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Fundamentals in Selective Catalytic Reduction (SCR), Filter, and Protocol

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PACIFIC NORTHWEST NATIONAL LABORATORY

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ACE023

Overview

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Timeline

- Status: On-going core R&D
- Particulate/filtration activity originated in FY03

Budget

- FY18 funding - $450K
  - SCR - $300K
  - Multi-functional device - $110K
  - Protocol - $40K

Barriers

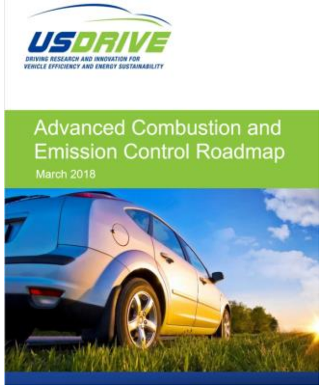
- Emission controls contribute to durability, cost and fuel penalties
  - Low-temp performance is now of particular concern
- Improvements limited by:
  - Available modeling tools
  - Chemistry fundamentals
  - Knowledge of material behavior
- Effective dissemination of information

Partners

- DOE Advanced Engine Crosscut Team
- CLEERS Focus Group
- 21CTP partners
- USCAR/USDRIVE ACEC team
- Oak Ridge National Lab
- Kymanetics, Inc.
- Cummins, JMC, FCA

Relevance

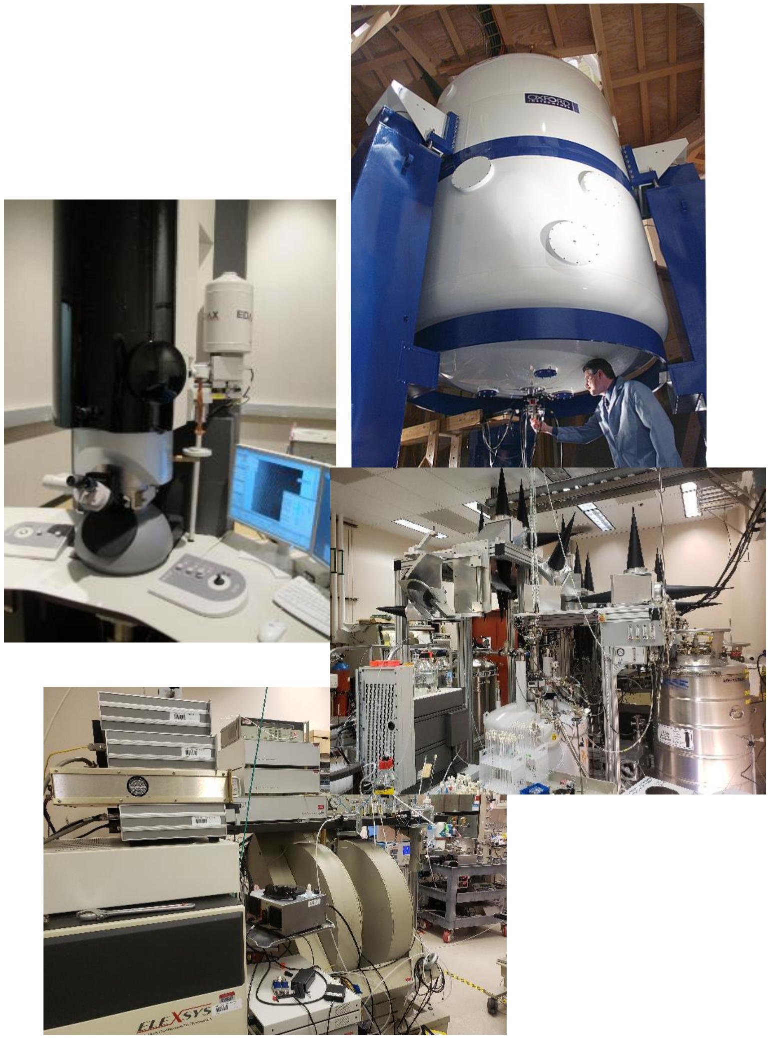
- Increasing internal combustion engine efficiency through advanced aftertreatment
  - Technologically-proven and cost-effective approach to:
    - Improving the fuel economy of the nation's fleet in near- to mid-term.
    - Reducing dependence on foreign oil and reducing carbon emissions.



- Driven by U.S. EPA Tier 3 Bin 30 emission standard.
- Requires aftertreatment technologies integrated with the combustion approaches.
- Achieve greater than 90% conversion of criteria pollutants (NO_x, CO, HCs) at 150°C for the full useful life of the vehicle (defined as the longer of 150,000 miles or 15 years).
- Need to develop models and simulation tools ranging from the molecular level to the system level to predict performance and better understand catalytic processes.

Approach/Strategy

- Build on our strong base in fundamental sciences to unravel the fundamental barriers to the improvement of low temperature activity and high temperature durability:
  - Institute for Integrated Catalysis (IIC)
  - Environmental Molecular Sciences Laboratory (EMSL)
- Orient strongly towards applications and commercialization
  - OEMs
  - TIER 1 suppliers
- Work closely with our partners and sponsors
  - ORNL
  - DOE Advanced Engine Cross-Cut Team



Technical Milestones and Go/No-Go Decisions

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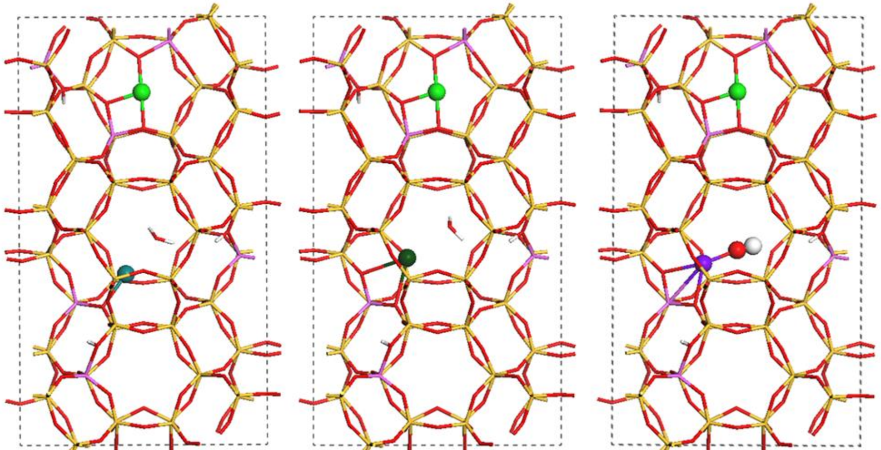
Milestones:

- Understand the degradation mechanism of Cu/SAPO-34 — 1/31/2019 √
- Understand the mechanisms of enhanced stability and performance by cocations on Cu/SSZ-13 — 3/31/2019 √
- Understand the site requirement and low temperature constraints for fast SCR on Fe/SSZ-13 and Fe/BEA — 9/30/2019 on track

