2022 DOE AMR Review

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

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ACE027

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Overview

Timeline

- Start: March 2020
- End: March 2023
- 70% complete

Budget

- Total project funding: $1,800,000
  - DOE share: $900,000
  - Cummins cost share: $900,000
- Funding for 2022: $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

Supports the DOE Vehicle Technology Office's goals for enabling U.S. economic growth by ensuring efficient and cost-effective ICE-equipped equipment, machinery, and vehicles across U.S. industrial sectors

- Early-stage research to improve the understanding of emissions control technologies and barriers that they face, including low-temperature activity and durability

- Meeting off-road Tier 5 regulations
  - Low-load cycle (LLC) – low temperature performance
  - Extended useful life – durability
  - GHG emissions, e.g, N_2O

- Emissions of low carbon fuels, renewable fuels (e.g., e-methane, R-NG)

Objectives

Uncover and inform on the science behind the barriers that current and emerging aftertreatment technologies face

- **Barriers – low temperature activity, durability, long useful life, efficient PGM usage**
- **Hard-to-electrify applications that are aligned with industrial priorities**

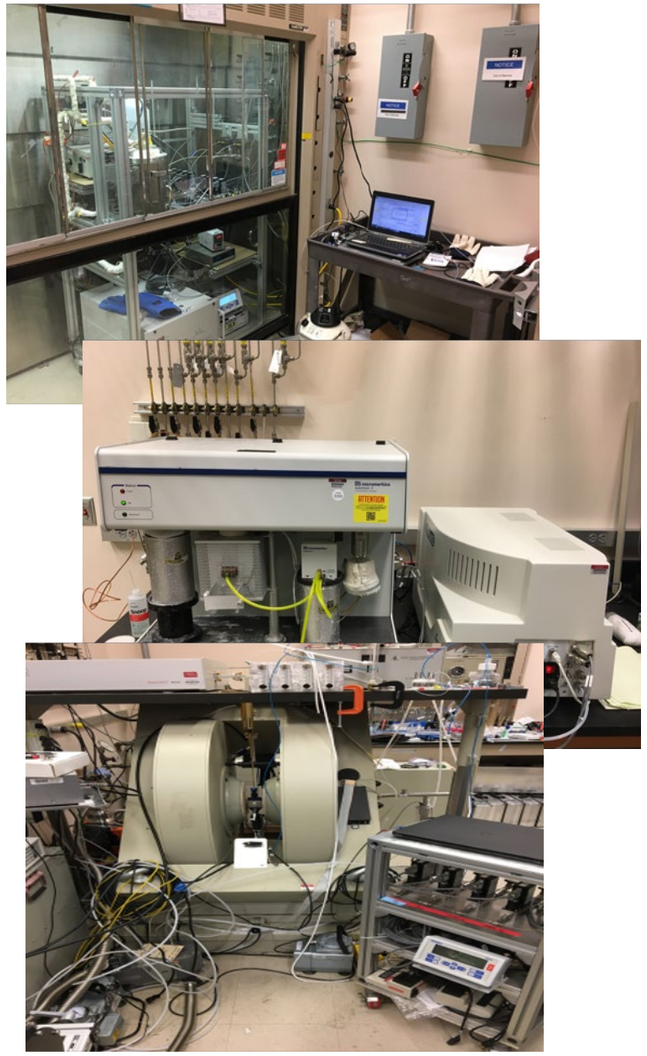
- Develop characterization tools to monitor dynamic changes upon progressive aging.
- Characterize field-aged samples, identify and model the changes in active sites.
- Develop accelerated procedures to simulate real-world aging (RWA) of SCR catalysts.

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	Complete	02/28/2022	100%
➢ Generate models to describe the performance degradation	On track	02/28/2023	30%

