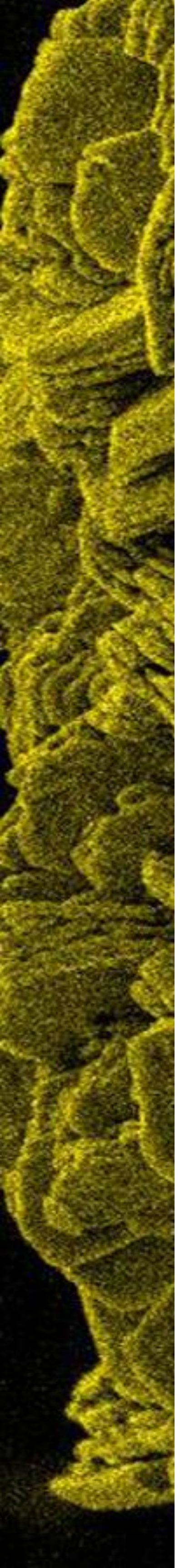


Pacific Northwest NATIONAL LABORATORY | Institute for INTEGRATED CATALYSIS

Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS): Fundamentals and Coordination

Yong Wang, Feng Gao,

Konstantin Khivantsev,

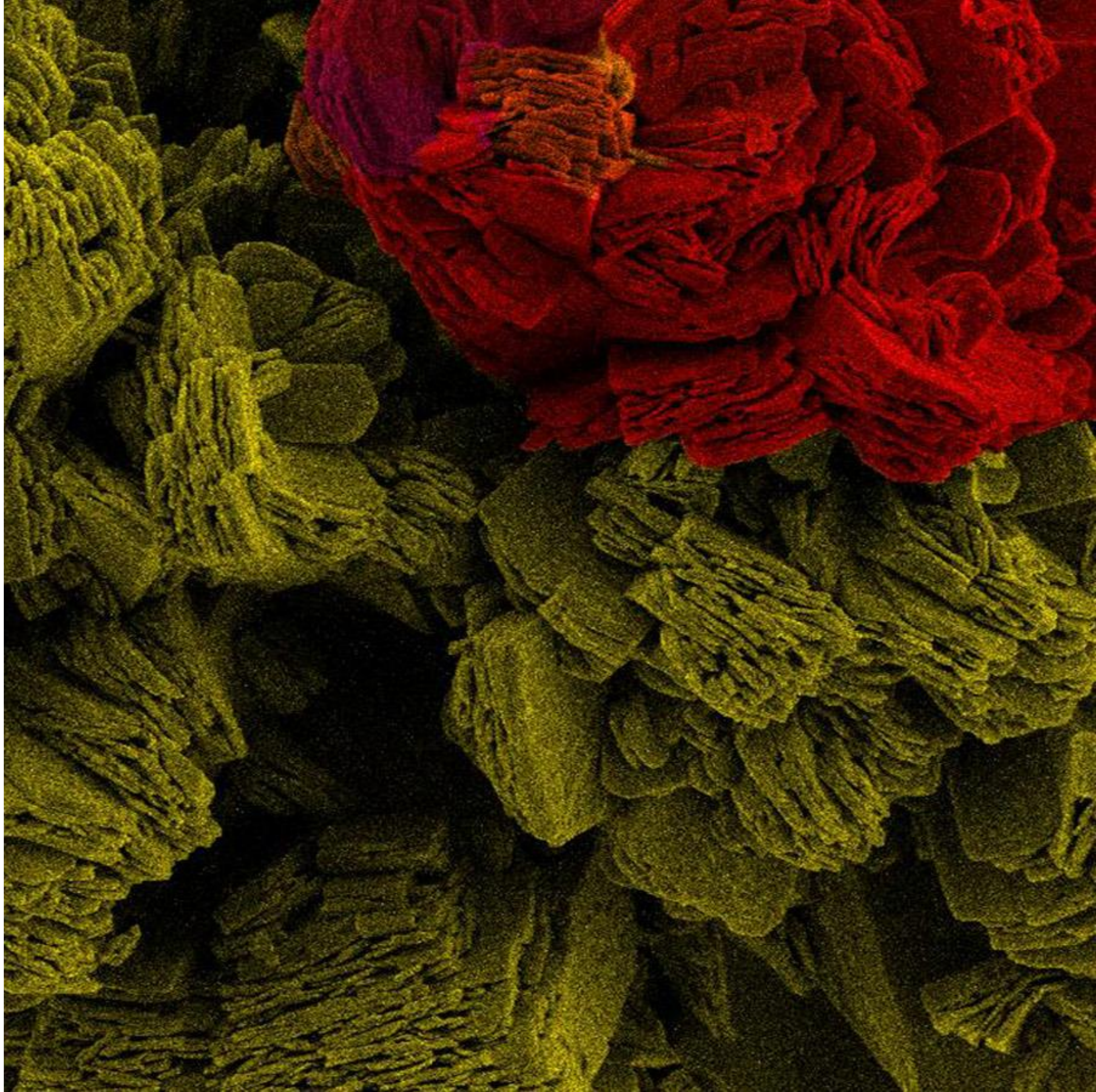
Ken Rappe, Mark Stewart, Janos Szanyi

June 23, 2021

ACE023

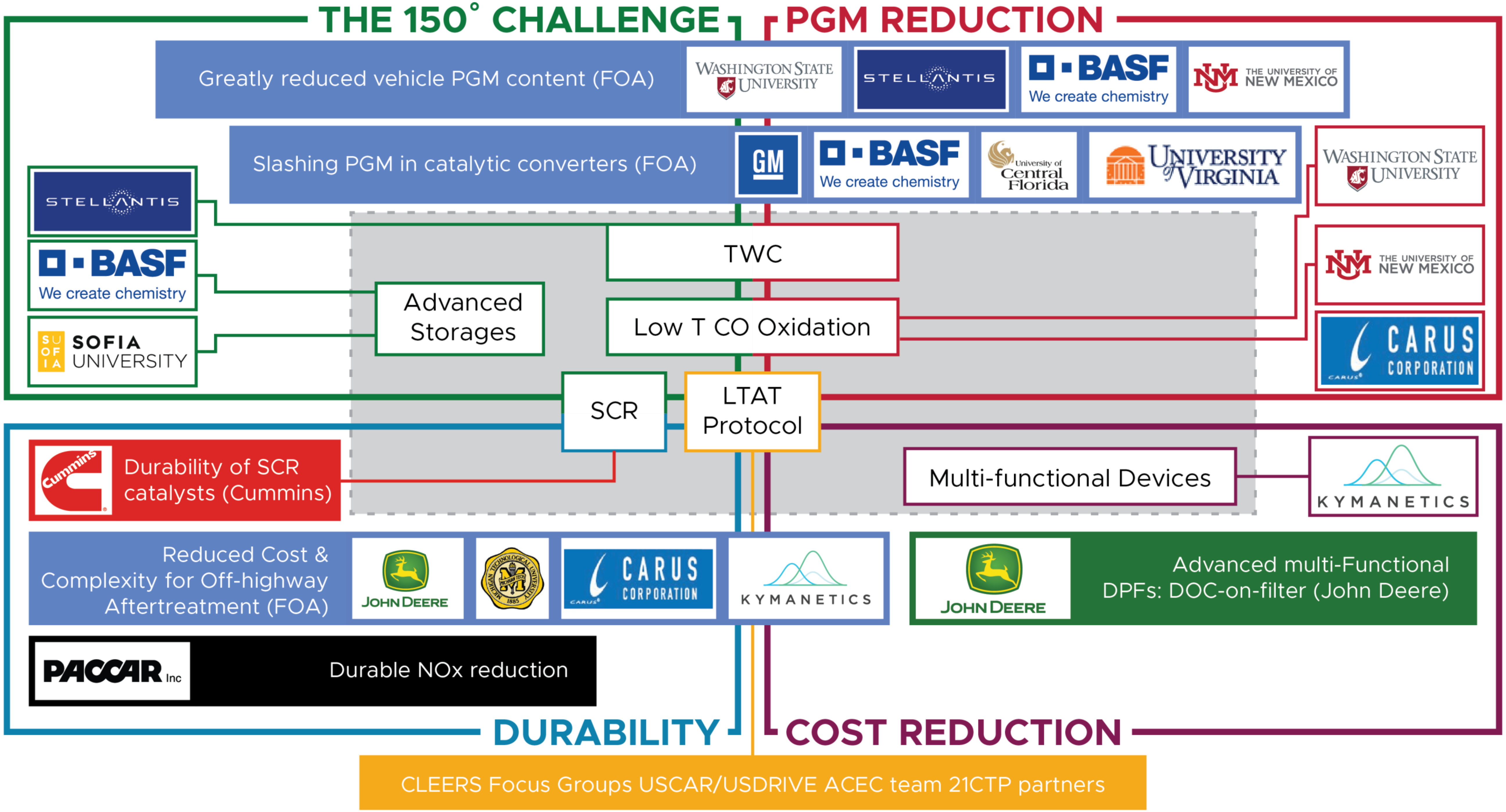
BATTELLE

PNNL is operated by Battelle for the U.S. Department of Energy



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

ACE169 FOA (Yong Wang)
ACE118 (Janos Szanyi)
ACE027 (Feng Gao)
ACE159 FOA (Ken Rappe)



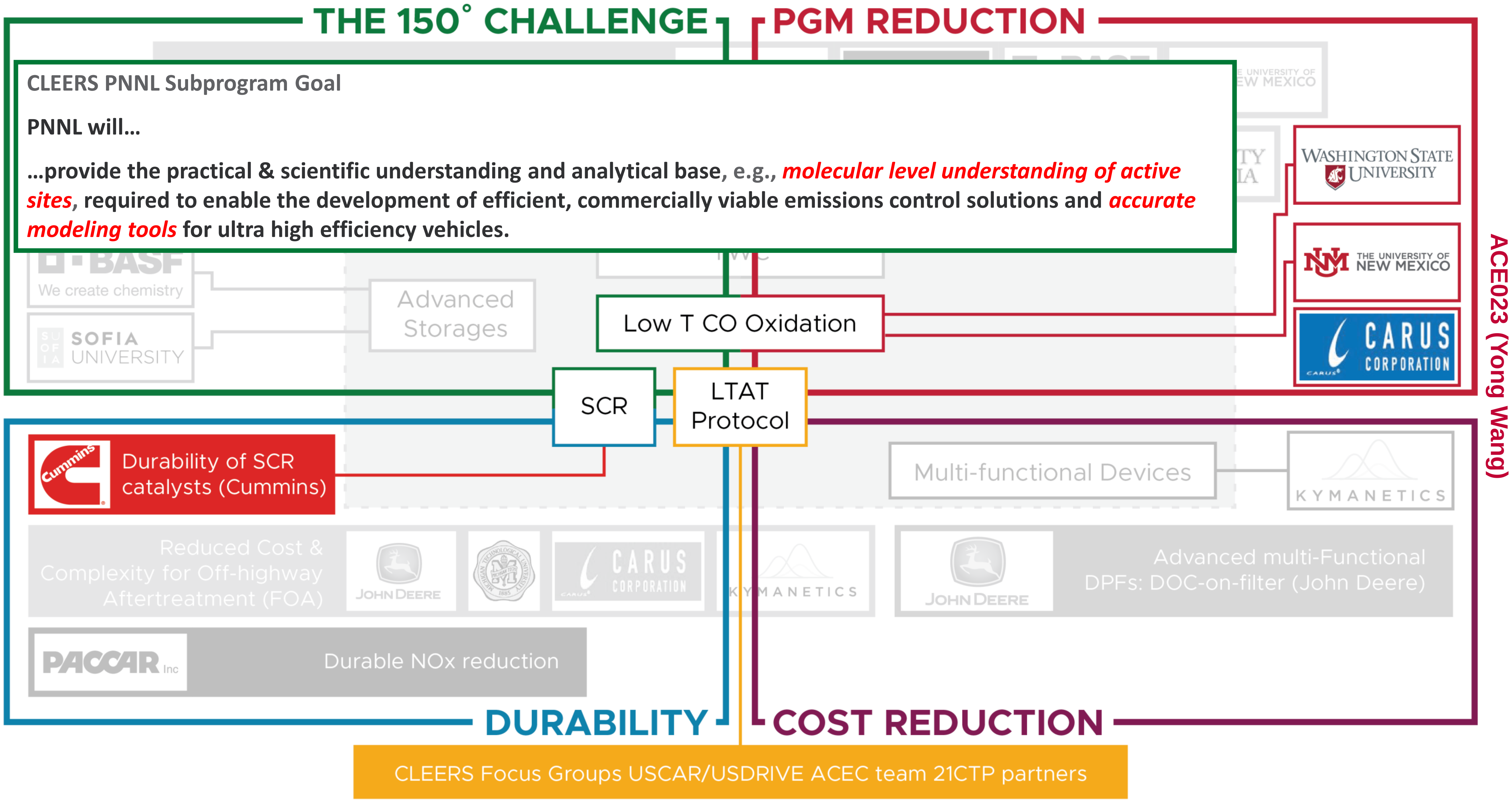
ACE158 FOA (GM)
ACE056 (Konstantin Kivantsev)
ACE023 (Yong Wang)
ACE119 (Ken Rappe)