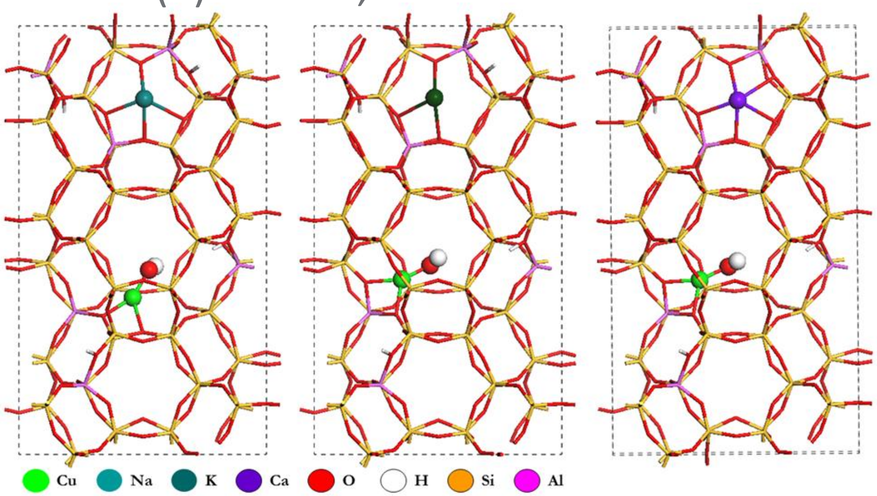
Go/No-Go Decisions:

- Demonstrate sufficient catalyst activity at 160˚C — 5/31/2019 √
- Identify key barriers to overcoming the “150˚C Challenge”, and demonstrate a clear path to achieve sufficient catalyst activity at 150˚C — 9/30/2021 on track

Accomplishments – SCR:
DFT Simulations Guide the Selection of Co-cations

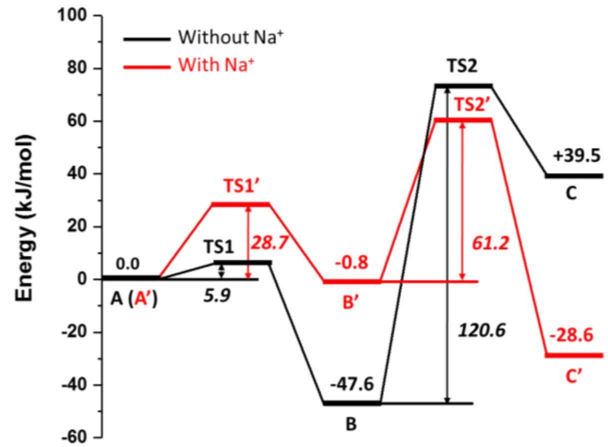


Cu(II) in 6MR, cocation in 8MR



Cu(II) in 8MR, cocation in 6MR

	Na^+/Cu^{2+}	K^+/Cu^{2+}	Ca^{2+}/Cu^{2+}
ΔE ($kJ\ mol^{-1}$)	+43.0	+20.6	-101.6



- Na^+ and K^+ delay dealumination, but they do not compete with Cu^{2+} to occupy windows of 6MR. However, they also destabilize $Cu(OH)^+$, causing CuO_x cluster formation much more readily. Their presence can promote maximization of Cu^{2+}-2Z sites when their contents are properly chosen.
- Ca^{2+} competes with Cu^{2+} for the thermodynamically most stable sites. They do not show beneficial co-cation effects.

Accomplishments – SCR: Formulating Cu/SSZ-13 SCR Catalysts with Co-cation for Improved Activity and Hydrothermal Stability

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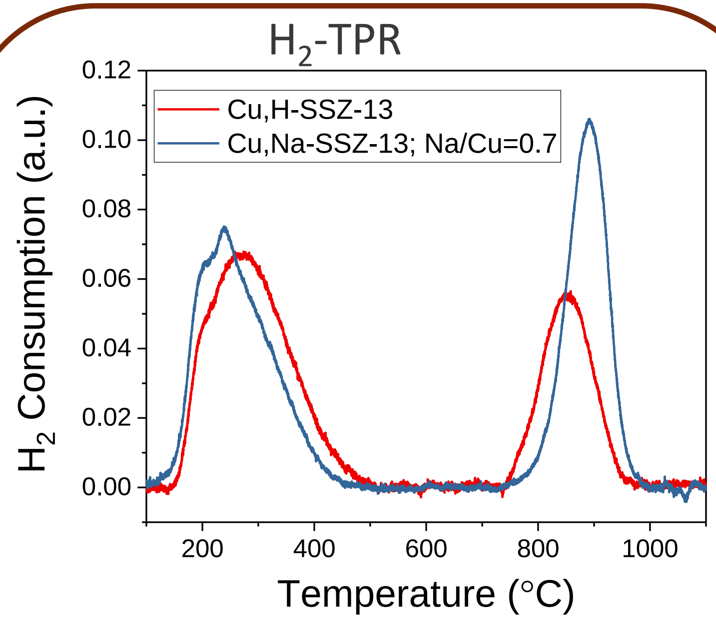
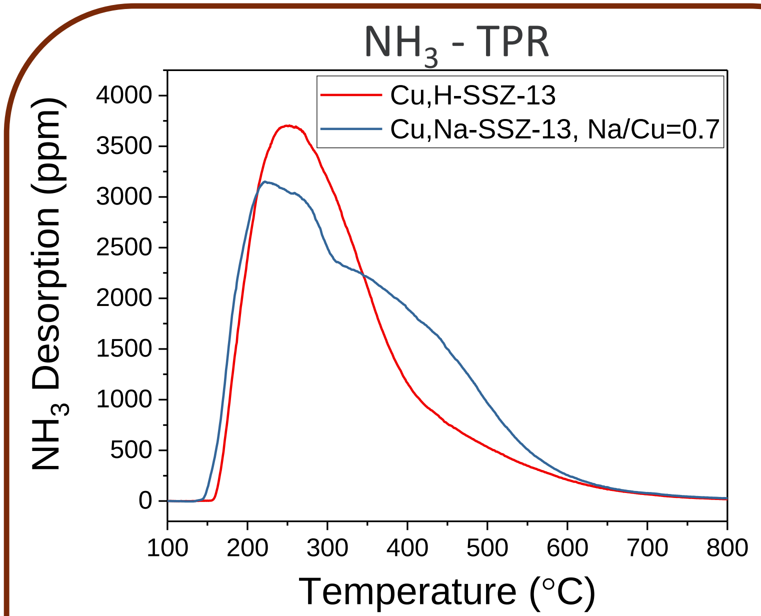
Ion-exchange H-SSZ-13 + $Cu(NO_3)_2$ + $NaNO_3$ → Slurry drying + calcination → Hydrothermal aging (800 °C, 16 h)

