

CLEERS: Aftertreatment Modeling and Analysis

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Pacific Northwest National Lab

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ACE023

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Overview

► Timeline

- Status: On-going core R&D
- DPF activity originated in FY03
- Now also includes LNT (and PNA), SCR, and LTAT technologies

► Budget

- FY14 funding - \$750K
- FY15 funding - \$750K
 - SCR task
 - DPF task
 - PNA task (limited)
 - LTAT activities



► Barriers

- Emission controls contribute to durability, cost and fuel penalties
 - Low-temp performance is now of particular concern
- Improvements limited by:
 - available modeling tools
 - chemistry fundamentals
 - knowledge of material behavior
- Effective dissemination of information

► Partners

- DOE Advanced Engine Crosscut Team
- CLEERS Focus Groups
- 21CTP partners
- USCAR/USDRIIVE ACEC team
- Oak Ridge National Lab
- NSF/DOE-funded program with partners at Purdue, Notre Dame, WSU, Cummins and ANL

Relevance (and Goals)

- ▶ “CLEERS is a R&D focus project of the Diesel Cross-Cut Team. The overall objective is to promote development of improved computational tools for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems.”

CLEERS PNNL Subprogram Goal

Working closely with our National Lab partners, the CLEERS industrial/academic team and in coordination with our CRADA portfolio, PNNL will...

...provide the practical & scientific understanding and analytical base required to enable the development of efficient, commercially viable emissions control solutions and modeling tools for ultra high efficiency vehicles.

- ▶ VT program goals are achieved through these project objectives:
 - interact with technical community to identify relevant technological gaps
 - understand fundamental underlying mechanisms and material behavior
 - develop analytical and modeling tools, methodologies, and best practices
 - apply knowledge and tools to advance technologies leading to reducing vehicle emissions while improving efficiency
- ▶ Specific work tasks in support of the objectives are arrived at through:
 - focus group industrial monthly teleconferences, diesel cross-cut meetings
 - yearly workshops and surveys
 - Ongoing discussions on program priorities with the VT office

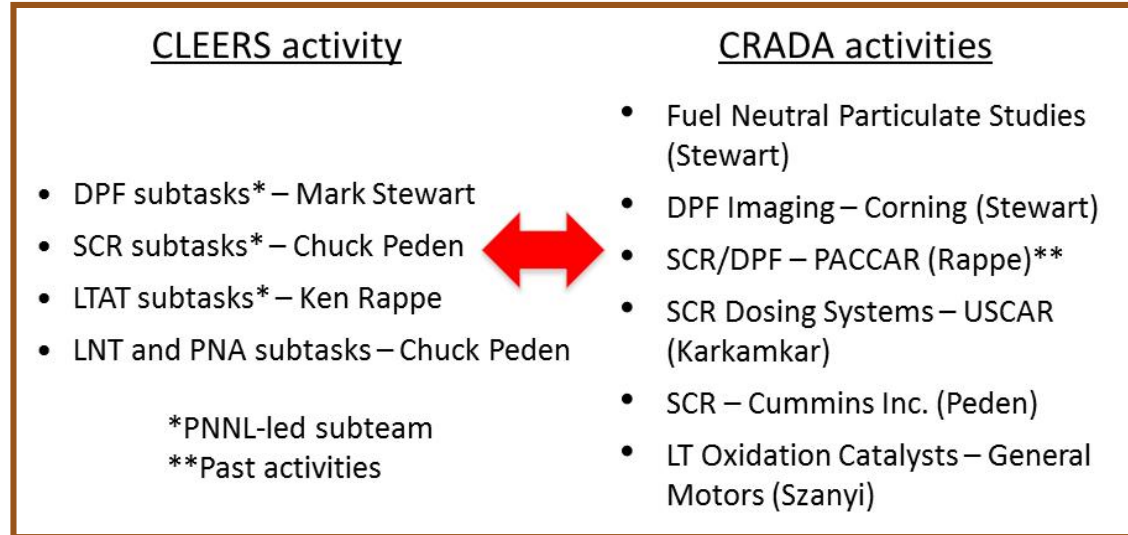
Technical Milestones (FY2014/2015 Scope Objectives)

- ▶ The overall performance measure of the project is inextricably linked to the interests of industry
 - PNNL CLEERS activities have resulted in the formation of new CRADAs
 - Tremendous success of the annual workshops
 - Strong participation in the monthly teleconferences
 - Specific performance measures are developed with the industrial/academic partners and captured in SOW
 - Specific technical targets and major milestones are described in our AOPs and annual reports to VT
- ▶ Selective Catalytic Reduction (SCR)
 - ✓ Prepare a range of model SCR catalysts for fundamental studies ; to include Fe/SSZ-13, Cu/SAPO-34 with varying Cu loading, and Cu/SSZ-13 with varying Si/Al ratios and Cu loadings.
 - ✓ Work with ORNL to apply data from SCR ammonia storage isotherm experiments.
- ▶ Low-temperature (LT) Aftertreatment
 - ✓ With the ACEC LTAT team, develop a catalyst testing protocol.
 - ✓ Initiate fundamental studies of low temperature oxidation catalysts.
- ▶ Diesel Particulate Filter (DPF)
 - ✓ Extend micro X-Ray CT analysis to multi-functional SCR filters with various catalyst loading levels

Approach/Strategy

► Approach - “Science to Solutions”

- We build off of our strong base in fundamental sciences and academic collaborations
 - Institute for Integrated Catalysis (IIC)
 - Environmental Molecular Sciences Laboratory (EMSL)
- With a strong pull towards industrial applications and commercialization
 - OEMs
 - TIER 1 suppliers
- Working closely with our partners and sponsors
 - ORNL (coordination of website, workshops, etc.)
 - DOE Advanced Engine Cross-Cut Team



► Strategy – “Balanced portfolio”

- Utilize open CLEERS work to support industry CRADA activities
- Maintain clear separation between CLEERS and CRADA activities

Technical Accomplishments (Outline)

► SCR

- Collaboration with ORNL on the modeling of SCR protocol and NH_3 storage experiments
- Materials characterization/mechanistic studies
 - Optimum preparation of model Cu/SAPO-34 catalysts: solid-state ion exchange (SSIE) and one-pot synthesis.
 - Characterization and reactivity of Cu/SAPO-34 as a function of Cu loading – effects on low and high temperature performance.
 - New studies of Fe/SSZ-13 catalysts as a function of Fe loading for wider temperature performance window.
 - Effects from Si/Al ratio on Brønsted acidity and Cu ion locations in Cu/SSZ-13.

► LTAT

- With ACEC LTAT team, developed a reaction protocol for testing of candidate LT-oxidation catalysts
- Initiating fundamental studies of candidate low temperature oxidation catalysts

► PNA

- Submitted several publications describing last few years of high temperature LNT studies .
- Initiated fundamental studies of passive NOx adsorber materials for low temperature applications.

► DPF

- Demonstrated that methods developed to distinguish catalyst from substrate in 3D CT images of multi-functional filters can be applied at various catalyst loadings
 - Correlated observed catalyst volumes with nominal loadings
 - Performed micro-scale filtration simulations with multiple larger sub-domains for a more representative picture of catalyst effects on filtration behavior

Experimental Studies of State-of-the-art Cu SCR Catalysts

- ▶ Cu/SSZ-13, Fe/SSZ-13, and Cu/SAPO-34 catalysts synthesized and studied at PNNL – *these model catalysts allow for fundamental studies of their catalytic and material properties*
 - Cu loaded into SSZ-13 via aqueous ion exchange is straightforward.
 - Fe loading via ion exchange requires low P(O₂) environments.
 - Many methods explored to incorporate Cu into SAPO-34. Very difficult to obtain reproducible model catalysts but significant progress has been made.
- ▶ Progress obtained this past year have included:
 - Initiated studies of the mechanism(s) of N₂O formation.
 - Synthesis of SSZ-13 with various Si/Al ratios (6, 12, 35) and multiple Cu ion exchange levels to address full range of effects of Cu loading and acid-site density.
 - Synthesis of Fe/SSZ-13 and Fe/beta using improved solution ion exchange methods.
 - One-pot synthesis of Cu-Fe/SSZ-13 and Cu-Fe/SAPO-34 *without* aqueous ion exchange.
 - Effects of Si/Al ratios on low-temperature reactivity (i.e., “light-off”).
 - Effects of Fe and Cu loading on reactivity, and studies of the fundamental differences between Fe- and Cu-based CHA catalysts.
 - Our latest results have been documented this year in:
 - 7 peer-reviewed publications; and
 - 11 presentations (5 invited) at scientific conferences.

