

Emissions Control for Lean Gasoline Engines

Project ID: ace033

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National Transportation Research Center

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 - *Pat Szymkowicz, Wei Li, Paul Battiston, Arun Solomon, Paul Najt*



- **Collaboration with partners at Umicore:**
 - *Ken Price, Ryan Day, Hari Krishnan, Tom Pauly*

Overview

Timeline

- Year 3 of 3-year program
 - Project start date:** FY2019
 - Project end date:** FY2021
- Builds on previous R&D in FY16-FY18
- Task 3 of larger ORNL project “Controlling Emissions from High Efficiency Combustion System” in response to 2018 VTO Lab Call

Budget

FY19	FY20	FY21
\$500k	\$500k	\$500k

Barriers Addressed

U.S. DRIVE Advanced Combustion & Emission Control 2018 Roadmap Barriers & Targets:

- Lack of cost-effective aftertreatment for lean-burn systems
- Compliance with U.S. EPA Tier 3 Bin 30 emission standard
- Efficiency, durability, sulfur tolerance of aftertreatment systems

Collaborators & Partners

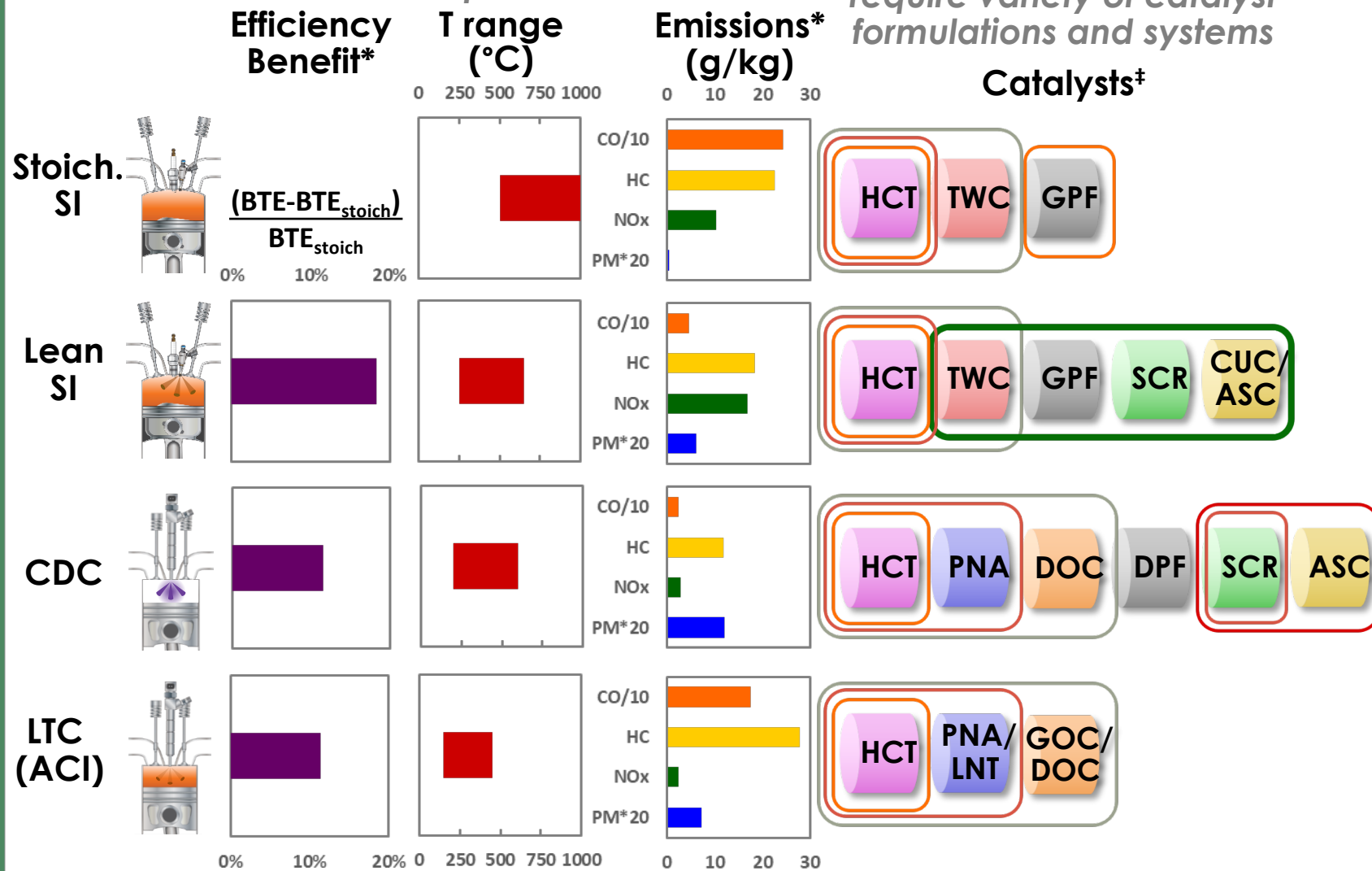
- General Motors
- Umicore
- Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS)