Optimized catalyst composition for Si/Al = 6: Cu loading 3.0 wt%, Na/Cu = 0.7

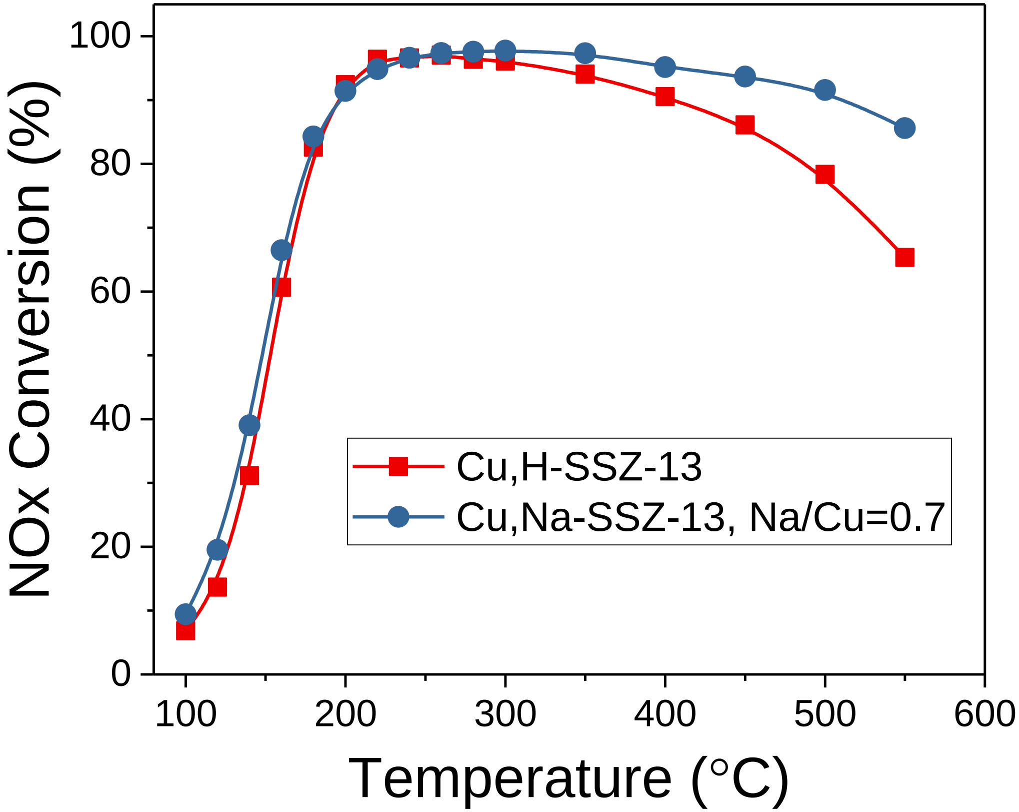


- Cu,Na catalyst contains more SCR active sites.



- Cu,Na catalyst contains more Brønsted acid sites (less dealumination).

Accomplishments – SCR:
Formulating Cu/SSZ-13 SCR Catalysts with Co-cation for Improved Activity and Hydrothermal Stability, cont'd



Standard SCR
GHCV ~ 100k h^{-1}.

- 60% NOx conversion at 160°C, and > 90% NOx conversions between 200-500°C in a harshly hydrothermally aged form – making significant progress towards the 150 Challenge.
- Na^+ co-cation plays import roles in preventing catalyst dealumination. This allows improved Cu dispersion during aging. Therefore, both structural integrity and active site preservation are improved at optimized Na/Cu ratios.

Accomplishments – SCR: Both *in situ* Advanced Characterization and Theory Unraveled the Mysterious Failure of Cu/SAPO-34 and Provided Guidance in Mitigating the Issue

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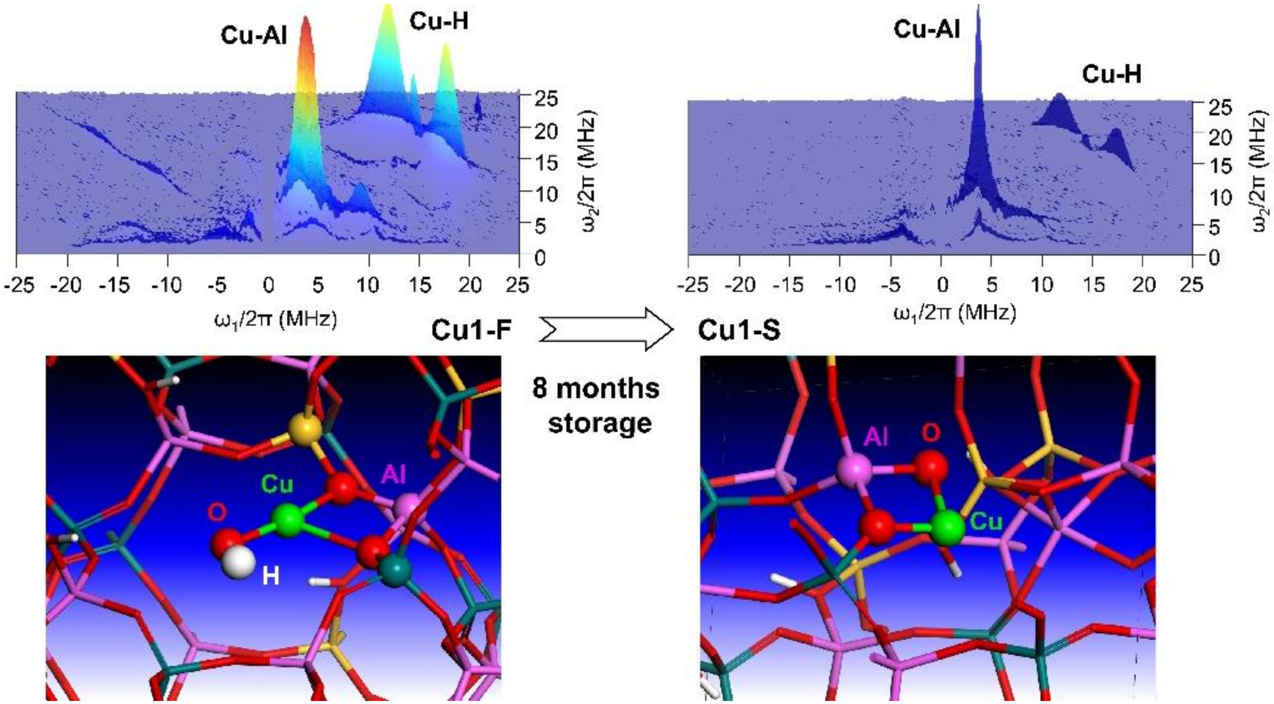
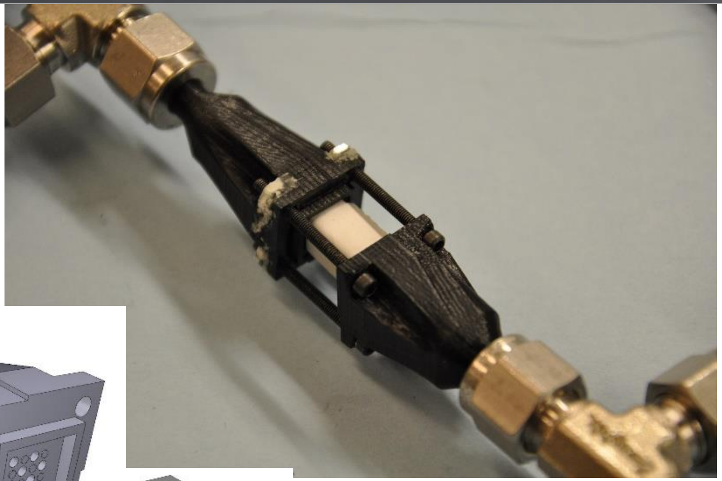