Technical Accomplishments – SCR Studies

- ▶ Synthesis of Cu-Fe/SSZ-13 and Cu-Fe/SAPO-34 model catalysts to address both fundamental and applied scientific questions in NH_3 -SCR.
 - ▶ Formation of Cu-Fe/SAPO-34 *without* aqueous ion exchange:
 - **Solid-state ion exchange** with nanosized CuO at high temperatures in the presence of H_2O
 - **One-pot synthesis:** addition of Cu-TEPA co-SDA to the synthesis gels.
 - **One-pot synthesis:** addition of Fe-TEPA co-SDA to the synthesis gels.
 - ▶ Synthesis of SSZ-13 with various Si/Al ratios (6, 12, 35):
 - Model catalysts with a vast variety of Si/Al and Cu/Al ratio combinations to address siting and nature of catalytically active Cu ion sites.
 - Brønsted acid site density (affecting both Cu ion location and NH_3 storage) is varied using the same approach.
 - One-pot synthesis of Cu-Fe/SSZ-13 via addition of Cu(Fe)-TEPA co-SDA to the synthesis gels.
 - ▶ Synthesis of Fe/SSZ-13 and Fe/beta using improved solution ion exchange methods:
 - Ion exchange using FeSO_4 and SSZ-13 under the protection of N_2 .
 - Ion exchange using $^{57}\text{FeSO}_4$ prepared in house and SSZ-13 under the protection of N_2 .

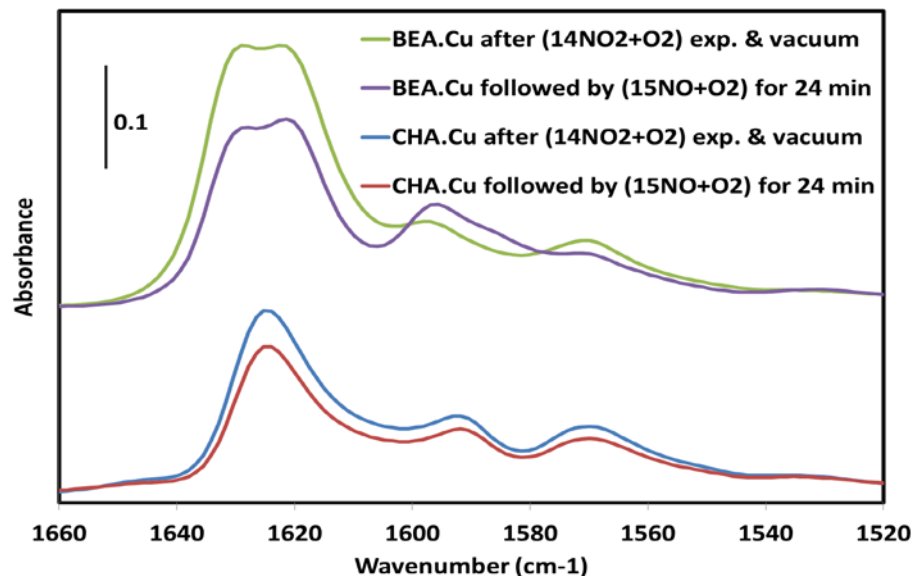
Technical Accomplishments – SCR Studies

- ▶ Synthesized catalysts used to address the following issues this year:
 - ▶ Model Cu/SSZ-13 catalysts:
 - Have addressed some specific issues with engine- and vehicle-tested catalyst materials.
 - Effects of Cu loading on reactivity and hydrothermal stability.
 - Effects of Si/Al ratios (6, 12, 35) on low-temperature reactivity (i.e., “light-off”).
 - Effects of co-cations (alkali and alkaline-earth cations, e.g., Na^+ , K^+ , Ca^{2+}) on Cu ion location, reactivity and hydrothermal stability.
 - ▶ Fe/SSZ-13 catalysts:
 - Fe loading effects on reactivity and hydrothermal stability.
 - Fe catalysts show considerably lower “light-off” temperatures during “fast SCR” reaction in contrast to Cu/SSZ-13.
 - What fundamental differences between Fe- and Cu-based CHA catalysts account for this and other differences?
 - Comparison between Fe/SSZ-13 and commercialized Fe/beta.
 - ▶ Cu,Fe/SSZ-13 catalysts.
 - Synergy between Cu and Fe ions in improving light-off and operational temperature window.

Technical Accomplishments (SCR task):

Studies of N_2O formation with Hai-Ying Chen, JM

One question specifically addressed was why Cu/CHA catalysts produce significantly less N_2O than other Cu/zeolites such as Cu/beta?



- ❑ FTIR results (above) show no exchange of nitrates with isotopically labeled NO for Cu/CHA.
- ❑ Formation of nitrates is also much more facile on Cu/beta relative to Cu/CHA (see reference below).



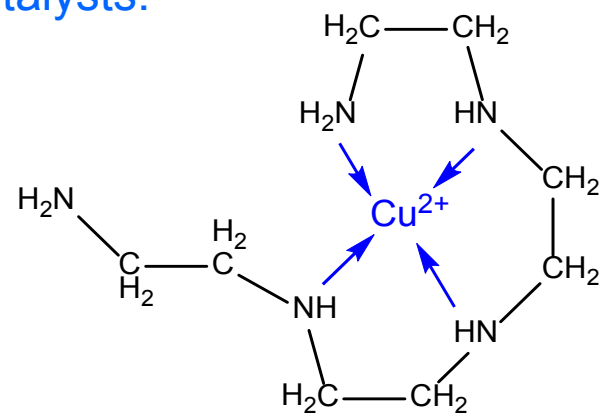
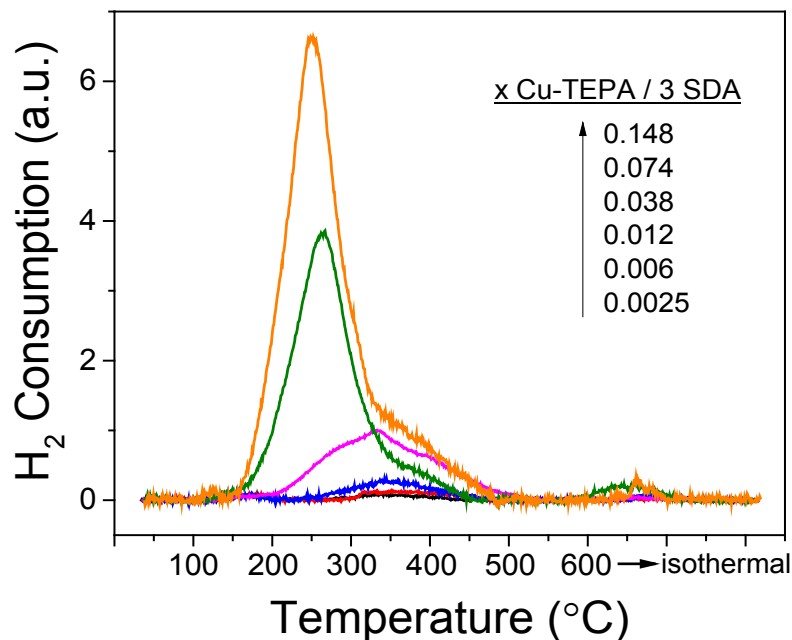
Johnson Matthey's Hai-Ying Chen (right) shows results from his summer sabbatical at PNNL to EERE Deputy Assistant Secretary for Transportation, Reuben Sarkar (second from right).

HY Chen, Z Wei, M Kollár, F Gao, Y Wang, J Szanyi, CHF Peden, *Journal of Catalysis*, submitted for publication.