Advanced combustion technologies improve efficiency, but lean low temperature exhaust creates emissions challenges that must be addressed before commercialization

Higher fuel efficiency = lower exhaust temperatures

Unique emissions profiles require variety of catalyst formulations and systems

ORNL R&D portfolio spans wide range of applications, technologies, size scales, commercial readiness



Tasks

- CLEERS (ACE022)**
Model new trap materials and aging effects on SCR catalysts
- Low Temperature Emissions Control (ACE085)**
Discover new low T catalysts & traps
- Lean Gasoline Emissions Control (ACE033)**
Develop pathways for lean gasoline engines to meet emissions with minimum fuel penalty
- Chemistry & Control of Cold Start Emissions (ACE153)**
Understand how exhaust chemistry impacts device performance & design
- Cummins Emissions Control CRADA (ACE032)**
Understand how aging affects properties and performance of SCR catalysts

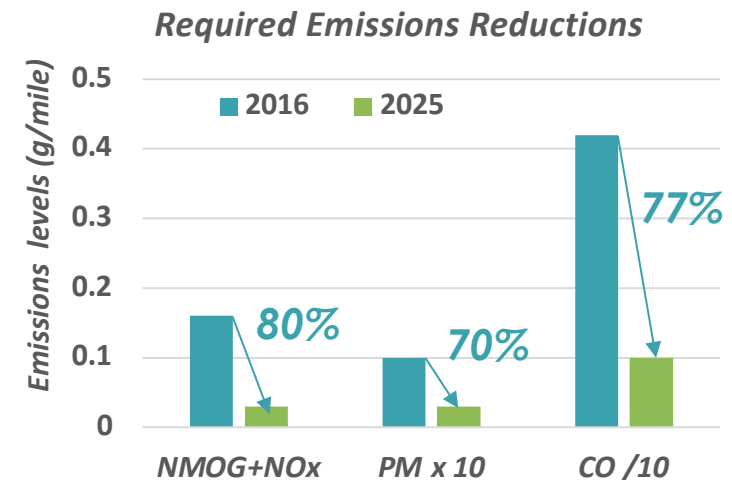
*(efficiency and emissions at 2000 rpm, ~2 bar BMEP) ‡Abbreviations in backup slides

Objectives and Relevance

Enabling lean-gasoline vehicles to meet emissions regulations will achieve significant reduction in petroleum use

- Objective:

- Demonstrate technical path to emission compliance that would allow the implementation of lean gasoline vehicles in the U.S. market
 - Lean vehicles offer 5–15% increased efficiency over stoichiometric-operated gasoline vehicles
 - Compliance required: U.S. EPA Tier 3
- Investigate strategies for cost-effective compliance
 - Minimize precious metal content while maximizing fuel economy