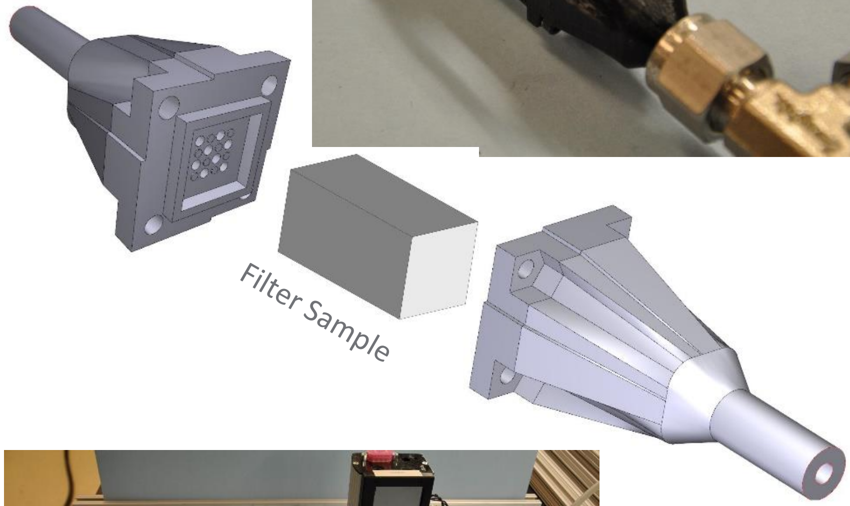
- Condensed H_2O in SAPO-34 pores facilitates the following three elementary steps, leading to permanent catalyst deactivation:
  - ZCuOH hydrolyzes to free $Cu(OH)_2$.
  - ≡Si-O(H)-Al ≡ hydrolyzes to generate terminal ≡Al.
  - Interaction between $Cu(OH)_2$ and terminal ≡Al to form SCR inactive Cu-aluminate.
- Catalyst stability can be improved by minimizing the contact of water with Cu, and optimizing Cu loading

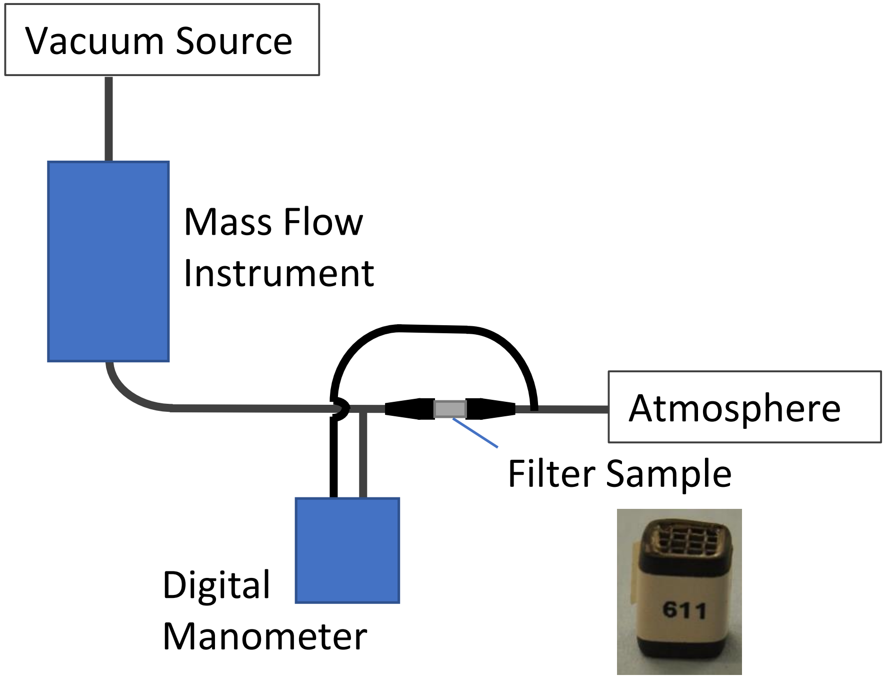
A.Wang, Y.Chen, E.D. Walter, N.M. Washton, D.Mei, T.Varga, Y.L.Wang, J.Szanyi, Y.Wang, C.H.F. Peden, F.Gao. ***Nature Communications***, 2019, 10:1137. https://doi.org/10.1038/s41467-019-09021-3

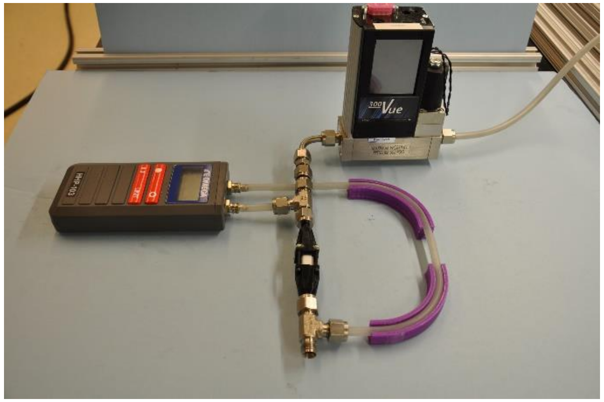
Technical Accomplishments (Multi-functional device task):
Measurement of Local Permeability

- New technique developed for measuring local permeability in multi-functional filters with zoned catalyst coatings.
- 3D printed manifolds allow fast and efficient mounting of filter sections.
- Printed features and flexible gaskets seal ends of channels in checkerboard pattern, forcing wall flow.









Technical Accomplishments (Multi-functional device task):