Approach

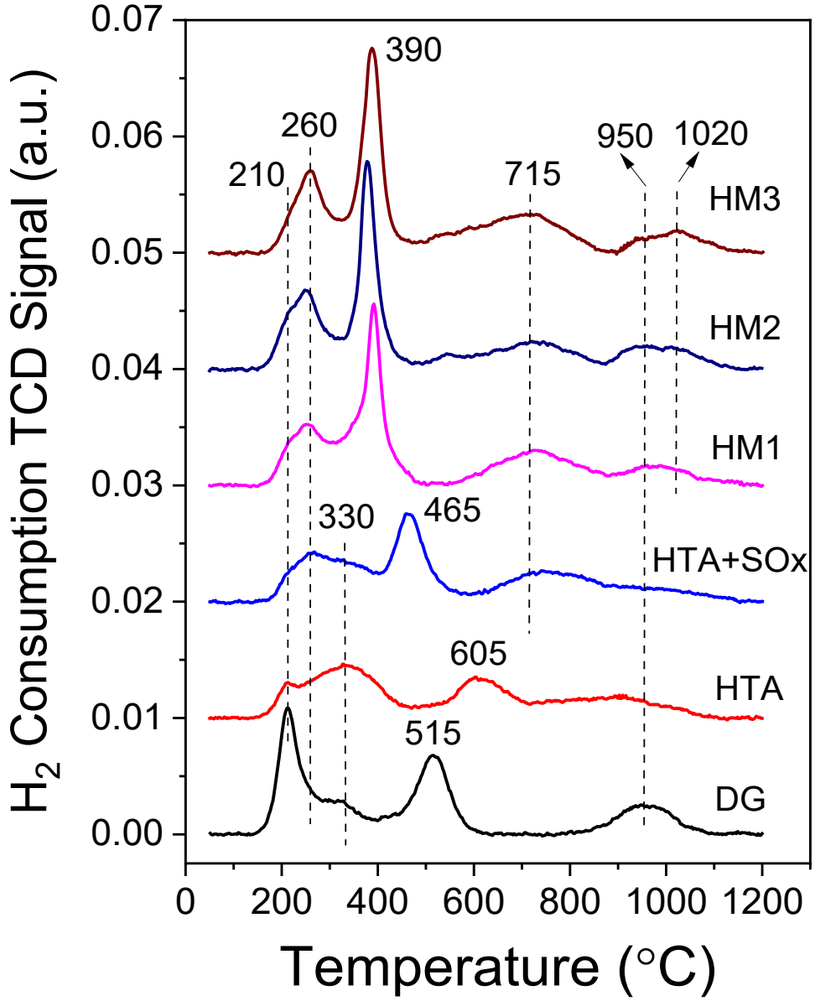
- Harness PNNL's strengths in fundamental sciences to clarify and circumvent / mitigate the barriers to highly efficient emission control with improved low temperature activity, extended useful life, and reduced cost.
  - Institute for Integrated Catalysis (IIC)
  - Environmental Molecular Sciences Laboratory (EMSL)
- Orient strongly towards applications and commercialization through close collaboration with our CRADA partner Cummins, Inc.



Technical Accomplishments

- Identified gaps between field-aged and existing simulated aged catalyst behavior.
- Developed model catalyst synthesis and aging protocols.
- 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.
  - Utilized detailed kinetic analysis of standard SCR, NH_3/NO oxidation reactions to develop structure-performance correlations.

Technical Accomplishments: Precise Cu speciation



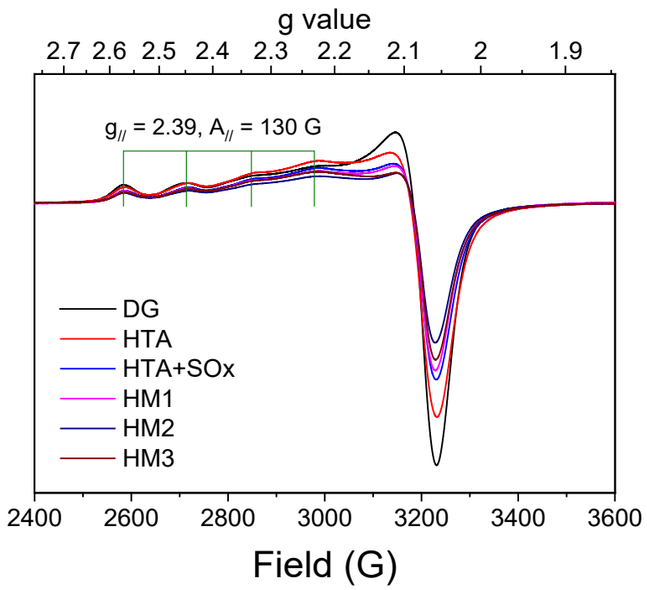
H_2-TPR, lab-aged vs. real-world

- Based on H_2-TPR (probed via both TCD and Mass Spec) and *in situ* XPS, all reduction peaks are now properly assigned.

