Pacific Northwest NATIONAL LABORATORY | Institute for INTEGRATED CATALYSIS

Controlling NOx Reduction and Low Temperature Oxidation

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ACE023

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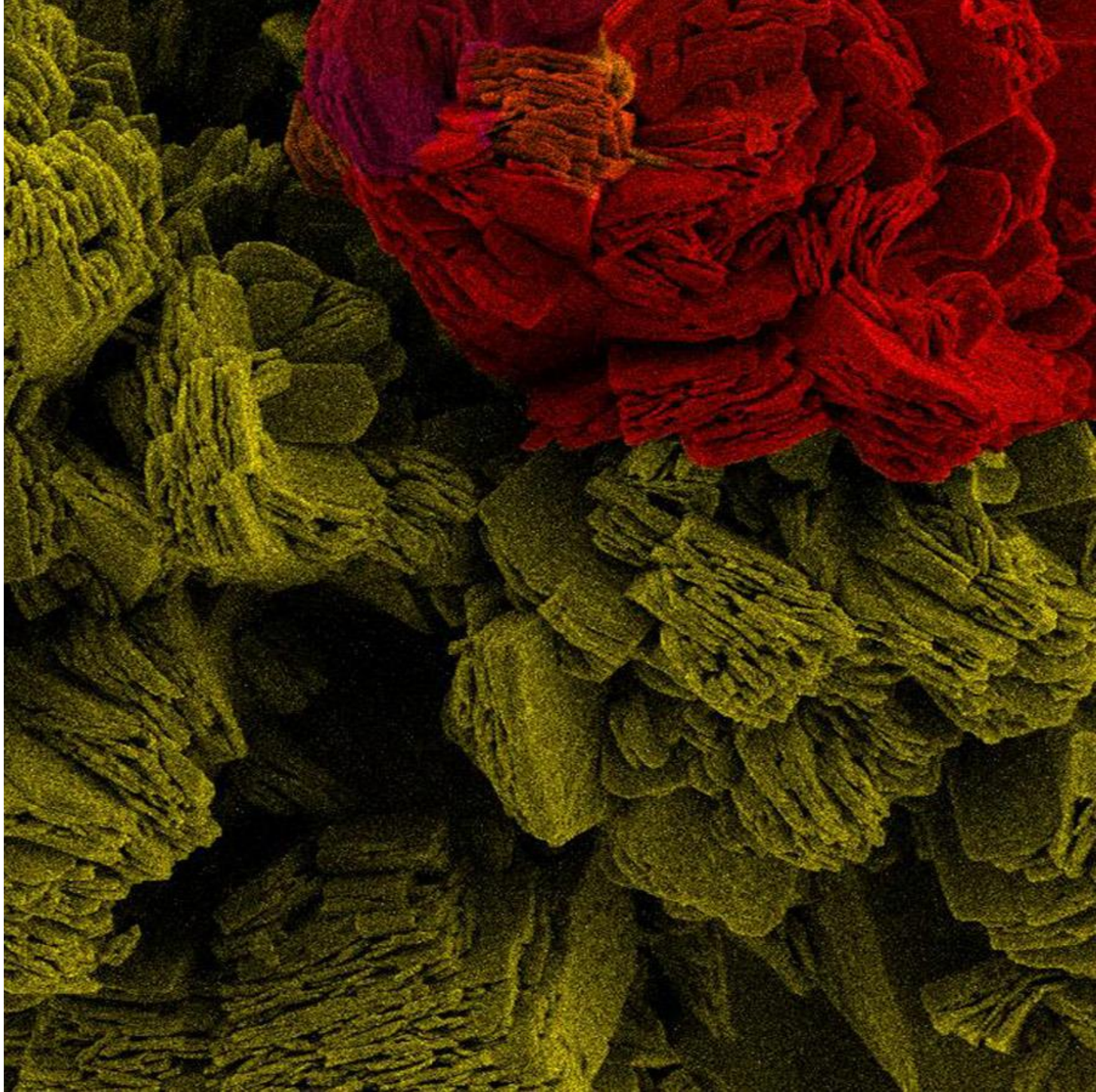


Overview

Timeline

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

Budget –

- FY21 funding: $1.2M
- FY22 funding: $350K

Barriers

- ***Durable*** emission controls add ***cost*** and incur ***fuel penalties*** for applications hard to electrify
  - Low-temp performance under low load cycles
  - Extended useful life
  - Emissions of low carbon fuels, renewable fuels (e.g., e-methane, R-NG)
- Improvements limited by:
  - Chemistry fundamentals
  - Knowledge of material behavior
- Effective dissemination of information

Partners

- DOE Advanced Engine Crosscut Team
- 21CTP partners
- Oak Ridge National Lab
- Cummins, BASF, John-Deere, Caterpillar, Carus, UNM, WSU

Relevance and Objectives

- Supporting 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
  - The knowledge generated enables industry (often through collaboration) to develop the next generation of fuels, engines, and emission controls.
- Meeting off-road Tier 5 regulations
  - Low-load cycle (LLC) – low temperature performance
  - Extended useful life – durability
  - GHG emissions, e.g, N_2O
- Controlling emissions from low carbon fuels, renewable fuels (e.g., e-methane, R-NG)

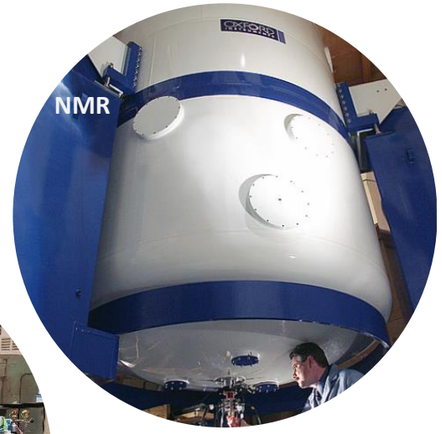
Objectives – Generate knowledge on how to improve low temperature activity, extend useful life, reduce usage of PGMs and cost associated with emission control from low carbon fuels for the applications that are difficult to electrify while aligning with industrial priorities

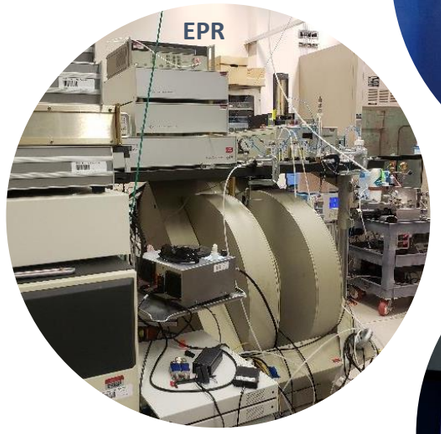
Technical Milestones

Month/Year	Description of Milestone or Go/No-Go decision	Status
06/2021	Complete initial studies of NO_x storage function and application to TWCs for stoichiometric combustion engines	Complete
09/2021	Understand & characterize the site requirement for low-temperature fast SCR on Fe/zeolites	Complete
09/2021	Understand the activation, deactivation and regeneration of Pd/FER	Complete
09/2022	Understand & characterize site requirement for N_2O formation	On track
09/2022	Demonstrate sulfur tolerance and catalyst regeneration on single atom catalysts based on non-PGMs	On track

Approach/Strategy

- 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 PGM and cost.
  - Institute for Integrated Catalysis (IIC)
  - Environmental Molecular Sciences Laboratory (EMSL)
- Orient strongly towards applications and commercialization through formal and informal engagements with:
  - OEMs
  - TIER 1 suppliers
- Work closely with our partners and sponsors
  - ORNL
  - DOE Advanced Engine Cross-Cut Team

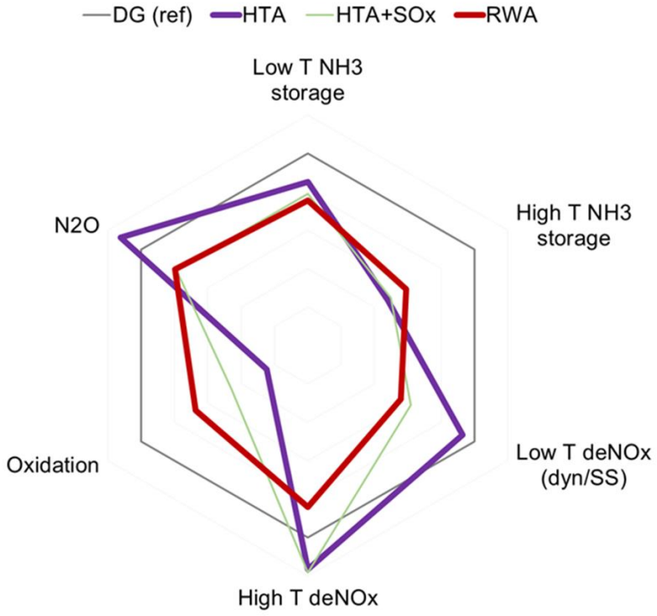




Technical Accomplishments and Progress (SCR durability)

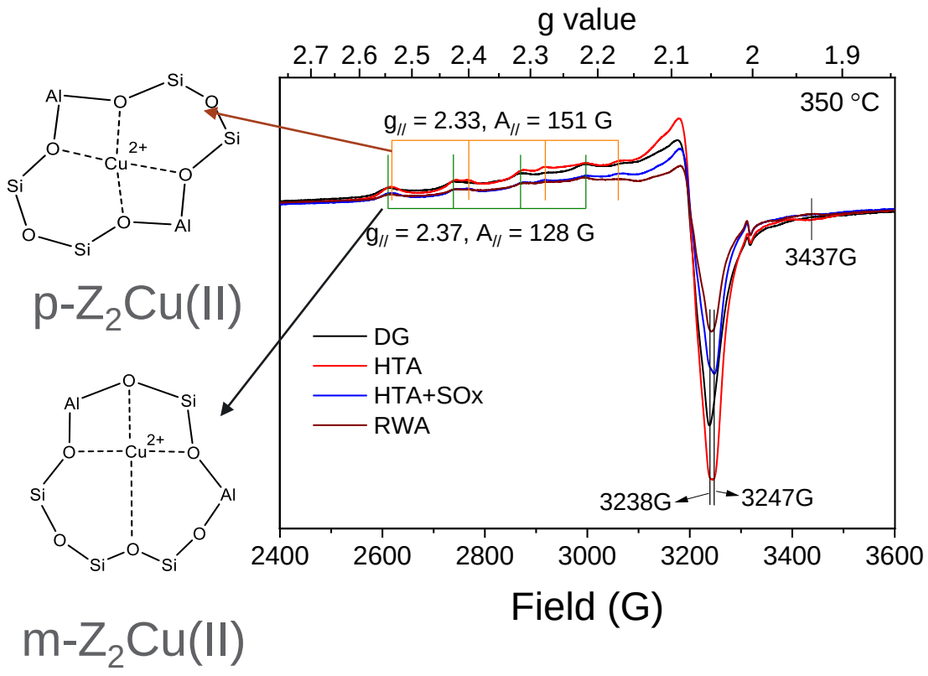
Developed lab-aging protocols in the presence of SO_x at temperatures < 650 °C to better mimic real-world aging