Pore-scale Characterization and Flow Models

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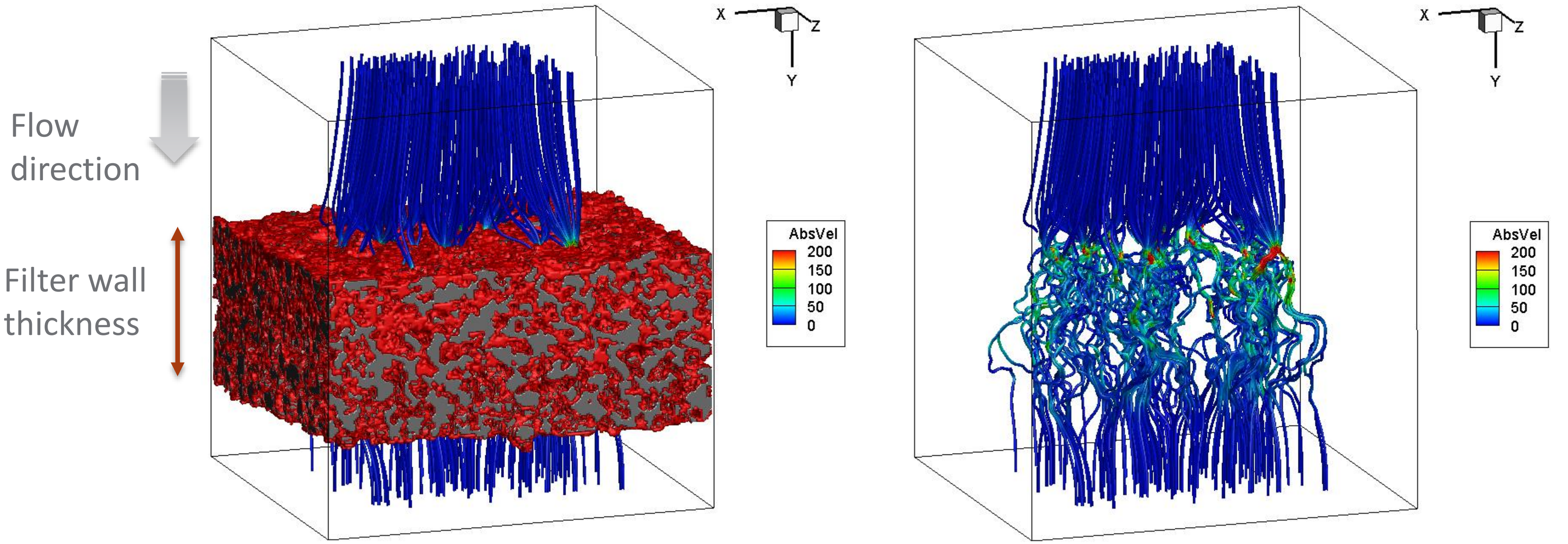
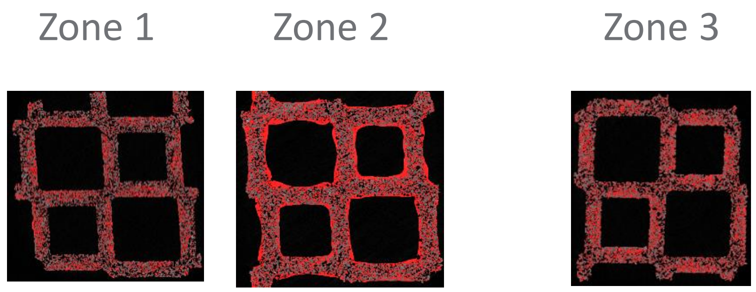
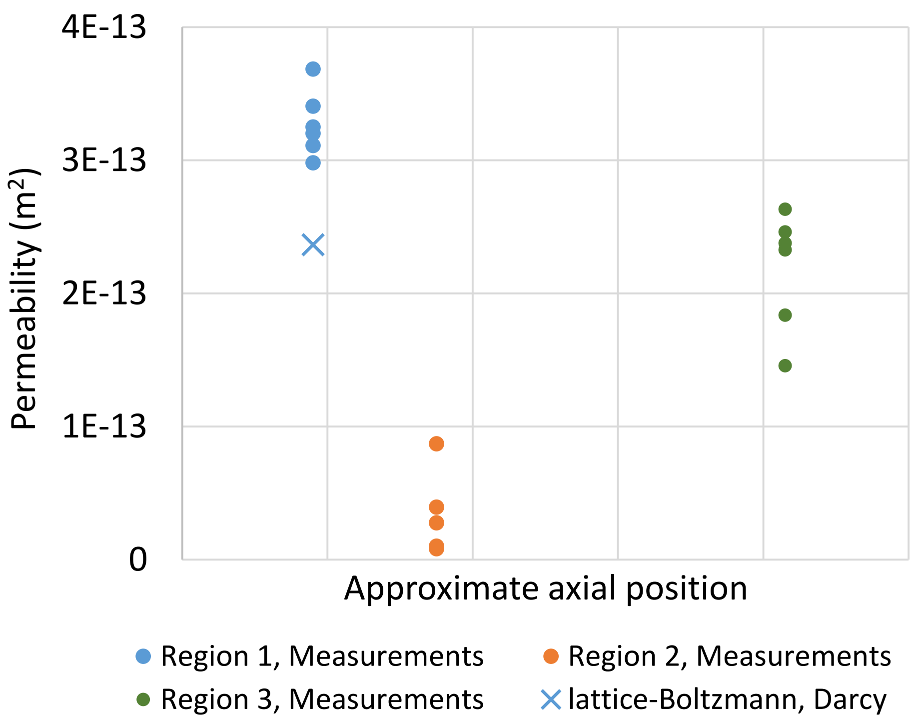


- Micro X-ray CT data was used to create 3D reconstructions for pore-scale lattice-Boltzmann flow simulations.
- Example shown is for first of three zones observed in multi-functional SRC-filter, with relatively thin catalyst coating from the upstream side of the filter wall.
- Catalyst voxels can be considered solid or assigned a sub-grid Darcy resistance, consistent with internal porosity and feature sizes.
- Predicted permeability can be compared to measured values.

Technical Accomplishments (Multi-functional device task):
Measured Permeability Related to Structure



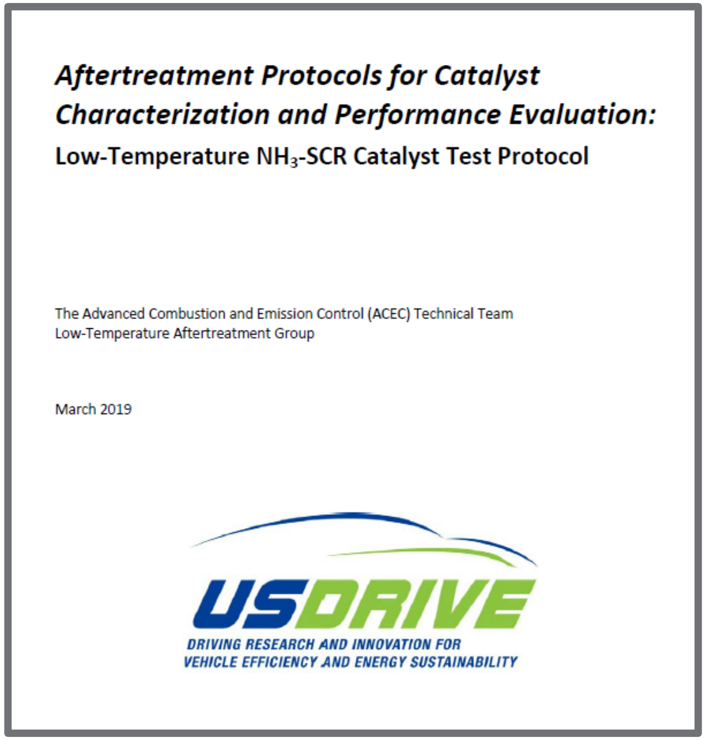


- Measured permeabilities show significant variation among the three observed axial zones.
- Some of the scatter observed in the permeability measurements may be attributed to variations in coating among the small sections examined.
- Example LB simulation in Zone 1 with sub-grid Darcy resistance gives a permeability close to the range of measurements for that zone.
- Device-scale models are being created to show effects of zone properties on performance (pressure drop, soot distribution, NO_X conversion, etc.).