Reduction Temp.	Assignment	Note
210 °C	$ZCu^{II}OH$	All samples
260 °C	CuOx clusters	S-containing samples
330 °C	Z_2Cu^{II}	Lab aged samples
390 °C	Cu-sulfates	HM1, HM2, HM3
465 °C	Cu-sulfates	HTA+SOx
515 °C	ZCu^{I} (8MR)	DG
605 °C	ZCu^{I} (8MR)	HTA
715 °C	SO_4^{2-}	S-containing samples
950 °C	ZCu^{I} (6MR)	All samples
1020 °C	SO_4^{2-}	S-containing samples

Technical Accomplishments: Precise Cu quantification

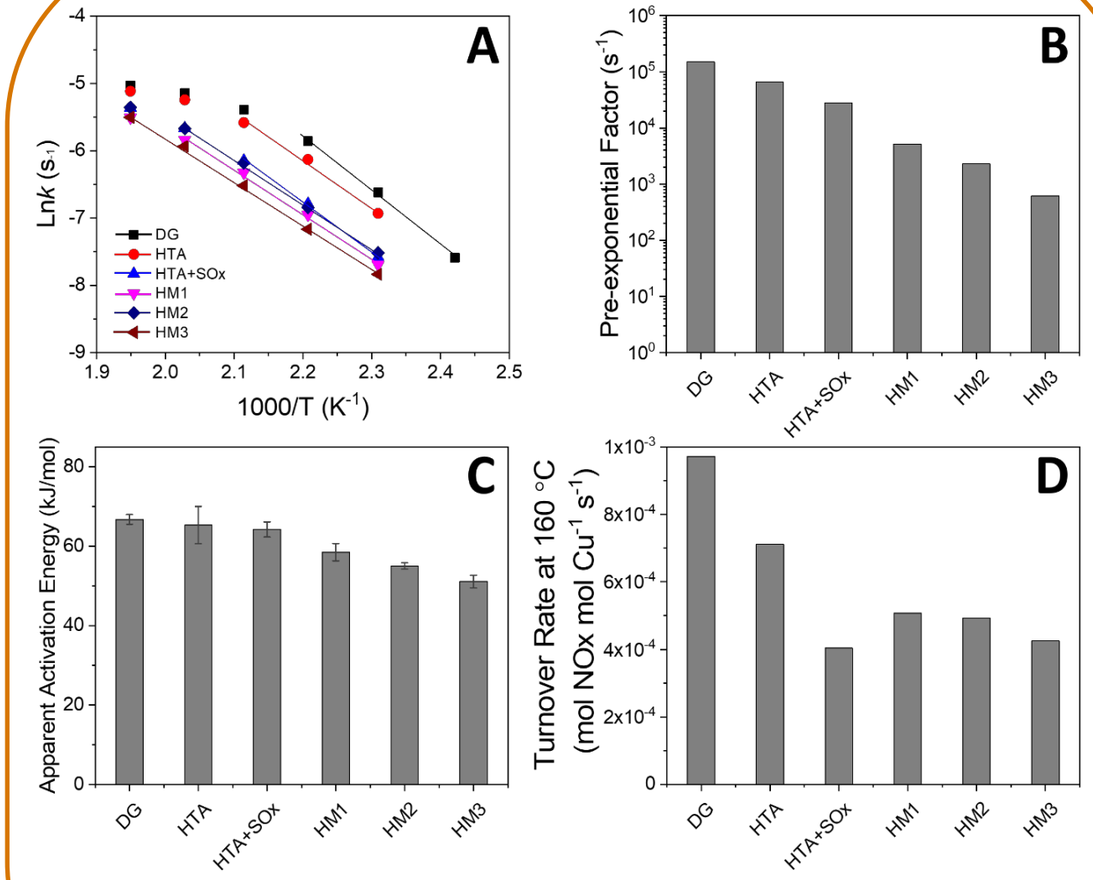
Sample	Cu content		Isolated Cu(II) EPR (wt%)	Reducible Cu NO+NH_3 titration (wt%)	S content		S:Cu molar ratio	
	ICP (wt%)	XPS (wt%)			ICP (wt%)	XPS (wt%)	ICP (wt%)	XPS (wt%)
DG	2.31	2.62	2.32	2.27	-	-		
HTA	2.42	2.93	2.35	2.27	-	-		
HTA+SOx	2.38	3.89	1.84	2.09	0.14	0.15	0.12	0.08
HM1	2.42	3.39	1.45	1.48	0.22	0.25	0.18	0.15
HM2	2.50	2.88	1.67	1.82	0.31	0.40	0.25	0.28
HM3	2.50	2.77	1.65	1.54	0.58	0.64	0.46	0.46



- Hydrothermal aging at 650 °C does not lead to agglomeration of isolated Cu-ions.
- CuOx formation must be due to the presence of SOx.
- EPR silent Cu (or non-reducible Cu by NO+NH_3) is not CuOx alone, nor $CuSO_4$ alone, but the mixture of the two with stoichiometries between CuOx·$CuSO_4$ and $CuSO_4$.