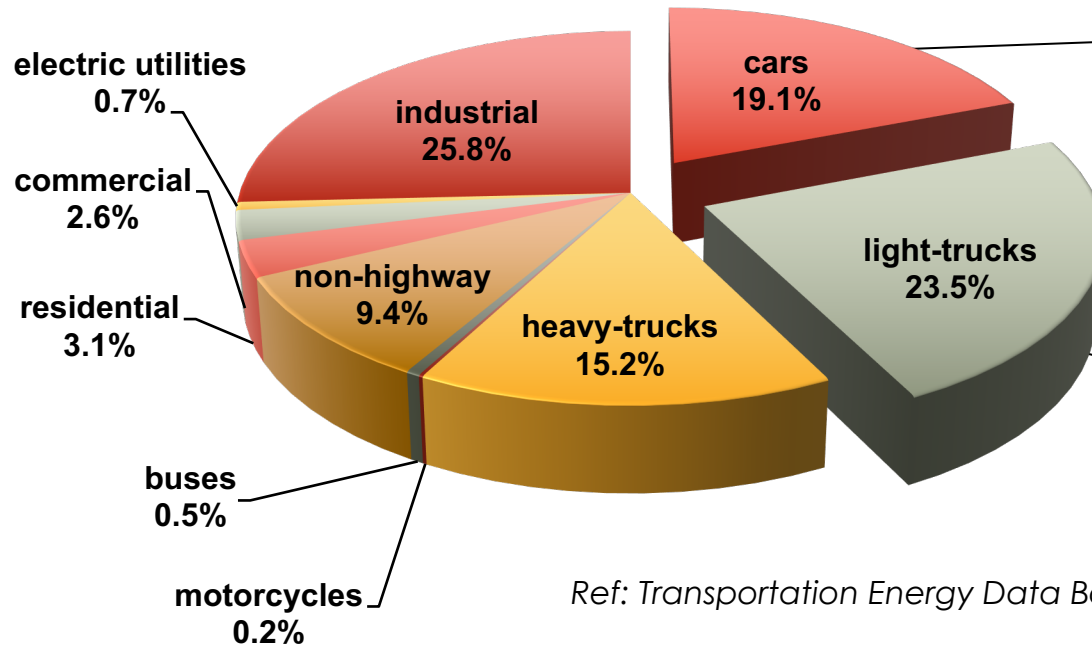


- Relevance:

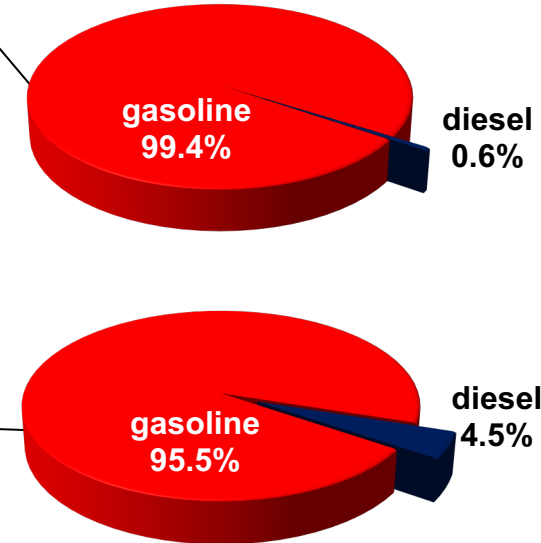
- U.S. passenger car fleet is dominated by gasoline-fueled vehicles
- Enabling introduction of more efficient lean gasoline engines can provide significant reductions in overall petroleum use
 - thereby lowering dependence on foreign oil and reducing greenhouse gases

Small improvements in gasoline fuel economy significantly decreases fuel consumption