Technical Accomplishments (Protocol task): Low-Temperature Catalyst Test Protocol Development

- Low-Temperature NH_3-SCR Catalyst Test Protocol
  - Completed this year
  - Reviewed & approved by the ACEC tech team and the Advanced Powertrain Technology Leadership Council
- In press:

  Aftertreatment protocols for catalyst characterization and performance evaluation: low temperature oxidation, storage, three-way, and NH_3-SCR catalyst test protocols
  - Open literature release of all four low-temperature catalyst test protocols



Aftertreatment Protocols for Catalyst Characterization and Performance Evaluation:

Low-Temperature NH_3-SCR Catalyst Test Protocol

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

March 2019

- On-going interaction with the ACEC tech team and the LTAT sub-group
  - Bi-monthly ACEC and AE Crosscut participation
  - Bi-weekly LTAT sub-group participation
  - Prioritization of activities moving forward

Organized & Moderated CLEERS Workshop Panel Discussion

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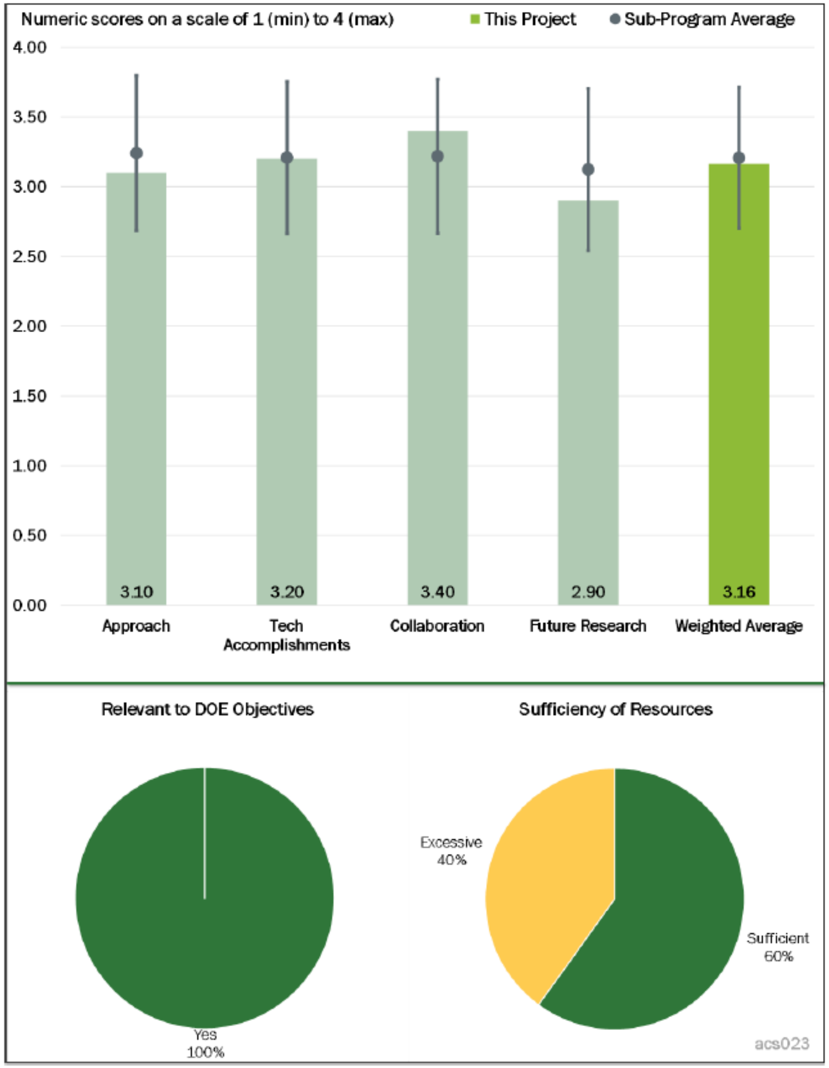
- Topic – Emission Control Challenges and Opportunities for Hybrid Electric Vehicles (HEVs)
- Panel participants
  - Gary Salemme, Cummins
    - Overview of architectures & characteristics that impact emissions
    - Focused on hybrid electric commercial vehicles, highlighted the opportunity to manage engine operation for optimal system performance
  - Manish Sharma, BASF
    - Market projection & vehicle roadmap
    - Unique challenges HEVs present to emission control
  - Matti Maricq, Ford
    - Measuring HEV emissions, key metrics, relation to real-world driving
    - What we need to know about current and (likely) future legislation
  - Haiying Chen, JM
    - Potential emission solutions for HEVs, pros & cons of select strategies
    - Other solutions: electric heating (GHG implications), thermal energy storage

Accomplishments – Responses to Previous Year Reviewers' Comments

- SCR and multifunctional filter efforts were reviewed as part of CLEERS in 2018. Nearly all the comments from the reviewers last year were very supportive and complimentary.
- Some comments/recommendations included:
  1. . value of micro (X-ray CT) will be to demonstrate using the wall-scale coating distribution to predict filter-scale performance (pressure drop, filtration, etc.). Even if directionally correct, that will be a big step forward.
  2. ….S tolerance and reactivation….. The reviewer cautioned that this ought to be addressed sooner rather than later because the proposed project directions may make the matter worse.
- PNNL response:
  1. This is the primary focus of FY19 and continued work in the near future.
  2. Already started looking into the real samples provided by industrial collaborators



Collaboration and Coordination with Other Institutions

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Collaborators/Coordination

- DOE Advanced Engine Crosscut Team (this group is the primary sponsor and overseer of all activities)
- CLEERS Focus Groups
- USCAR/USDRIVE ACEC team
- 21CTP partners
- Oak Ridge National Lab: Melanie Debusk, Jim Parks, Josh Pihl, Vitaly Prikhodko, Todd Toops
- Cummins: Krishna Kamasamudram, Yuhui Zha, Xiang Wang
- Johnson Matthey: Haiying Chen
- FCA: Craig DiMaggio
- Kymanetics, Inc.: Carl Justin Kamp

Acknowledgements

- DOE Vehicle Technologies Program: Gurpreet Singh and Ken Howden.

Remaining Challenges and Barriers

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SCR

- Generation of enough NO_2 and dose reduction at low temperature for fast SCR.
- Distinguishing thermal degradation, hydrothermal degradation and chemical degradation for examining aged (used) catalysts, and identification of representative descriptor for aging from such complexity.
- Linkage of the learning from lab accelerated model materials with field-aged commercial catalysts.

Multi-functional devices

- Detailed performance models needed for production multi-functional exhaust filters, including SCR/DPF and TWC/GPF.
- Lack of fundamental understanding of interactions between advanced substrates, advanced catalyst coatings, and ash, and their effects on device performance as a function of time.

Proposed Future Work

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SCR

- Understand the roles of the Fe sites, NH_4NO_3 elimination, reaction mechanisms for fast SCR on Fe-zeolites and study the long term stability of the catalysts.
- Study the mechanisms for the oxide promoted low temperature NOx conversion to enable the development of zeolite + oxide hybrid SCR catalysts, and understand how these two phases influence each other's long-term stability.
- Develop new spectroscopic methods in examining aged and on-road catalysts, and develop correlations between mileage and catalyst performance.