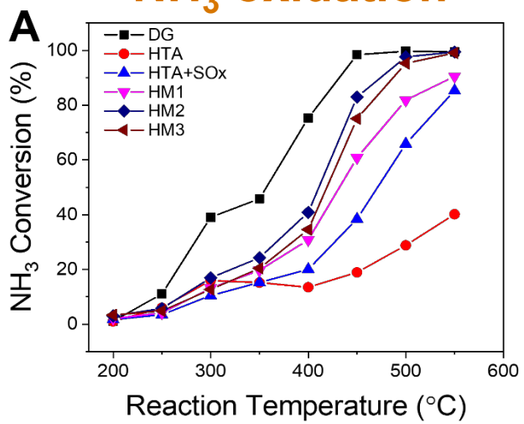
Technical Accomplishments: SCR and NH_3/NO oxidation kinetics

Standard SCR

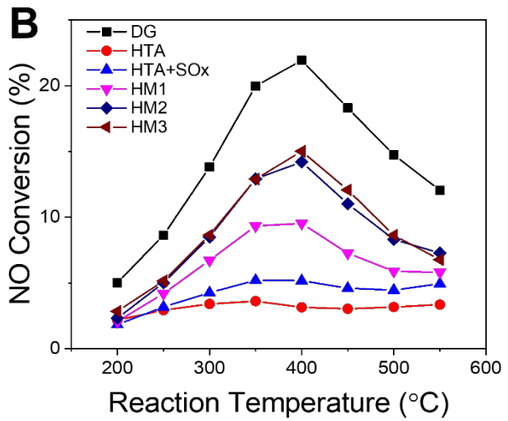


$$k = \frac{r}{[NOx]_0} = Ae^{\frac{-E_a}{RT}}$$

NH_3 oxidation

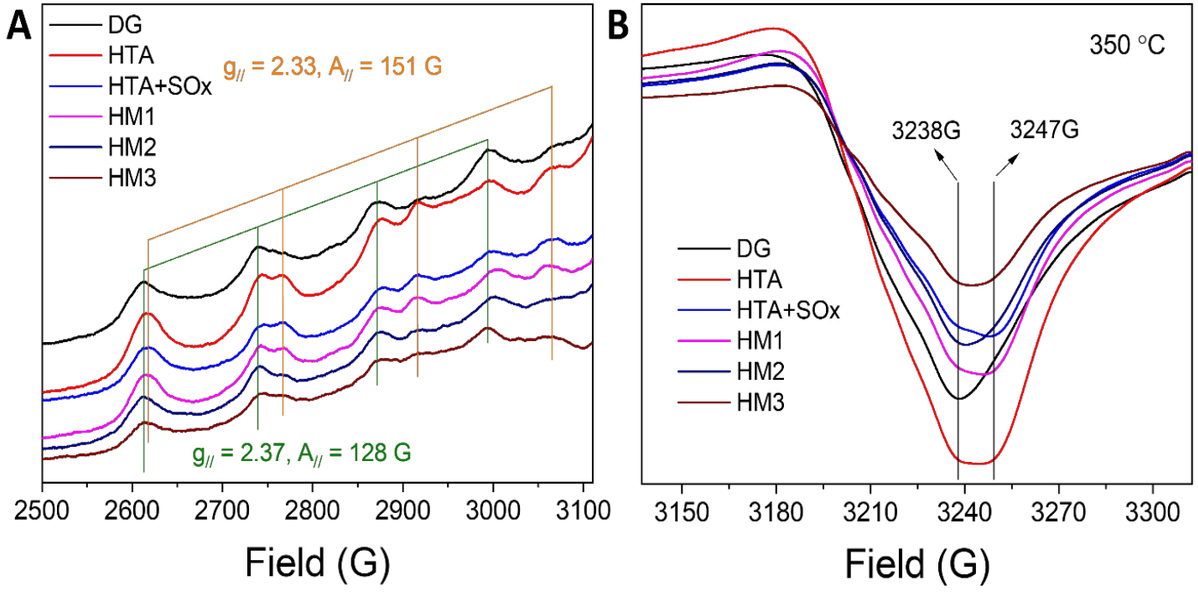


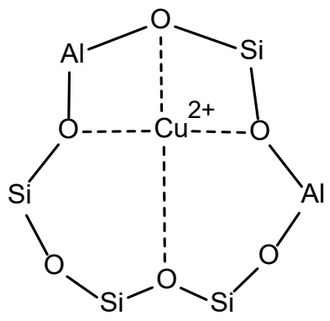
NO oxidation



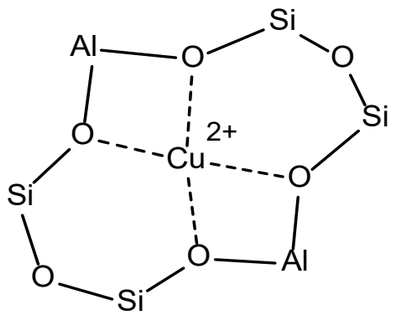
- Hydrothermal aging induces ~30% atomic efficiency loss for SCR, whereas HTA+SOx and RWA induce ~50% loss.
- NH_3 and NO oxidation tests indicate that hydrothermal aging severity during RWA is lower than that in lab aging. This is consistent with H_2-TPR.
- Sulfur poisoning and chemical aging of catalyst due to the presence of sulfur in the exhaust is more responsible than HTA in catalyst degradation.

Technical Accomplishments: Operando EPR - HTA severity descriptor





