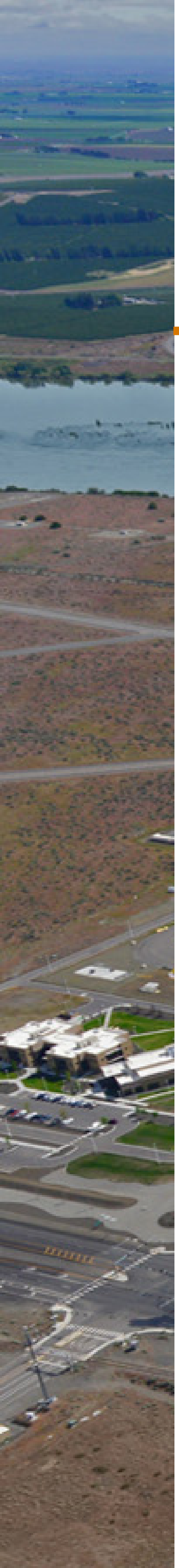

2021 DOE AMR Review

Fundamental Understanding of Copper-Zeolite Selective Catalytic Reduction (SCR) Catalyst Aging Mechanism

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Pacific Northwest National Laboratory

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Cummins Inc.

Program Managers: Siddiq Khan, Ken Howden, Gurpreet Singh

The work was funded by the U.S. Department of Energy (DOE), Vehicle Technologies Office.

ACE027

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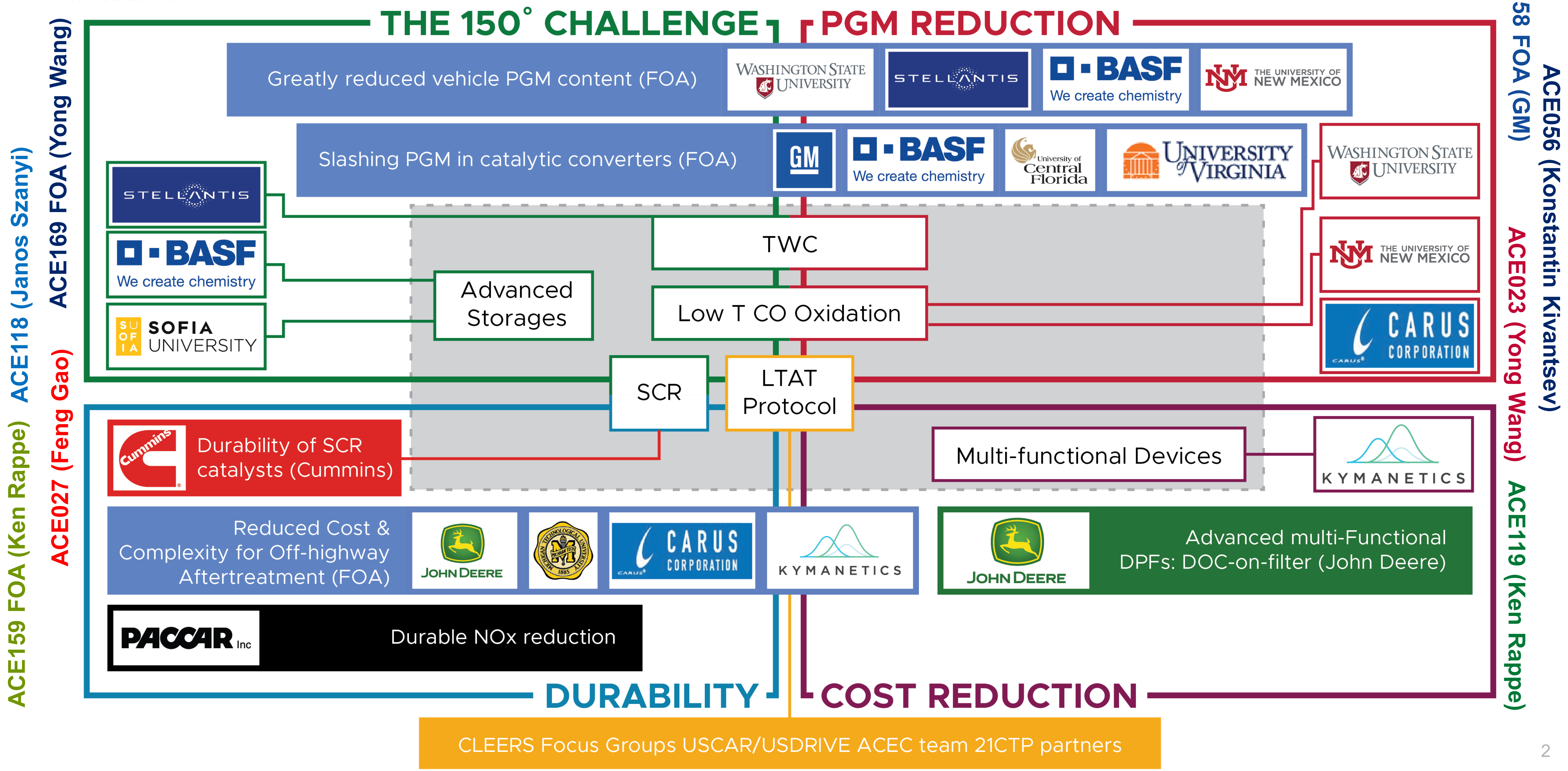
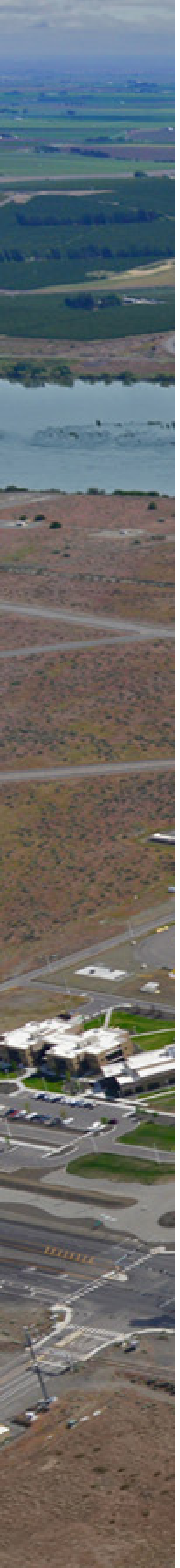
PNNL Fundamental and CRADA Projects:

1) Address the "150 °C Challenge", PGM Reduction, Durability, and Cost;
2) Aligns with Industrial Priorities - Exemplified by 8 AMR Presentations