Technical Accomplishments (SCR task): Simple “wet” method in Cu/SAPO-34 synthesis: One-pot with Cu-TEPA co-SDA

Solution ion-exchange is clearly not the best way to generate well-defined (active centers homogeneously dispersed) Cu/SAPO-34 catalysts.

x Cu-TEPA: 0.6 SiO₂ : 0.83 P₂O₅ : 1 Al₂O₃ : 3MOR : 60 H₂O
(x = 0.0025, 0.006, 0.012, 0.038, 0.074, 0.148)

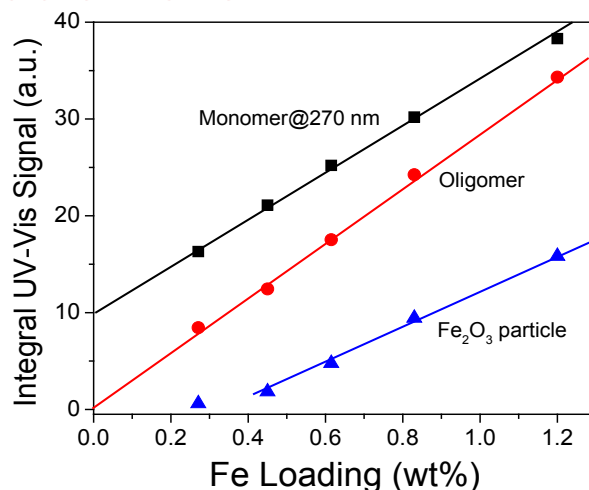
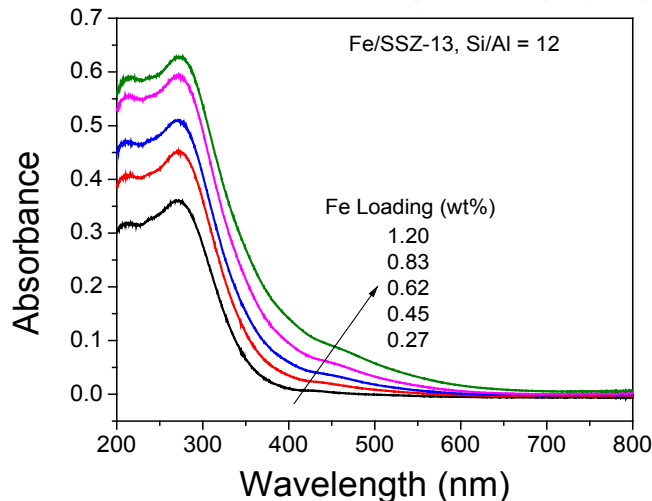


Cu-TEPA Complex

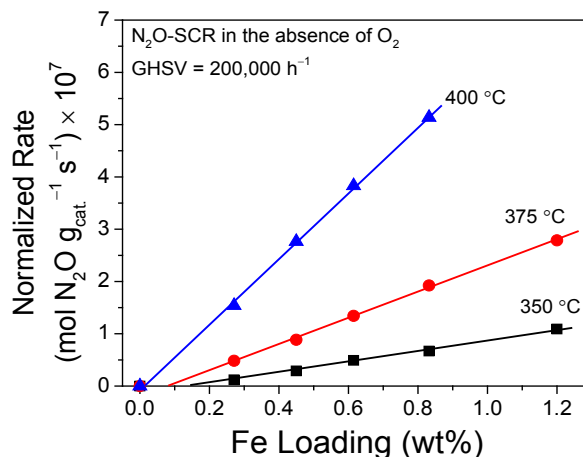
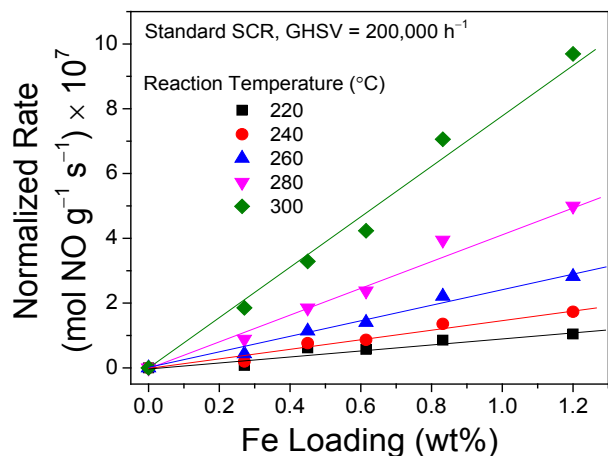
Use Cu-TEPA as a co-SDA, but not the only SDA. Fe-TEPA also works.
Stir the gel during synthesis for uniform Cu(Fe) dispersion.
These “well-defined” model catalysts will be used for fundamental studies.

Fe/SSZ-13 Catalysts: effects of varied Fe loadings

UV-Vis characterization



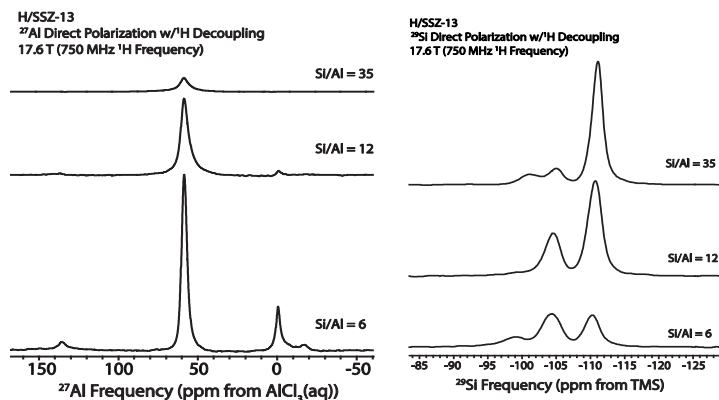
- Structure-function relationships in a large number of SCR-related reactions: NO and NH₃ oxidation, SCR, N₂O decomposition and SCR.
- Collaboration ongoing with Prof. Bill Schneider's theory group at Notre Dame (NSF/DOE program) on structure/function in Fe/SSZ-13 catalysts.



F. Gao, C. Paolucci, R. Kukkadapu, M. Kollar, Y. Wang, J. Szanyi, W.S. Schneider, C.H.F. Peden, in preparation.

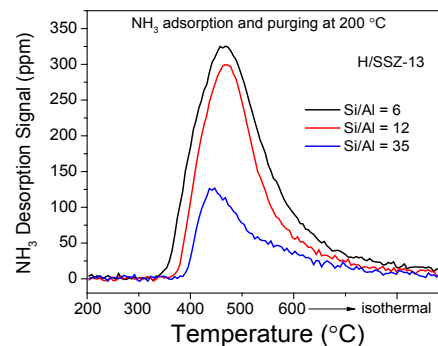
Technical Accomplishments (SCR task): Cu/SSZ-13 Catalysts: effects from Si/Al ratio and Brønsted acidity

Synthesis and utilization of a vast number of model catalysts with Si/Al = 6, 12, 35 and various Cu/Al ratios.

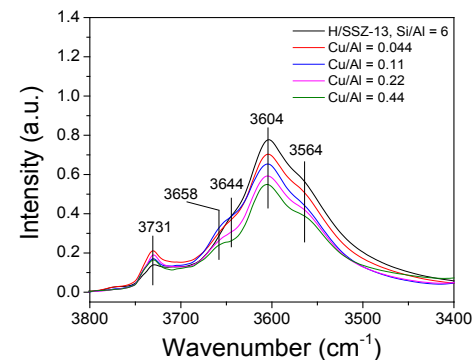


Solid-state NMR

H₂-TPR

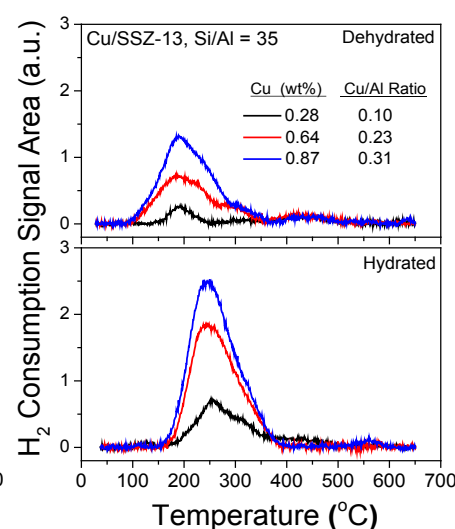
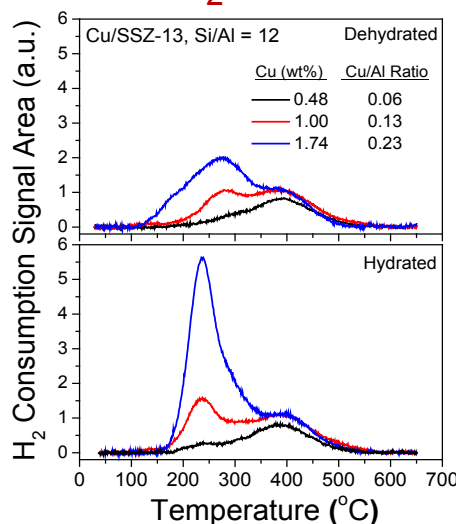
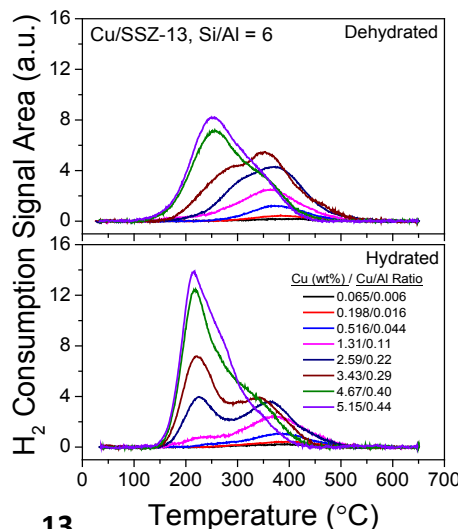


NH₃-TPD



DRIFTS

Various spectroscopic methods to probe Al, Si distribution; Cu²⁺ redox, Brønsted acidity and acid site density.