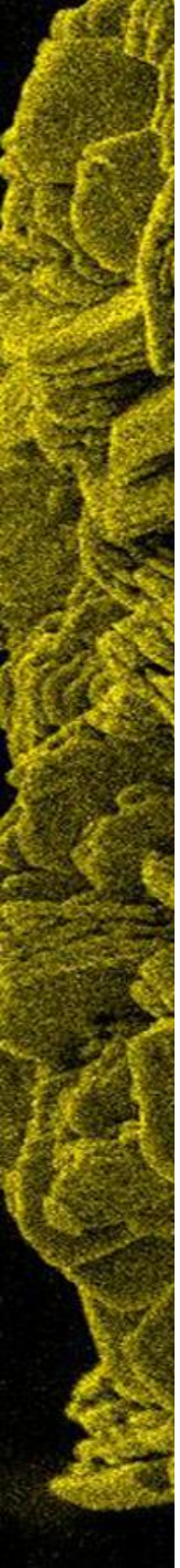
Three Fundamental Tasks (SCR, LTAT, Multifuntional Devices) Focus on Four Important Areas and Align With Industrial Priorities

CLEERS PNNL Subprogram Goal

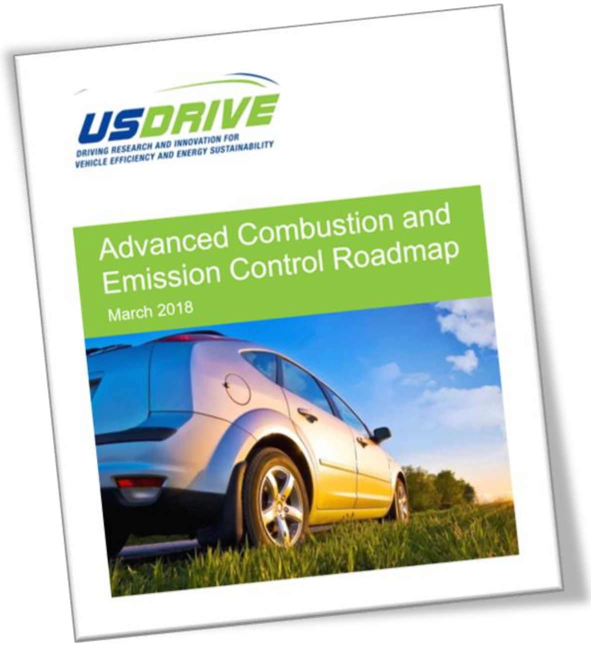
PNNL will…

…provide the practical & scientific understanding and analytical base, e.g., *molecular level understanding of active sites*, required to enable the development of efficient, commercially viable emissions control solutions and *accurate modeling tools* for ultra high efficiency vehicles.



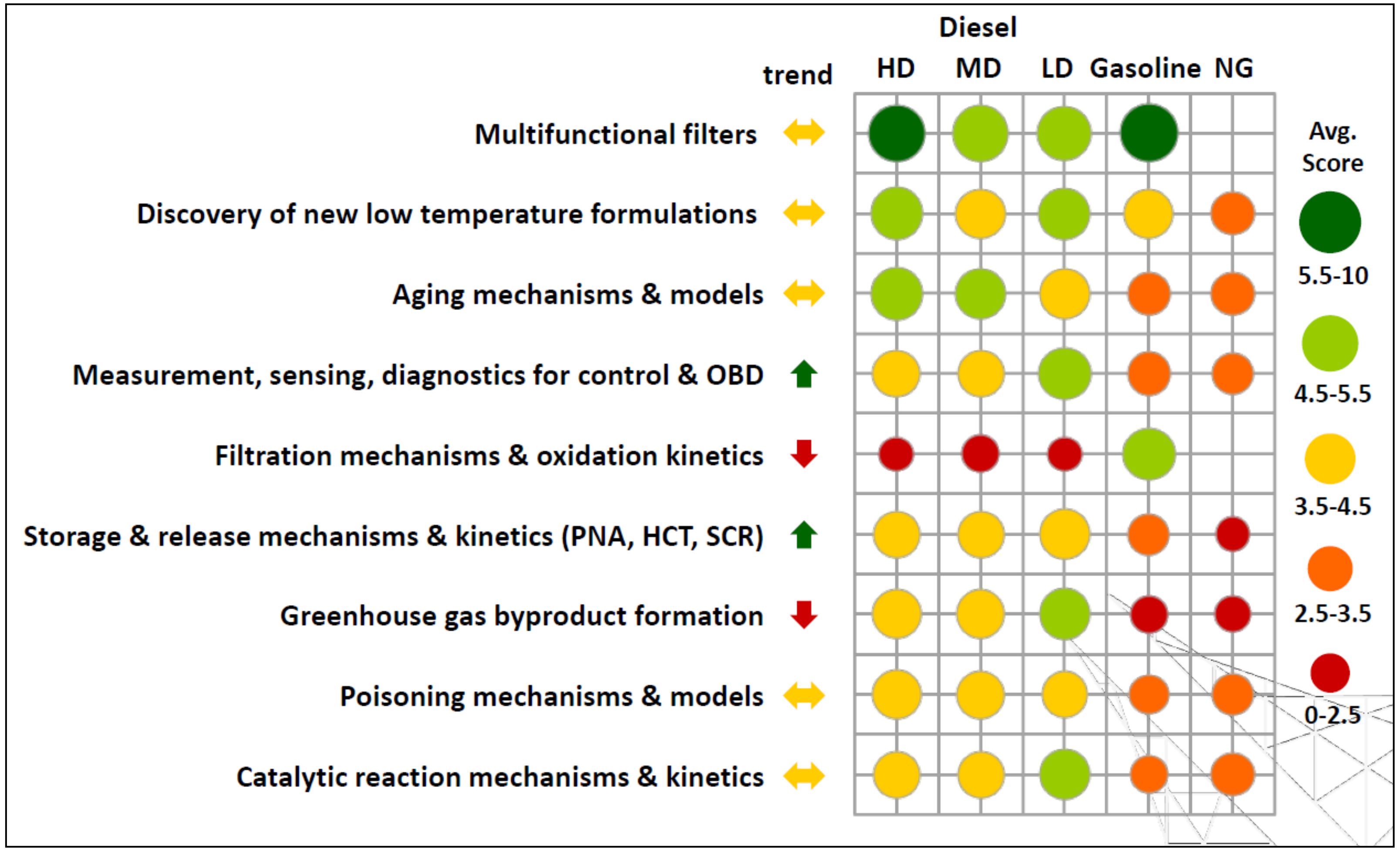


Relevance



2018 Advanced Combustion and Emission Control Roadmap

- Increase internal combustion engine efficiency through advanced aftertreatment (driven by U.S. EPA Tier 3 Bin 30 emission standard).
- Achieve greater than 90% conversion of criteria pollutants (NOx, CO, HCs) at 150°C for the full useful life of the vehicle.*
- Reduce the Platinum Group Metal (PGM) content to mitigate commercial risk to PGM market volatility.
- Reduce cost, size, and complexity of emission control system with multifunction catalysts that combine multiple components onto one substrate.
- Develop models and simulation tools (molecular to the system level) to predict performance and better understand catalytic processes.



High Priority Research Areas (Industrial Survey)

- Multifunctional filters
- Low temperature catalysts
- Aging

*defined as the longer of 150,000 miles or 15 years

Overview

Timeline

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

Budget

- FY21 funding: $490K
  - SCR: $210K
  - LTAT: $280K

Barriers

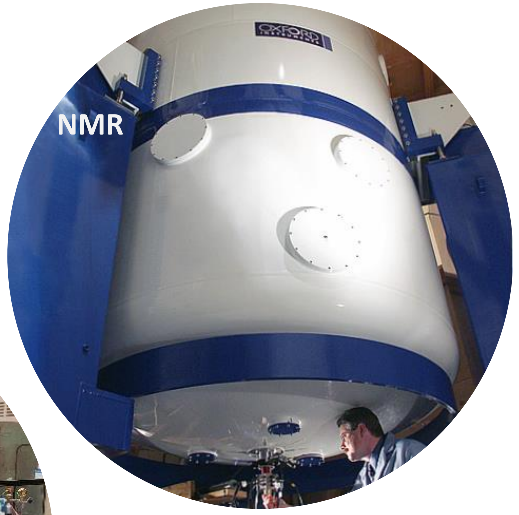
- Emission controls contribute to durability, cost and fuel penalties
  - Low-temp performance is now of particular concern
- Improvements limited by:
  - Available modeling tools
  - Chemistry fundamentals
  - Knowledge of material behavior
- Effective dissemination of information

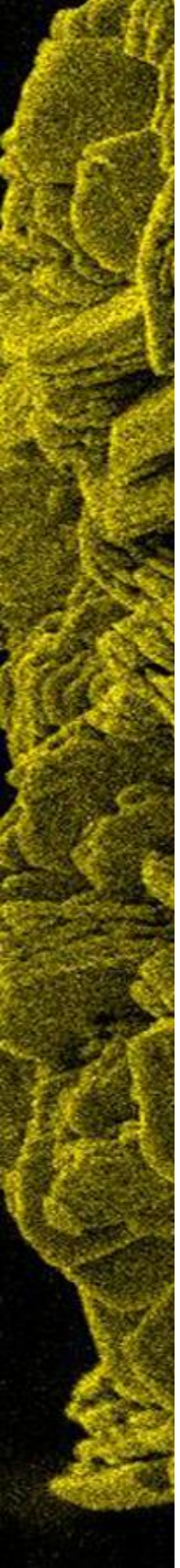
Partners

- DOE Advanced Engine Crosscut Team
- CLEERS Focus Group
- 21CTP partners
- U.S. CAR/U.S. DRIVE ACEC team
- Oak Ridge National Lab
- Cummins, Stellantis, Carus, Kymanetics, UNM, WSU

Approach/Strategy

- Build on PNNL's strong base in fundamental sciences to unravel the barriers needed to improve 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



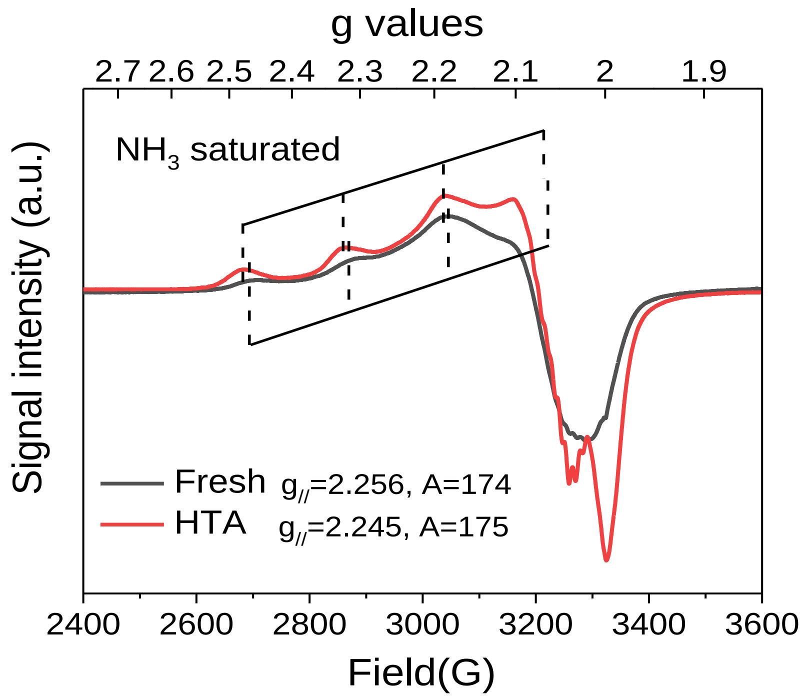


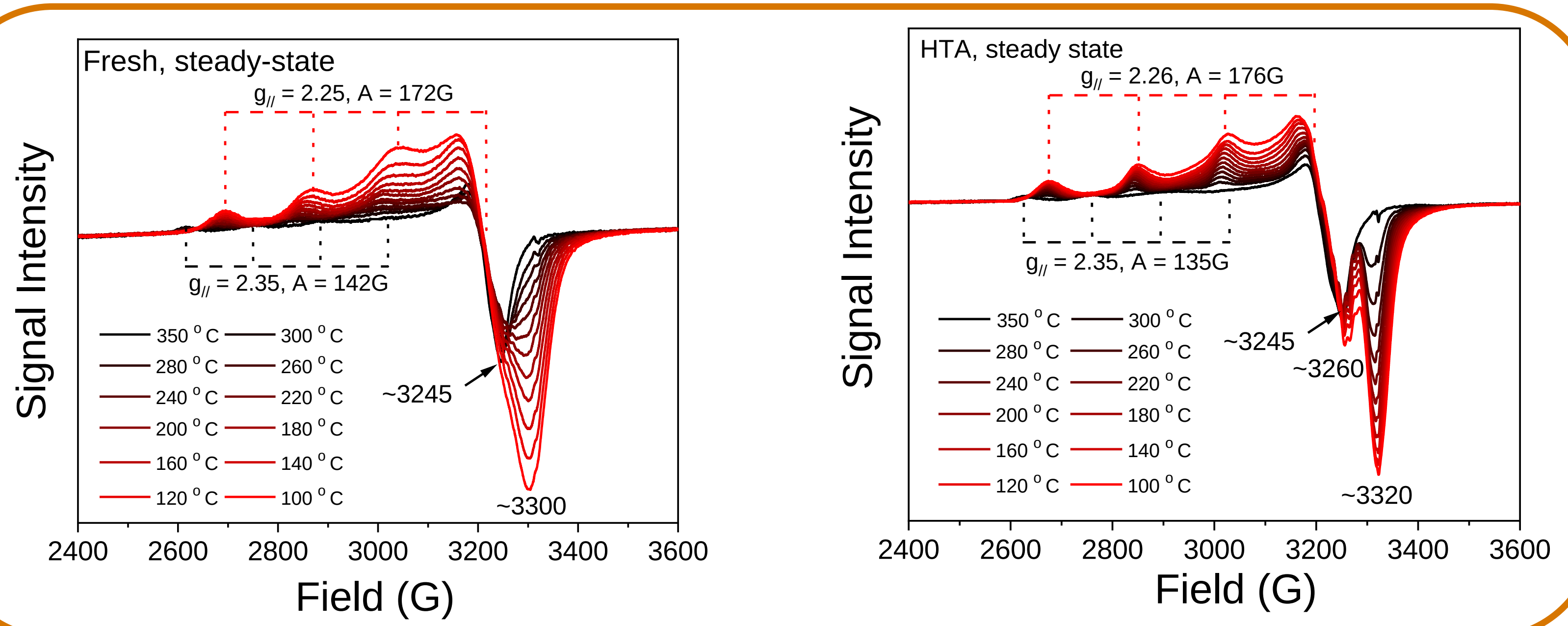
Technical Milestones

Milestones	Date	Status
Complete multi-scale modeling of zone-coated SCR-filter	12/31/2020	√
Demonstrate sulfur tolerance & catalyst regeneration on single atom catalysts based on non-PGMs	12/31/2020	√
Develop new synthesis method to control Al distribution of SSZ-13 and crystallinity of SAPO-34 supports for enhanced stability	3/31/2021	√
Understand & characterize site requirement for low-temperature fast SCR on Fe-exchanged zeolites	9/30/2021	on track
Understand sulfur poisoning mechanisms on Cu single atom catalysts	3/31/2022	on track

