEERS Workshop
  - Student/faculty exchanges

Future Work

- **CLEERS Coordination:**
  - Analyze and report on 2013 Industry Survey results
  - Continue planning, focus group, workshop, website, and DOE lab coordination
  - Accelerate data and modeling tool expansion
    - recruit postdoctoral fellow
  - Incorporate low-temperature emission control priorities into CLEERS activities & plans
- **CLEERS Kinetics:**
  - SCR:
    - Develop simple, accurate NH_3 storage modeling and parameter estimation strategies
    - Propose mechanisms for NO oxidation and NO SCR, emphasizing low T chemistry
  - LNT:
    - Estimate kinetic parameters for BMW GDI LNT, emphasizing low T operation
    - Further refine mechanisms for N_2O formation
  - Low temperature emissions control technologies:
    - Identify modeling strategies and key parameters for passive adsorber devices
    - Develop a CLEERS adsorber protocol and begin experimental characterization

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 & protocols; data & model source for parallel DOE projects and CRADAs
  - Fundamental understanding and modeling of commercial catalyst mechanisms
- **Collaborations**
  - PNNL; ICT Prague; Politecnico di Milano
  - Collaborations among industry, national laboratories, universities, and foreign institutions through CLEERS organizational structure
- **Future Plans**
  - Continue coordination activities: workshop, telecons, website, priorities survey
  - Accelerate data and modeling exchange expansion
  - 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