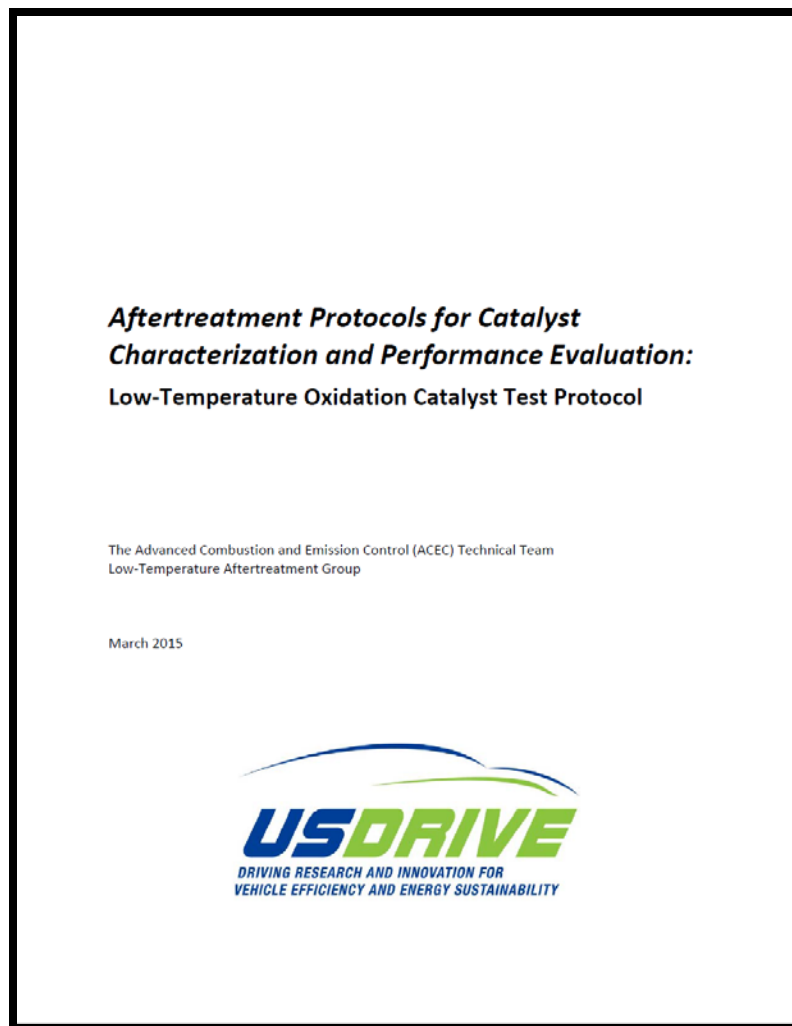


Technical Accomplishments – Low Temperature Aftertreatment (LTAT)

- ▶ With ACEC LTAT team, developed a reaction protocol for testing of candidate LT-oxidation catalysts.
- ▶ Initiating fundamental studies of candidate low temperature oxidation catalysts

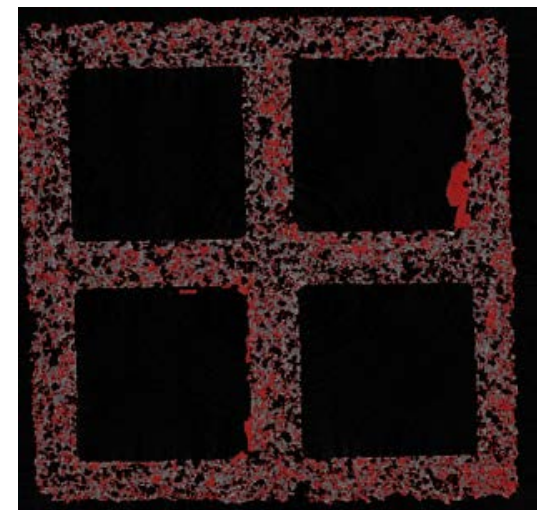
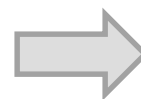
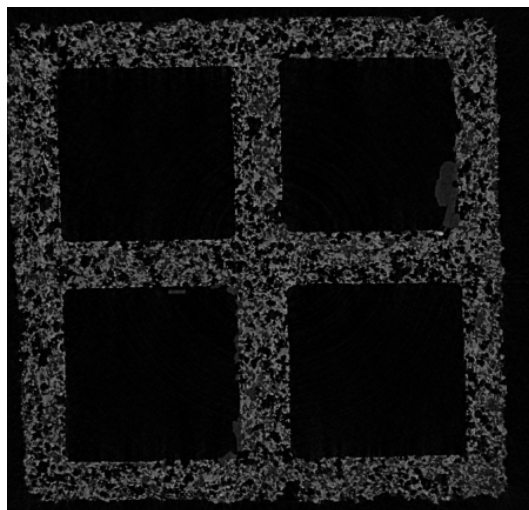
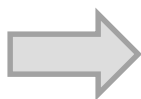
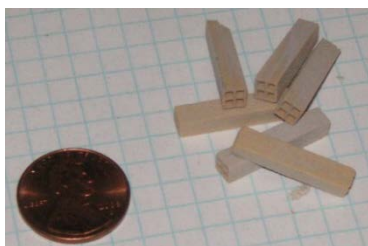
LTAT Protocol Development with ACEC Tech Team

- ▶ Low temperature aftertreatment (LTAT) research needs highlighted by the ACEC group under USDRIVE, and workshop report published in 2013.
- ▶ Need for protocols to enable accurate baseline testing of candidate low temperature emission control catalysts identified as a top priority by ACEC.
- ▶ PNNL (Ken Rappe) has taken the leadership role in developing the first of these protocols for candidate low temperature oxidation catalysts. This protocol is now being approved by USDRIVE leadership for publication.
- ▶ Ken Rappe now leading a new effort on a protocol for testing of candidate low temperature adsorber catalysts.