Multi-functional devices

- Conduct multiple micro-scale flow simulations with realistic sub-grid catalyst permeability to relate microstructure to measured permeability values
- Create device-scale models to relate macroscopic catalyst distribution and zone properties to aftertreatment system performance

Protocol

- On-going interaction with the ACEC tech team and the LTAT sub-group

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

Summary

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SCR

- Detailed atomic-level understanding on the beneficial or detrimental roles of alkali and alkaline co-cations was used as an example to guide the formulation of Cu,M/SSZ-13 (M = Na^+ or K^+) catalysts with significantly improved low temperature activity and high temperature durability.
- Advanced *in situ* characterization coupled with theory was used to propose, for the first time, detailed Cu/SAPO-34 deactivation pathways during low-temperature moisture treatment and storage, and two suggestions are provided for its prevention.

Multi-functional devices

- A new technique was developed for measuring local permeability in multi-functional filters with zoned catalyst coatings.
- Micro X-ray CT data was used to generate three dimensional reconstructions for pore-scale flow simulations.

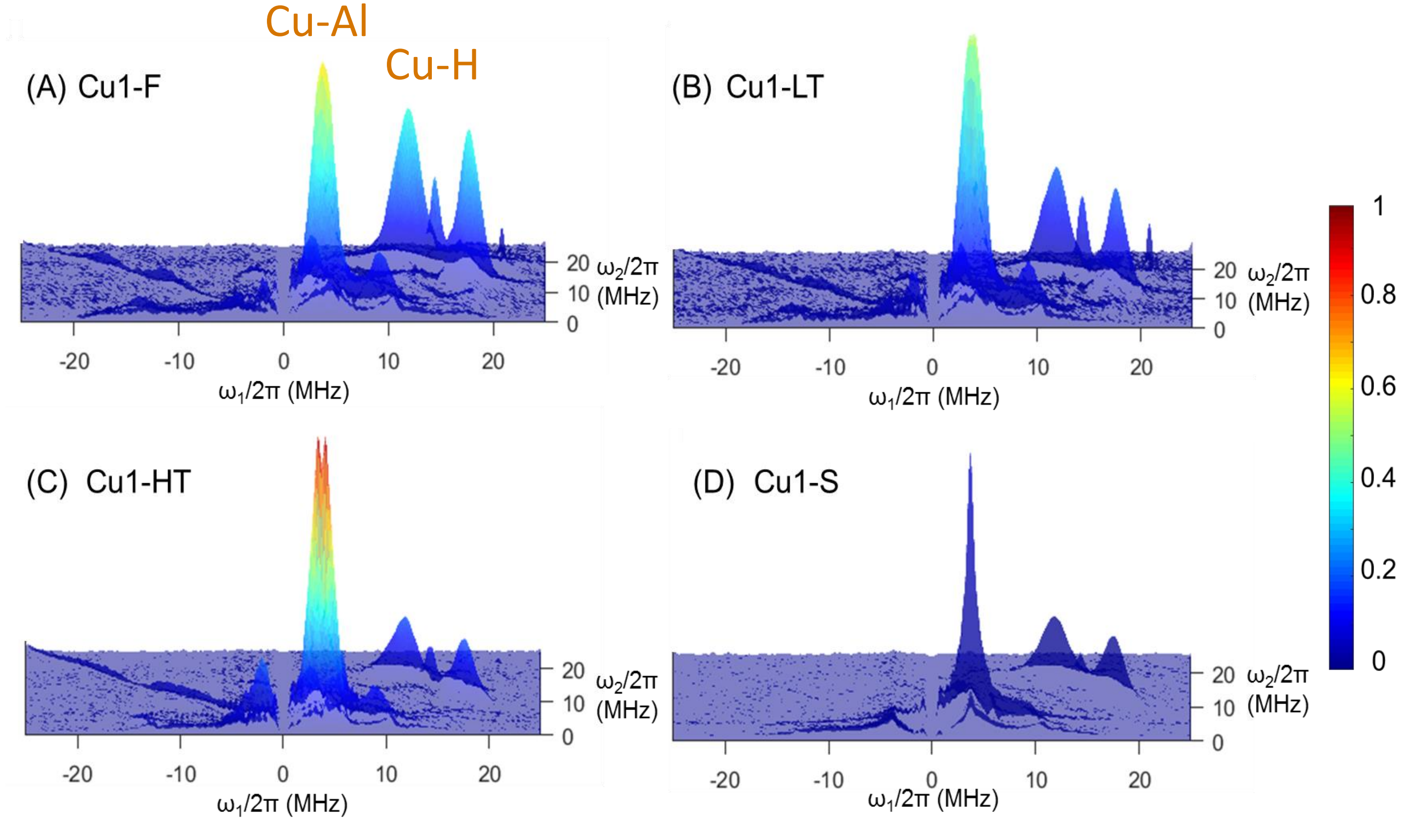
Protocol

- On-going interaction with LTAT sub-group of the ACEC Tech Team to prioritize activities moving forward.
- Longer term activity testing of single atom Pt1/CeO_2 for CO oxidation.

Technical Backup Slides

Cu/SAPO-34 Deactivation Pathways During Low-Temperature Moisture Treatment and Storage

For the first time, hyperfine sublevel correlation (HYSCORE) spectroscopy, a two-dimensional (2D) pulsed electron paramagnetic resonance (EPR) technique, was used to trace Cu(II) ions in Cu/SAPO-34.



High-temperature hydrothermal treatment converts ZCuOH to Z_2Cu, however low-temperature hydrothermal treatment and storage lose SCR active Cu.

Cu/SAPO-34 Deactivation Pathways During Low-Temperature Moisture Treatment and Storage

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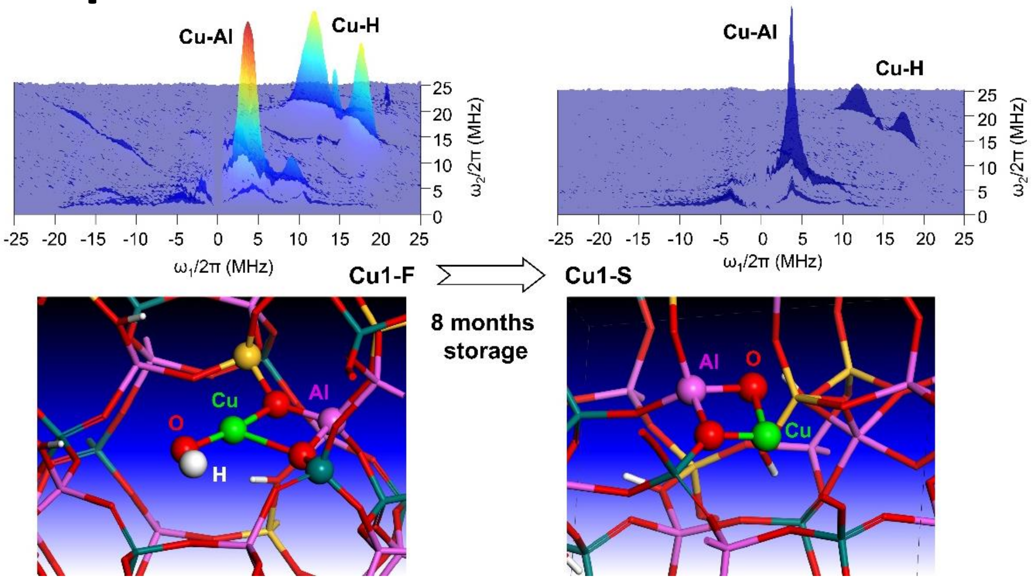
Institute for INTEGRATED CATALYSIS