m-Z_2Cu^{II}



p-Z_2Cu^{II}

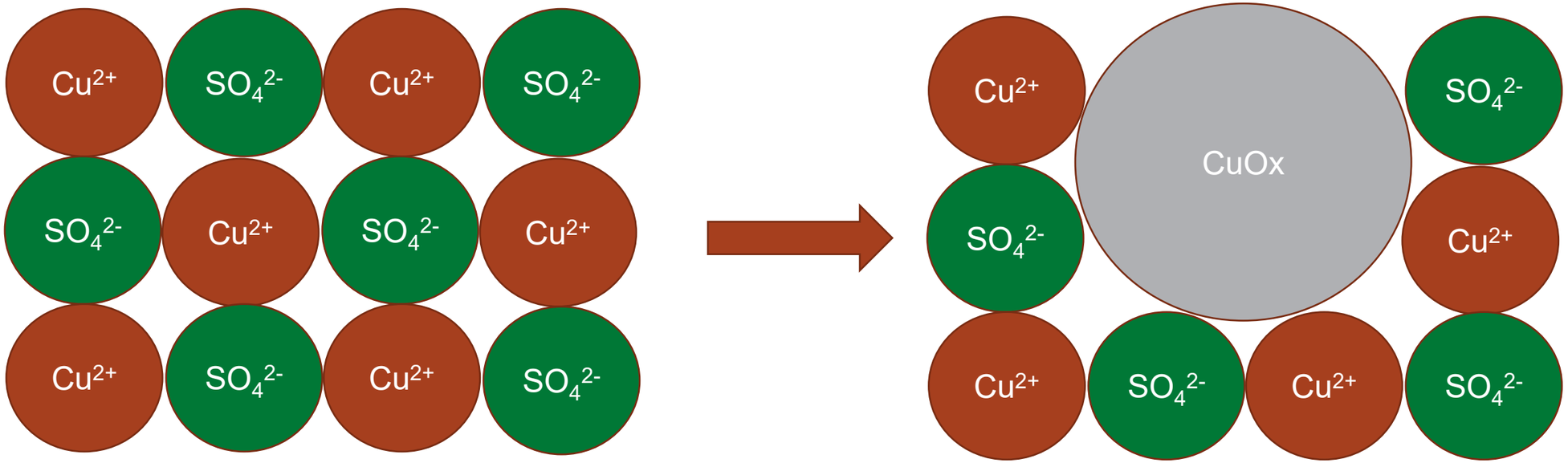
- Formation of p-Z_2Cu^{II} as a good descriptor for HTA severity.
- HTA severity order: HTA > HTA+SOx > HM1 > HM2 ≈ HM3.
- HM2 and HM3 catalysts underwent milder desulfation treatments than HTA+SOx and HM1.

Technical Accomplishments: Desulfation pathways

(1) $Z\text{-}CuOH + SO_2 + \frac{1}{2} O_2 \rightarrow Z\text{-}Cu\text{-}HSO_4 \rightarrow ZH + CuSO_4$

(2) $CuSO_4 \rightarrow (CuSO_4)n$

(3) $(CuSO_4)n \rightarrow CuOx \cdot CuSO_4$



Responses to Previous Year Reviewers' Comments

Q1: zeolite structure and acidity may also affect the catalyst NOx conversion and thus should be examined.

A1: we indeed utilized ^{27}Al NMR and NH_3-TPD to examine catalyst acidity.

Q2: it would be better if there were more concrete evidence that Cu-sulfate formation occurs.