Gaps between lab and real-world aging

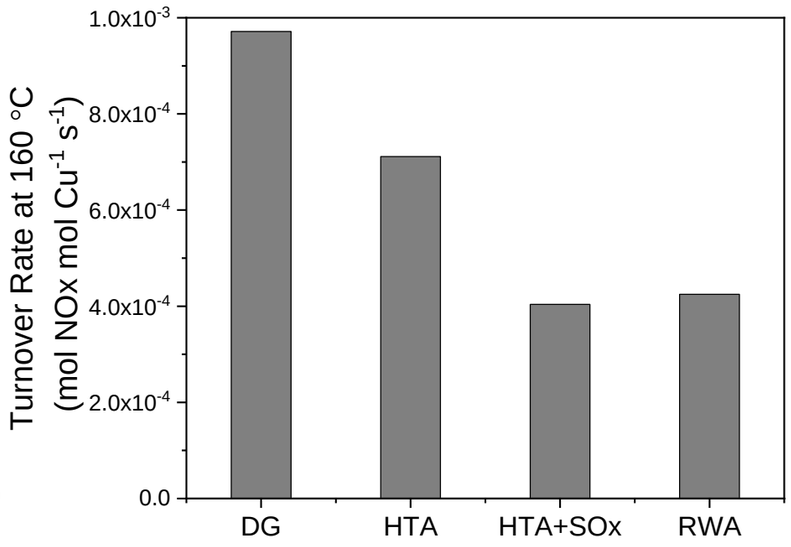


DG:	550 °C, 4h
HTA:	650 °C, 100h
HTA+SOx:	650 °C, 60h

operando EPR at 350 °C



SCR turnover rates at 160 °C

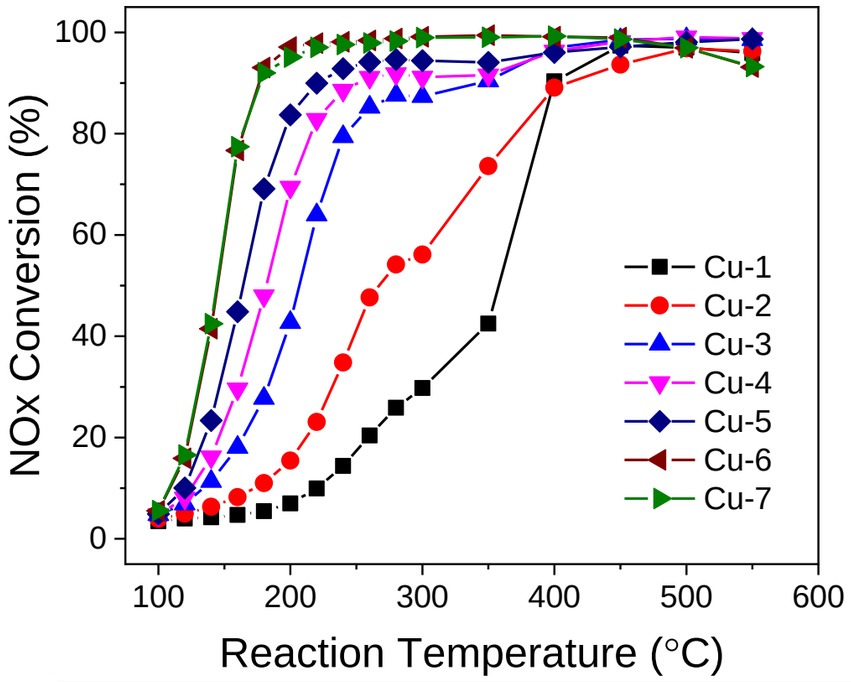


Details in ACE027 by Feng Gao

- Formation of p-Z_2Cu(II) as a good descriptor for the severity of hydrothermal aging.
- p-Z_2Cu(II) is more stable (i.e., less reactive) than m-Z_2Cu(II). This explains why HTA induces catalyst deactivation even without loss of active site density.
- The low atomic efficiency for RWA is due more to sulfur poisoning than to hydrothermal aging.

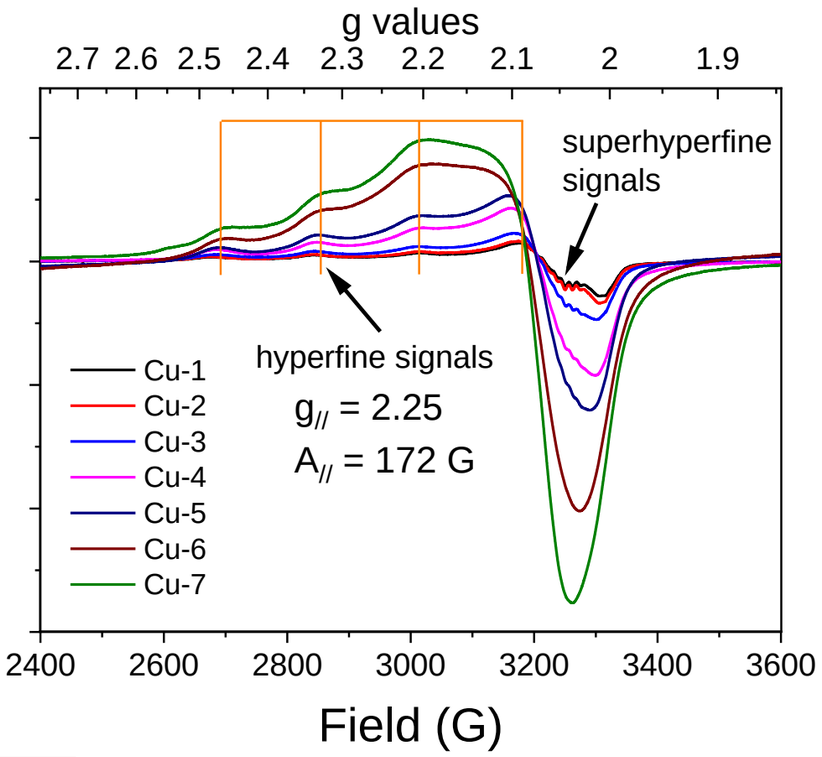
Low temperature standard NH_3-SCR activity is controlled by Cu species with the highest inter-cage mobility

NOx conversion as a function of temperature for standard SCR on 7 Cu/SSZ-13 catalysts

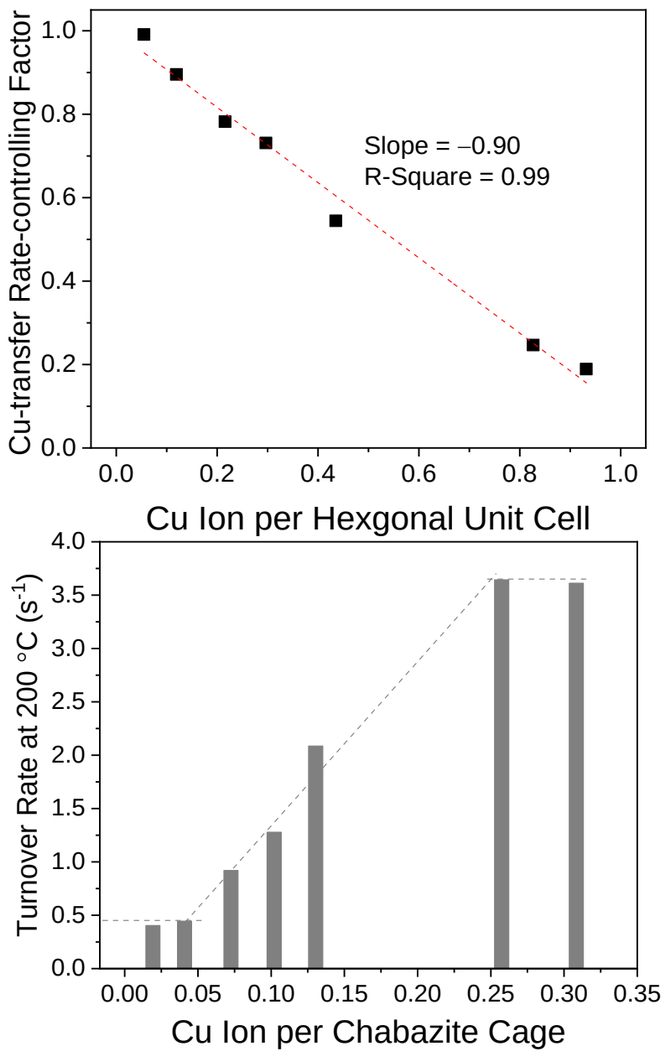


350 ppm NOx (including ~10 ppm NO_2), 350 ppm NH_3, 2.5% H_2O, 10% O_2, and balanced N_2 at a GHSV of ~2×10^5 h^{-1}

operando EPR at 200 °C



Increased Cu atomic efficiency with Cu loading



- Low-temperature atomic efficiency increases with Cu loading up to ~1/3 Cu ion per cage.
- Mobility of Cu-ions and inter-cage transfer of Cu-ions increase with Cu loading.