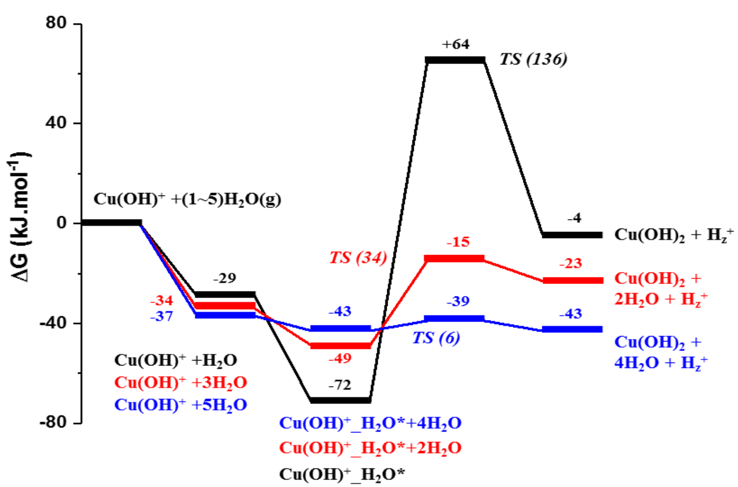
Three simple steps lead to permanent catalyst deactivation:

(1) ZCuOH hydrolyzes to free $Cu(OH)_2$.

(2) ≡Si-O(H)-Al ≡ hydrolyzes to generate terminal ≡Al.

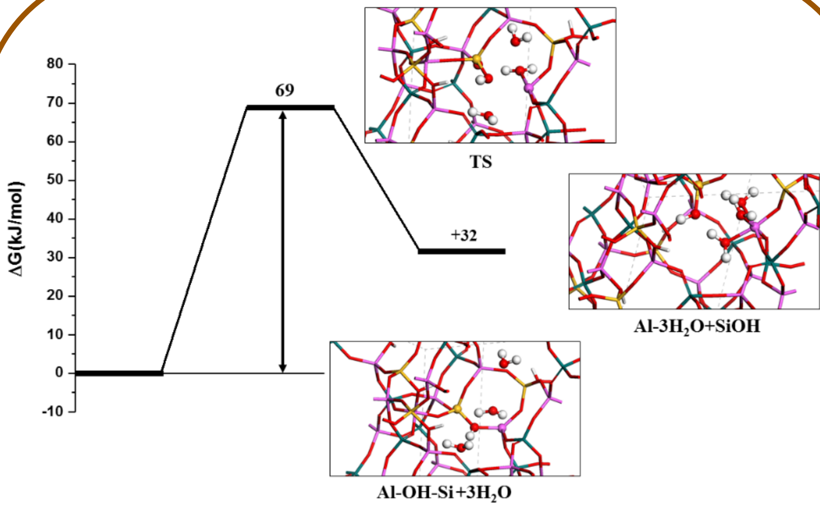
(3) Interaction between $Cu(OH)_2$ and terminal ≡Al to form SCR inactive Cu-aluminate.

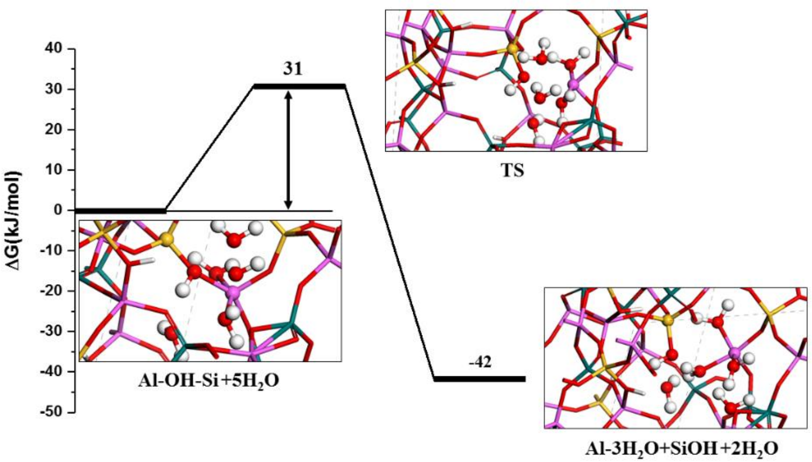
These chemistries are greatly facilitated by condensed H_2O in SAPO-34 pores.



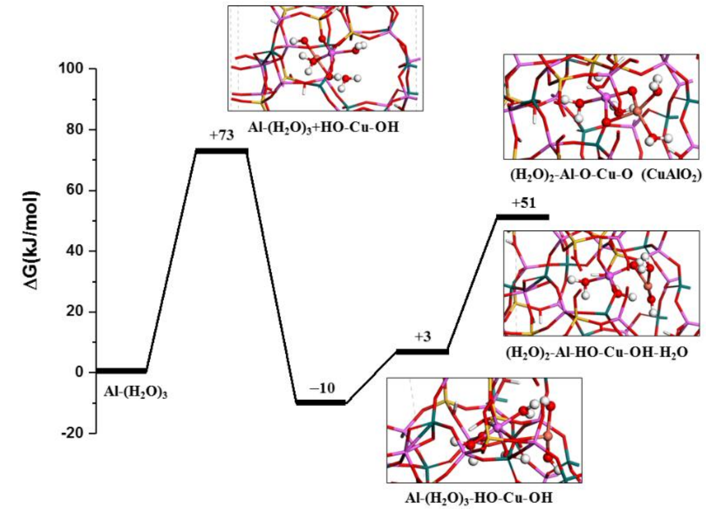
ZCuOH hydrolysis chemistry

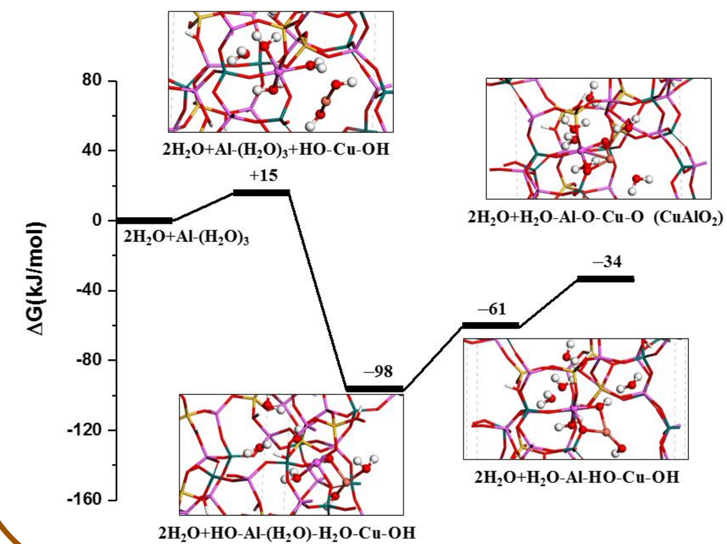
Condensed Water Promotes All Three Reactions





≡Si-O(H)-Al ≡ hydrolysis chemistry





Cu-aluminate formation chemistry