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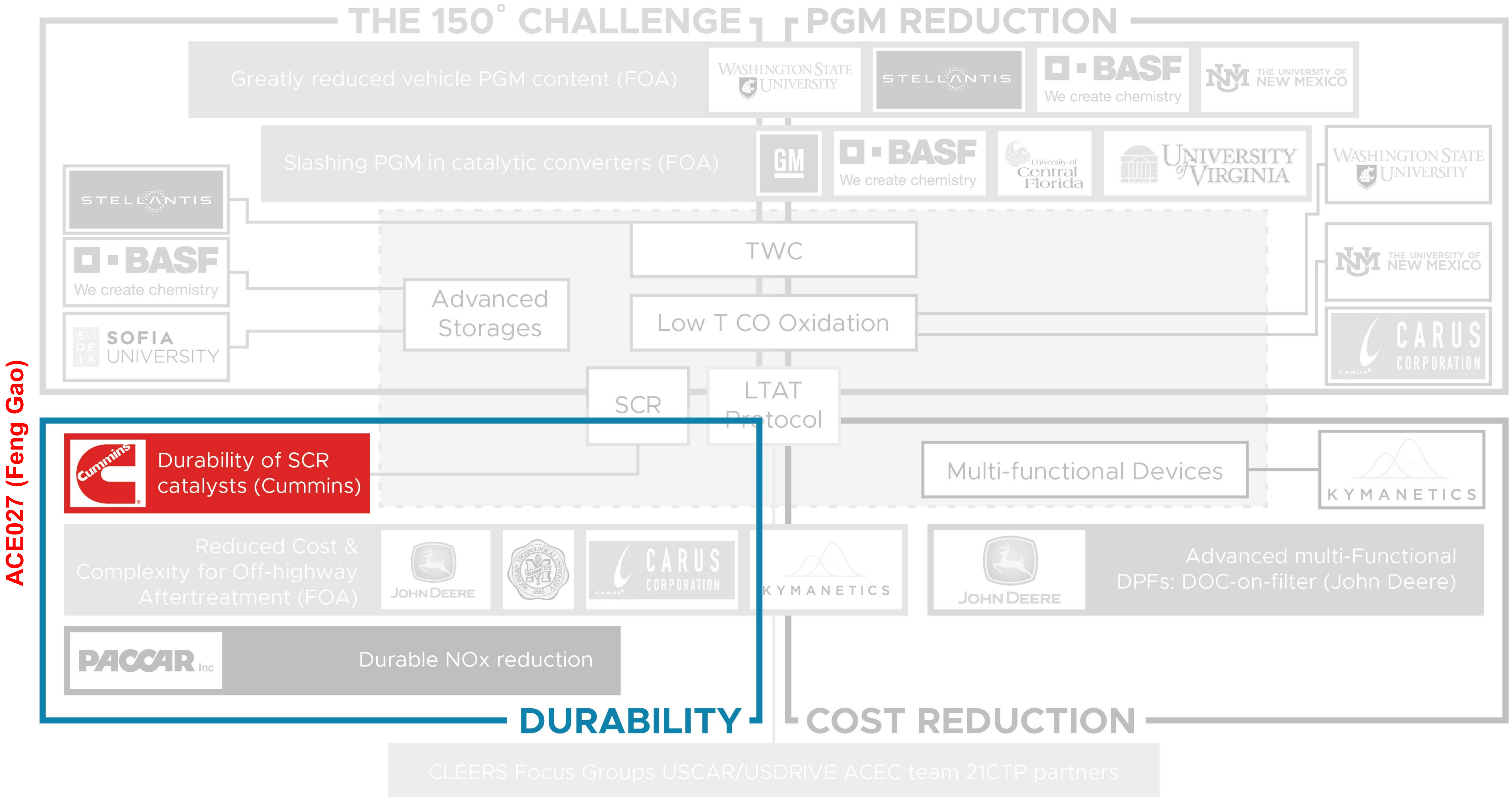
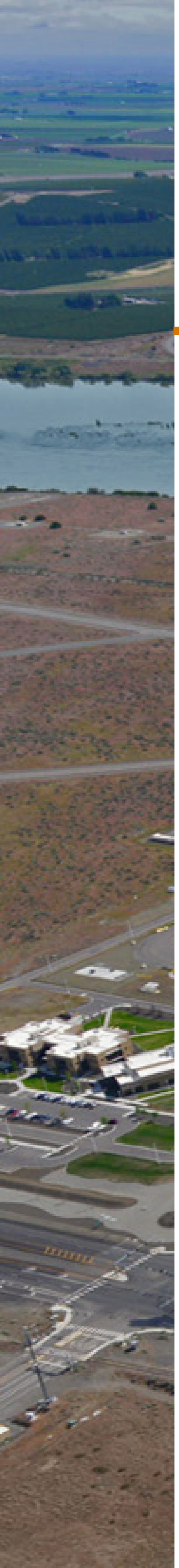
Cummins CRADA Project Specifically Addresses the SCR Durability through Fundamental Understanding of Aging Mechanisms





Overview

Timeline

- Start: March 2020
- End: March 2023
- 40% complete

Budget

- Total project funding: $1,800,000
  - DOE share: $900,000
  - Cummins cost share: $900,000
- Funding for 2021: $300,000

Barriers

- Real world aging shows characteristics very different from aging based on current accelerated lab aging protocols.
- Accurate predictive aging and performance models are needed.
- Extending emission warranty requires much deeper understanding of SCR catalyst aging mechanisms than our current comprehension.

Partners

- CRADA project
  - Cummins, Inc.
  - PNNL.

Relevance

2018 roadmap of the U.S. DRIVE Partnership

*Emission control technology research needs for combustion strategies. (√=need for emission-control technology, **?** =further research required to determine applicability)*

	Low Temperature Combustion		Dilute Gasoline Combustion		Clean Diesel Combustion
	LTC-G (Gasoline Fuel)	**LTC-D** (Diesel Fuel)	**S-GDI** (Stoichiometric)	**L-GDI** (Lean)	
Lean NOx Catalysts	✓	✓		✓	✓
Three-Way Catalyst			✓	✓	
CO/HC Oxidation Catalysts	✓	✓			✓
HC Traps	✓	✓	?	?	?
Passive NOx Adsorbers	✓	✓	?	?	✓
Particulate Filters	✓	✓	✓	✓	✓
Multifunction Devices/Systems	✓	✓		✓	✓

This CRADA benefits (1) Cummins in developing new technologies to address the future aftertreatment challenges, (2) PNNL/DOE in improving domestic fuel efficiency in the transportation sector and environment protection.

Objectives

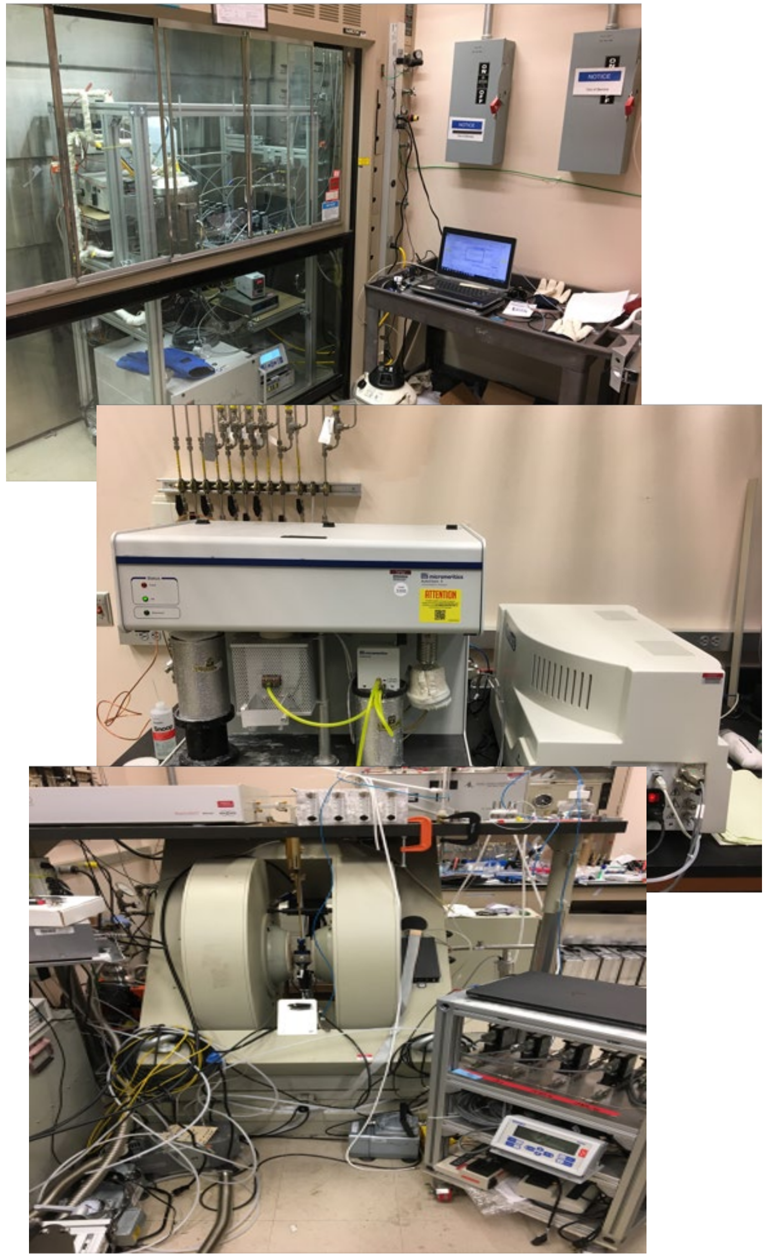
- Develop characterization tools to monitor the dynamic changes upon progressive aging.
- Characterize field-aged samples, identify and model the changes in active sites.
- Develop accelerated procedures to simulate real-world aging (RWA) of SCR catalysts.