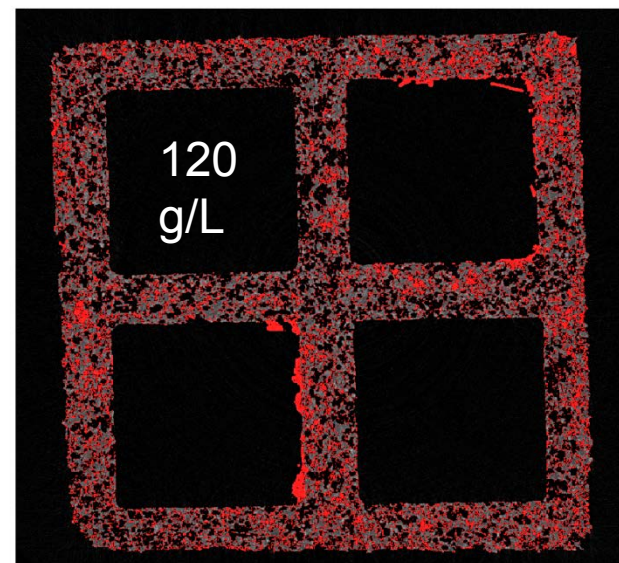
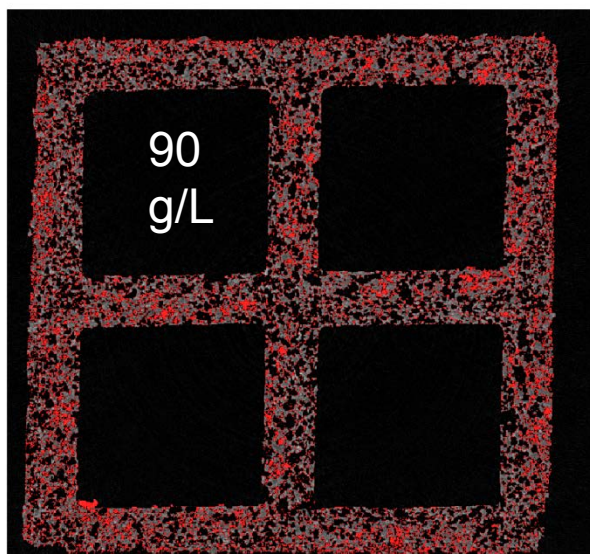
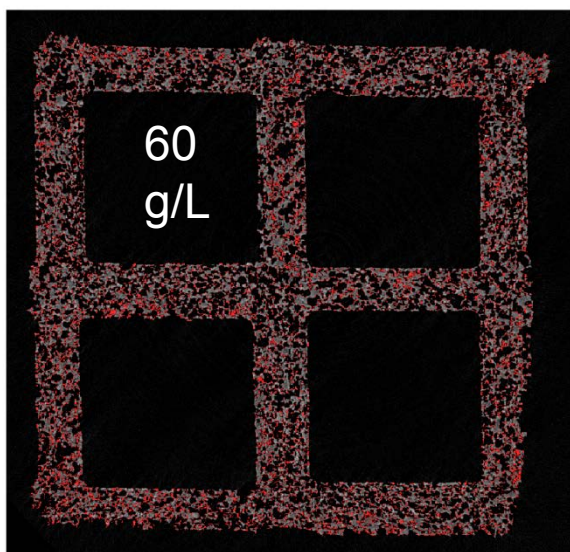
Micro X-Ray CT analysis of multi-functional filters

- ▶ High resolution X-Ray CT data obtained for 3 SCRF samples coated with Cu-CHA SCR catalyst by a major catalyst company: 60 g/L, 90 g/L, 120 g/L
- ▶ 2x2 channel samples were sectioned from 1"x1.5" mini-DPFs
- ▶ About 1 cm of each sample was scanned, or roughly 2% of the original mini-DPF volume
- ▶ Imaging processing methods were developed to distinguish catalyst from substrate and void volume in the 3D data - showing catalyst location and morphology



Micro X-Ray CT analysis of multi-functional filters

- ▶ Last year we showed preliminary analysis of the heavily loaded sample
- ▶ In FY14/15 the method was further developed and applied to the light and intermediately loaded samples to understand effects of loading level
- ▶ The catalyst was coated from one direction in the pre-plugged monoliths
 - Deposits of catalyst on the wall surfaces only existed on one side
 - In most, but not all locations, there was a clear gradient in catalyst loading across the wall thickness from one side to the other

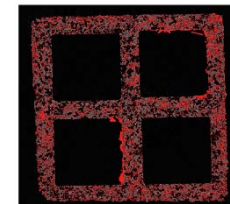
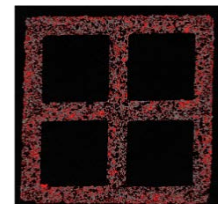
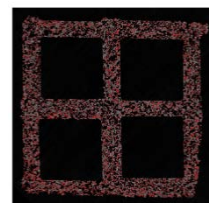


Cu-CHA catalyst shown in red

Observed catalyst loading and location

How much of the expected catalyst volume do we see?

Nominal Loading	Catalyst observed	Catalyst inside filter wall
~60 (g/L)	57.0 (mL/L)	96.7 %
~90 (g/L)	89.1 (mL/L)	97.6 %
~120 (g/L)	106.8 (mL/L)	93.8 %



Approximate zeolite properties:

CHA crystal density: 2.0-2.2 g/mL

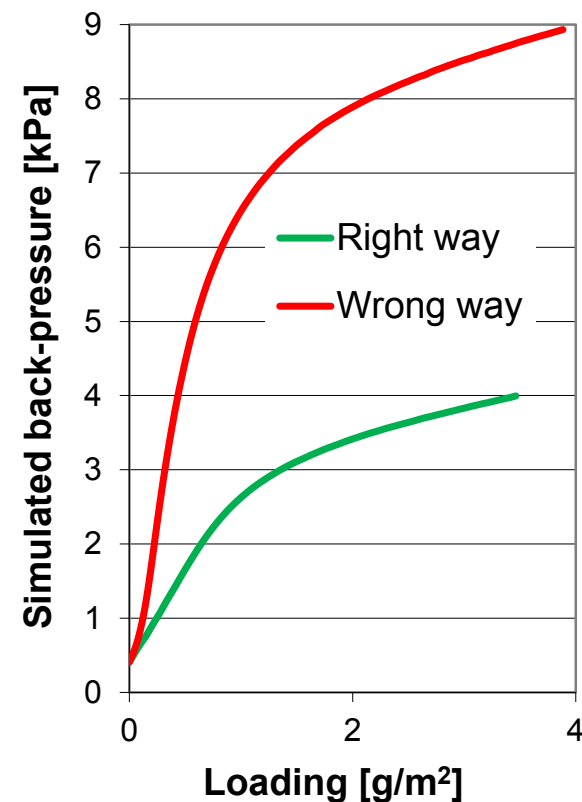
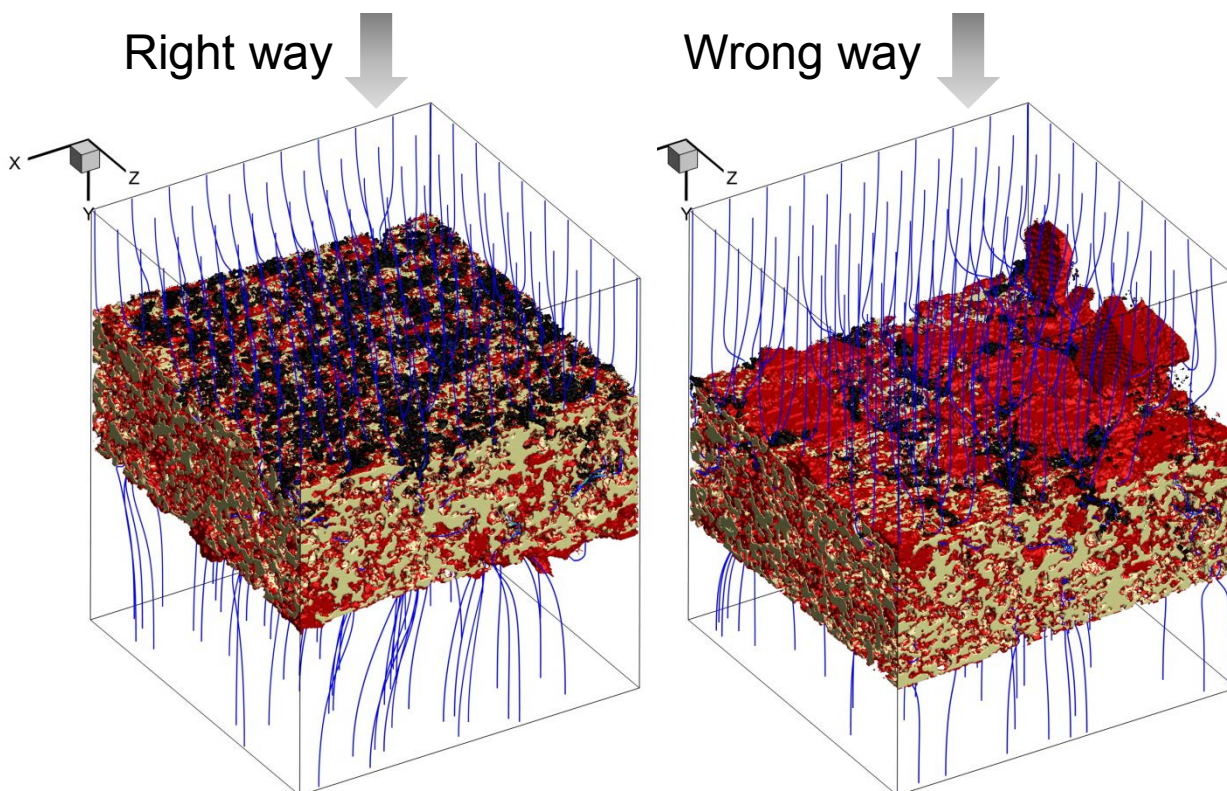
zeolite bulk density: 0.8-1.1 g/mL