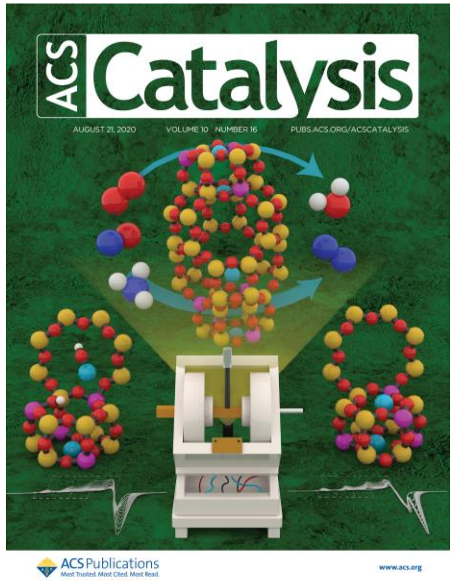
Accomplishments (SCR)
Understanding of Cu Transformation During Hydrothermal Aging using *in situ* EPR Allows Accurate Modeling of SCR Catalyst Aging Behaviors

2.1wt%Cu/SSZ-13 (Si/Al = 12)





- EPR analysis of NH_3-saturated samples provides “fingerprints” of different Cu species, e.g., strongly anchored Cu sites in HTA samples.
- *in situ* EPR during SCR:
  - Provides identification of SCR relevant Cu species
  - Establishes correlation between spectroscopic results and SCR turnover rates.

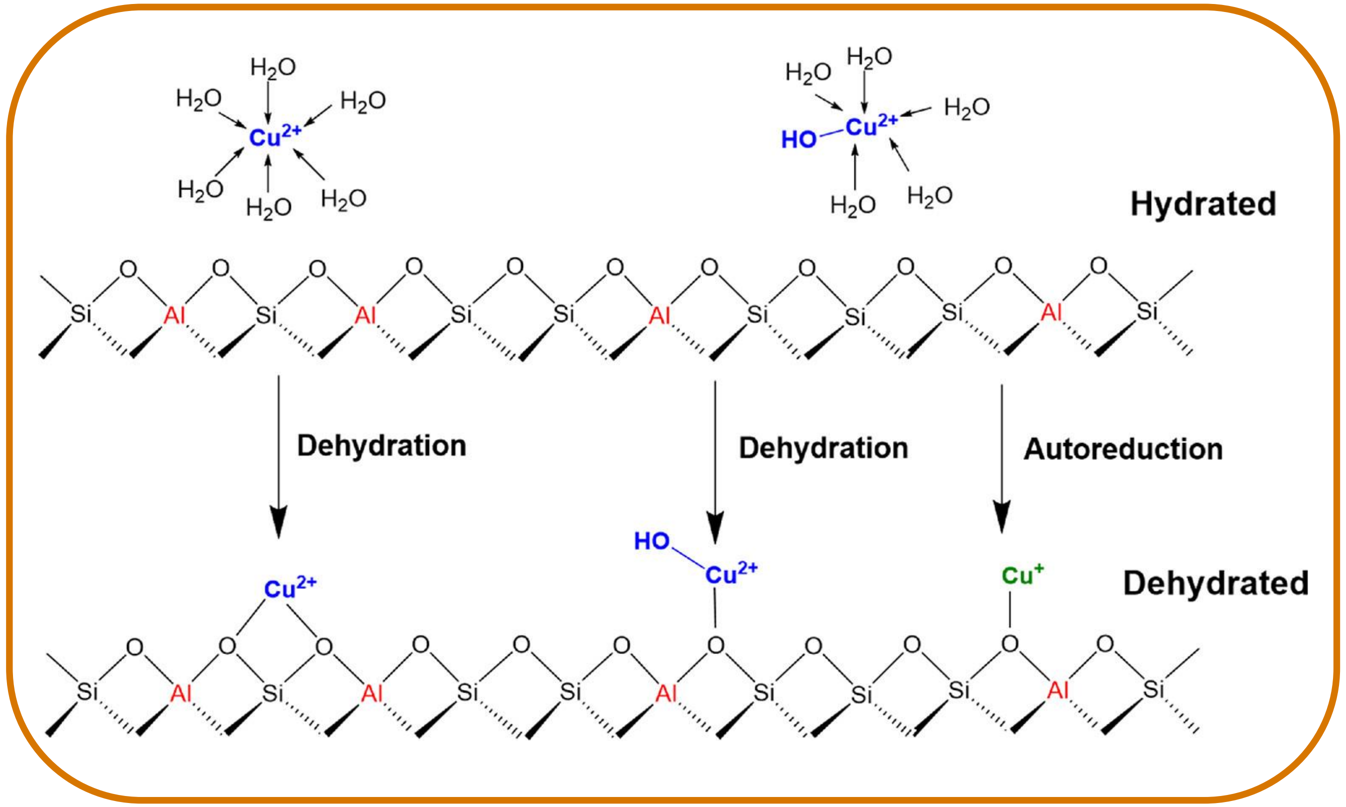


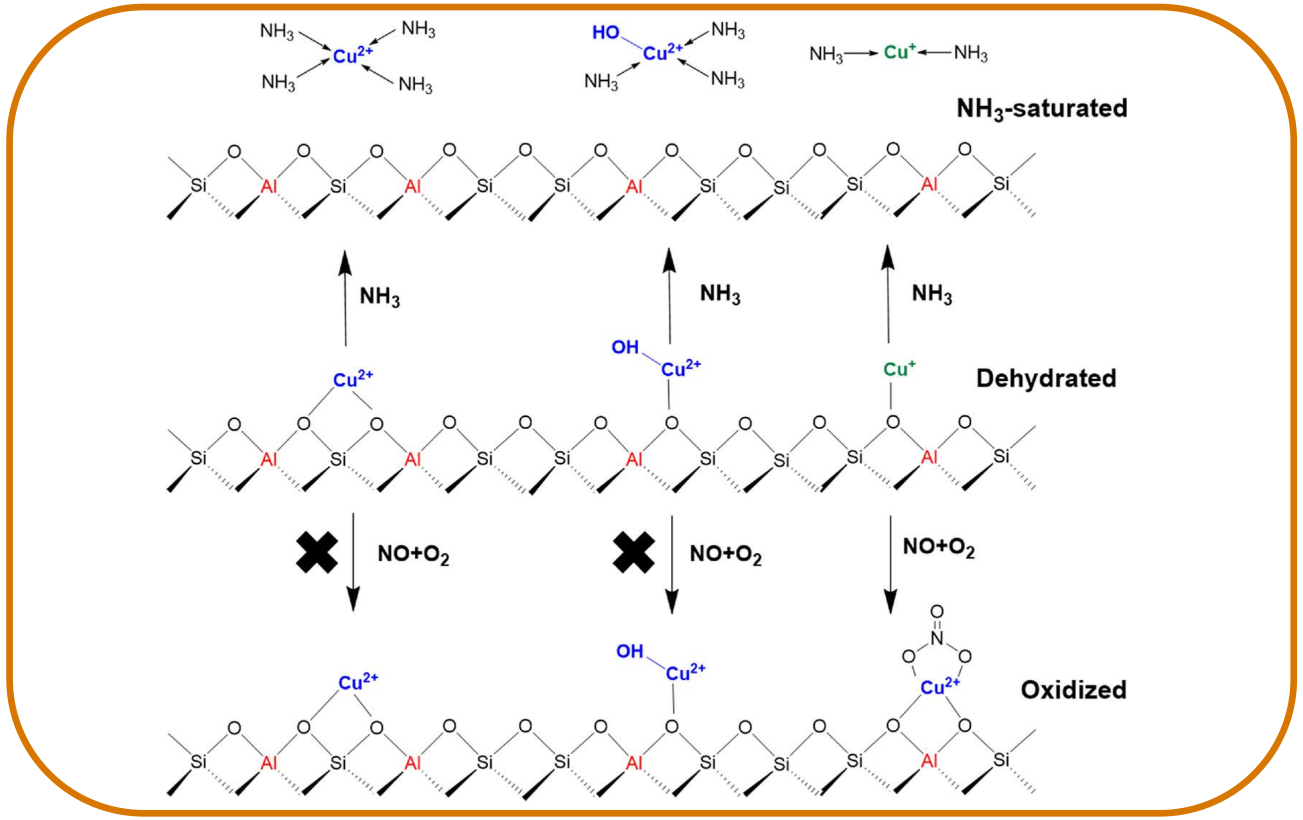
ACS Catalysis Cover Story

Yani Zhang, Yue Peng, Junhua Li, Kyle Groden, Jean-Sabin McEwen, Eric D. Walter, Ying Chen, Yong Wang, and Feng Gao, ***ACS Catal***. 2020, 10, 9410−9419.

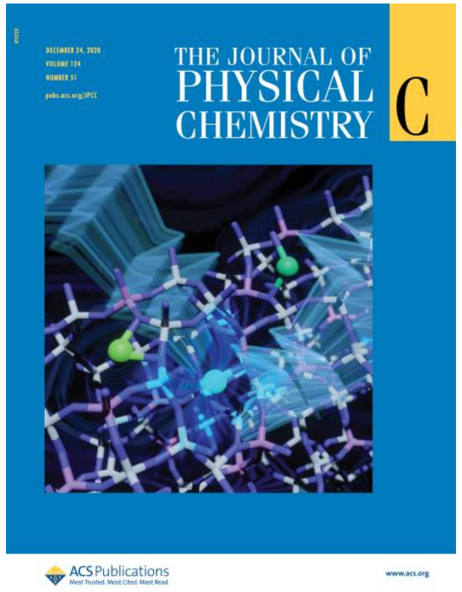
Accomplishments (SCR)

Cu Species Quantified by EPR Are Critical for Accurate Modeling of SCR



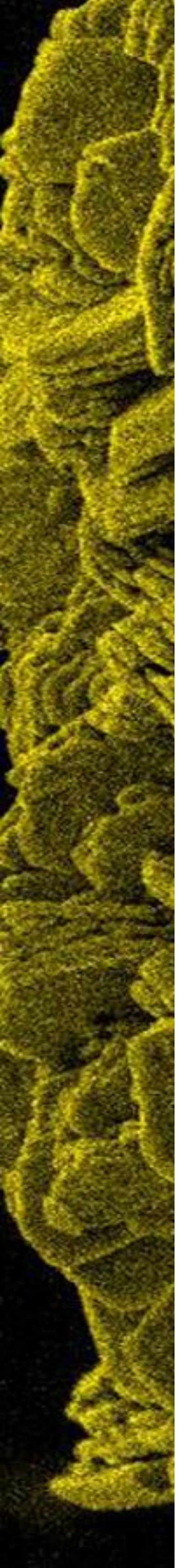


- EPR analysis under the conditions of hydration/dehydration, ammonia adsorption, and $NO+O_2$ adsorption allows for the quantification of Z_2Cu^{II}, $ZCu^{II}OH$ and ZCu^{I}.
- This method quantifies the SCR-active Cu species and provides molecular insight into the transformations of active sites during SCR and/or pre-treatments.