Wu *et al*, ***J.Am.Chem.Soc*** (revisions submitted)

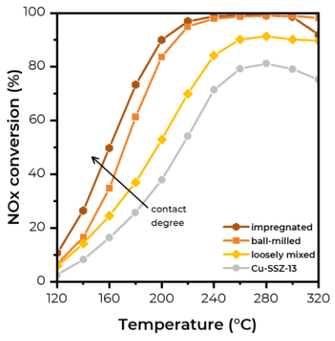
Technical Accomplishments and Progress (SCR low temperature activity)

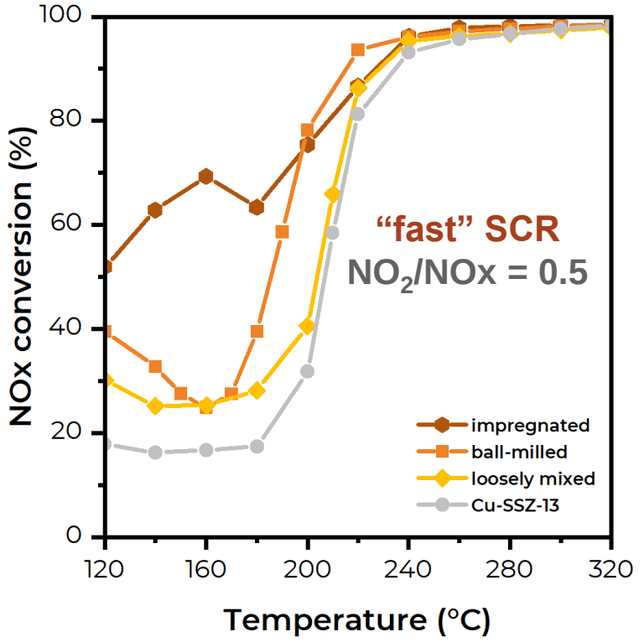
Overcome the barrier of Cu redox chemistry and inhibition of NH_4NO_3 by SCO

SCO: $Ce_{0.7}Mn_{0.3}O_X$; SCR: Cu-SSZ-13
SCO-SCR: 1:3 (by wt)

Reaction conditions:
175 ppm NO
0 or 175 ppm NO_2
350 ppm NH_3
15% O_2, 8% CO_2, 6% H_2O
SV = 400 L g^{-1} h^{-1}

NO_2/NOx = 0
"standard" SCR

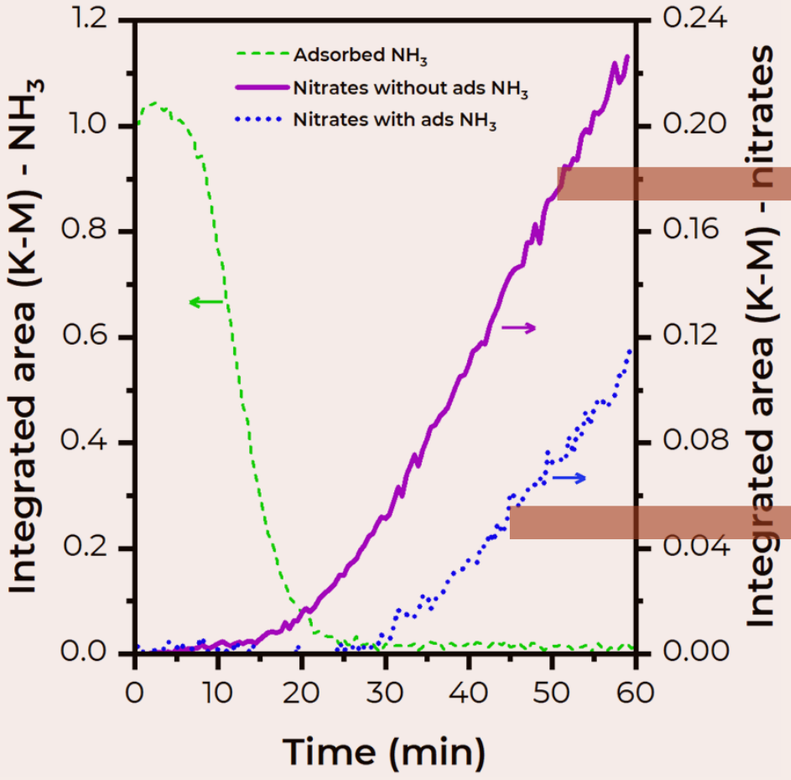


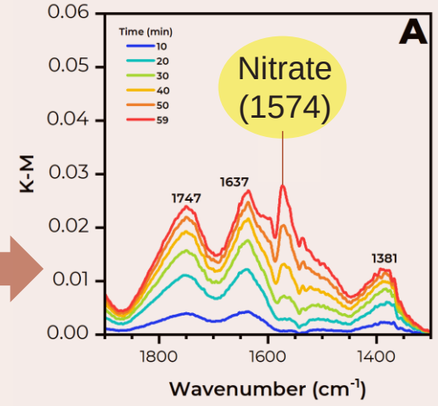


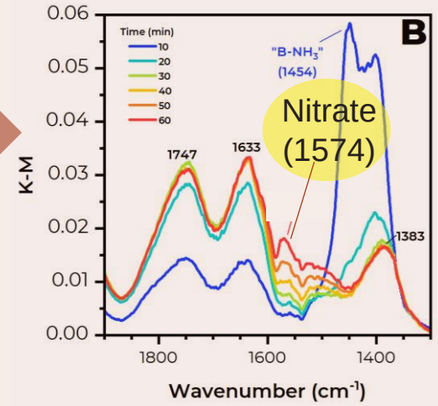
- Positive impact of SCO-SCR observed in both "standard" and "fast" SCR
- SCO catalyst (closely coupled to SCR) reduces NH_4NO_3 inhibition
  - Beneficial to "fast" SCR
  - Practical solution to low-temperature SCR activity

in situ DRIFTS spectra of SCO/HSZ (ball-milled) in a NO/O_2 mixture

Reaction conditions:
175 ppm NO,15% O_2, 6% H_2O



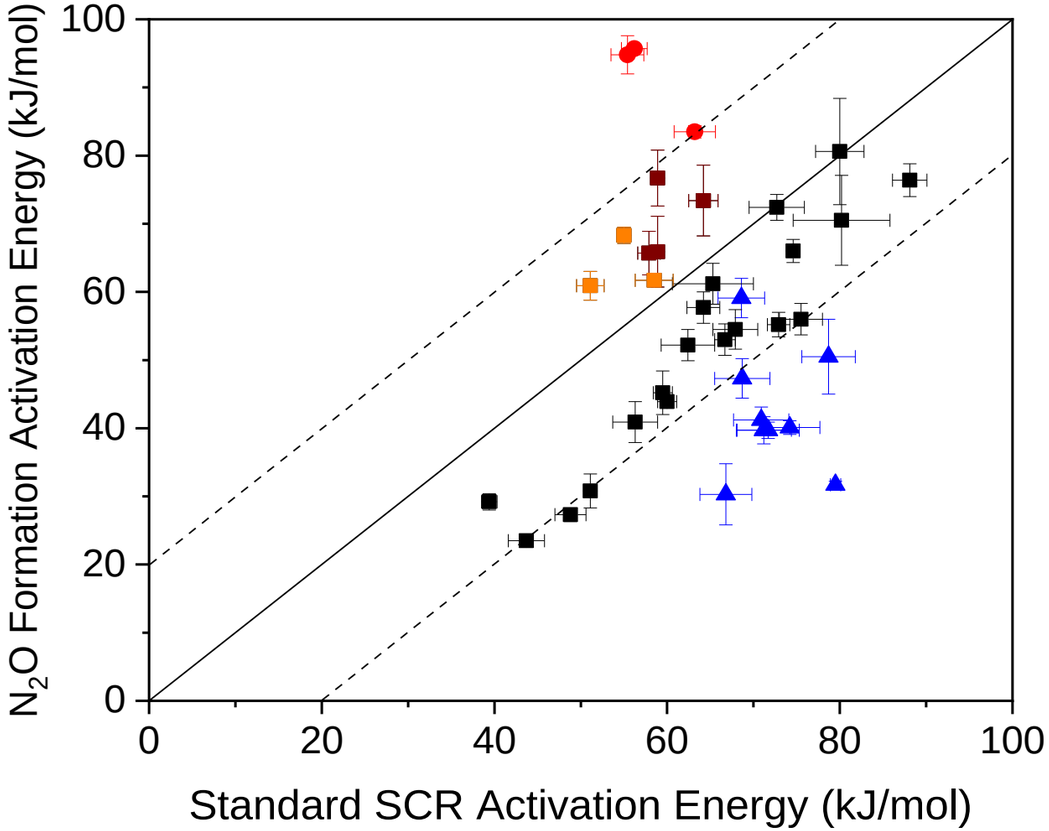




- SCO supplies reactive species to zeolite
  - Superior SCR activity
  - Reduced NH_4NO_3 inhibition on Cu-SSZ-13

Andana *et al*, ***Applied Catalysis B: Environmental*** (revisions submitted)

N_2O formation is SCR catalyst-dependent and mechanisms are complex



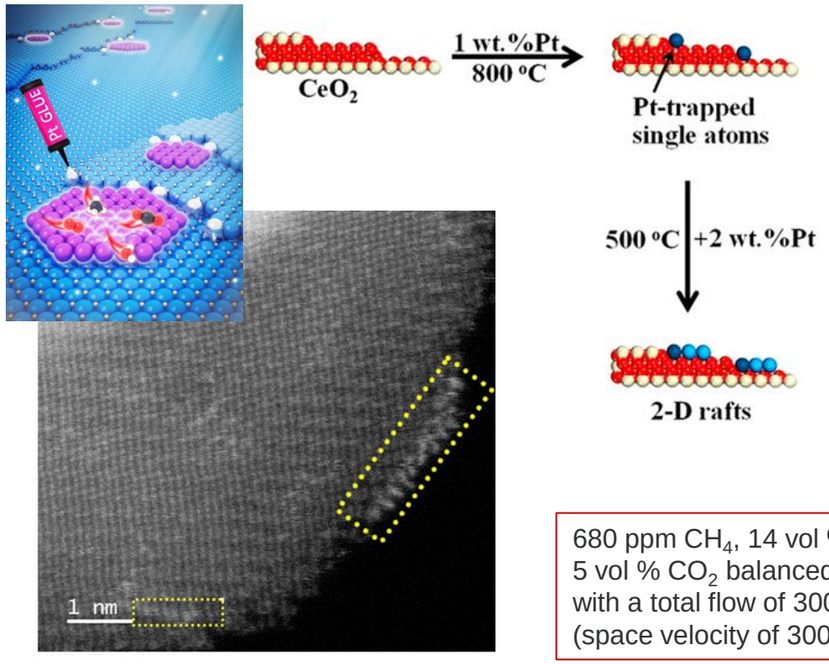
- The Cu/SSZ-13 catalysts we studied in the past, fresh or HTA, display in most cases N_2O formation activation energies 0-20 kJ/mol less than the corresponding SCR activation energies. (■) majority
- Some Cu/SSZ-13 catalysts display slightly higher N_2O formation activation energies than SCR. (■) sulfur poisoned catalysts; (■) solid-state ion exchanged catalysts.
- A few Cu/SSZ-13 catalysts display N_2O formation activation energies substantially higher than SCR. (●) high Si/Al ratio catalysts.
- Cu/SAPO-34 catalysts, fresh or HTA, typically display N_2O formation activation energies at least 20 kJ/mol less than the corresponding SCR activation energies. (▲)

- NH_4NO_3 is the most stable species in standard SCR. If N_2O formation originates purely from NH_4NO_3 decomposition, then N_2O formation activation energy should not be lower than that of standard SCR.
- Low-temperature N_2O formation mechanism must be complicated, including decomposition of NH_4NO_3, and decomposition of other less stable intermediates that are not fully understood.