Total petroleum consumption by sector



Energy consumption by fuel type

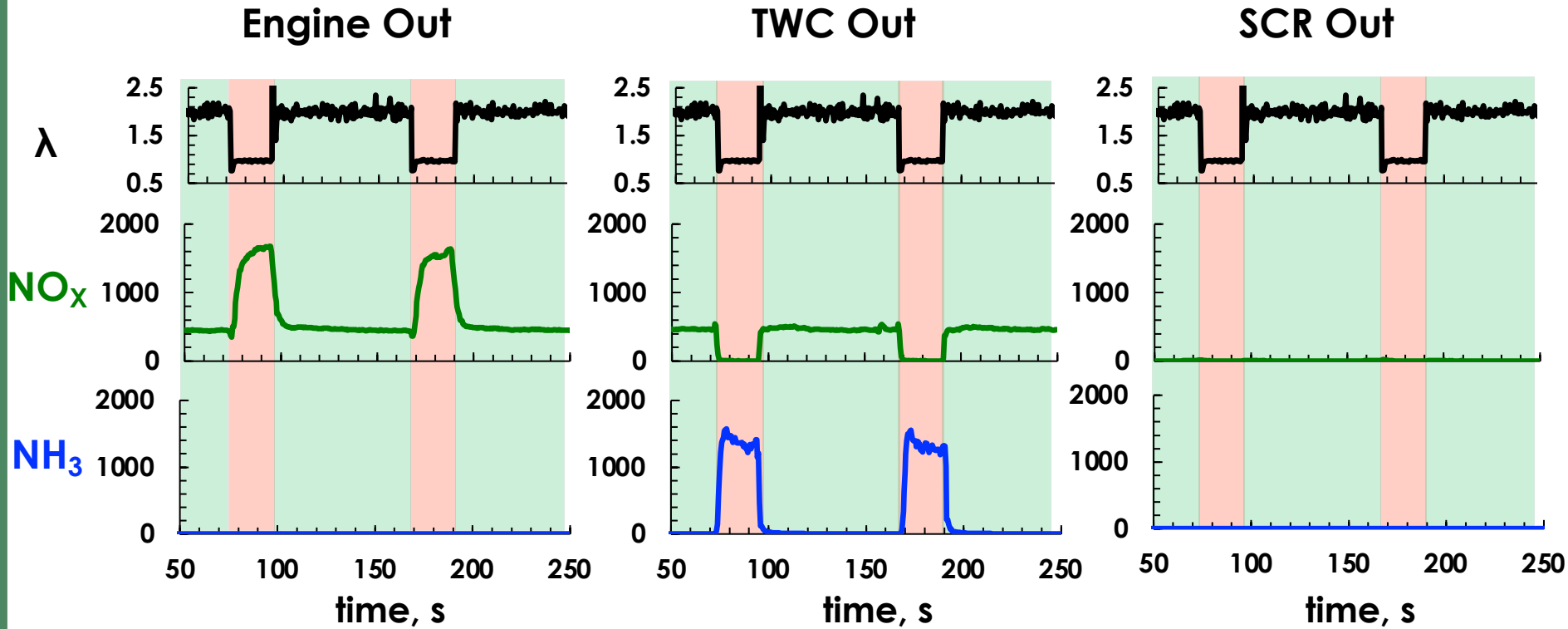


Ref: Transportation Energy Data Book, Ed. 36.1, 2018 (2015 data)

- U.S. car and light-truck fleet dominated by gasoline engines
- 10% fuel economy benefit has significant impact
 - Potential to save 13 billion gallons gasoline annually
- HOWEVER...emissions compliance needed!!!

Lean gasoline vehicles can decrease US gasoline consumption by ~13 billion gal/year

Passive SCR is non-urea approach to lean gasoline NOx control



Passive SCR is a potential low cost strategy for reducing lean gasoline NOx emissions

- Makes use of TWC already onboard to generate NH₃
- Eliminates urea tank, injector, refills
- Potentially reduces PGM relative to TWC+LNT