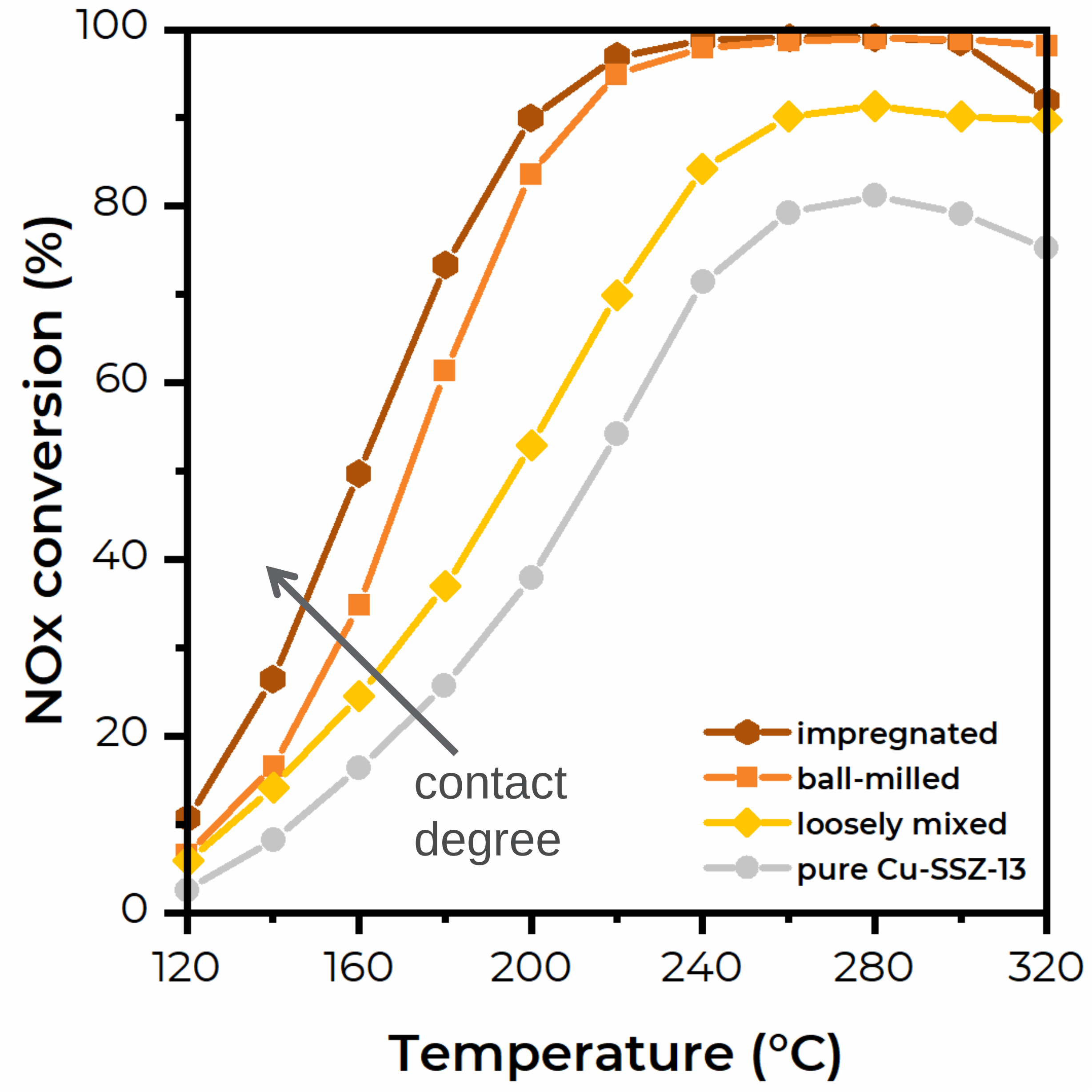


JPCC Cover Story

Yani Zhang, Yiqing Wu, Yue Peng, Junhua Li, Eric D. Walter, Ying Chen, Nancy M. Washton, Janos Szanyi, Yong Wang, and Feng Gao, ***J. Phys. Chem. C*** 2020, 124, 28061−28073.



Controlling Proximity between SCR and SCO Is Critical to Low Temperature SCR Performance



Test condition: 350 ppm NO, 350 ppm NH_3, 15% O_2, 6% H_2O, 8% CO_2 (balanced N_2), 150 mg catalyst, SV = 400 L g^{-1} h^{-1}

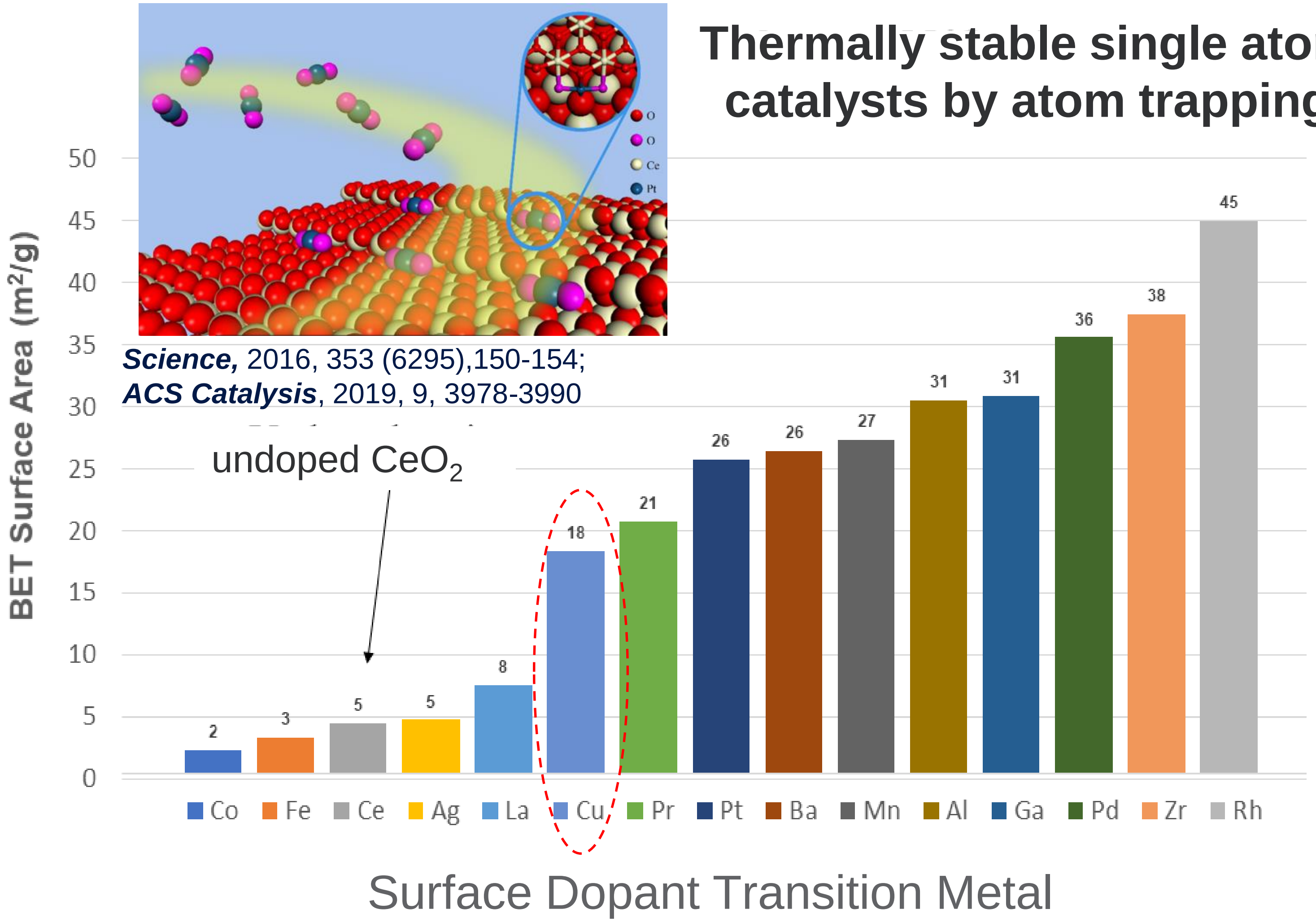
SCO component: **ceria-manganese oxide**, $Ce_{0.7}Mn_{0.3}O_x$)
SCR component: **Cu-SSZ-13** (1.4 wt% Cu)
SCO-SCR weight ratio: **1:3**
Coupling technique: **impregnation**, **ball milling**, **loose mixture**

- Proximity between SCO–SCR component, tailorable via preparation technique, is the key to a synergistic low temperature SCR reaction

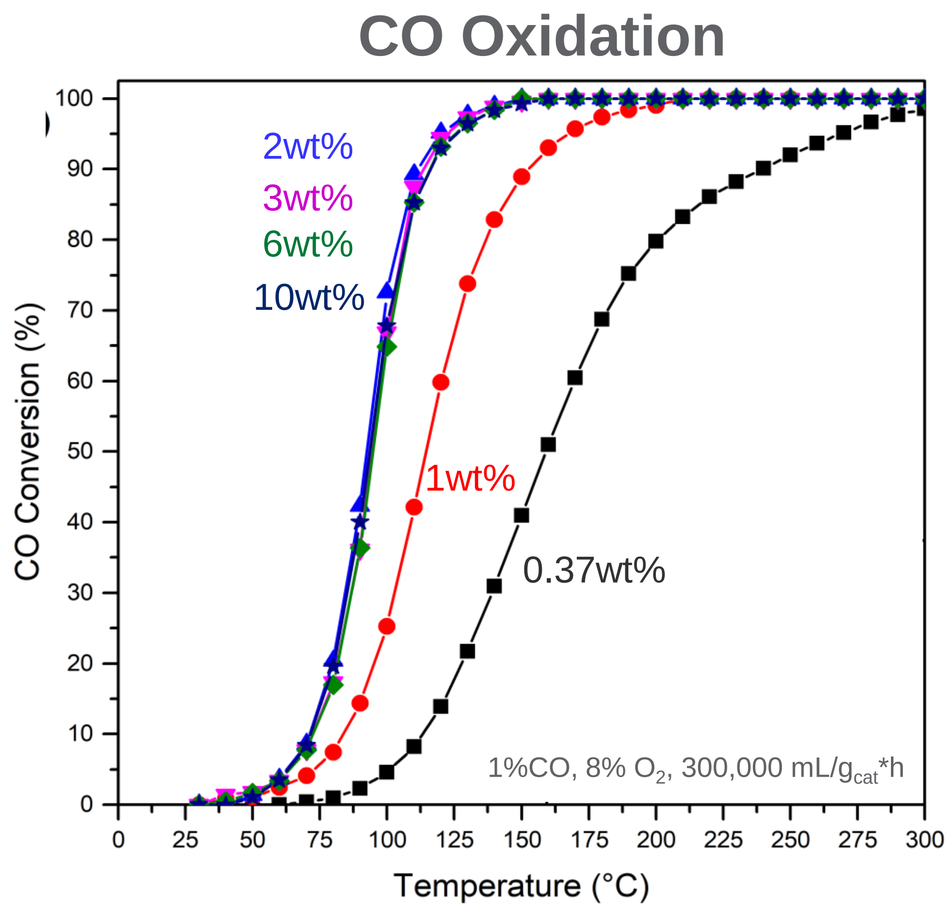
Accomplishments (CO Oxidation)

Thermally Stable Cu Single Atom Catalysts Prepared by Atom Trapping Achieve 100% CO Conversion at <150 °C

Thermally stable single atom catalysts by atom trapping



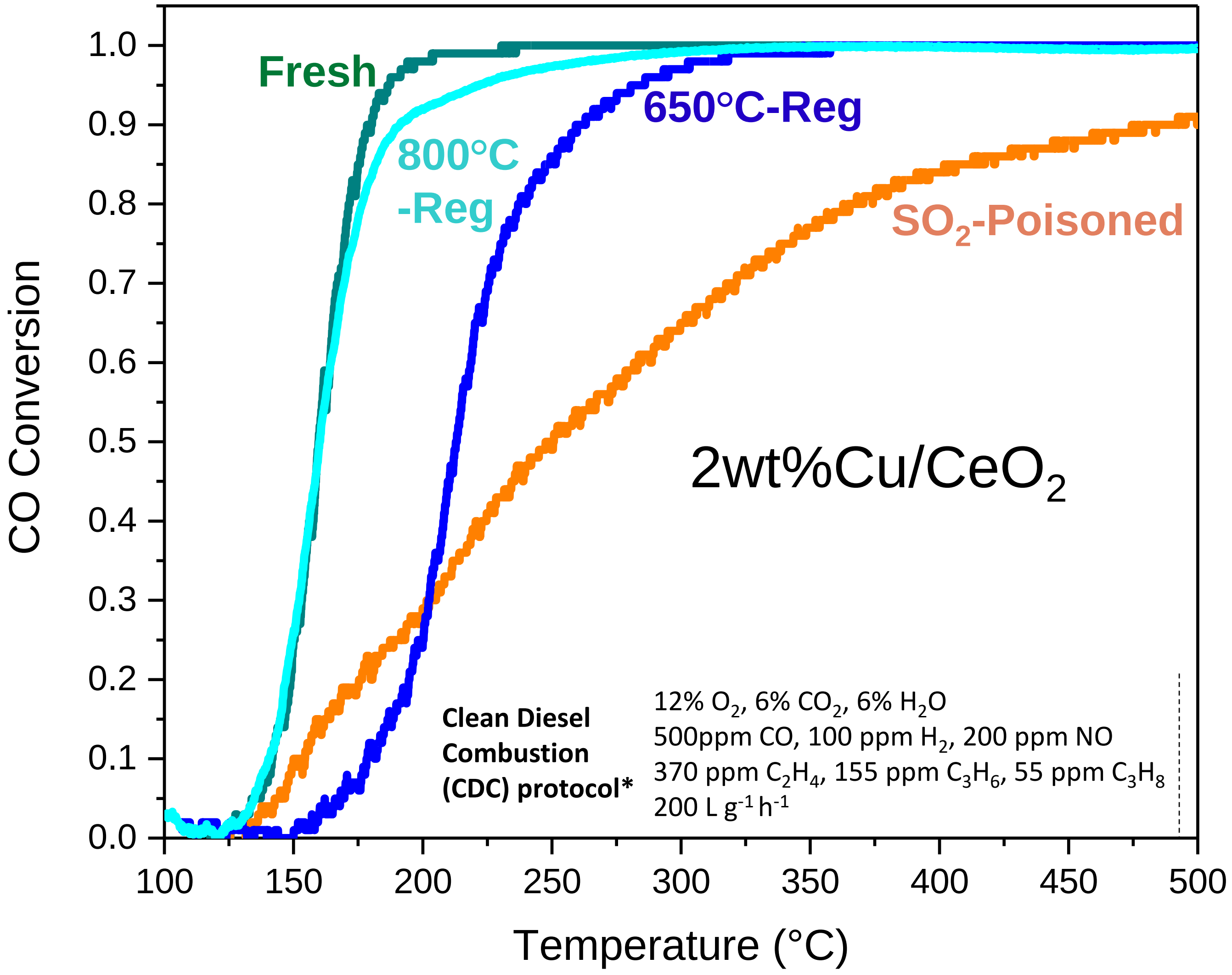
Alcala *et al*, ***Appl.Catal.B,*** 2021, 10.1016/j.apcatb.2020.119722)



- Thermally stable single atom catalysts including Cu can be prepared by atom trapping (800 °C in air) as indicated by stabilized BET surface area of ceria with 0.88 mol% M
- 2wt% Cu single atom catalyst is highly active for CO oxidation, achieving 100% CO conversion at <150 °C.