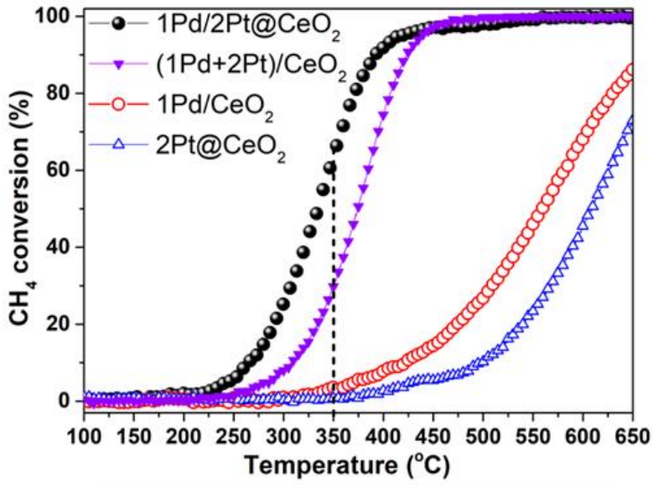
Technical Accomplishments and Progress (low temperature methane oxidation)

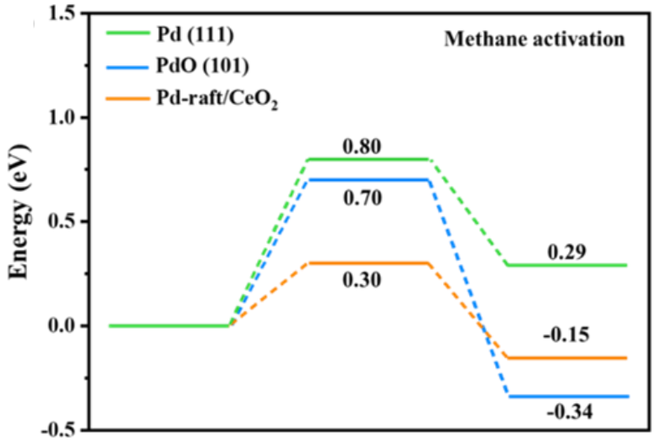
Modification of ceria support by atom trapping of Pt stabilizes PdO_x 2-D rafts for water-tolerant methane oxidation

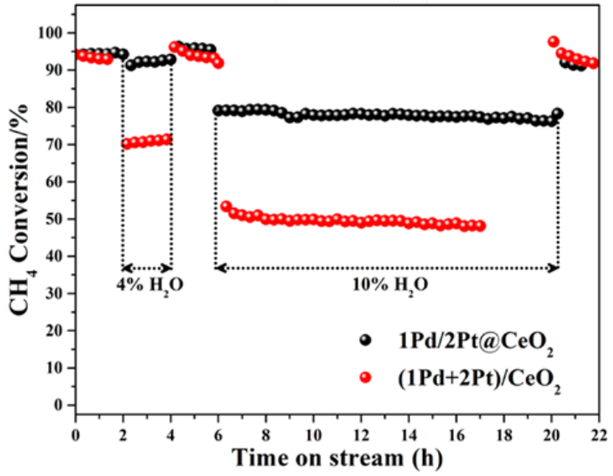
2-D PdOx rafts on Pt@ceria SACs

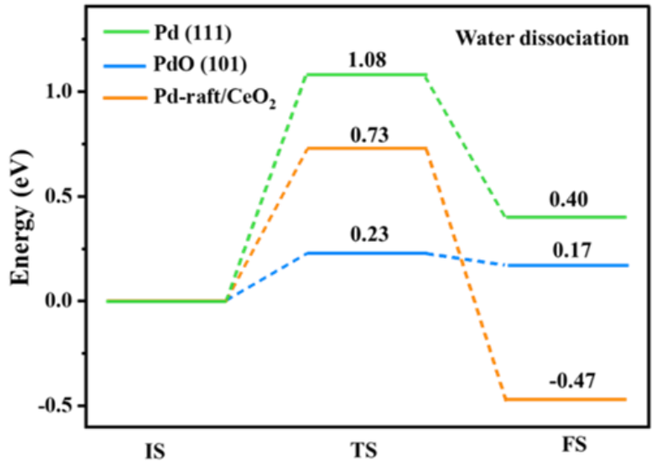


680 ppm CH_4, 14 vol % O_2 and 5 vol % CO_2 balanced with N_2 with a total flow of 300 mL/min (space velocity of 300 L/g_{cat}/h)







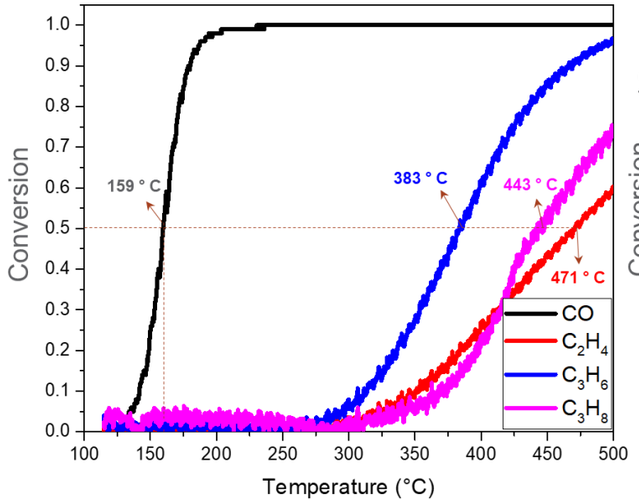


- Modification of ceria support with Pt single atoms by atom trapping leads to controlled nucleation and growth of PdO_x, forming 2-D PdO_x rafts, which favors CH_4 activation with less water inhibition.
- Enhanced sulfur tolerance tested using US.DRIVE protocols.

Xiong, *et al* ***Nature Catalysis***, 2021, 4, 830-839

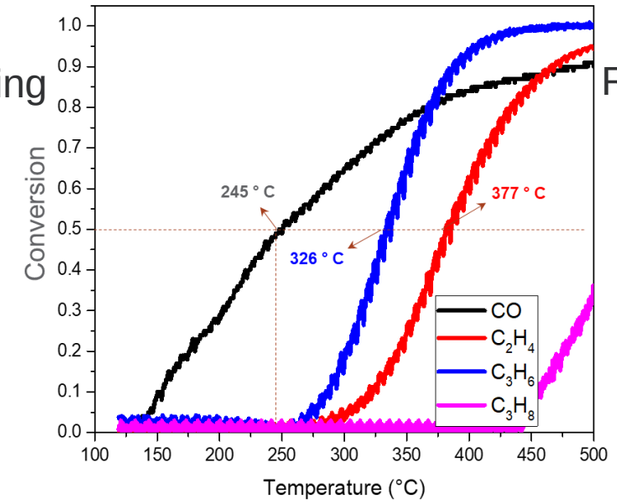
Technical Accomplishments and Progress (low temperature oxidation with non-PGM)

Highly active and durable 2wt%Cu@CeO_2 by atom trapping can be readily regenerated after sulfur poisoning



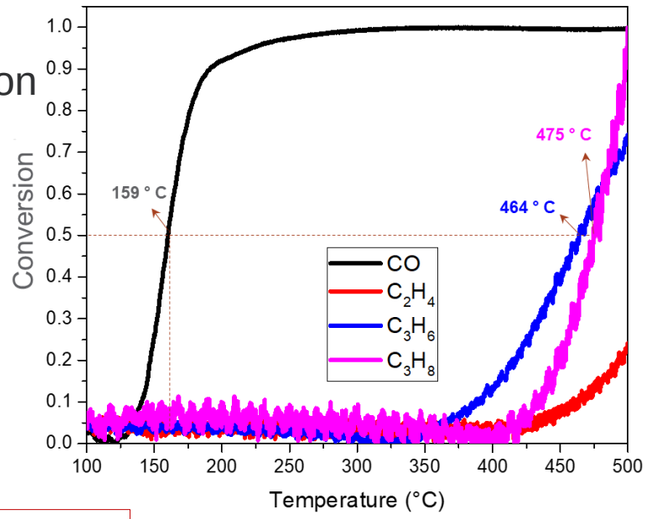
Sulfur poisoning

12% O_2
6% H_2O
5ppm SO_2
200 L g^{-1} h^{-1}
75 min
300 °C

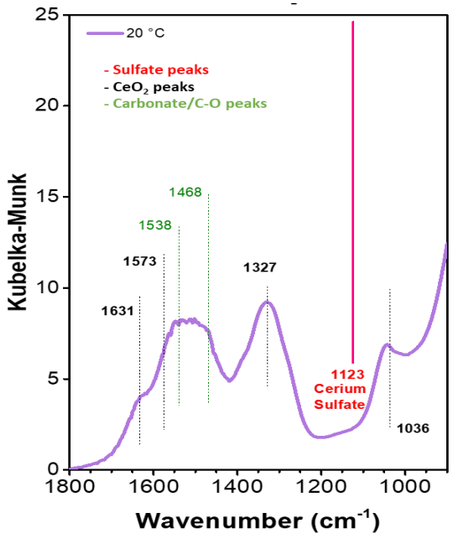


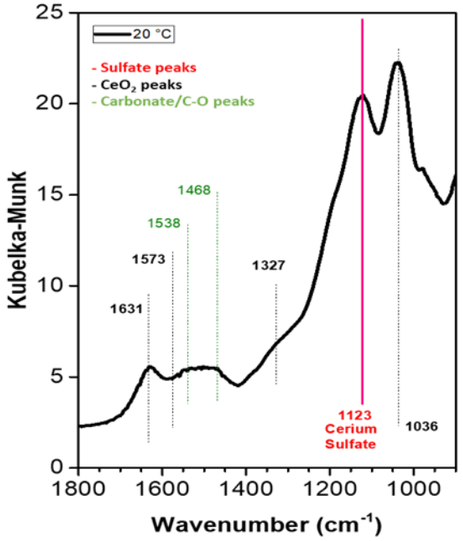
Regeneration

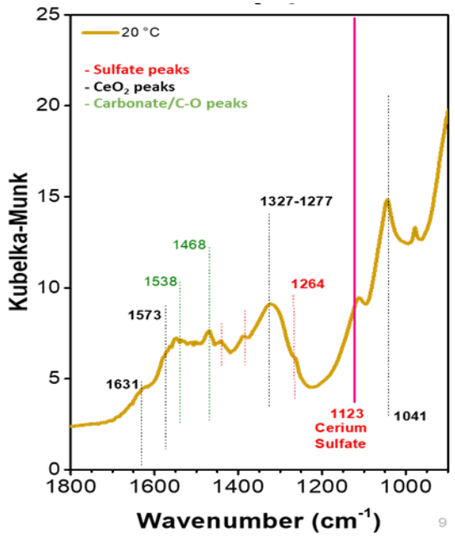
12%O_2
6%CO_2
6% H_2O
200 L g^{-1} h^{-1}
30 min
800 °C