Milestones

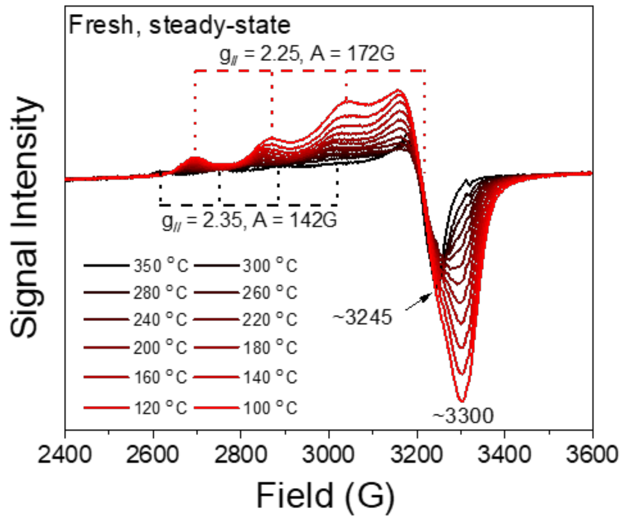
Milestone	Status	Time	Percentage
➢ Generate representative samples using various aging protocols and compare with field aged samples	Complete	09/30/2020	100%
➢ Complete characterization of representative field- and lab-aged samples to identify cause of deactivation, including poisoning by sulfur and changes in Cu species	Complete	03/31/2021	100%
➢ Develop *in situ* characterization tools such as electron paramagnetic resonance (EPR) for monitoring the changes in active sites on real-world and representative lab-aged conditions	On track	02/28/2022	60%
➢ Generate models to describe the performance degradation	not initiated	02/28/2023	0%

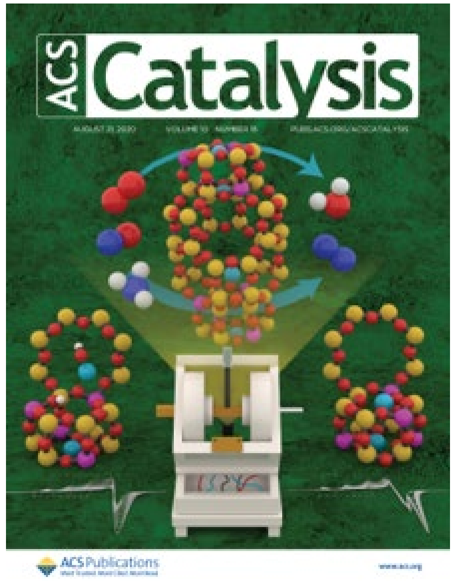
Approach

- Prepare and Process Catalyst Materials
  - Lab and field-aged catalysts are characterized by Cummins and PNNL.
  - Model SCR catalysts prepared by PNNL, with compositions similar to those of the field-aged samples.
  - Utilize expertise and state-of-the-art catalyst characterization and testing facilities at PNNL's Institute for Integrated Catalysis (IIC) and Environmental Molecular Sciences Laboratory (EMSL) to address mechanisms and structure/function.
    - XRD, XPS, NMR, EPR, TEM/EDS and SEM/EDS
    - NH_3 and NO_x TPD, H_2 TPR
    - Lab-based EXAFS and XANES
    - Lab reaction systems
- Cummins facilities: Lab and Field aging facilities allowing the generation of representative samples, *in situ* FTIR and chemical characterization.

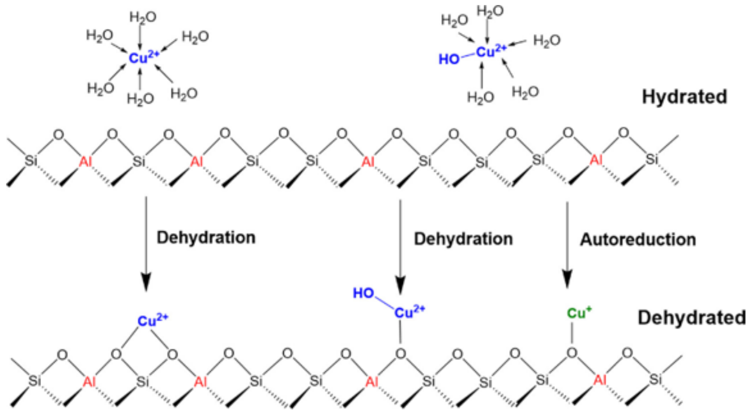


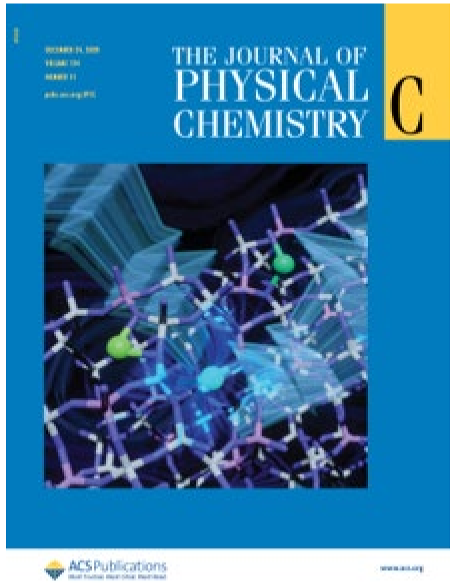
Approach: development of *in situ/operando spectroscopy* capabilities as an example



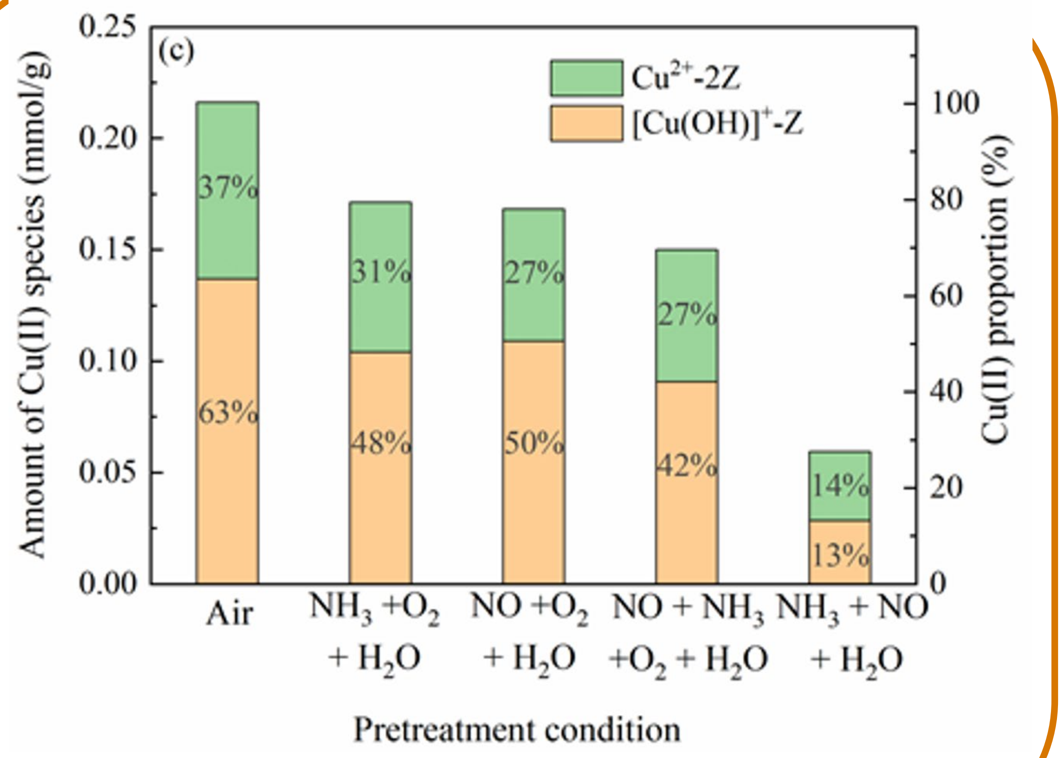


ACS Catal. 2020, 10, 9410−9419.