Accomplishments (CO Oxidation)

Highly Active and Durable Cu Single Atom Catalysts Can Be Readily Regenerated at 800 °C Using US DRIVE Protocols



Fresh

De-greening: 700°C, 4h, 10% O_2, 5% H_2O, 200L g^{-1} h^{-1}.

SO_2-Poisoned

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

650 °C-Reg.

Pretreatment: 600°C, 20min, 12% O_2, 6% H_2O, 6% CO_2, 200L g^{-1} h^{-1}.

800°C-Reg.

Pretreatment: 650°C, 20min, 12% O_2, 6% H_2O, 6% CO_2, 200L g^{-1} h^{-1}.

U.S.DRIVE Protocols

*K. Rappé et al. *Emiss. Control Sci. Technol.* **2019**. 5:183-214

- Catalyst activity can be readily regenerated at 800 °C using U.S.DRIVE protocols after exposure to SO_2.

Accomplishments (CO Oxidation)

Atomistic Level Understanding of Active Sites and Reaction Mechanisms Helps Accurate Modeling

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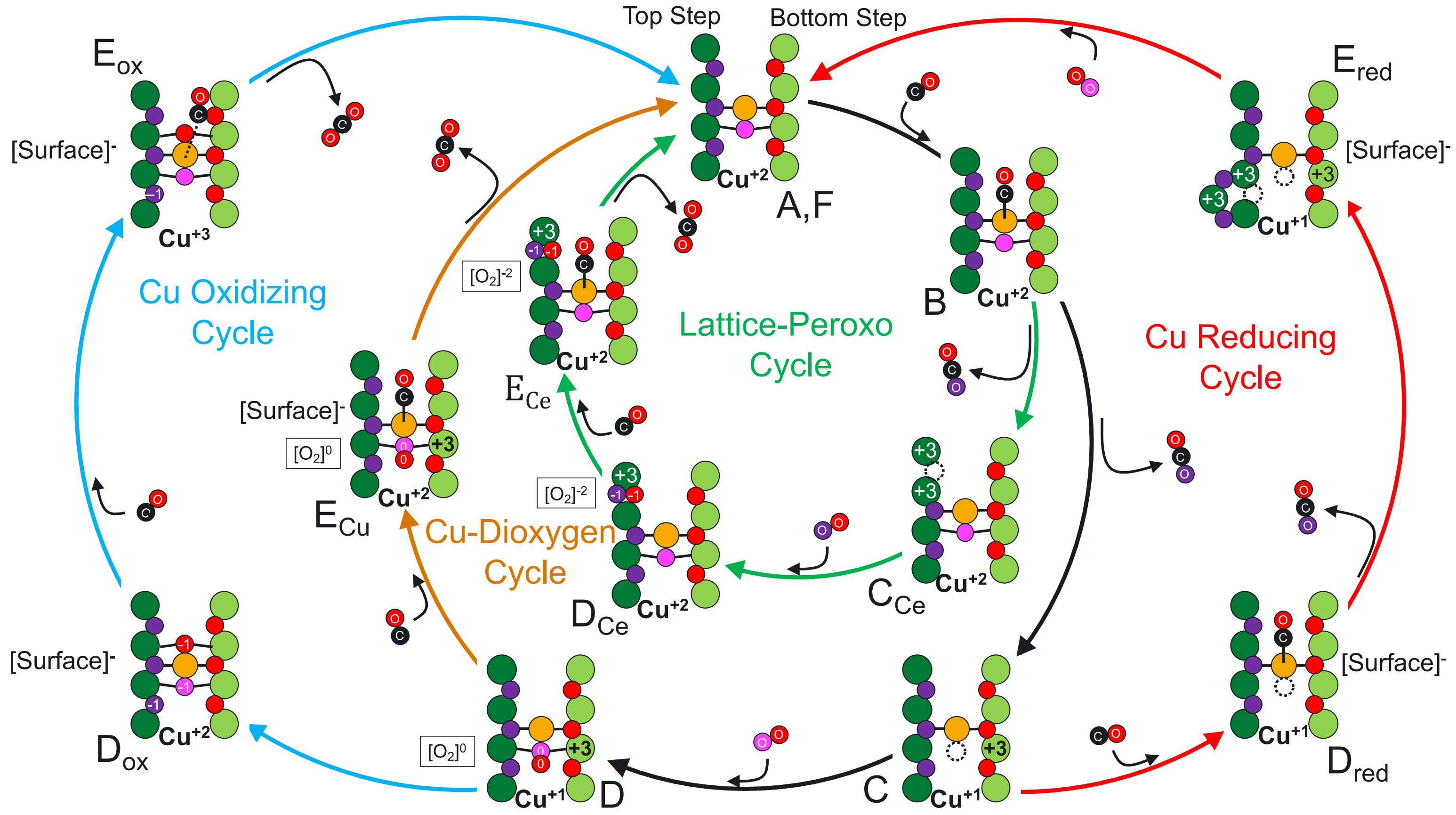
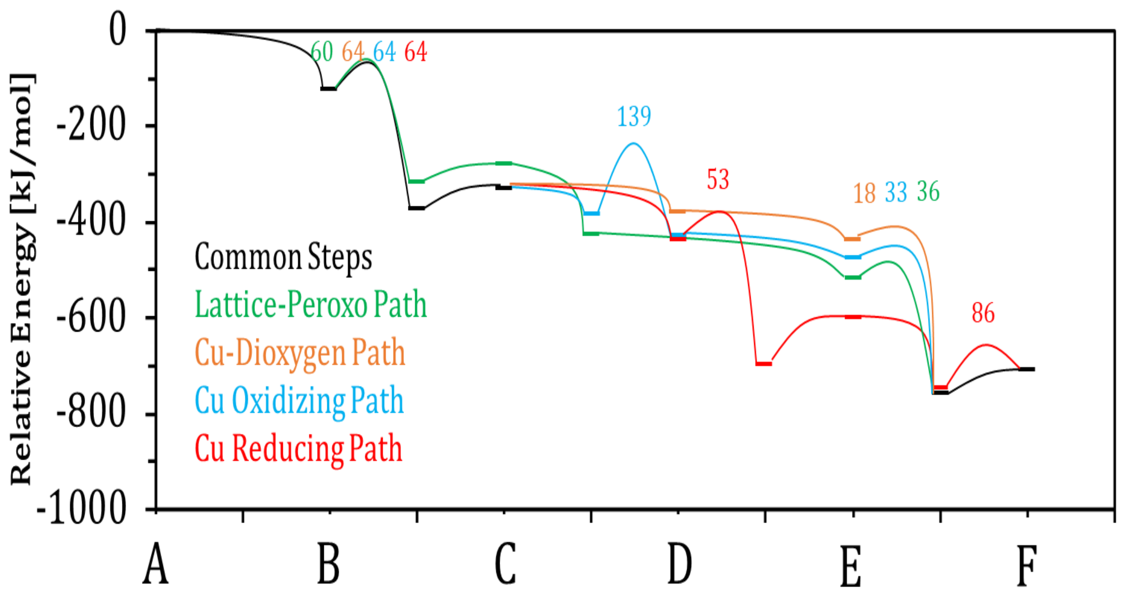
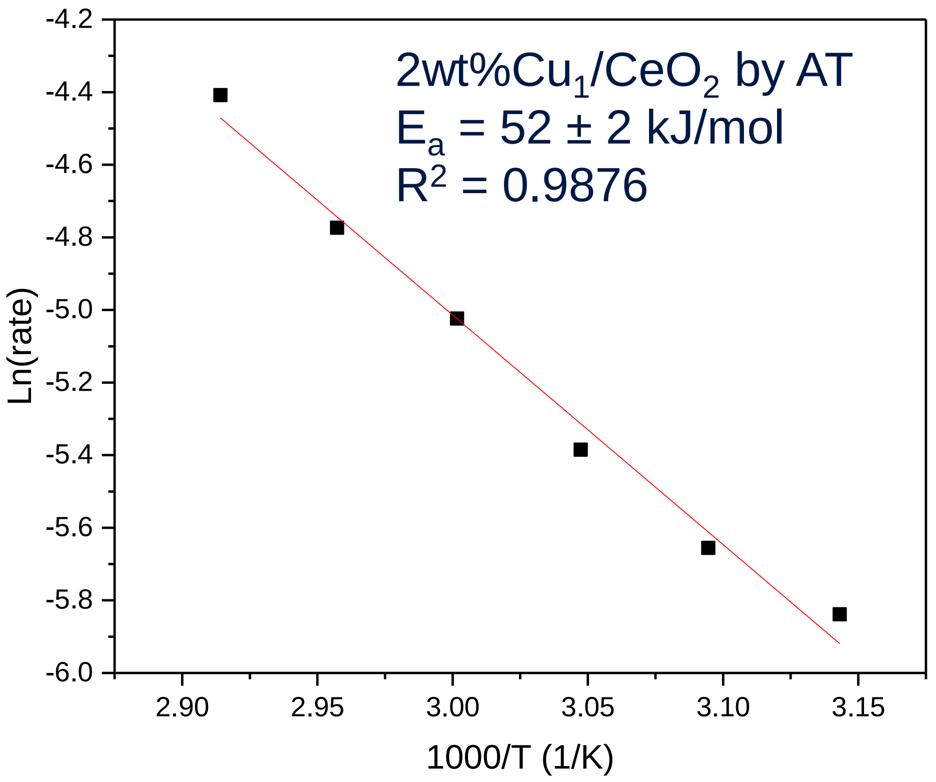






- Both Lattice-Peroxo and Cu-Dioxygen Cycles are favorable with $E_{a,eff}$ of ~60 kJ/mol, matching experimentally measured 52 kJ/mol
- The Cu Oxidizing Cycle has a prohibitively high barrier
- The Cu Reducing Cycle is potentially competitive

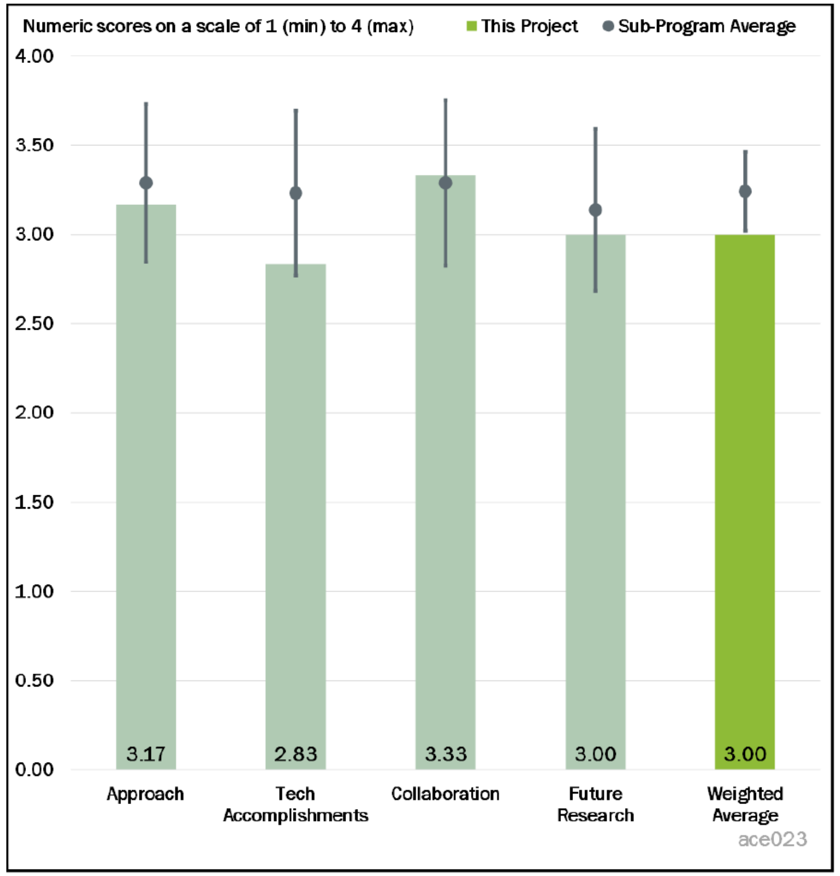
Accomplishments (LTAT team)

Catalyst Test Protocols and PGM Utilization

- Road-mapping and planning efforts surrounding lowering PGM usage in emission control catalysts
  - Presentation prepared for the ACEC Tech Team and the APTLC
    - ***Current State of Automotive Aftertreatment Catalysis****: Addressing the Need to Lower Catalyst PGM Usage For Cost Effective SULEV30 Emissions Control*
    - Summarized current status of PGM research towards reduced usage in aftertreatment, including compilation of recent relevant literature review articles, technical articles, and BES overview
- 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 2020 CLEERS workshop panel discussion

Responses to Previous Year Reviewers' Comments

Reviewers' Comments	PNNL Responses
It might be good to break up this project into several smaller projects where each is focused on one catalyst technology	TWC is presented separately in ACE056, and this presentation only focuses on SCR and LTAT
Aging of closed couple SCRs in heavy-duty applications also needs to be considered.	Working with OEMs on clear guidance including chemical poisoning, thermal stability improvement with controlling Al distribution and SSZ-39 support
The team needs to investigate sulfur poisoning and desulfation on the Mn-Ce-modified SCR catalyst, since sulfur inhibits the low-temperature activity of SCR catalysts	Currently being addressed by closely working with Carus