→ catalyst porosity: 45%-64%

- ▶ Volumes of catalyst observed in the light and intermediate samples are consistent with a catalyst bulk density of ~1.0 g/mL
- ▶ Somewhat less catalyst was observed in the heavily loaded sample than expected
 - More of the catalyst is present as lumps and flakes on the wall surfaces and in the corners of the channels
 - The distribution of the catalyst is less even, and it may be harder to get a representative sub-sample

Effects of catalyst location on back-pressure

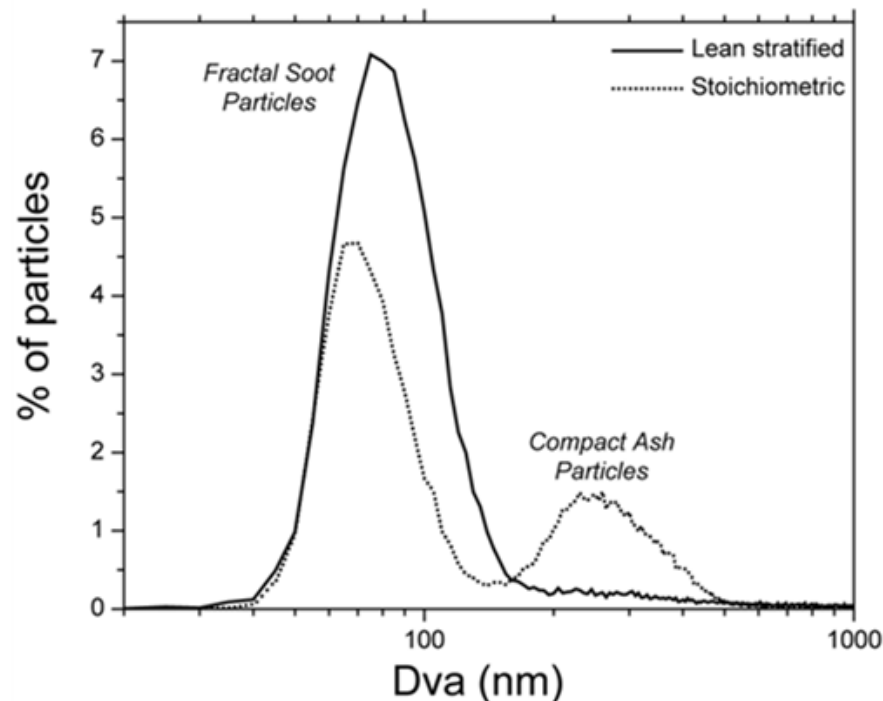
- ▶ Lattice-Boltzmann simulations of a very small sub-domain had demonstrated last year that catalyst distribution could explain observed differences in pressure drop during filtration - depending upon the orientation of the filter
- ▶ Larger simulations spanning more filter area also support that understanding



Compare to experimental observations: Rappe', Industrial & Engineering Chemistry Research 53-45 (2014) 17547-17557

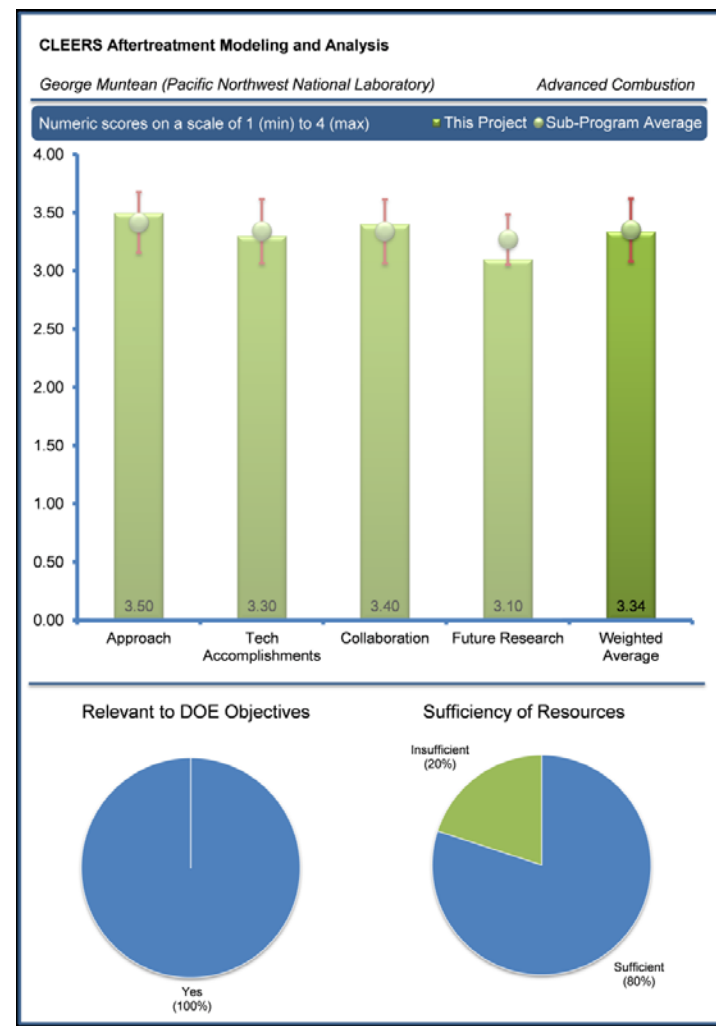
Characterization of particulates from production SIDI

- ▶ Completed analysis of data collected during cooperative experiments at ORNL with production SIDI engine
 - 2008 BMW 1-series 120i (E87))
 - 20 engine operating conditions, including lean homogeneous, lean stratified, and stoichiometric
 - With and without TWC aftertreatment
- ▶ Distinct sub-populations of particles were observed:
 - Diesel-like fractal soot
 - Compact Ca-rich ash
 - Volatile nuclei mode organics
- ▶ Stoichiometric conditions produced far fewer total particles
 - Higher proportions of Ca-rich ash (associated with lube oil)
 - Higher proportions of nuclei mode volatile particles (removed by TWC)
- ▶ Particulates produced under lean conditions dominated by Diesel-like fractal soot



Response to Previous Reviewer Comments

- ▶ Nearly all the comments from the reviewers last year were very supportive and complementary.
- ▶ Some comments/recommendations included:
 - ...for excellence, the project could add an industry survey (such as from the [USCAR] or 21st Century Truck Partnership partners) to confirm/identify needs and interests.
 - investigating deactivation pathways of candidate PNAs earlier in the project is recommended.
 - Add some aging/deactivation work for SCR catalysts.
- ▶ PNNL response:
 - PNNL (and ORNL) use a CLEERS survey to identify needs.
 - We agree with the reviewer. We do note, however, that (as supported by reviewers) PNNL focusses on fundamental issues with catalyst and filter materials.
 - PNNL's studies of aging of SCR catalysts are carried out as part of a CRADA program with Cummins.