J. Phys. Chem. C 2020, 124, 28061−28073.



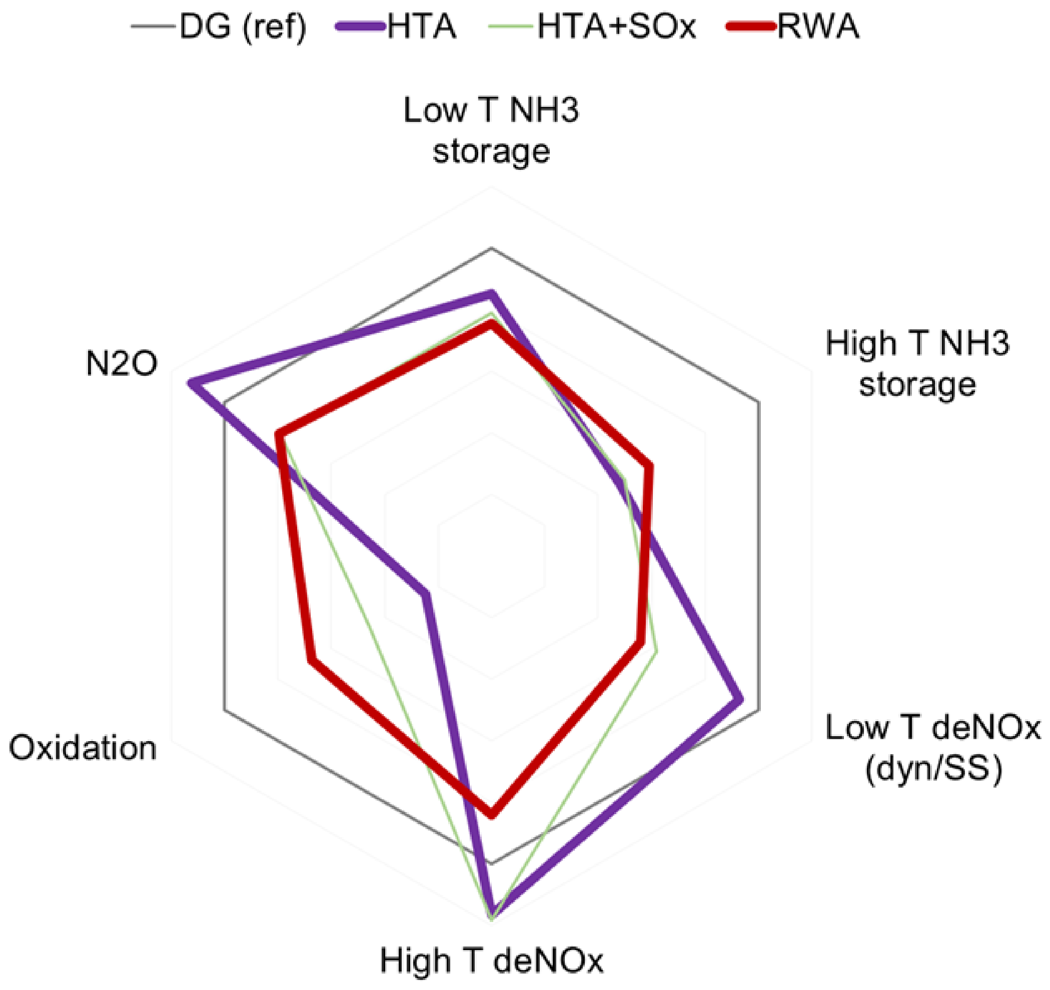
Chem. Commun., 2021, 57, 1891-1894.

Such new capability development has been mainly under PNNL's "CLEERS" foundational emission control research, which directly benefits this CRADA project.

Technical Accomplishments

- Identified gaps between field-aged and existing simulated aged catalyst behavior.
- Developed model catalyst synthesis and aging protocol development.
- Utilized new tools and methods in studying field-aged catalysts.
  - H_2-TPR coupled with *in situ* XPS to probe the nature of Cu species and the nature of sulfur poisons.
  - Utilized *operando* electron paramagnetic resonance (EPR) facilities for catalyst characterization and evaluation.
  - Utilized new quenching plus chemical titration method to probe status of the Cu active species under SCR conditions (*quasi-operando* method).