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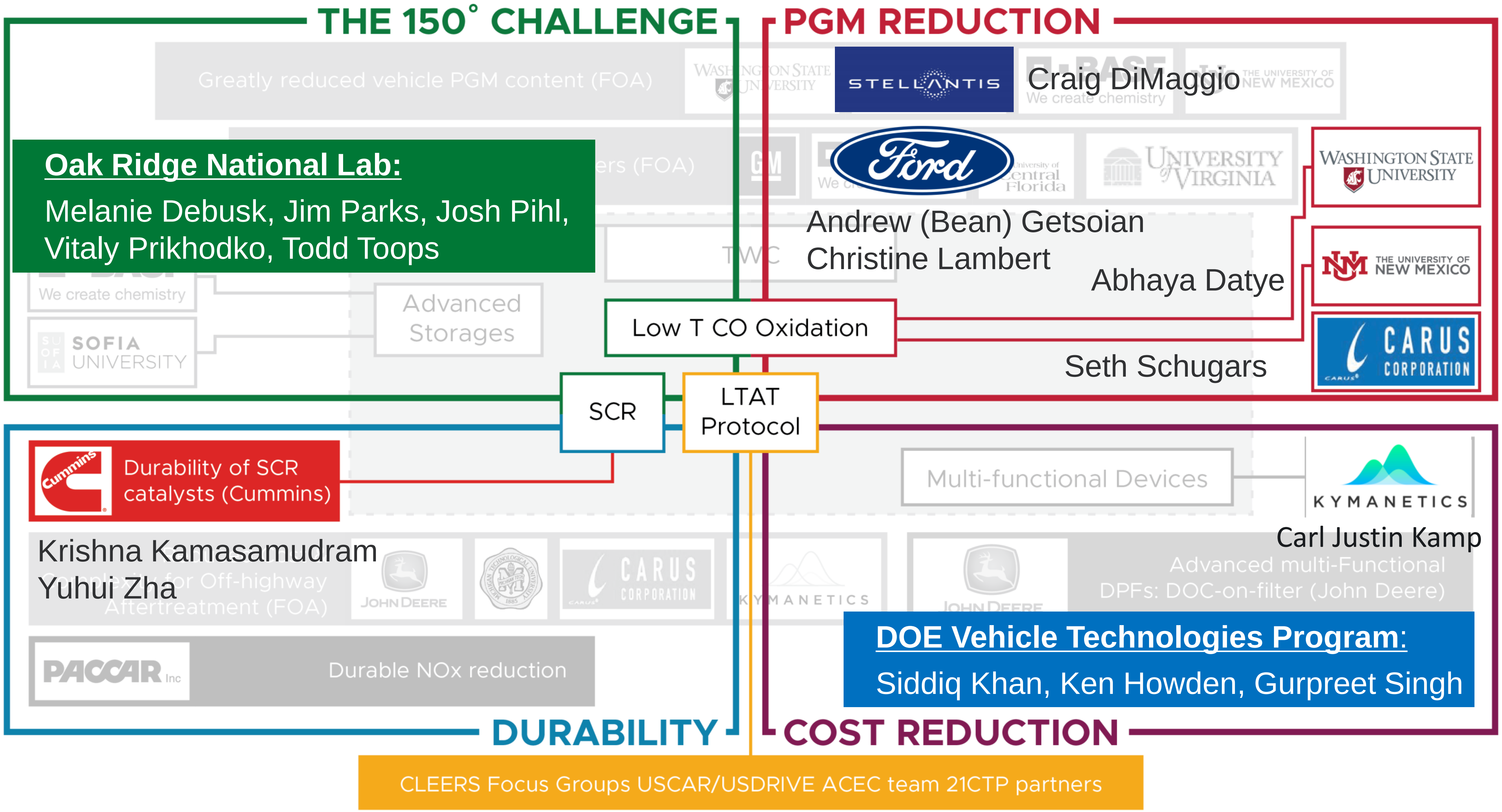
Collaboration and Coordination with Other Institutions



Remaining Challenges and Barriers

- Linking learning from lab accelerated model materials with field-aged commercial catalysts.
  - Distinguishing thermal degradation, hydrothermal degradation, and chemical degradation for examining aged (used) catalysts, and identification of representative descriptor for aging from such complexity.
- SCO-SCR – turning learning into opportunity to design the next generation low-temperature SCR catalysts
- Translating efficiency gains of single atom catalysts prepared by atom trapping to production scale while ensuring Bin30/SULEV30 emissions compliance.
- Understanding of multi-functional filters with respect to washcoat placement, permeability, and catalyst usage efficiency.

Proposed Future Work

SCR

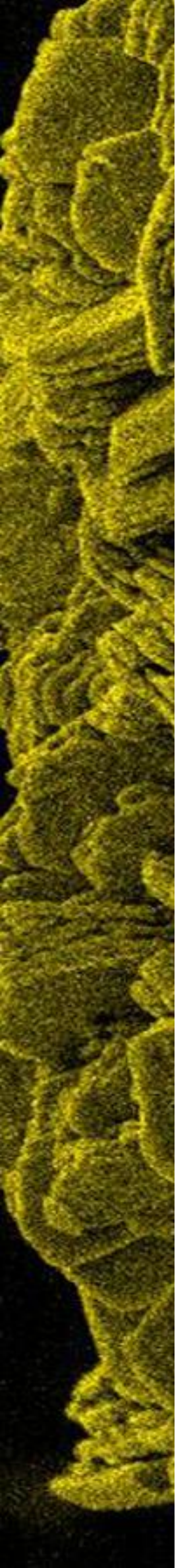
- Study effects of SSZ-13 support framework Al distribution and SAPO-34 crystallinity on Cu speciation, low-temperature performance, high-temperature stability, and resistance to sulfur poisoning.
- Utilize newly developed spectroscopic methods to examine aged- and on-road catalysts and develop correlations between mileage and catalyst performance.
- Understand pathway and nature of chemical exchange (e.g., active intermediates, stable products) between SCO & SCR phases as a function of proximity (e.g., impregnated, ball-milled, loosely mixed)

LTAT

- Understand activation of oxygen and oxygen storage by single atoms via atom trapping and their roles in low temperature oxidation activity
- Further improve sulfur tolerance and regeneration strategies of thermally stable single atom catalysts
- Continue PGM road-mapping efforts, including possible PGM review article with ORNL, and early planning of PGM workshop, e.g., analogous to 150°C Grand Challenge Workshop
- Plan to support update to ACEC Tech Team Roadmap in CY2021

Multi-functional devices

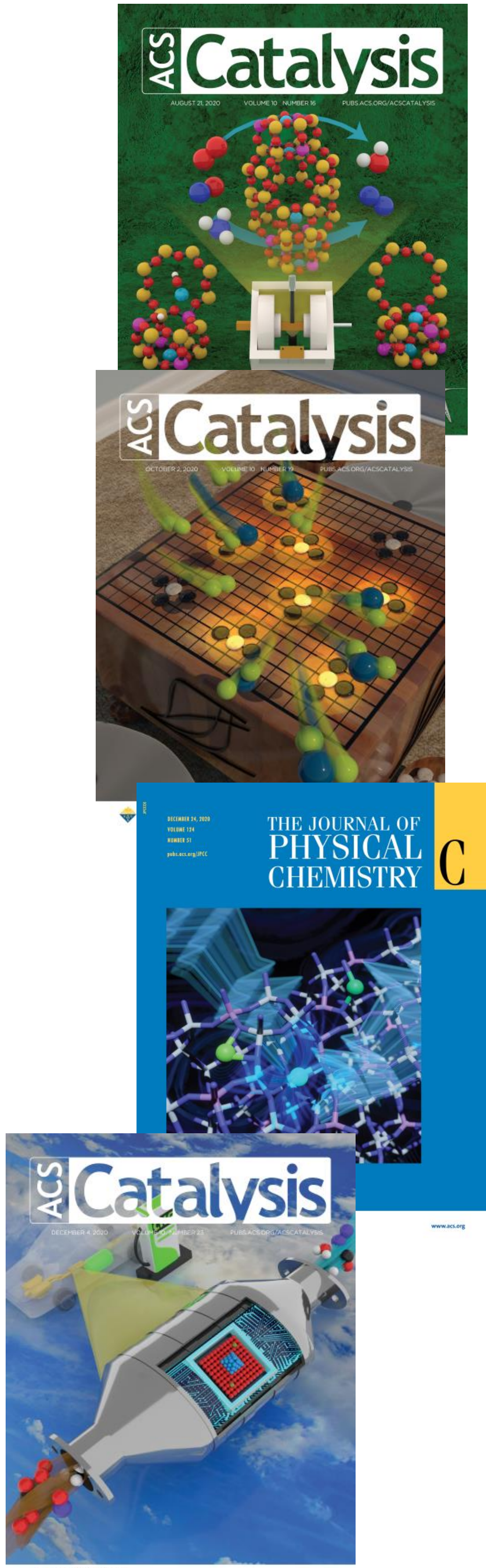
- Characterize catalyst distribution in a state-of-the-art SCR-Filter using Micro X-Ray CT
- Examine effects of SCR catalyst placement on pore-scale flow patterns and transport phenomena

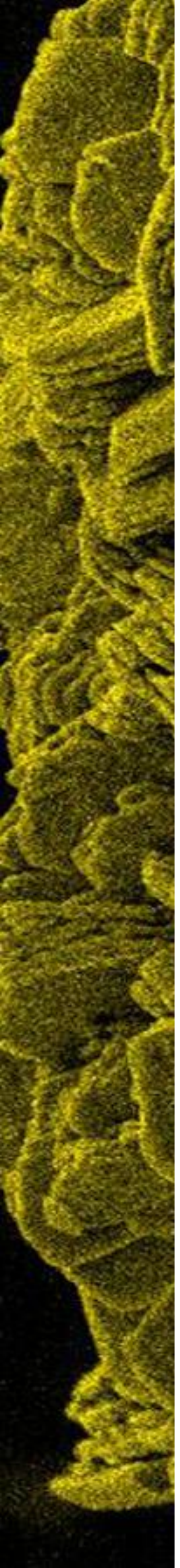


Summary

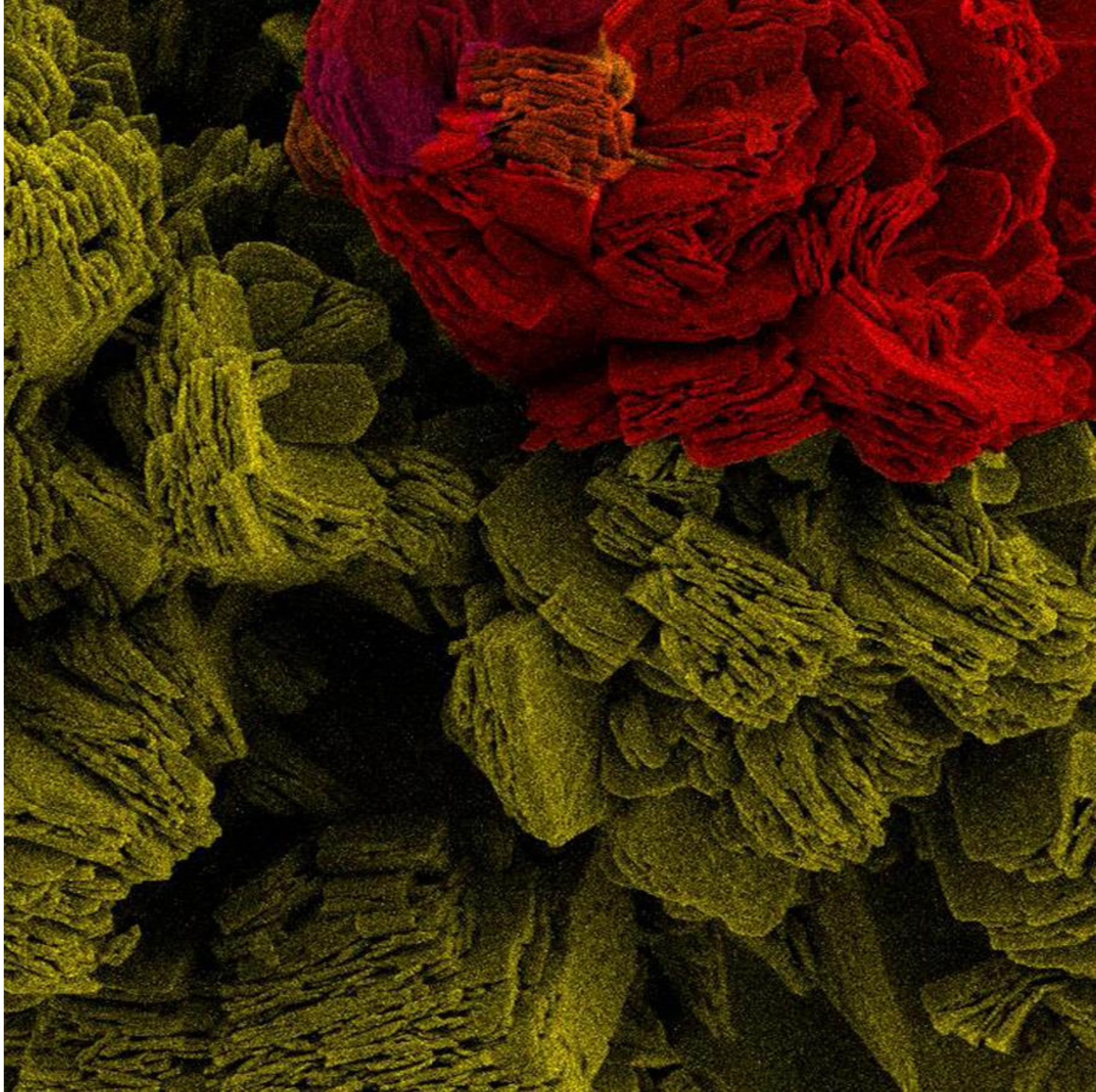
- *in situ and ex situ* electron paramagnetic resonance (EPR), in both 1D (continuous wave) and 2D (pulsed) modes, provides unprecedented insight on Cu/SSZ-13 catalyst deactivation under full useful life aging which is essential in accurate modeling of SCR aging behaviors.
- Intimate contact between SCR and SCO phase enhances low temperature SCR activity.
- Thermally durable single atom Cu catalysts prepared by atom trapping exhibit high activity in CO oxidation and can be readily regenerated by US DRIVE protocols after sulfur poisoning, contributing to PGM reduction and catalyst cost savings. Atomistic level understanding of active sites and reaction mechanisms helps accurate modeling.