A2: the combination of in situ XPS and H_2-TPR unambiguously demonstrate the formation of Cu-sulfate. Its EPR silent nature further indicates its presence as multinuclear aggregate.

Q3: elemental analysis of the field-aged parts seems to be urgently required.

A3: we indeed conducted wide scan of the catalysts with XPS. Except Al, Si, O, Cu and S, we didn't observe the presence of other poisons.

Q4: what techniques will be used to simulate a similar poisoning mechanism (between Lab and Field)?

A4: a combined reaction kinetics and in situ spectroscopy (in particular, EPR). Our data indicate more severe sulfur poisoning but less severe hydrothermal aging for the field catalysts (as compared to lab catalysts).

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	Collaboration with Professor Jeffrey T Miller in synchrotron-based studies at APS.
Argonne NATIONAL LABORATORY Advanced Photon Source	
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

- Aging model development with Cummins:
  - Spectroscopic characterization and kinetic data on lab-aged and real-world aged catalysts are being utilized to develop a continuous aging SCR redox model
  - This model incorporates:
    - Different ion-exchanged Cu configurations in the reduced and oxidized state
    - Cu^{II} site transformation during hydrothermal aging
    - Sulfur poisoning and sulfur aging mechanisms
    - Influence of aging on NH_3 storage, SCR performance, oxidation functions and N_2O formation
  - The first version of this model should be available by end of Q2, 2022, with further development and validation work planned throughout 2022
- Transitioning from on-road to off-road research focuses.

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

Presentations and Publications

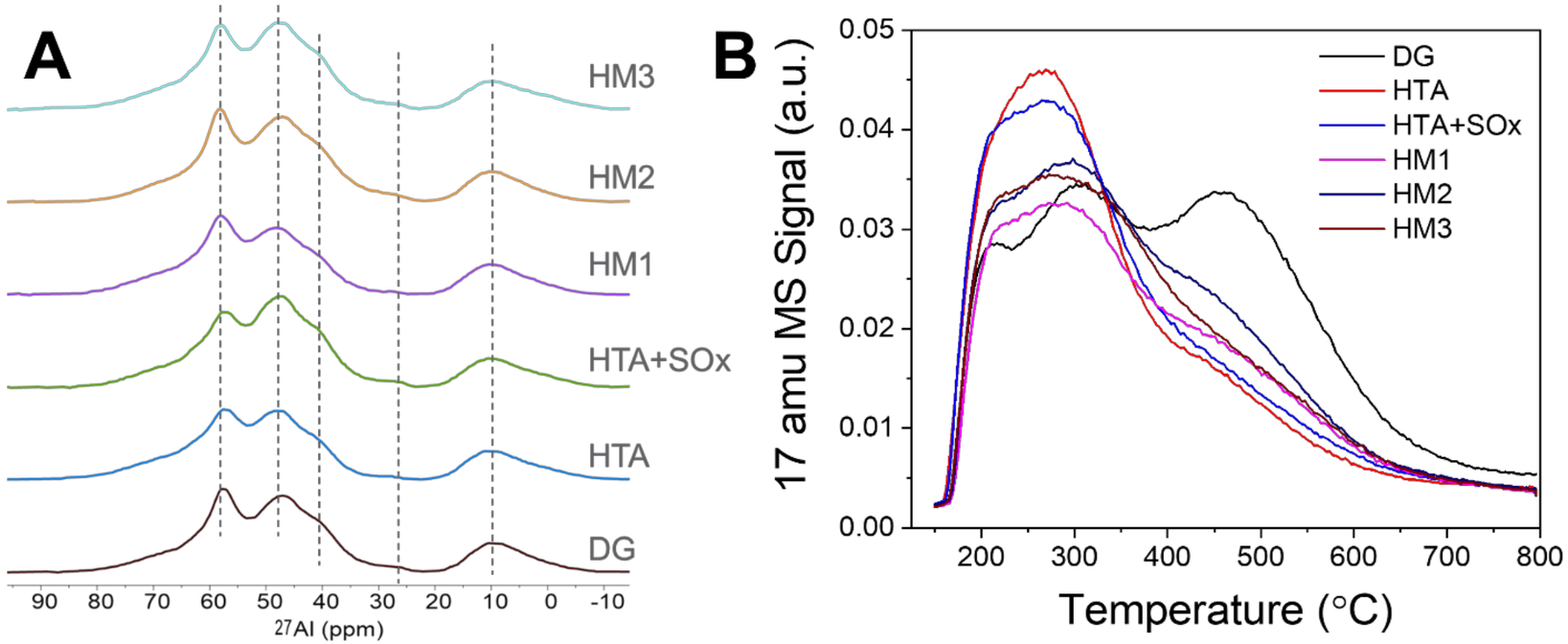
Yiqing Wu, Tahrizi Andana, Yilin Wang, Ying Chen, Eric D. Walter, Mark H. Engelhard, Kenneth G. Rappé, Yong Wang, Feng Gao*, Unmesh Menon, Rohil Daya, Dylan Trandal, Hongmei An, Yuhui Zha, Krishna Kamasamudram, A Comparative Study between Real-world and Laboratory Accelerated Aging of Cu/SSZ-13 SCR Catalysts, Applied Catalysis B, submitted.