Technical Accomplishments: Field vs. Lab aging Gaps

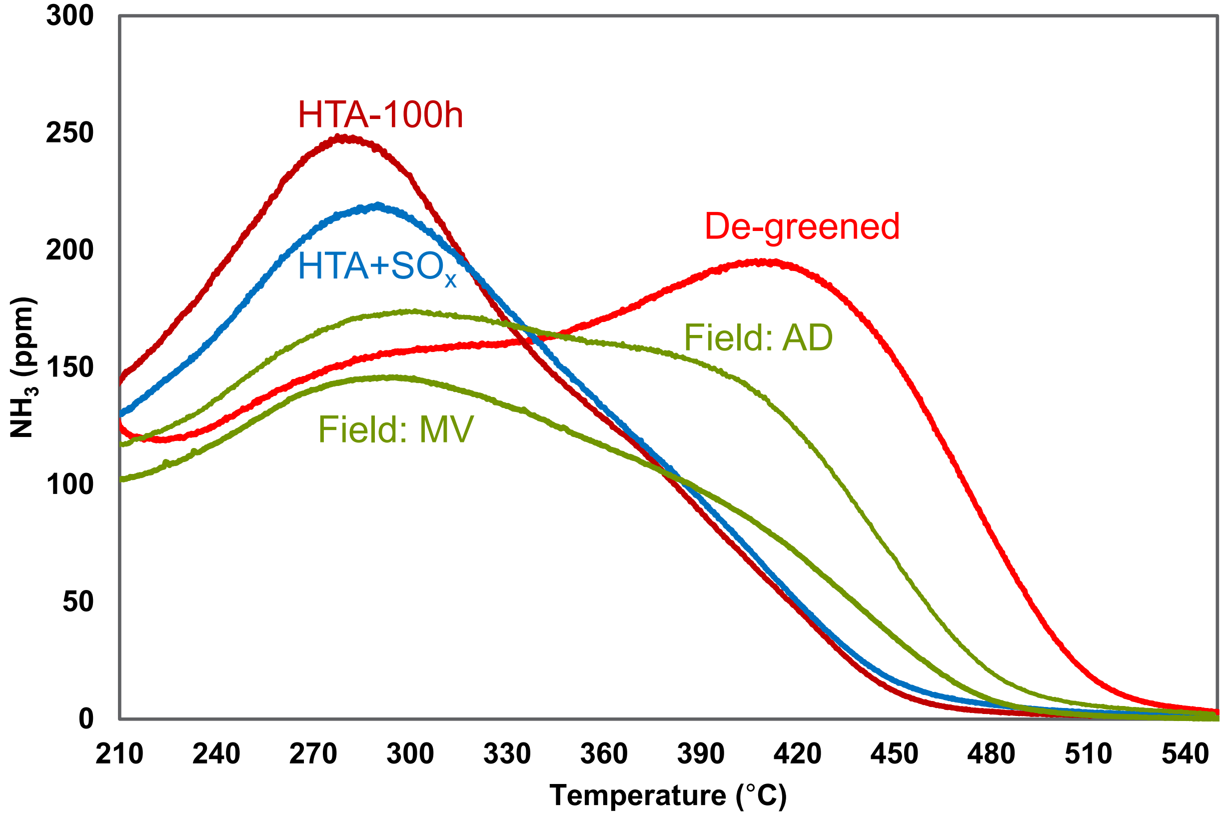


6-parameter catalyst evaluation

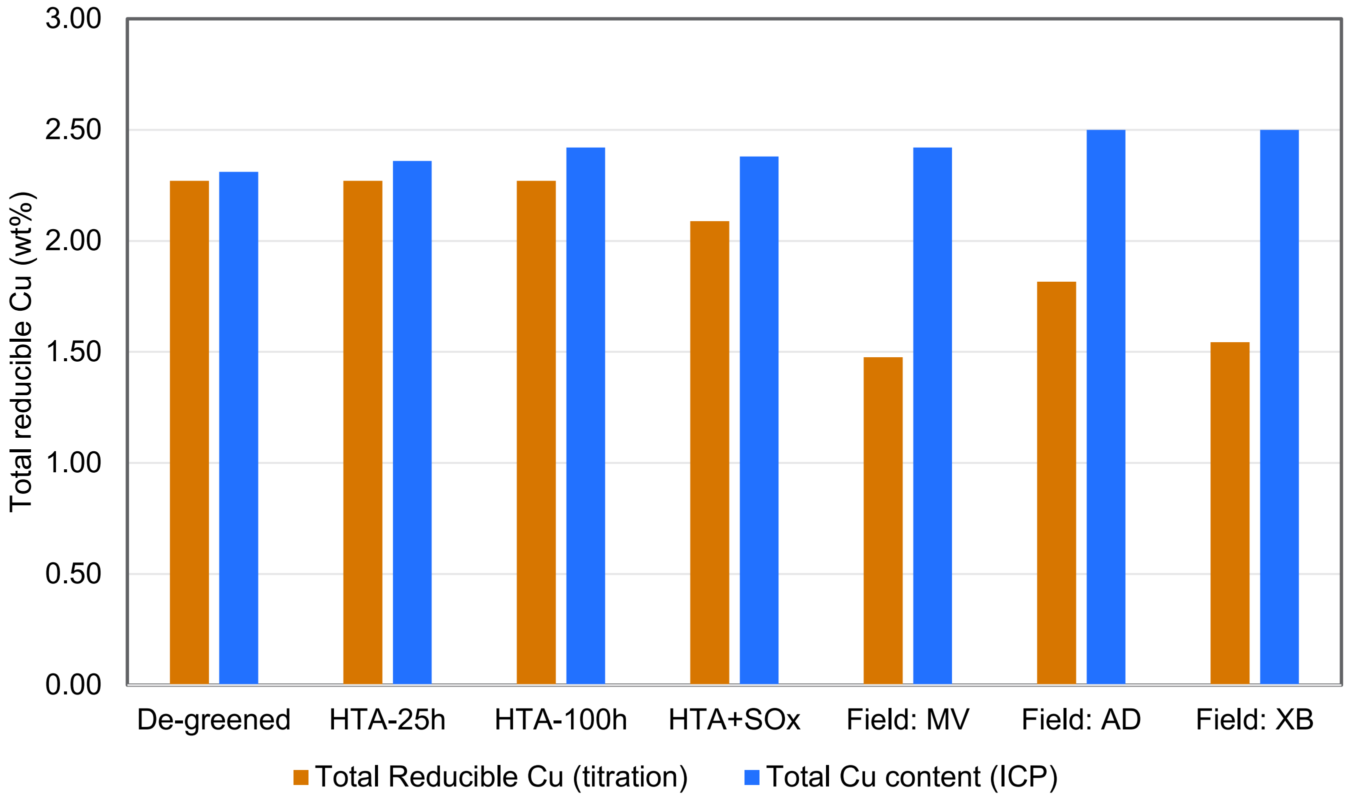
- The analysis of real-world healthy high mileage Cu-SCR catalyst showed changes in catalyst functions that cannot be explained by hydrothermal aging (HTA) alone.
- HTA+SO_x leads to an accelerated aging of Cu-SSZ-13. However, there are still key gaps between the sulfur-aged vs. engine-aged samples.
- The underlying aging mechanisms in real-world are not well-understood.
  - Additional poisons beyond sulfur;
  - Additional pathways for Cu deactivation, beyond HTA.
  - Multiple pathways for zeolite support degradation.
  - Interaction of deactivation pathways.

Technical Accomplishments: Field vs. Lab aging Gaps

NH_3 TPD



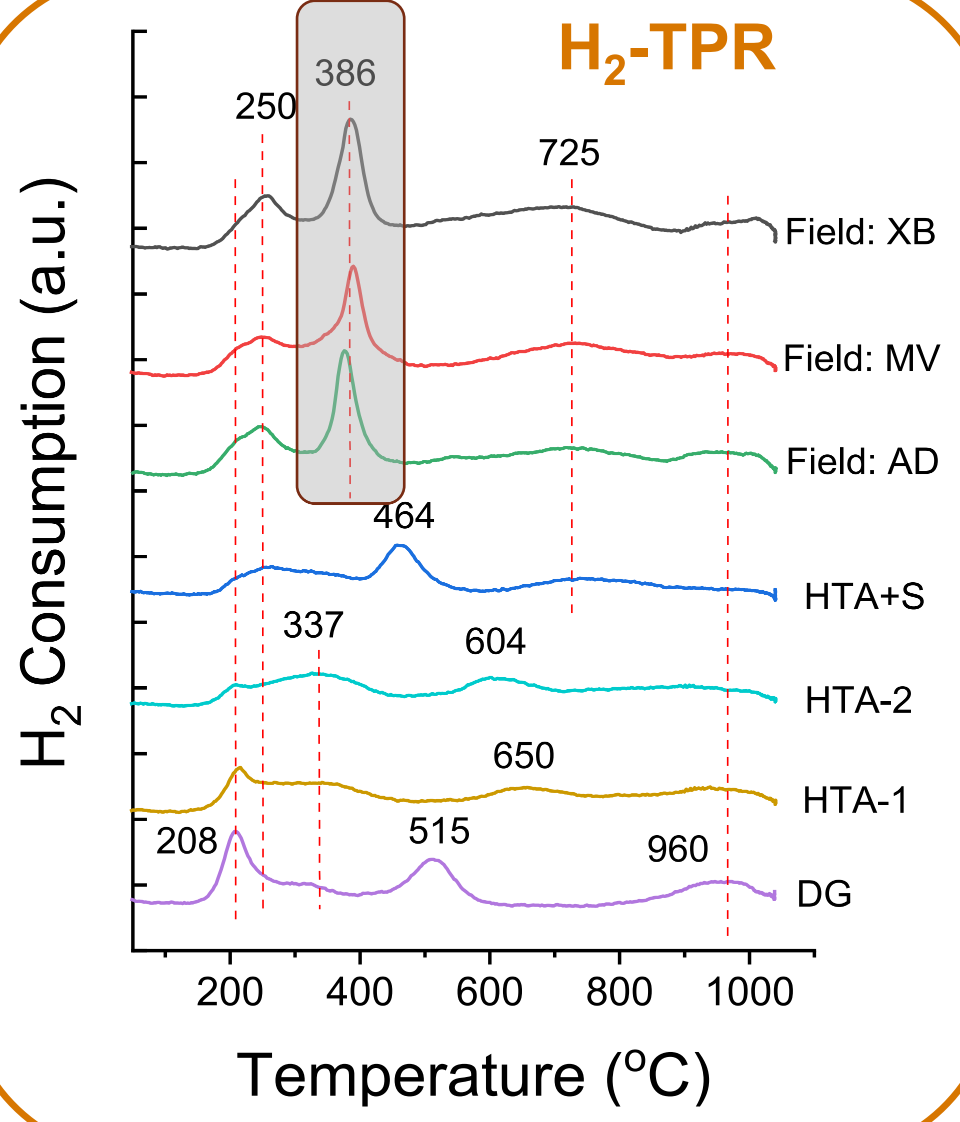
NO + NH_3 titration and ICP



- **NH_3 TPD** on the field aged samples cannot be represented by hydrothermal aging and sulfur exposure.
- Field aged samples show higher loss of reducible Cu than hydrothermal aging and sulfur exposure as quantified using **NO + NH_3 titration**.