Effective dissemination by 11 peer-reviewed publications in *Nature Comm, JACS Au, ACS Catalysis, Applied Catal. B.*

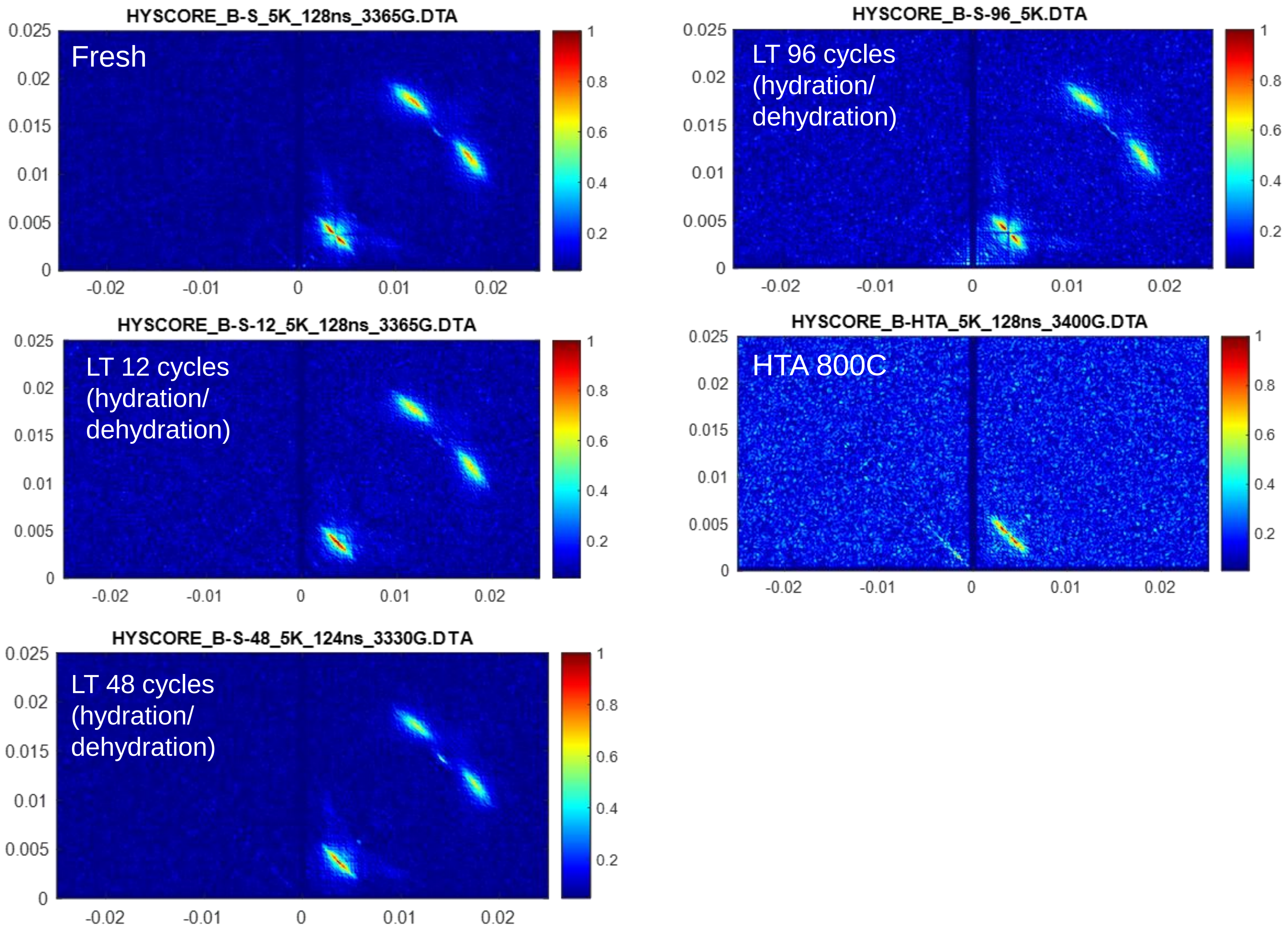




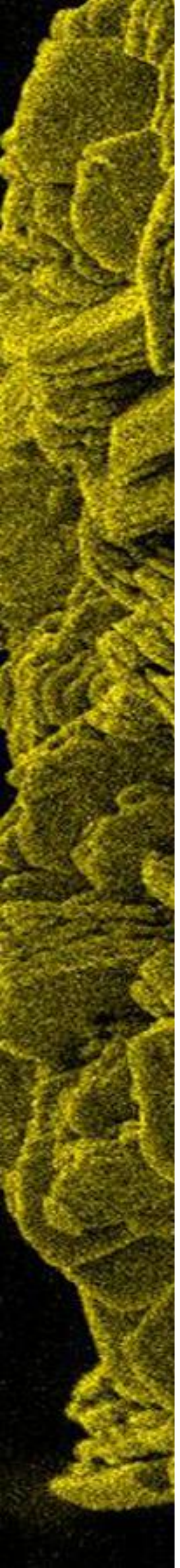
Technical Backup Slides



2-*D* EPR Examines Coupling between Isolated Cu(II) and Framework Al/H in Cu/SAPO-34



- Repeated hydration-dehydration treatment of Cu/SAPO-34 catalyst at low temperatures induces loss of Cu active sites.
- High temperature hydrothermal aging leads to both the loss of active sites and conversion of ZCuOH sites to Z_2Cu sites.



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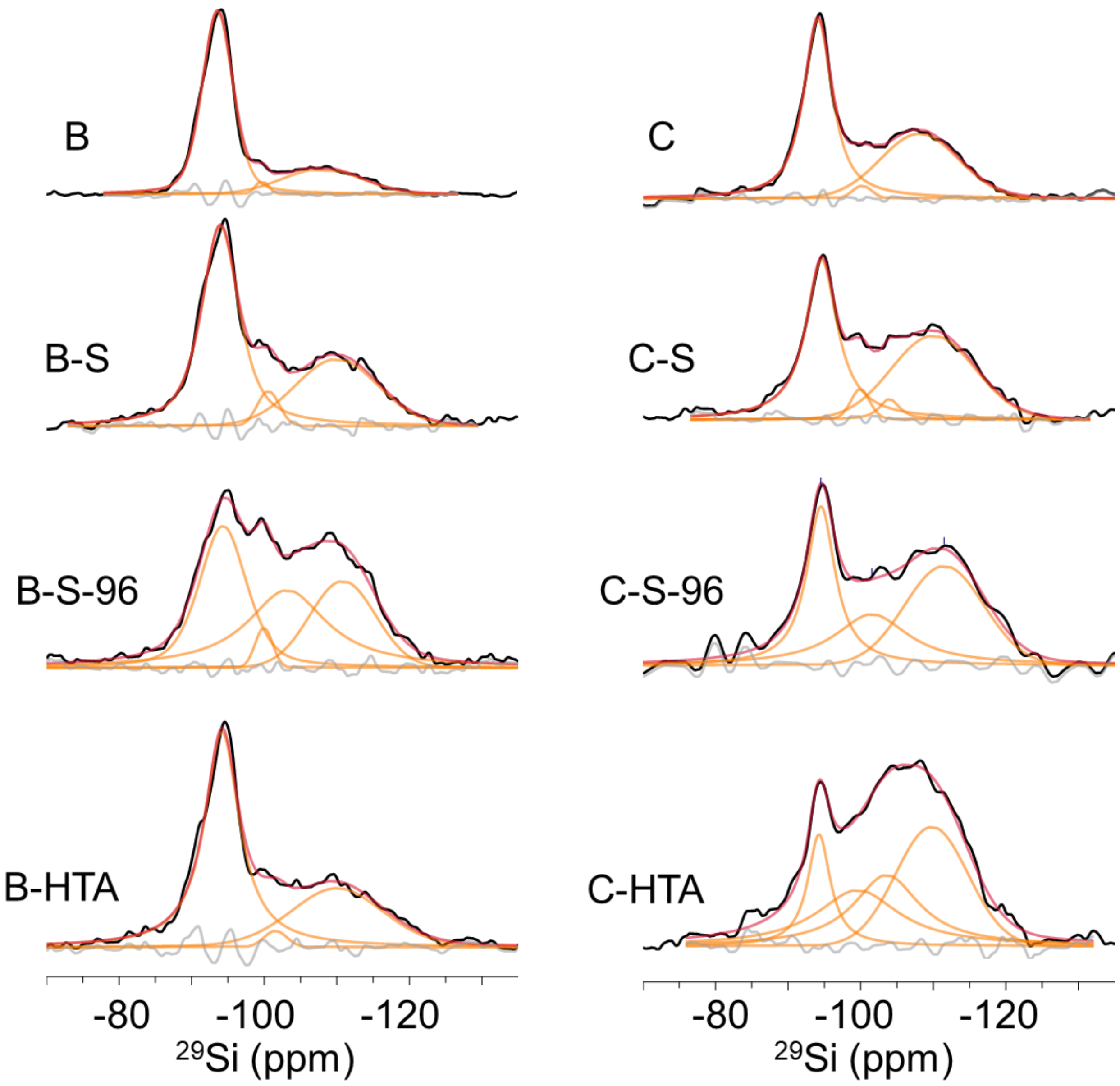
Solid-state ^{39}Si NMR Reveals How Silica Islands Form during Low- and High-temperature Hydrothermal Treatment of Cu/SAPO-34 Catalysts



- For SAPO-34 synthesized with morpholine as SDA (B), low-temperature moisture treatment induces strong Si island formation. However, this support is more stable during high temperature hydrothermal aging.
- For SAPO-34 synthesized with TEAOH as SDA (C), the behavior is the opposite: the catalyst is more stable than B at low temperature, but less stable than B at high temperature.