Summary

- Demonstrated clear gaps between Field and Lab accelerated aging that require molecular-level investigations to comprehend.
- Detailed characterization of 6 representative catalysts from Cummins (H_2-TPR, XPS, EPR etc.) coupled with SCR, NH_3/NO oxidation tests.
- The utilization of operando methods in studying catalysts under the most relevant SCR reaction conditions.
- As compared to lab-aged catalyst in the presence of SOx, real-world aged catalysts suffer from more severe sulfur poisoning, but less hydrothermal aging degradation. The combination of these two factors is responsible for gaps between lab-aging and real-world aging.

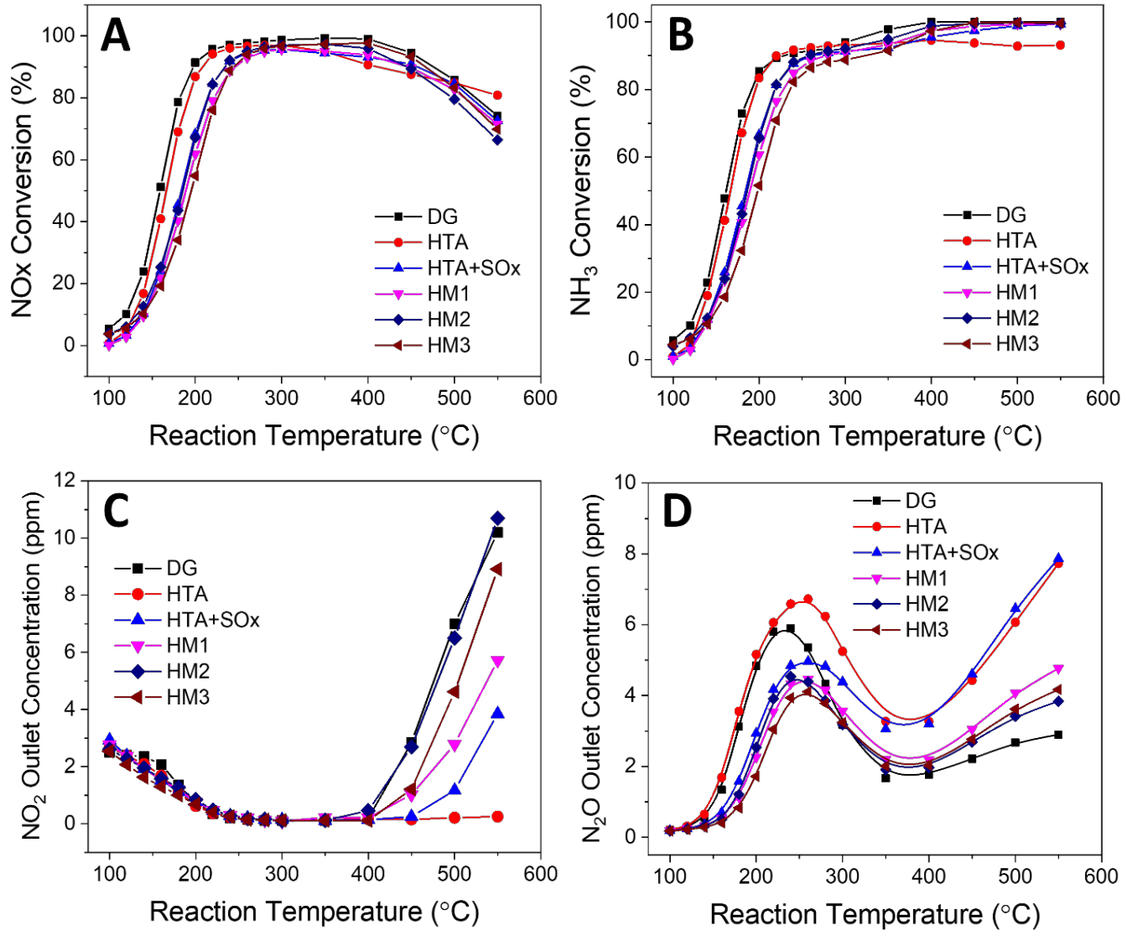
Technical Back-Up Slides

Technical Accomplishments: Probing acidity of the catalysts