R. Villamaina, et al., ACS Catal. 2019, 9, 8916−8927.

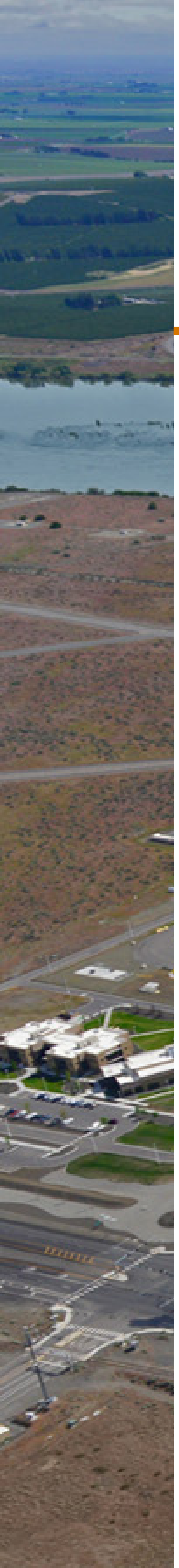
Technical Accomplishments: H_2-TPR, EPR and *in situ* XPS for Cu quantification



- A reduction state centered at 386 °C only appears in field-aged samples. The HTA+S sample shows a similar state at 464 °C.
- Possible origin for this reduction state: Cu-sulfates. However, H_2 consumption quantification suggests that this reduction state should be mainly Cu rather than S reduction.
- Field-aged and HTA+S samples have a unique reduction that may be described by the following prototypical reaction: $CuSO_4 + H_2 \rightarrow Cu(0) + H_2SO_4$.
- Nature of sulfur contamination is likely Cu-sulfate formation.

Responses to Previous Year Reviewers' Comments

This project was not reviewed last year.



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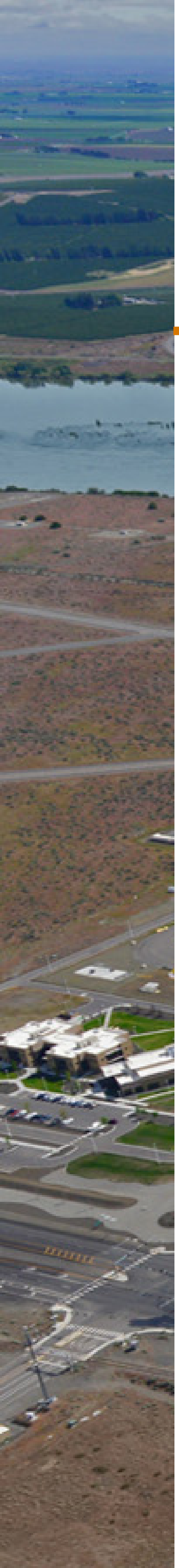
Cummins

Collaboration and Coordination with Other Institutions

Cummins	CRADA partner; provide "field-aged" catalysts, catalyst lab tests, and lead the aging model development. Monthly meetings and yearly face-to-face meetings.
EMSL	Environmental Molecular Sciences Laboratory for providing state-of-the-art instrumentation and expertise, for example in NMR, EPR spectroscopy and STEM imaging.
PURDUE UNIVERSITY Argonne NATIONAL LABORATORY Advanced Photon Source	Collaboration with Professor Jeffrey T Miller in synchrotron-based studies at APS.
清華大學 Tsinghua University	Visiting students working on foundational SCR studies (e.g., operando spectroscopy) that directly benefit this CRADA.



Remaining Challenges and Barriers

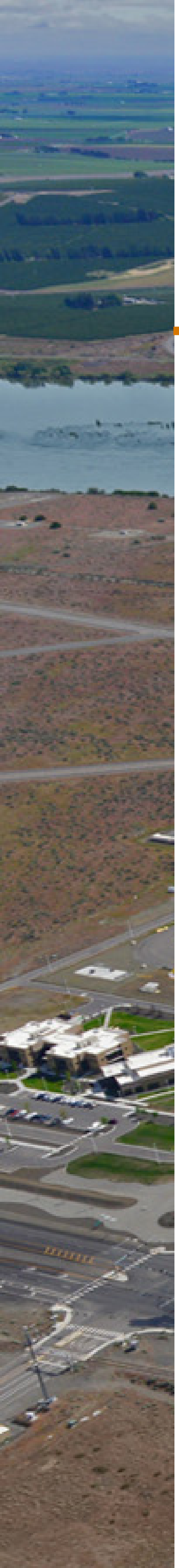
- Key Challenges include:
  - Upcoming EPA and CARB regulations
  - Increased duration of warranty legislation
  - Increased penetration of renewable fuels
- Key Barriers include:
  - Introducing representative poisons beyond sulfur into the aging protocols via rational approaches.
  - Possible aging mechanism changes beyond the current durability requirement.

Category	Warranty				EUL			
	Current	Step 1 MY 2022	Step 2 MY 2027	Step 2 MY 2031	Current	Step 1 MY2022	Step 2 MY 2027	Step 2 MY 2031
Heavy HD Class 8	100,000 mi 5 yrs 3,000 hrs	350,000 mi 5 yrs {}	450,000 mi 7 yrs 22,000 hrs	600,000 mi 10 yrs 30,000 hrs	435,000 mi 10 yrs 22,000 hrs	No change	600,000 mi 11 yrs 30,000 hrs	800,000 mi 12 yrs 40,000 hrs
Medium HD Class 6-7	100,000 mi 5 yrs 3,000 hrs	150,000 mi 5 yrs {}	270,000 mi 7 yrs 13,000 hrs	360,000 mi 10 yrs 18,000 hrs	185,000 mi 10 yrs {}	No change	360,000 mi 11 yrs {}	450,000 mi 12 yrs {}

Proposed Future Research

- Investigations on PNNL model catalysts:
  - Model catalysts with compositions similar to field-aged catalysts.
  - Aging of the model catalysts in the presence of relevant poisons.
  - Characterize the aged catalysts using PNNL state-of-the-art tools.
  - Correlate characterization results with catalytic performance.
- Initiate aging model development with Cummins:
  - Provide relevant data to Cummins (both realistic and model catalyst data).
  - Based on feedback from Cummins, modify aging protocols, and then provide updated data to Cummins.

The proposed future work is subject to change based on funding levels.



Presentations and Publications

None

Summary

- Demonstrated clear gaps between Field and Lab accelerated aging that require molecular-level investigations to comprehend.
- Detailed characterization of 7 representative catalysts from Cummins (H_2-TPR, XPS, EPR etc.) coupled with SCR tests.
- The utilization of operando and quasi-operando methods in studying catalysts under the most relevant SCR reaction conditions.
- Synthesis and aging of PNNL model catalysts for investigations in Year Two.