12% O_2, 6% CO_2, 6% H_2O, 500ppm CO, 100 ppm H_2, 200 ppm NO, 370 ppm C_2H_4 155 ppm C_3H_6, 55 ppm C_3H_8 , 200 L g^{-1} h^{-1}







- Regeneration removes sulfate species while preserving the low temperature CO oxidation

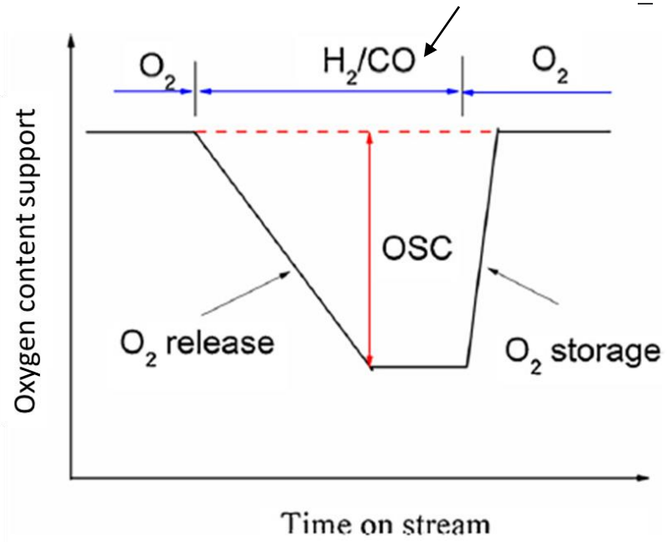
Improved oxygen storage capacity (OSC) in 2wt%Cu@CeO_2 by both USDRIVE protocol and dynamic OSC method

	Surface area (m^2/g)	Cu contents (μmol/g)	OSC at 550 °C (μmol/g)	OSC at 350 °C (μmol/g)	OSC at 150 °C (μmol/g)
CeO_2 (800)	26.3	~	211	135	0
2wt% Cu@CeO_2	39.2	315	744	483 (149)	249 (98)

Total OSC (USDRIVE's method)

i: switch between O_2 and CO

ii: OSC is **determined by** formed CO_2 amount

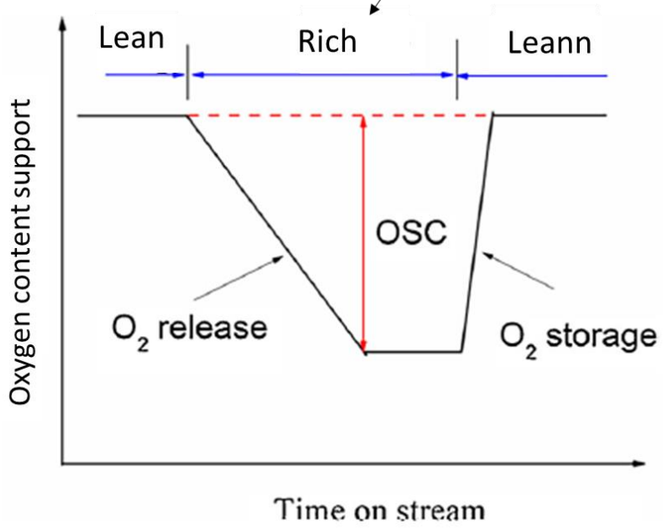


Rappe *et al* ***Emi.Cont.Sci and Tech***, 2019, 5:183-214830-839

Dynamic OSC (Theis's method)

i: switch between lean and rich conditions

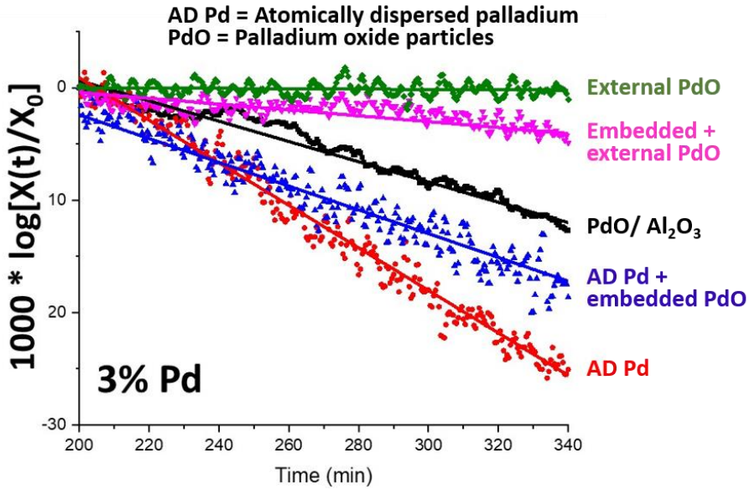
ii: OSC is **determined by** A/F ratio change



J.R.Theis *et al* ***SAE Techncial Paper***, 1996, 961900

ACEC Tech Team & AE Crosscut Team support

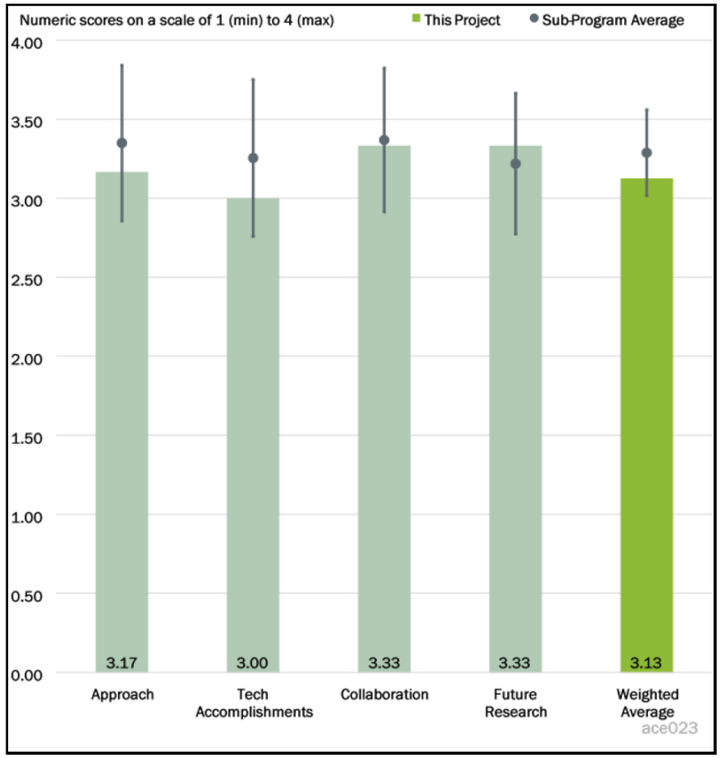
- USDRIVE highlights prepared
  - Small pore zeolite supported Pd as water-resistant methane combustion catalyst
  - Rh_1/CeO_2 single atom catalysts offer the ability to use significantly less Rh compared to current three-way catalysts
  - *in situ* EPR spectroscopy provides insight on SCR catalyst changes under mild aging



- Presentations
  - "Comparing Real-world and Accelerated Lab Aging of Cu/SSZ-13 SCR Catalysts"
    - Feng Gao to the AE Crosscut Team, 11-4-2021
  - Discussion on Aftertreatment Modeling Development Needs
    - LTAT group (Josh Pihl lead), 5-13-2021
- Organized & moderated 2021 CLEERS workshop panel discussion

Responses to Previous Year Reviewers' Comments

Reviewers' Comments	PNNL Responses
developing new tools such as electron paramagnetic resonance (EPR) spectroscopy …will lead to catalysts with improved thermal durability to meet the increased mileage requirements.	Continue pushing the capabilities of operando EPR, e.g., developing representative aging protocols
nice job on adding manganese (Mn)-cerium (Ce) to the SCR catalyst to increase the NO+ formation, thereby improving the low-temperature activity of the catalyst.	Continue the effort in fundamental understanding of the roles of SCO in circumventing low temperature SCR activity
single-atom catalysts (SAC) Cu catalysts for stoichiometric applications	Addressing this issue with a separate CRADA with Stellantis
collaboration with the industry helped the overall progress of the project.	Expanded collaboration with Caterpillar, John Deere, and BASF



Collaboration and Coordination with Other Institutions

Industry

- BASF – U.S. heavy-duty and off-road emission control
  - Future emission regulations for off-road applications
- Caterpillar – Natural Gas and Alternative Fuels Engine Research
  - Emissions from renewable & low-C fuels; future emission regulations for off-road
- John Deere – Advanced Technology and Integration
  - Off-road emission control, emissions from low carbon fuels
- Cummins – Advanced Technologies
  - Extended useful life of SCR
- Carus Corporation – Advanced Materials
  - Non-PGM catalyst structures

Academia & NLs

- University of New Mexico, Prof. Abhaya Datye – single atom catalysts
- Sofia University, Prof. Hristiyan A. Aleksandrov – molecular simulations
- SLAC, Simmon Bare – synchrotron capabilities
- Purdue University, Prof. Jeff Miller – synchrotron capabilities
- ORNL – Applied Catalysis and Emissions Research

DOE Vehicle Technologies Program:
Siddiq Khan, Gurpreet Singh

Remaining Challenges and Barriers

- Off-road low-load cycles: low-temperature performance
- Full useful life (FUL): durability and extended useful life of emission control catalysts
- Fuels: emissions from low carbon fuels, renewable fuels (e.g., e-methane, R-NG)
- Greenhouse gases (GNGs): controlling GHG emissions including N_2O, CH_4
- PGM use: cost reduction and reducing PGM usage

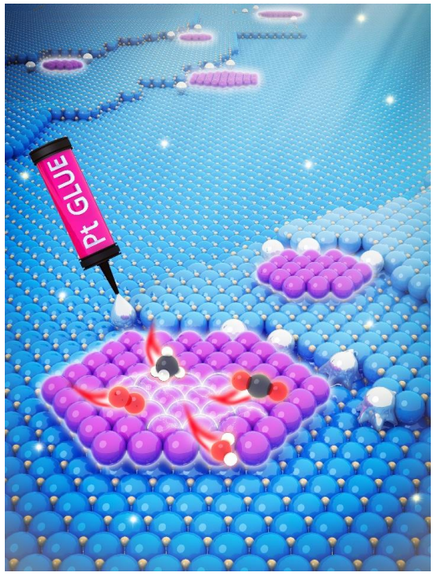
Proposed Future Work

- Clarify barriers to low temperature NH_3-SCR catalyst activity, propose pathways to circumvent
- Understand implications of S-poisoning and de-sulfation of SCO-SCR composite catalysts
- Develop and improve lab-aging protocols to more accurately mimic real-world aging of NH_3-SCR catalysts
- Understand origins and pathway of N_2O formation in NH_3-SCR catalysts, propose pathways to mitigate or circumvent
- Clarify the challenges that low-C and renewable fuels (e.g., e-methane, R-NG) present to low-temperature emission control and PGM usage

Summary

- *Operando* electron paramagnetic resonance (EPR) and kinetic analysis helped develop lab-aging protocols in the presence of SO_x at temperatures < 650 °C to better ***mimic real-world aging***.
- Identified two areas to target ***improved low temperature NH_3-SCR activity***:
  - Increasing Cu species with the highest inter-cage mobility
  - SCO-SCR composite catalysts overcome the barrier of Cu redox chemistry and inhibition from NH_4NO_3
- ***N_2O formation*** was found to be structure dependent in SCR catalysts; mechanisms are complex
- Modification of ceria support by atom trapping of Pt can stabilize PdO_x 2-D rafts for ***water-tolerant methane oxidation***
- 2wt%Cu@CeO_2 by atom trapping showed increased OSC and can be readily regenerated after sulfur poisoning, offering the potential for ***improved PGM usage***.