Collaboration and Coordination with Other Institutions

► Collaborators/Coordination

- DOE Advanced Engine Crosscut Team (this group is the primary sponsor and oversight of all activities)
- CLEERS Focus Group
- USCAR/USDRIIVE ACEC team
- 21CTP partners
- Oak Ridge National Lab
- Very active collaboration with an NSF/DOE-funded program with partners at Purdue, Notre Dame, WSU, Cummins and ANL

► Acknowledgements

- PNNL: Haiying Chen (Johnson Matthey), Laura Righini (Politecnico Milano), John Luo (Cummins), Gary Maupin, Alla Zelenyuk, Jacqueline Wilson
- ORNL: Stuart Daw, Jim Parks, Josh Pihl, John Storey, Vitaly Prikhodko, Samuel Lewis, Mary Eibl, and support from the ORNL team
- DOE Vehicle Technologies Program: Gurpreet Singh and Ken Howden

Future Work

- ▶ SCR
 - Experimentally address the continuing fundamental issues being identified in modeling studies.
 - Continue studies of the reaction mechanism for Cu-CHA relative to Fe-CHA catalysts:
 - Why differences in NO oxidation, low- and high-temperature performance, and sensitivity to NO/NO₂ ratios?
 - Are there differences in the structure and location of these metal cations?
 - In collaboration with partners in new NSF/DOE-funded program, probe the nature and stability of the active Cu species in the CHA-based catalysts, especially for SAPO-34 zeolite-based catalysts.
 - Cooperate with ORNL to improve SCR characterization protocols and experiments with fresh and aged samples for model development
 - Incorporate expanded NH₃ storage dataset and CLEERS SCR protocol data from improved bench reactor at ORNL into two-site SCR global kinetics model
- ▶ NSR
 - Focus will be on low-temperature NO adsorption. Reducible oxides such as ceria and titania appear to be useful for this but likely prone to aging and sulfur poisoning.
 - Studies this next year will probe mechanisms of NO adsorption and desorption.
- ▶ DPF
 - Analyze commercial SCRF products using micro X-Ray computed tomography techniques to identify catalyst location with respect to filter substrate structure

Summary and Remaining Challenges

► SCR

- The nature and location of the active Cu species in Cu-CHA SCR catalysts is changing during operation. This likely explains the “seagull”-shaped performance curves observed for these catalysts.
- Combined FTIR vibrational spectroscopy/DFT calculations are providing additional insights into the structure of these various active Cu species.
- Improved and standardized methods for characterizing NH_3 storage and SCR performance and incorporating into practical kinetic models are still needed.

► NSR

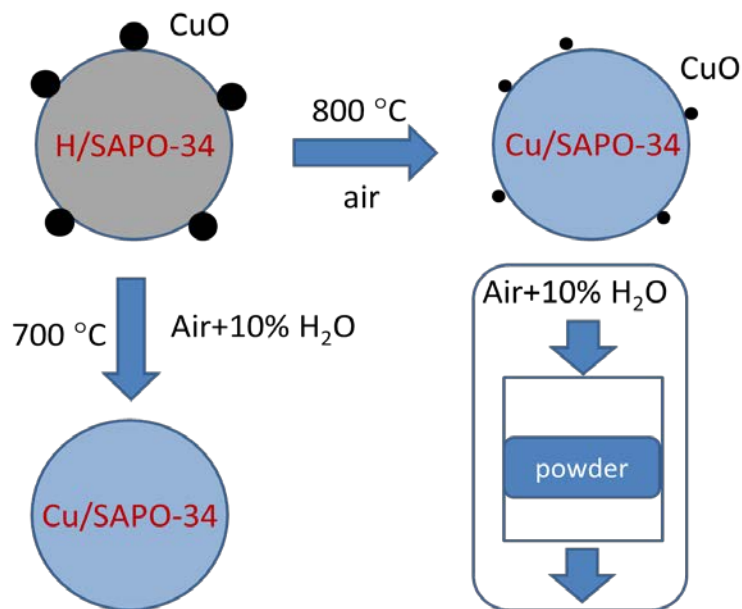
- Unlike Ba-based NSRs, K-based NSR catalysts on all support materials (Al_2O_3 , MgAl_2O_4 , TiO_2) studied to date are seriously degraded during hydrothermal aging. While promising high-temperature performance is achieved, efforts to stabilize K via the use of TiO_2 and $\text{K}_2\text{Ti}_6\text{O}_{13}$ supports were unsuccessful.
- Current studies are addressing the materials properties of low -temperature NO adsorption materials, and mechanisms for NOx adsorption/desorption.

► DPF

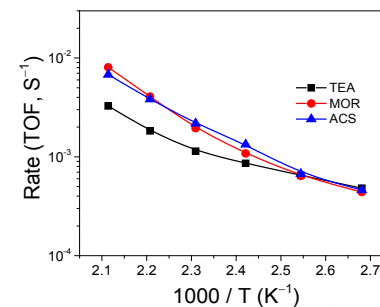
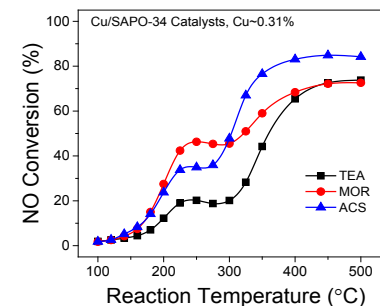
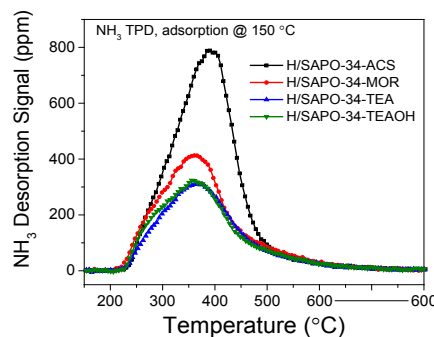
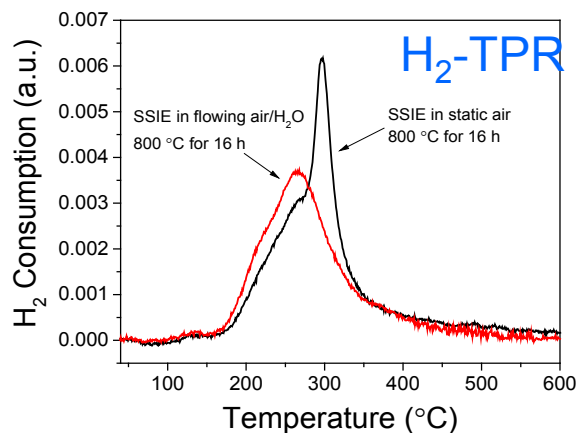
- Micro X-Ray CT analysis is a promising technique for understanding interactions between the porous substrate and catalyst coatings in multi-functional filters and the impacts those interactions have on filter performance
- Analogous techniques that do not rely on contrast between catalyst and substrate in the raw CT images may be necessary for other systems, such as TWC on GPF

Technical Back-Up Slides

Simple “dry” method in Cu/SAPO-34 synthesis: solid-state ion exchange

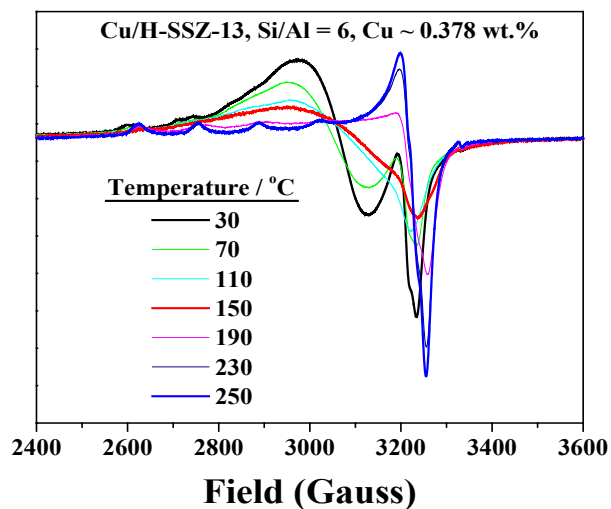


Developed a simple, readily adaptable method for the synthesis of Cu/SAPO-34 catalysts. H₂O promotes mobility of Cu ions at elevated temperatures without any sign of structural degradation (Brønsted acid density, BET area). More suitable for SAPO-34 than SSZ-13.

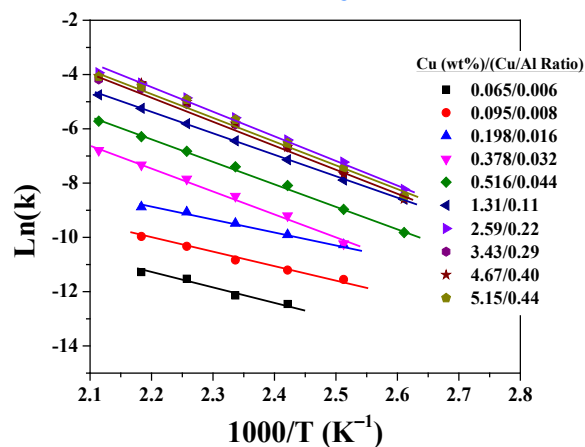


F Gao, ED Walter, NM Washton, J Szanyi, and CHF Peden, Appl. Catal. B 162 (2015) 501-514.