Technical Back-Up Slides

Technical Accomplishments:
H_2-TPR, EPR and *in situ* XPS for Cu quantification

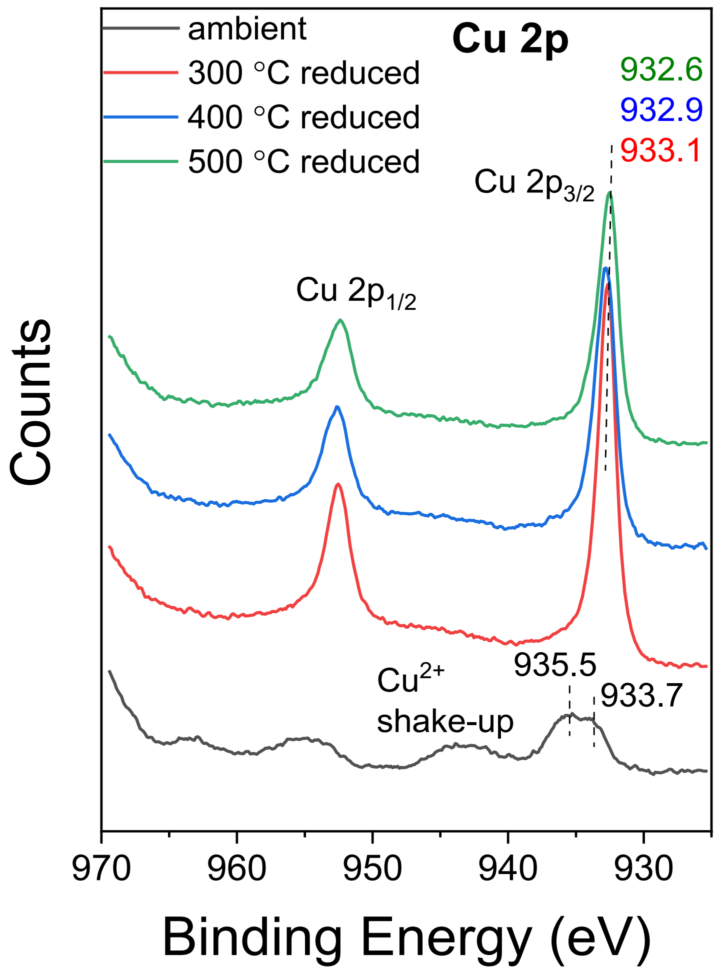
7 samples from Cummins

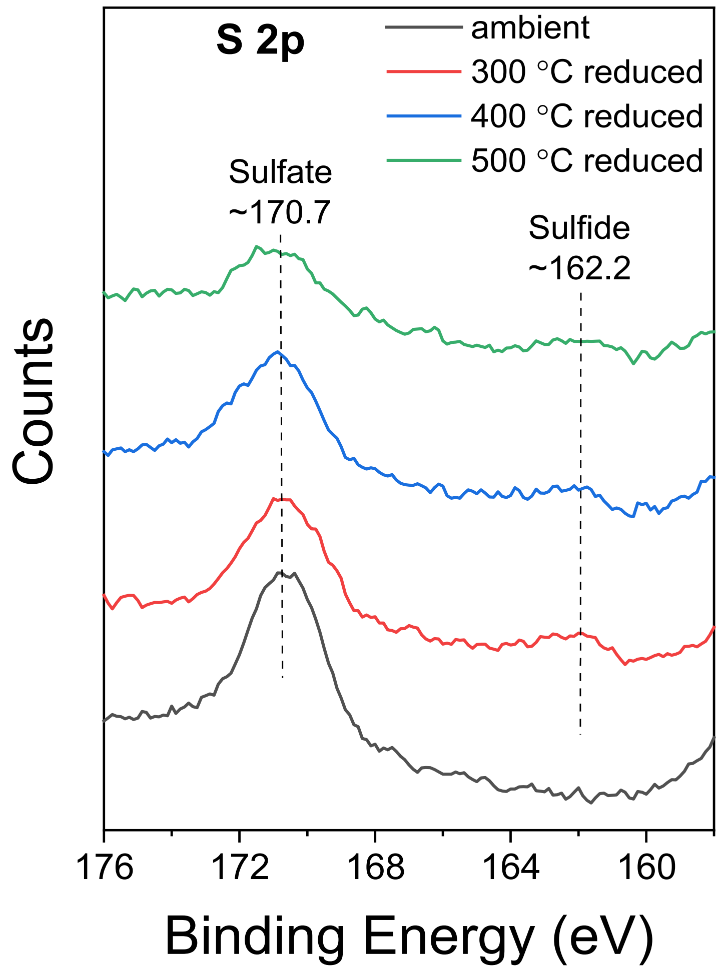
Sample	Cu content ICP (wt%)	Cu content XPS (wt%)	Isolated Cu(II) EPR (wt%)	Reducible Cu $NO+NH_3$ titration (wt%)	S content ICP (wt%)	S content XPS (wt%)
De-greened	2.31	2.62	1.39	2.27	-	-
HTA-25h	2.36	2.78	1.45	2.27	-	-
HTA-100h	2.42	2.93	1.41	2.27	-	-
HTA+S	2.38	3.89	1.10	2.09	0.14	0.15
Field: MV	2.42	3.39	0.87	1.48	0.22	0.25
Field: AD	2.50	2.88	1.00	1.82	0.31	0.40
Field: XB	2.50	2.77	0.99	1.54	0.58	0.64

- Consistency between ICP and XPS quantification in total Cu and S contents.
- Gaps between EPR and $NO+NH_3$ chemical titration in isolated Cu(II) contents.
- Aging in the presence of sulfur (both “field” and “lab” samples) induces loss of isolated Cu sites.
- Elemental quantification as the important first step in understanding aging mechanisms.

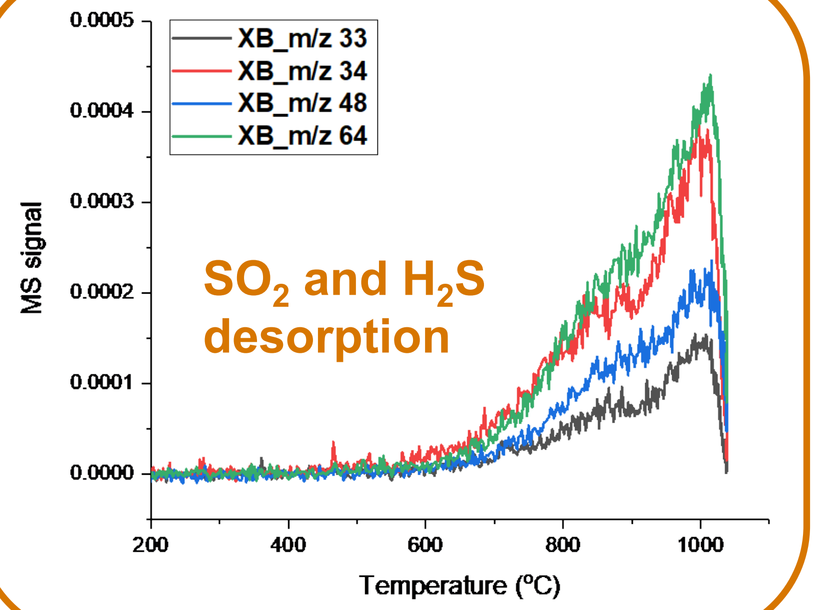
Technical Accomplishments: H_2-TPR, EPR and *in situ* XPS for Cu quantification

- Field aged XB as an example. In the XPS pretreatment chamber, ramp the samples in 10% H_2/He from ambient to the target temperatures 300-400-500 °C at 10 °C/min, and cool back to ambient naturally in the same gas.