Effective dissemination by 7 peer-reviewed publications in *Nature Catalysis*, *Nature Comm, Angewandte, Applied Catal. B., J.Catal* and 17 presentations



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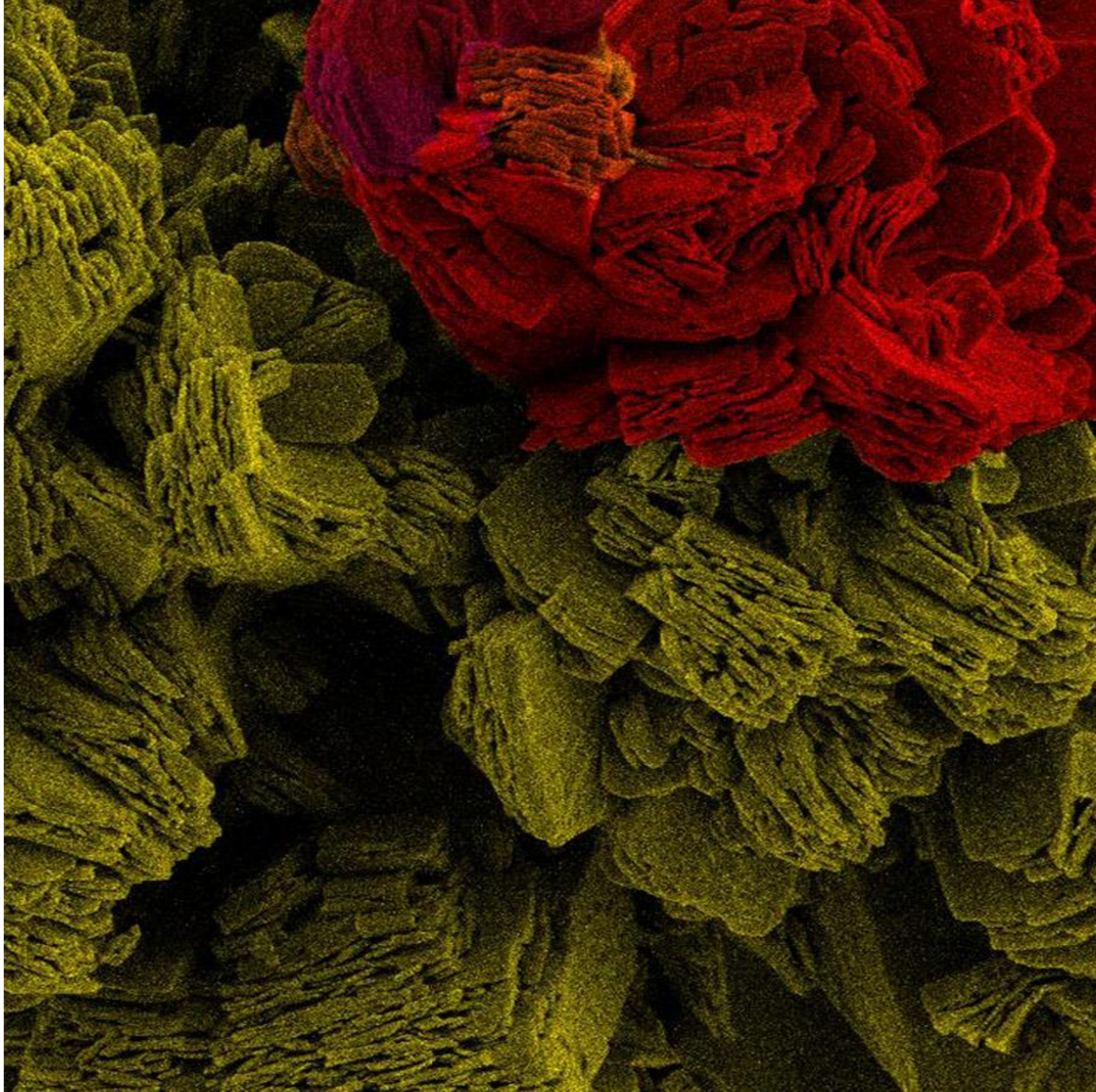
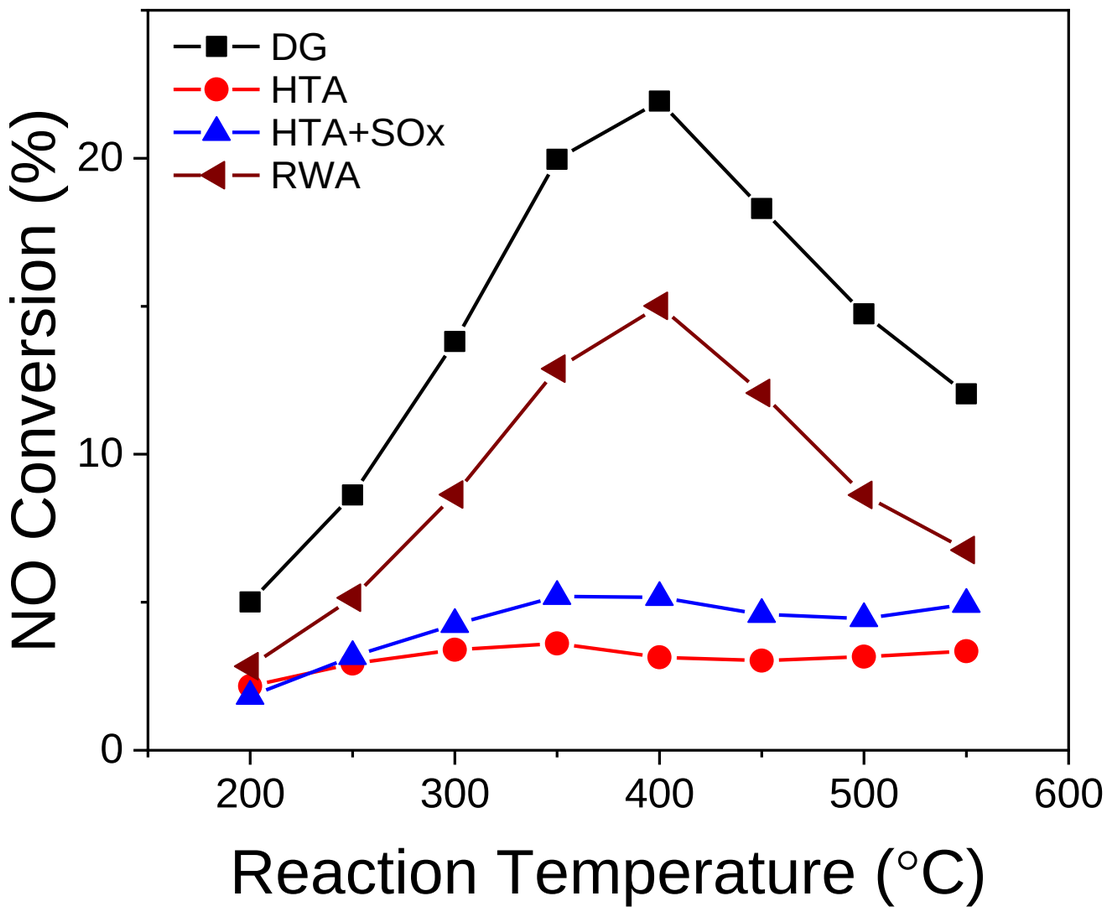
Technical Backup Slides