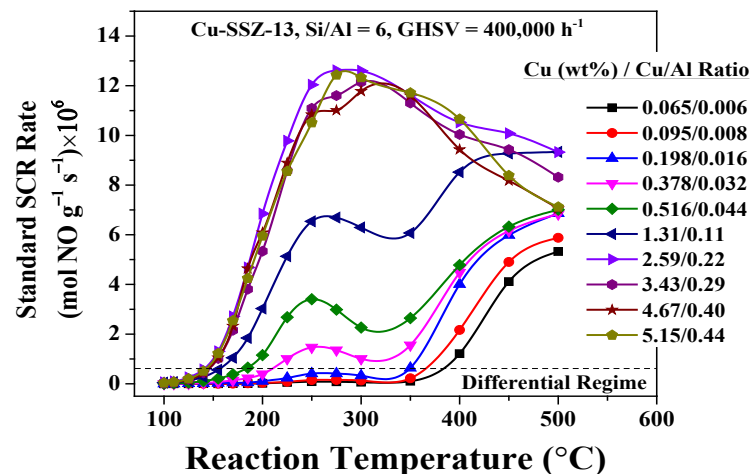
Cu/SSZ-13 Catalysts: effects from Cu loadings



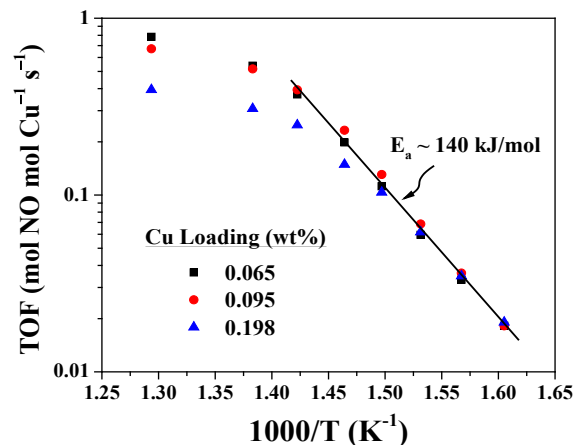
Cu ion mobility followed by EPR



Low-T Kinetic Regime



Normalized rates at different Cu loadings



High-T Kinetic Regime

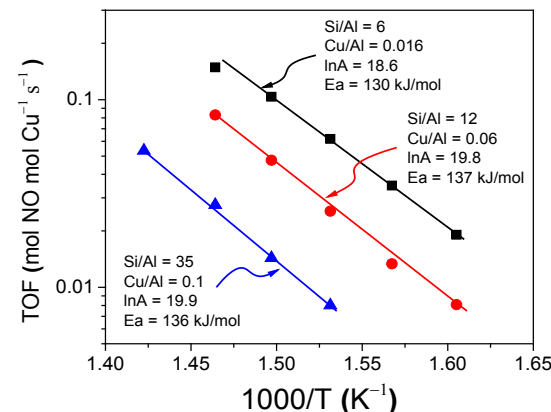
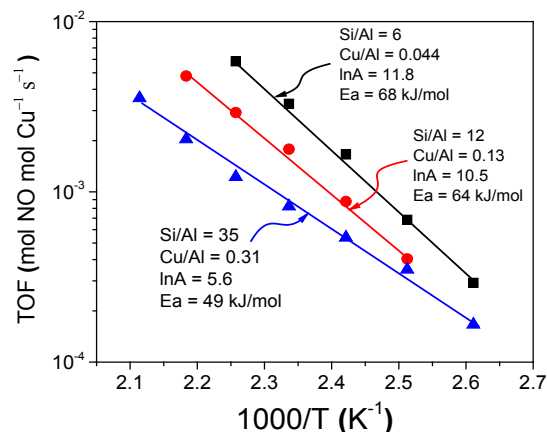
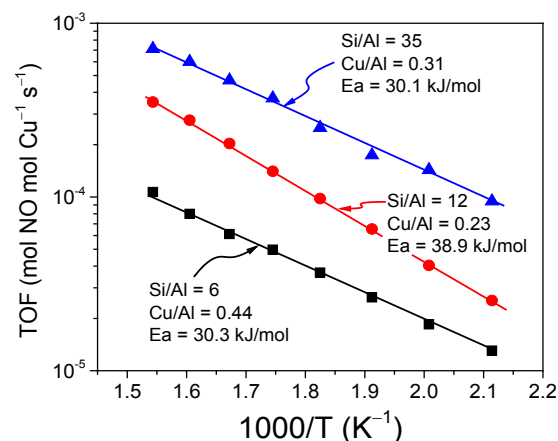
Identification of temperature-dependent kinetic regimes.

Correlate reaction rates with mobility of active centers.

Confirmation of isolated Cu²⁺ at 6MR active site for the high-T regime.

Cu/SSZ-13 Catalysts: effects from Si/Al ratio and Brønsted acidity

Synthesis and utilization of a vast number of model catalysts with Si/Al = 6, 12, 35 and various Cu/Al ratios.



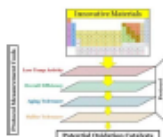
- NO oxidation follows a redox mechanism. Increasing Si/Al ratio promotes reaction by decreasing redox potentials for Cu active centers.
- NH₃ oxidation (not shown) and standard NH₃-SCR influenced by both redox of Cu active sites and Brønsted acidity.
- Rates at both low- and high-T regimes display dependence on NH₃ storage. Low-T activation energies determined by Cu-ion redox while high-T activation energies may reflect a demanding rate-limiting step, possibly –NH_{2(a)} formation.

F. Gao, E.D. Walter, M. Kollar, Y. Wang,
J. Szanyi, C.H.F. Peden, in preparation.

LTAT Oxidation Protocol described in poster presentation for the April 2015 CLEERS Workshop

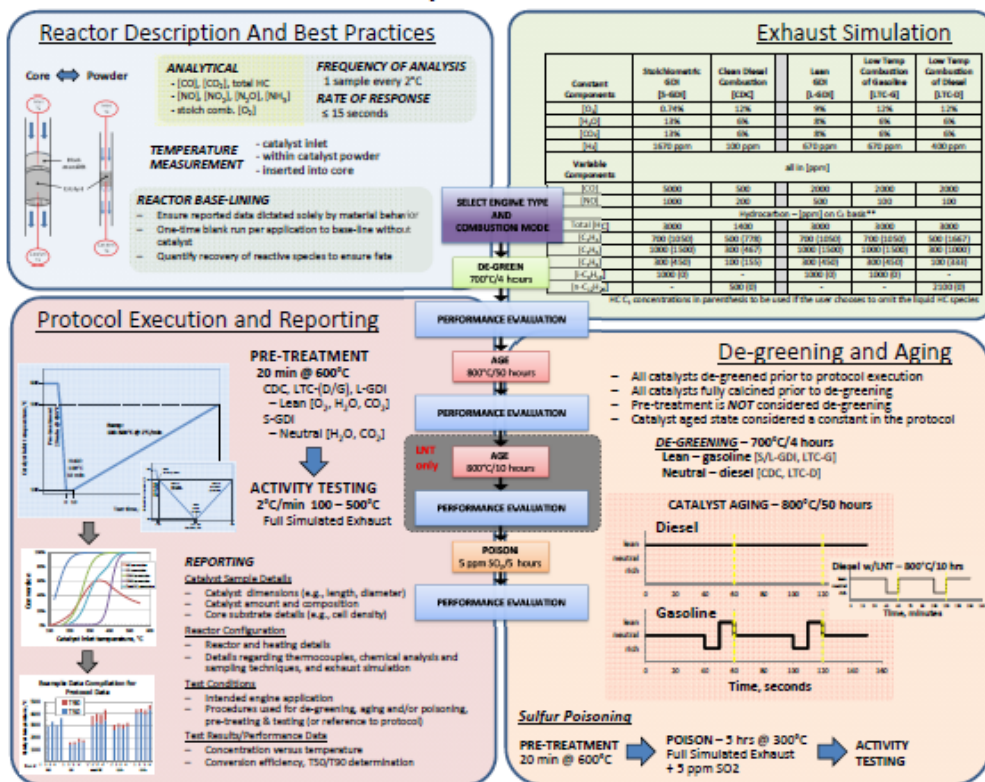


Low Temperature Aftertreatment (LTAT) Test Protocol Development



STEP 1

Low-Temperature Oxidation



Technical Accomplishments (PNA task): Focus on NO for Low Temperature Aftertreatment

Low temperature NSR storage likely limited by the light-off temperatures of DOCs for NO oxidation.