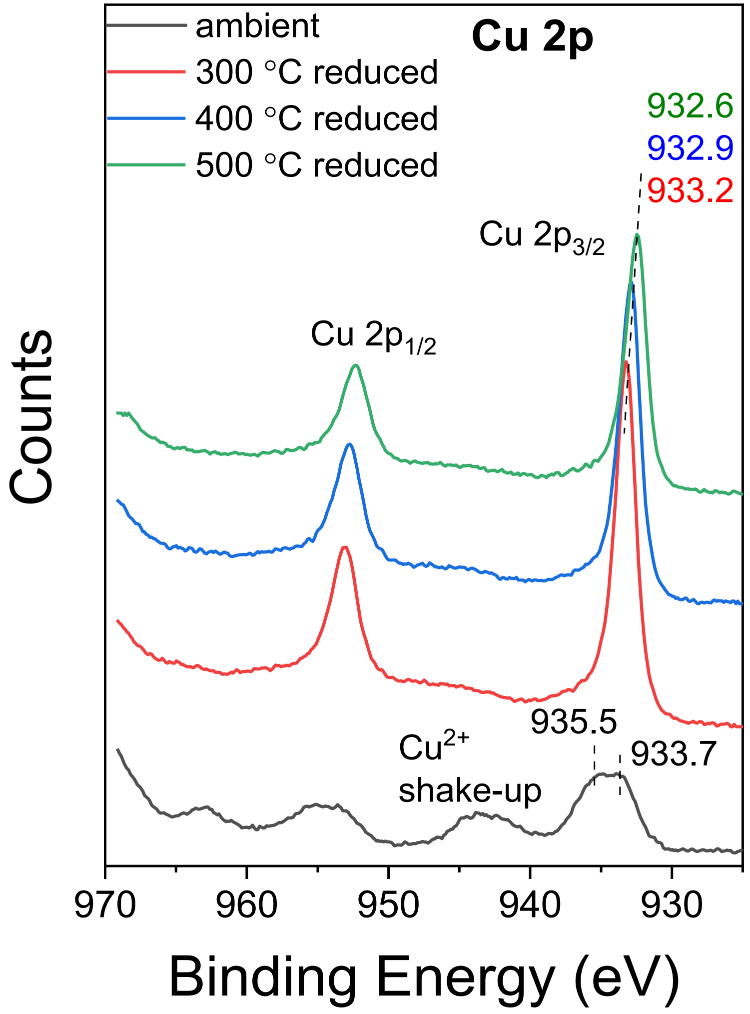
***in situ* XPS**

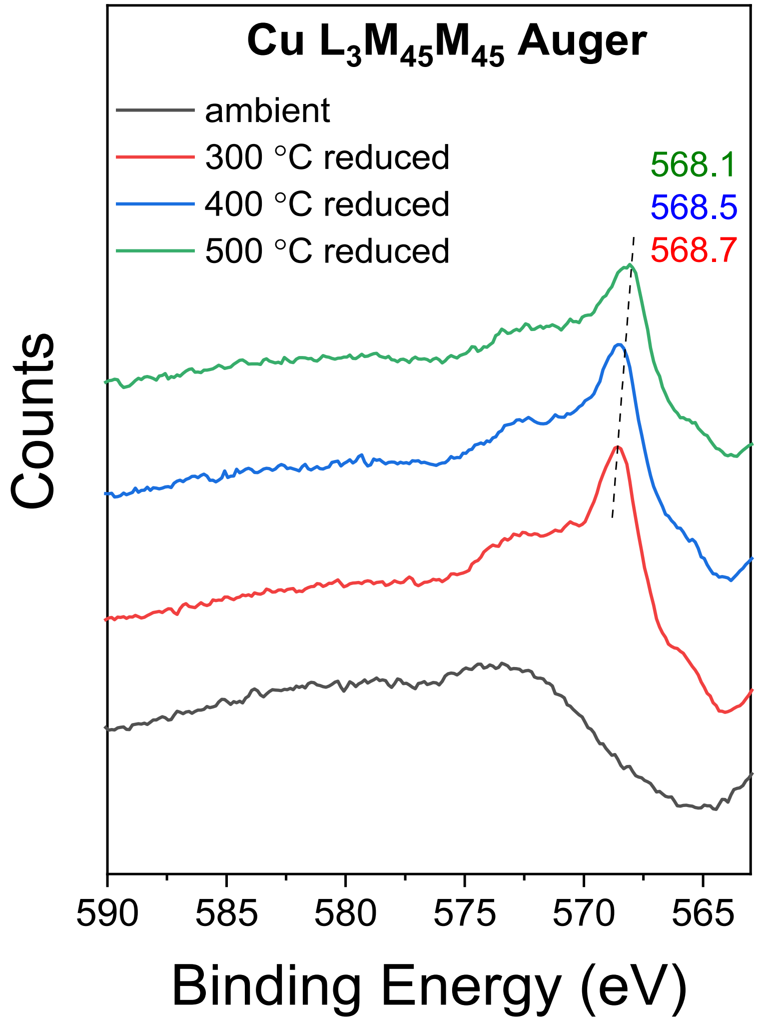


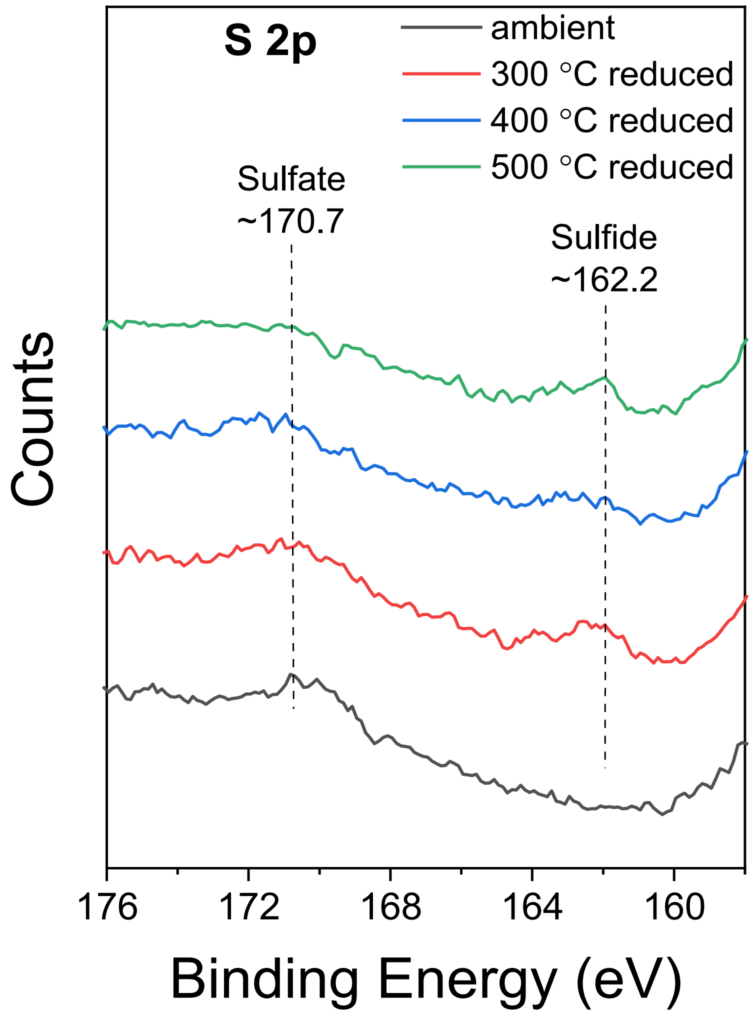
TPR-MS

The combination of various techniques allow for precise quantification of different Cu species in the catalysts, which clearly differentiates field versus lab aging.

XPS studies HTA+S sample







- HTA+S sample displays essentially identical reduction behavior as field-returned XB, suggesting similar nature of sulfur poisoning.

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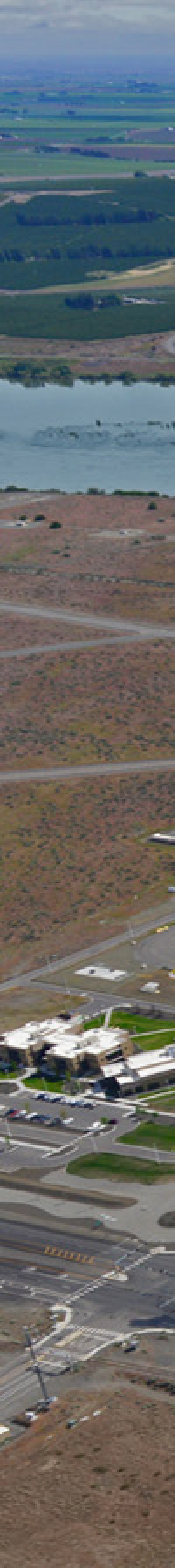

Thank you