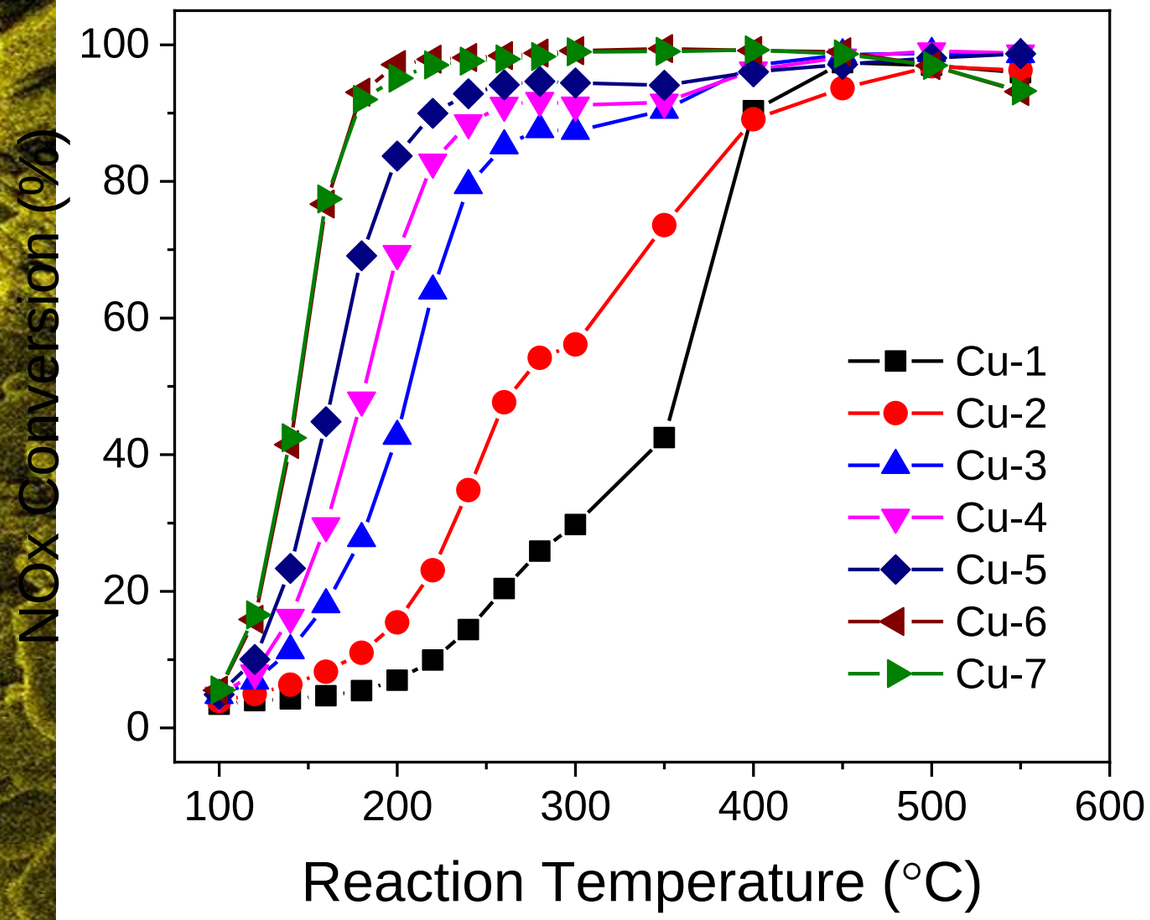


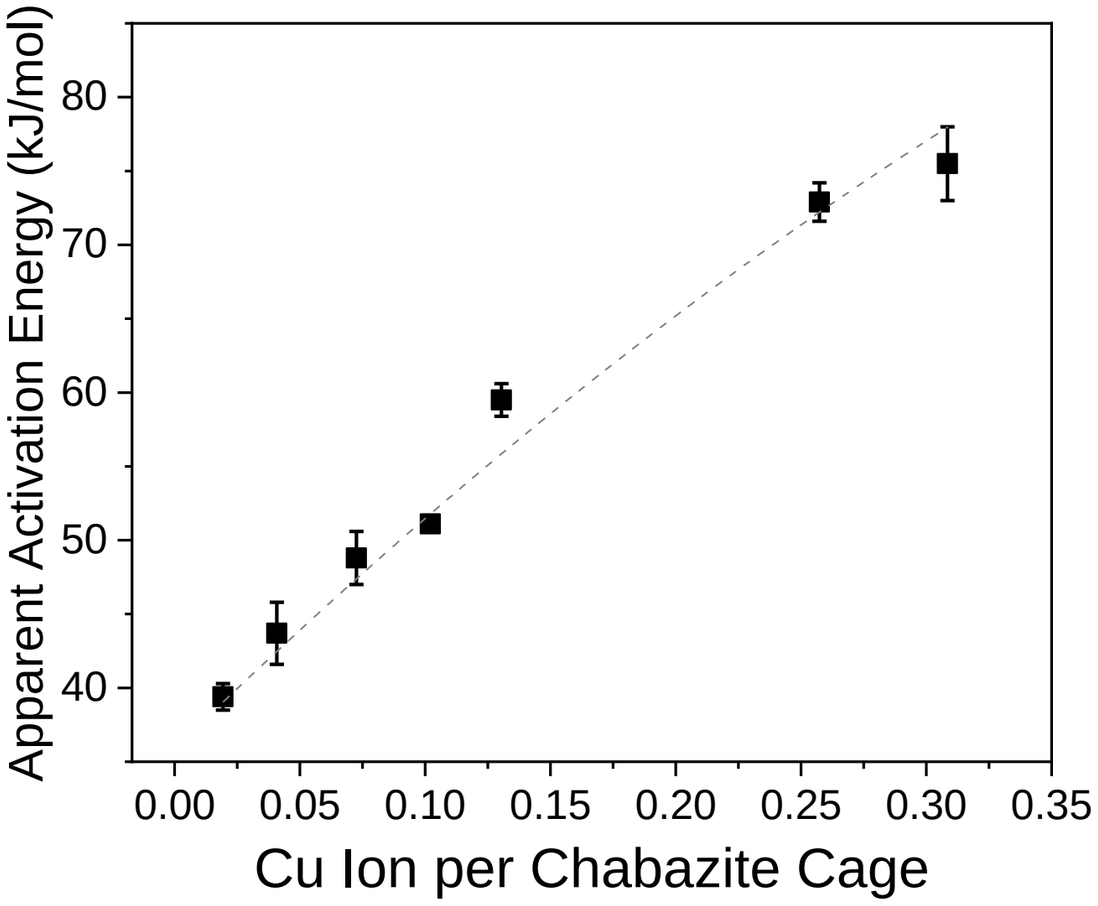
NO conversion as a function of temperature over the Cu/SSZ-13 catalysts in dry NO oxidation. The composition of the gas feed was 350 ppm NO, 10% O_2, and balance N_2. 240 mg of crushed core samples were used for these tests, and the total flow rate was 600 mL min^{-1}.



- "dry" NO oxidation ($NO + ½O_2 \rightarrow NO_2$) is much more sensitive than SCR towards severity of hydrothermal aging.
- RWA considerably milder than lab-aging in terms of severity of hydrothermal aging.

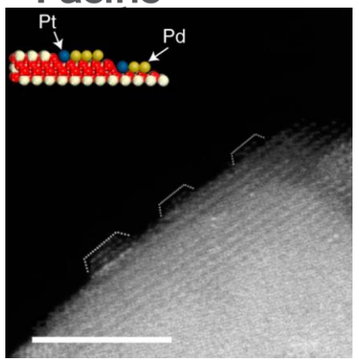
(Left) NOx conversion as a function of reaction temperature for standard SCR on the 7 Cu/SSZ-13 catalysts. The reactant feed contains 350 ppm NOx (including ~10 ppm NO_2), 350 ppm NH_3, 2.5% H_2O, 10% O_2, and balanced N_2 at a GHSV of ~2×10^5 h^{-1}. (Right) The corresponding apparent activation energies derived from Arrhenius analysis.

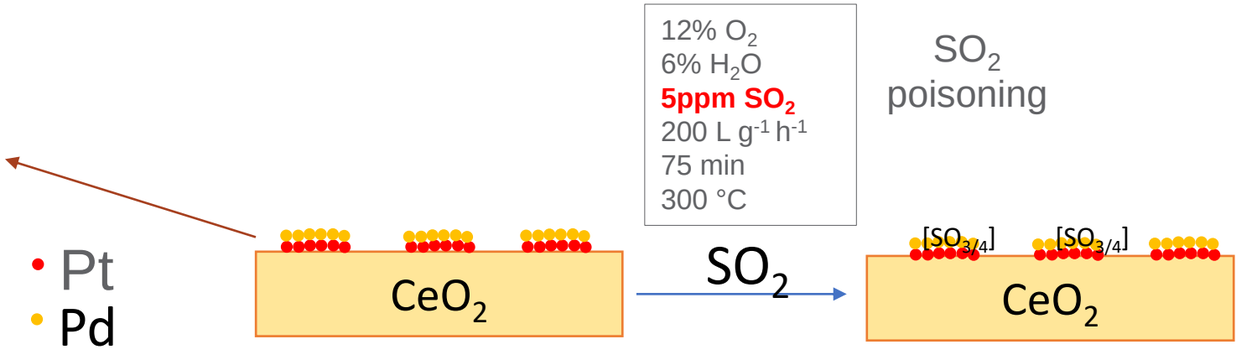




- Low-temperature atomic efficiency increases by increasing Cu loading up to ~1/3 Cu ion per cage.
- Contrary to the common wisdom, reaction activation energy *increases* with increasing atomic efficiency.

Modified-CeO_2 by Pt atom trapping, with anchoring sites for Pd, resulting in bimetallic PtPd 2D-rafts with superior activity and SO_2 resistance