Characterization by HRTEM, XRD and EXAFS Confirms Cu Single Atoms with 2wt% Cu

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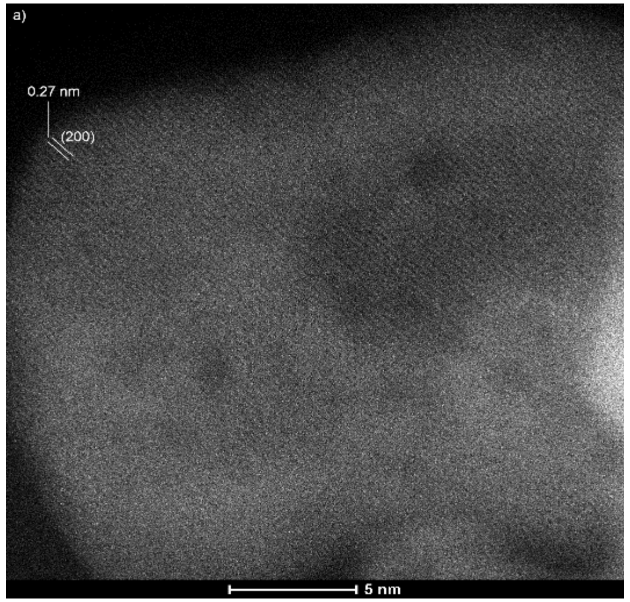
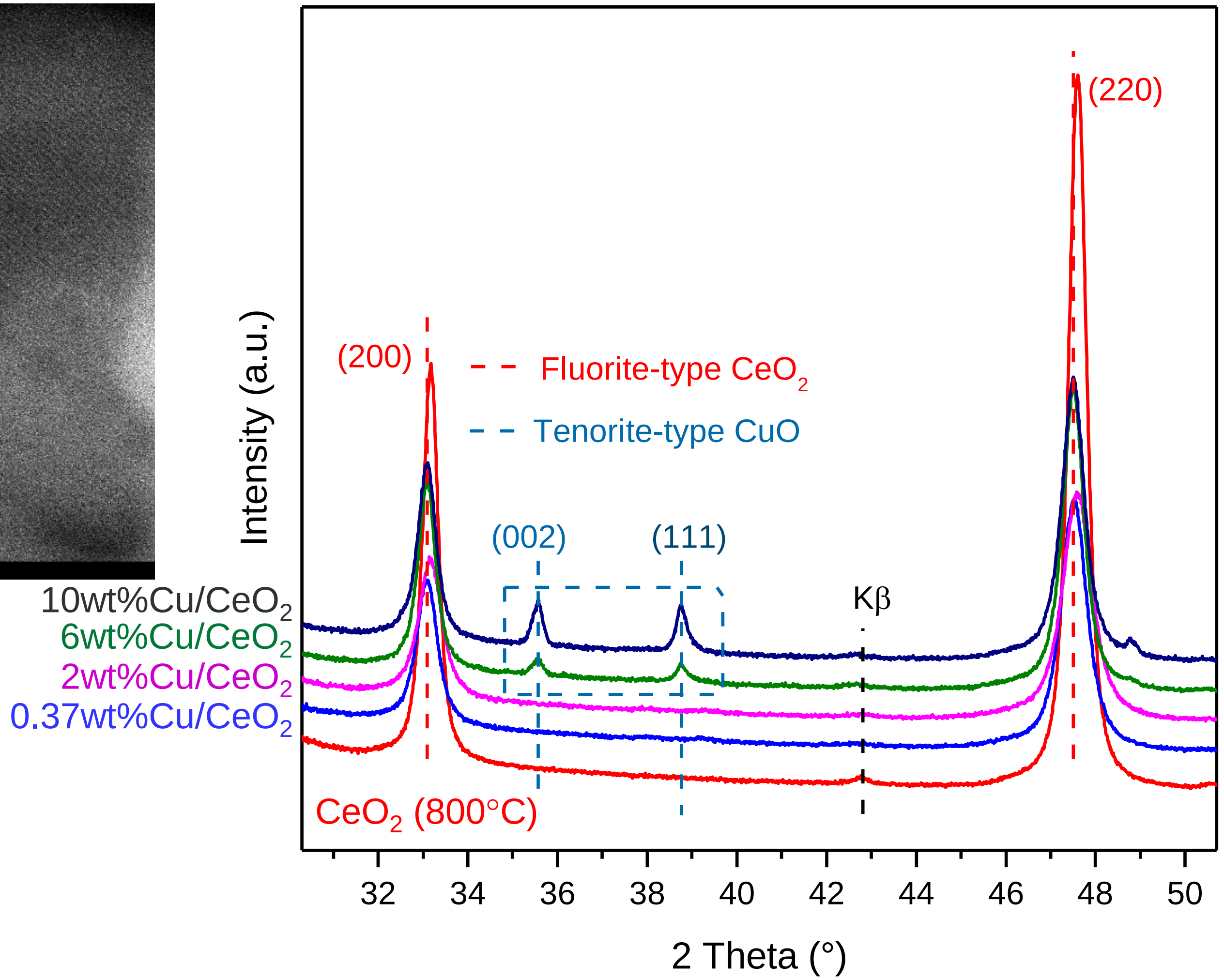
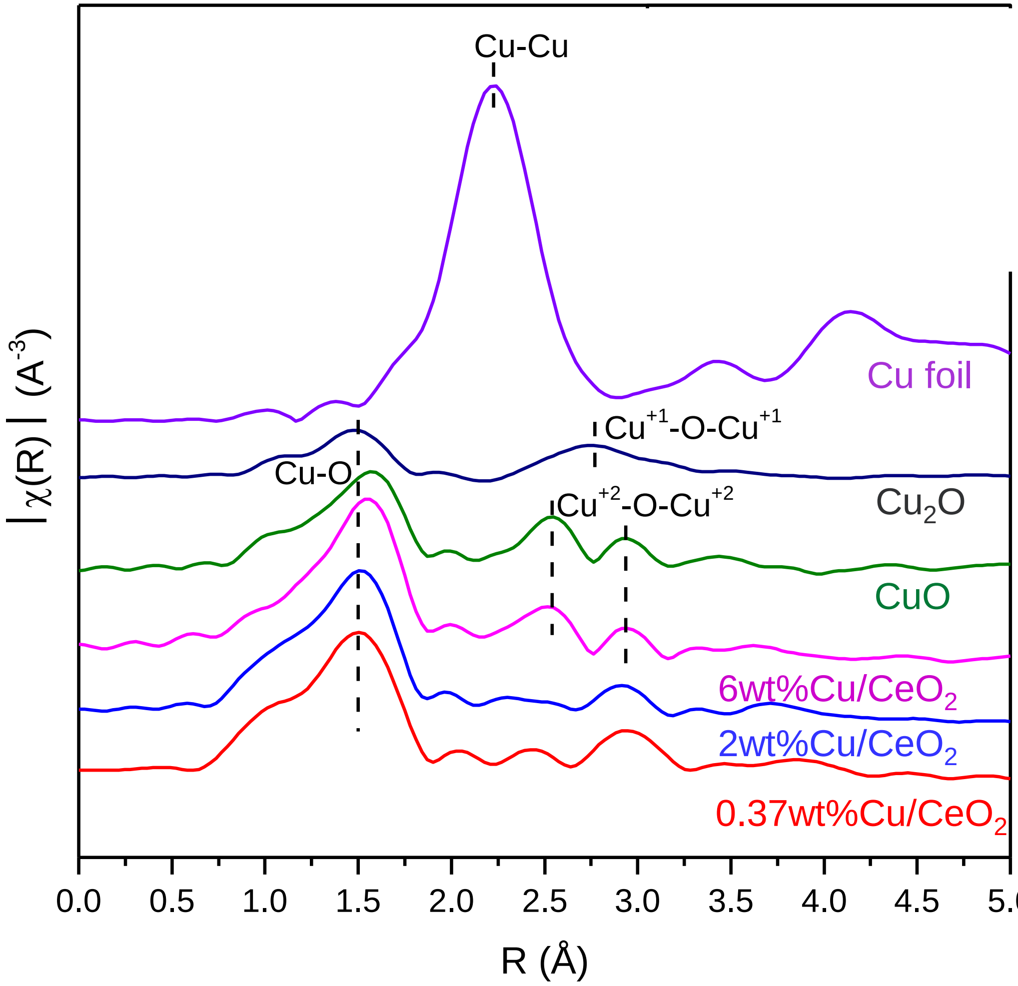
HRTEM



XRD



EXAFS



- No Cu/CuO particles observed by HRTEM
- CuO (002) and (111) diffraction peaks are detected only for the catalysts with 6 & 10wt.% Cu
- Cu is atomically dispersed as Cu^{2+} at up to 2wt% Cu

DFT Calculations Confirm that Cu-O-Ce Oxygen and Step Edge Ce-O-Ce Are Most Active in Cu Single Atom Catalysts

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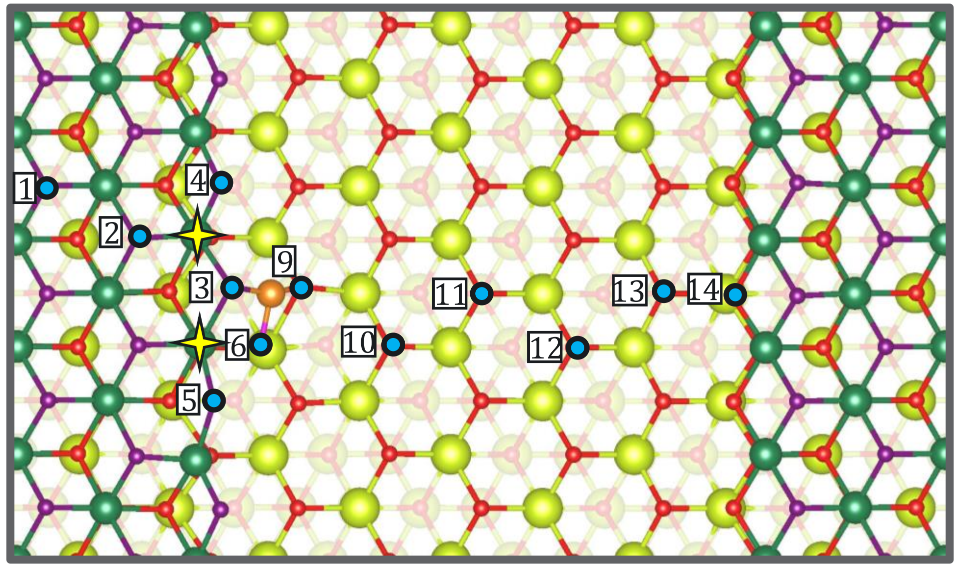
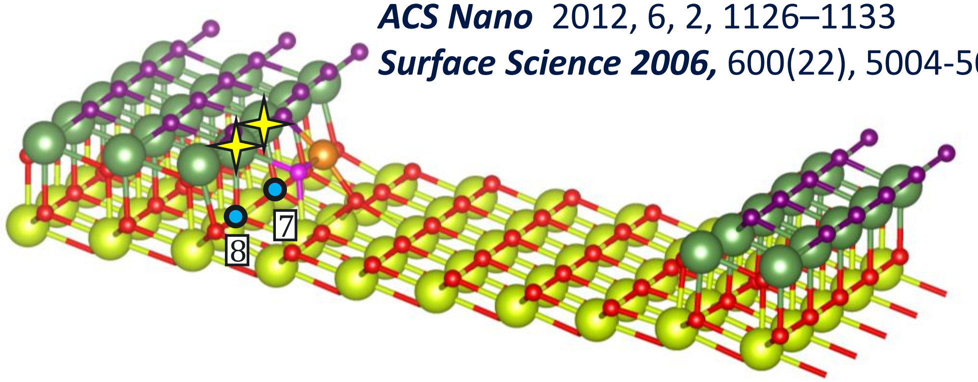
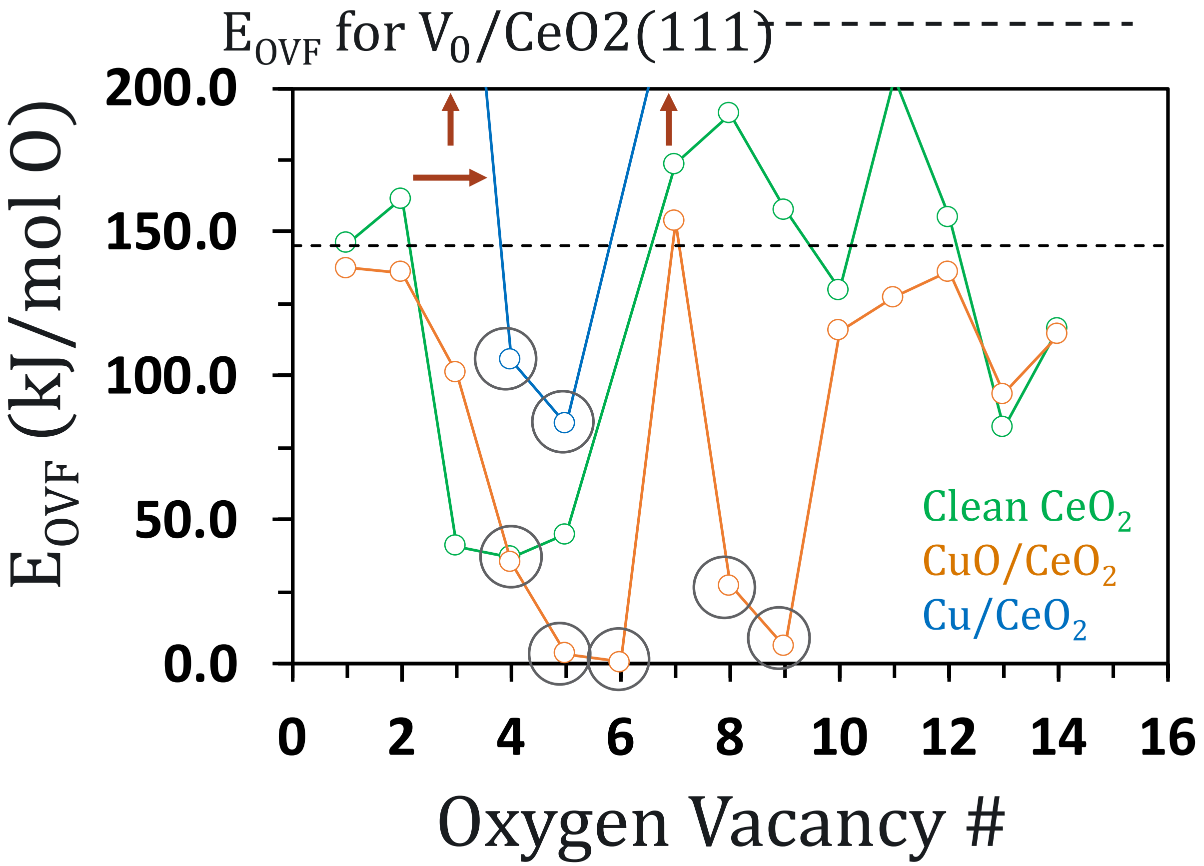




ACS Nano 2012, 6, 2, 1126–1133
Surface Science 2006, 600(22), 5004-5010.



Oxygen Vacancy Formation Reaction:

$$CeO_2 \rightarrow V_0/(CeO_2) + \frac{1}{2}O_2(g)$$

$$E_{OVF} = E_{V_0/CeO_2} + \frac{1}{2}E_{O_2(g)} - E_{CeO_2}$$

- Oxygen vacancy formation is favored in atomic CuO/CeO_2 including Oxygen # 4, 5, 6, 8, and/or 9.
  - Can eliminate #5 and #8 for steric reasons.
  - #9 vacancy filled by #6, so it is eliminated
  - Leaves #4 (Ce-O-Ce) and #6 (Cu-O-Ce)

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Organized & Moderated 2020 CLEERS Panel Discussion

- ***Dr. Bill Epling***, University of Virginia
  - Overview of the DOE-awarded GM-led project:

    "Slashing PGM in Catalytic Converters:
    An Atoms-to-Autos Approach"

- ***Dr. Yong Wang***, Washington State University
  - Overview of the DOE-awarded WSU-led project:

    "Greatly Reduced Vehicle PGM Content Using
    Engineered, Highly Dispersed Precious Metal Catalysts"

- ***Dr. Saeed Alerasool***, BASF
  - Review of Pt, Pd, Rh market projections, including Pd price premium over Pt and Rh shortage projection
  - BASF approach – Accelerating technology development from powder to fully-formulated catalysts
    - Intense R&D on LD gasoline and HD/LD diesel
    - Working closely with OEMs to optimize PGM ratio & reduce total PGM required
    - Participation in DOE sponsored projects, actively engaging in academic collaborations

- ***Dr. Wilfried Mueller***, Umicore
  - An Overview of PGM utilization efforts at Umicore