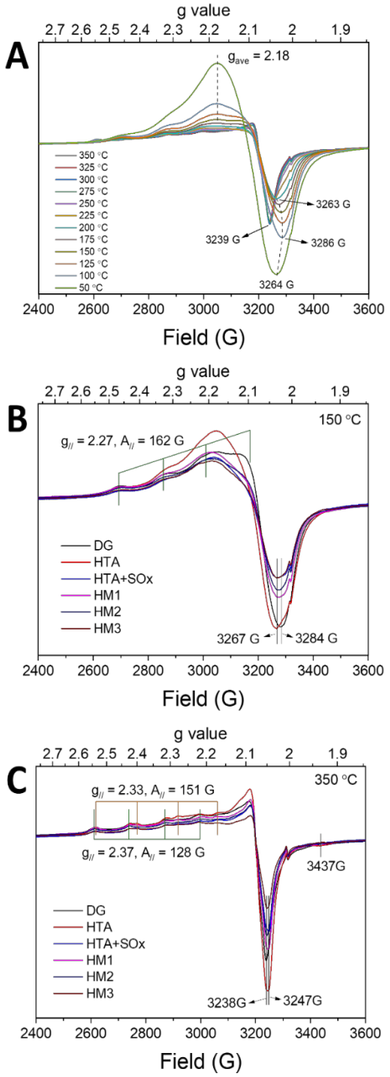
(A) ^{27}Al NMR spectra and (B) NH_3-TPD results for the Cu/SSZ-13 catalysts.

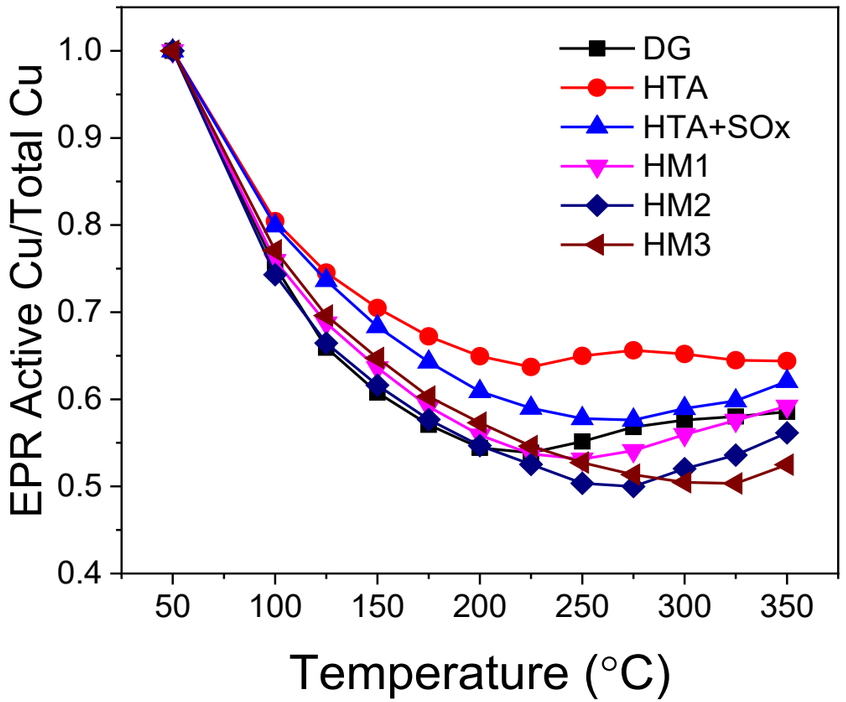
Technical Accomplishments: SCR testing results



(A) NOx conversion, (B) NH_3 conversion, (C) NO_2 outlet concentration, and (D) N_2O outlet concentration as a function of temperature over the Cu/SSZ-13 catalysts in standard SCR. The composition of the gas feed was 350 ppm NH_3, 350 ppm NO, 10% O_2, 2.5% H_2O, and balance N_2. 240 mg of crushed core samples were used for these tests, and the total flow rate was 600 mL min^{-1}.

Technical Accomplishments: Operando EPR results





EPR visible Cu/total Cu as a function of temperature over the Cu/SSZ-13 catalysts under operando SCR condition

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Thank you