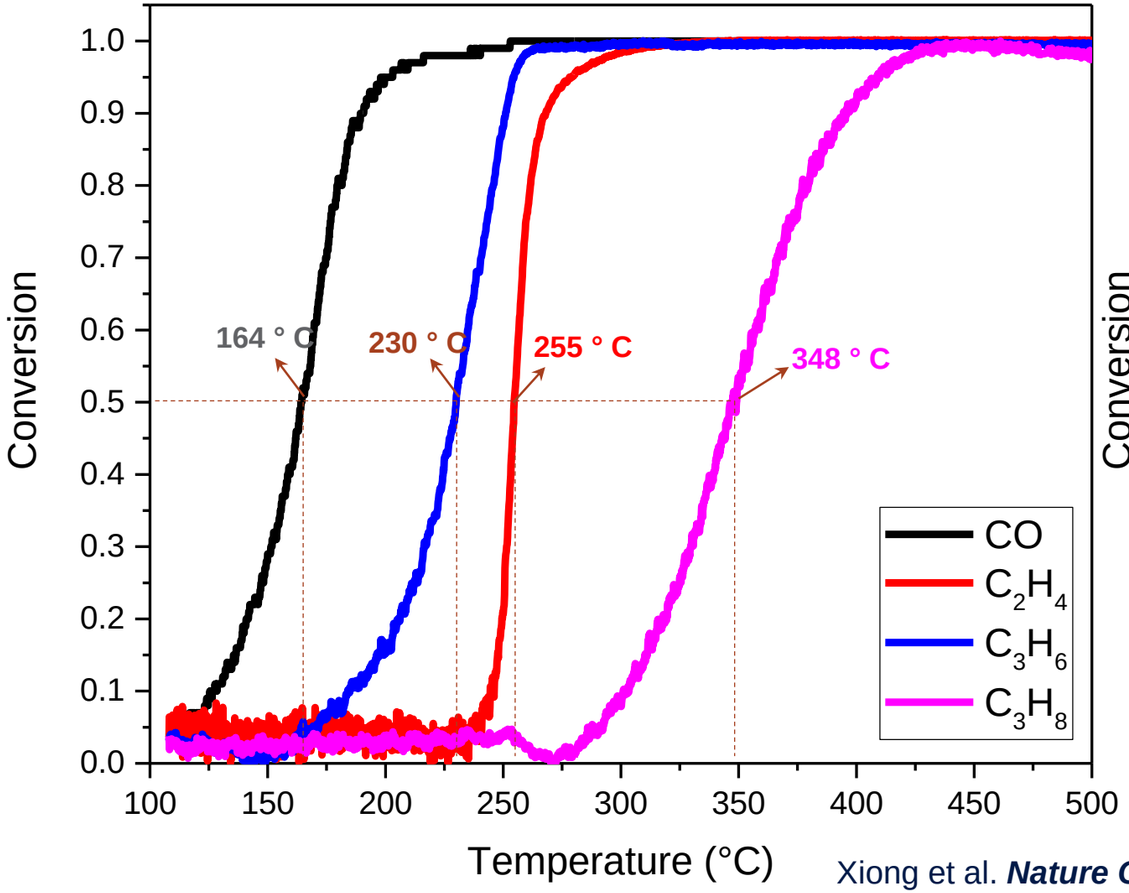


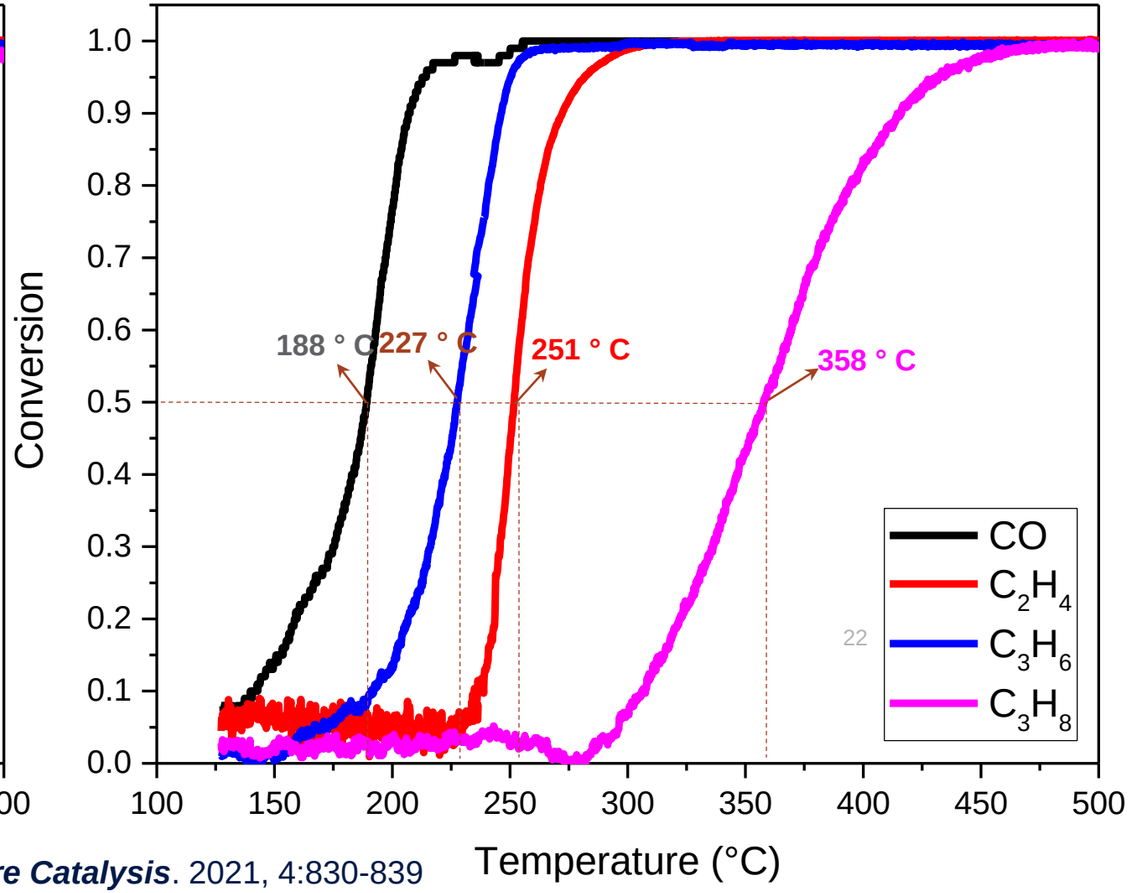
12% O_2
6% H_2O
5ppm SO_2
200 L g^{-1} h^{-1}
75 min
300 °C

SO_2 poisoning

Clean Diesel Combustion

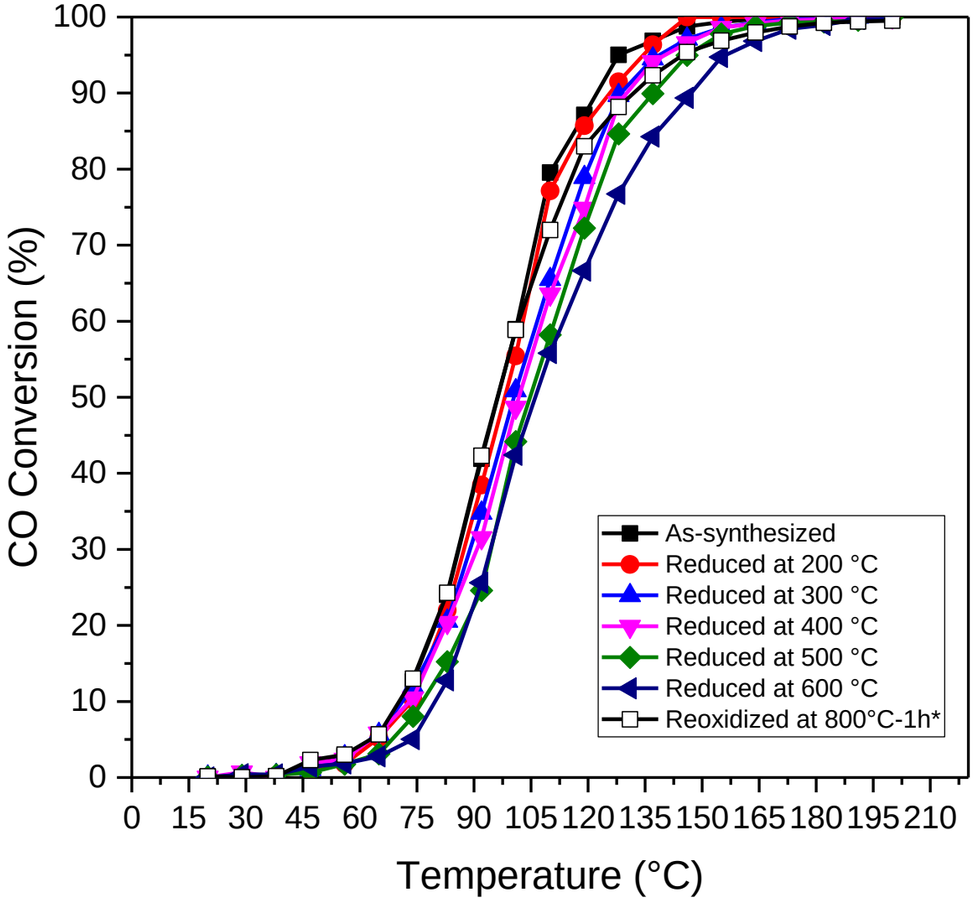
12% O_2
6% CO_2
6% H_2O
500ppm CO
100 ppm H_2,
200 ppm NO
370 ppm C_2H_4
155 ppm C_3H_6
55 ppm C_3H_8
200 L g^{-1} h^{-1}

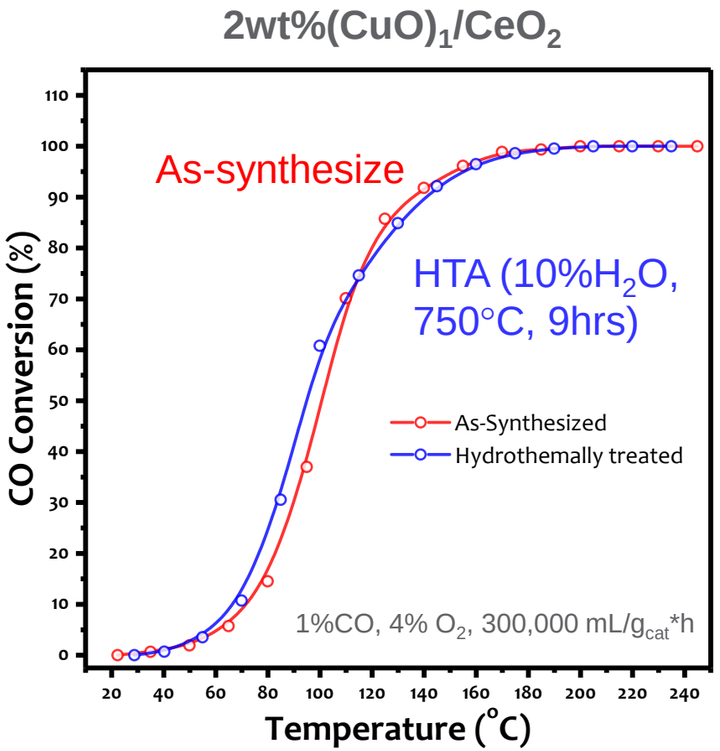




Xiong et al. ***Nature Catalysis***. 2021, 4:830-839

Reduction with CO does not significantly affect CO oxidation on Cu_1/CeO_2 (promising under fuel rich conditions)





- Hydrothermally stable

CO oxidation	1%CO, 8% O_2 300,000 mL g^{-1} h^{-1} 20 mg cat	**Reduction conditions**	5%CO 200 L g^{-1} h^{-1} / 30 min

Organized & Moderated 2021 CLEERS Workshop Panel Discussion

2021 CLEERS Virtual Workshop Panel Discussion

Monday, September 13
2:35 – 4:15 p.m. EDT

Aftertreatment Catalyst Durability: Information Gaps and Future Needs

Panelists
Tom Pauly (Umicore)
Christine Lambert (Ford)
Alissa Recker (Daimler Trucks N. A.)
Danan Dou (John Deere)

Moderator
Ken Rappe (PNNL)

Thank you to Haiying Chen (ORNL) for technical guidance

- **Dr. Tom Pauly**, Director Product Management
  - *Diesel (North America) at Umicore*
  - Aftertreatment Catalyst Durability: Information Gaps and Future Needs
- **Dr. Christine Lambert**, Manager, Aftertreatment Technology
  - *Ford Research and Innovation Center*
  - Accelerated aging protocol development, necessary considerations & best practices
- **Dr. Alissa Recker**, Catalyst Kit Engineer
  - *Daimler Trucks North America*
  - Upcoming 800K mile HD FUL requirement and important knowledge gaps
  - Fuel/lube considerations & opportunity in PC-12 development
- **Dr. Danan Dou**, Manager, Advanced Technology and Innovation
  - *John Deere*
  - Lessons learned from off-road, and Directions in off-road legislation and unique challenges
  - Replicating/accelerating on-bench (key considerations for the CLEERS community)