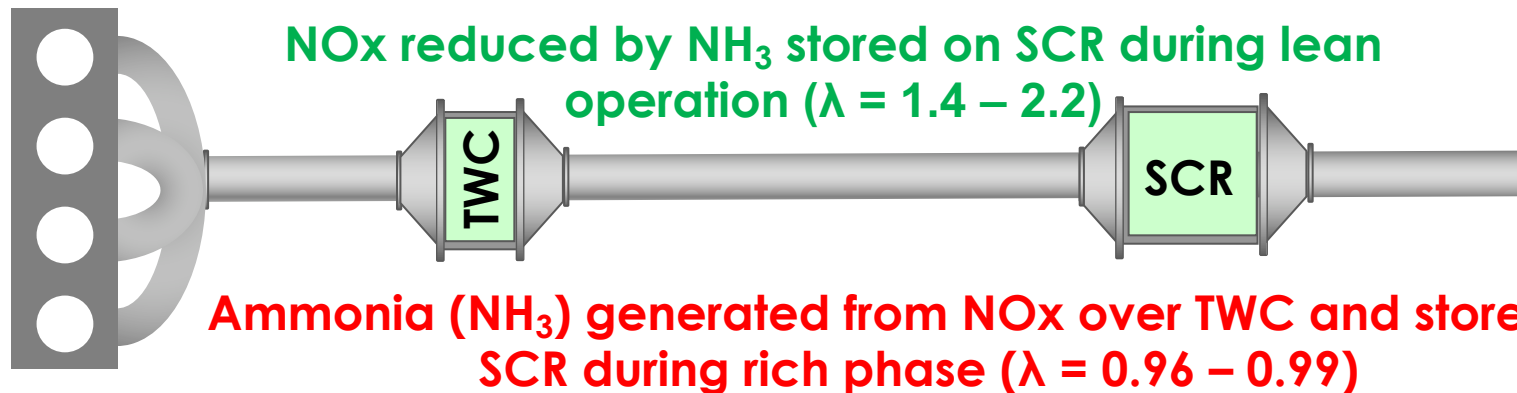
$$\lambda = \frac{AFR}{AFR_{stoich}}$$

AFR = air/fuel ratio

$\lambda < 1$: excess fuel

$\lambda = 1$: stoichiometric

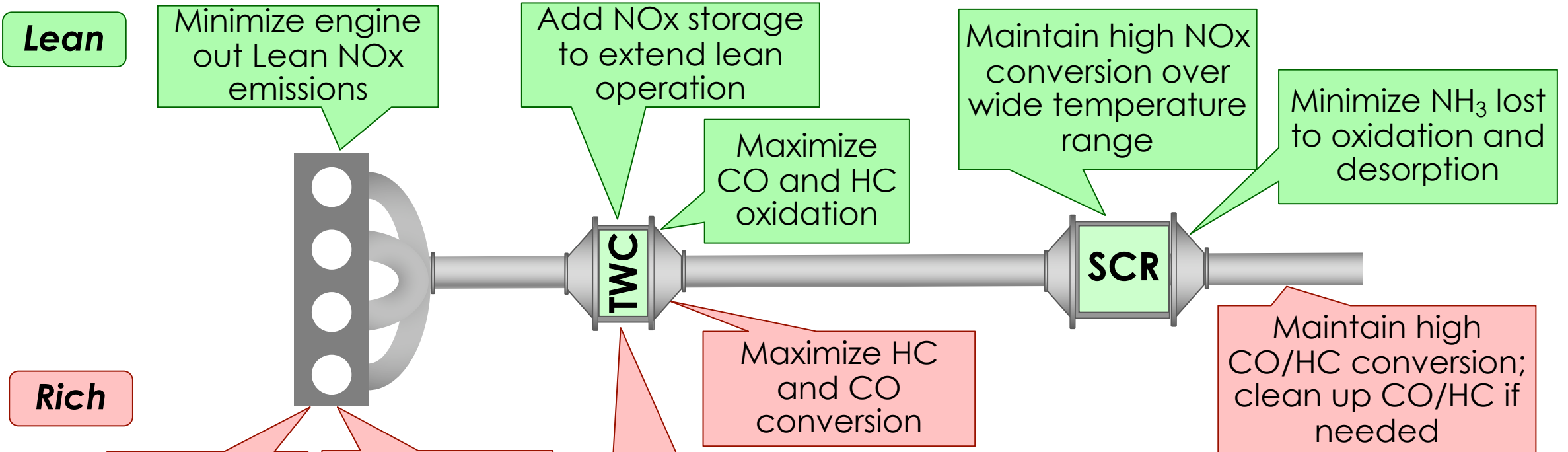
$\lambda > 1$: excess air



References:
SAE2010-01-0366,
SAE2011-01-0306,
SAE2011-01-0307

Approach focuses on engine and catalyst optimization of passive SCR

Key Principle: system fuel efficiency gain depends on optimizing NH_3 production during rich operation and NO_x reduction during lean operation

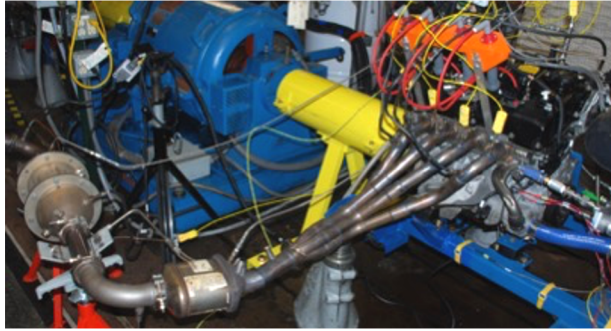


Other Core Principles:

- Expand operating temperature range
- Evaluate durability to aging and sulfur
- Understand precious metal utilization to minimize cost

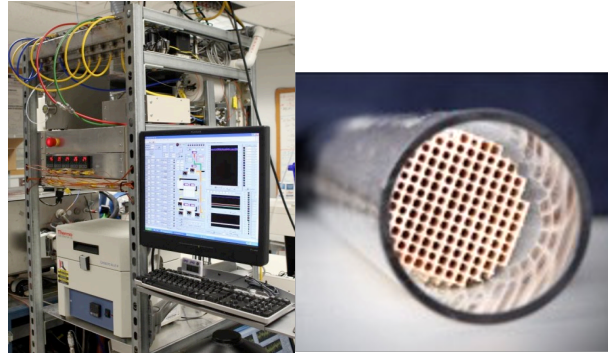
References: SAE2010-01-0366, SAE2011-01-0306

Iterative Flow Reactor + Engine Study Approach



BMW 120i lean gasoline engine platform with open controller

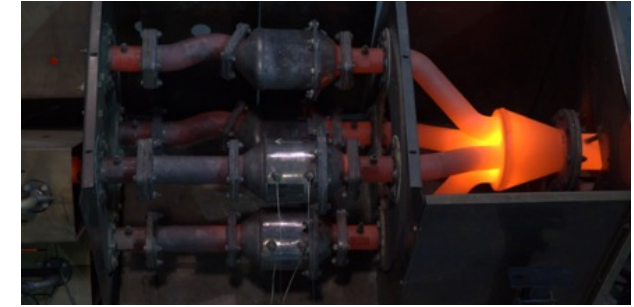
- Define relevant exhaust conditions
- Evaluation of selected catalyst components, system integration and optimization
- Measurement of fuel economy and emissions over pseudo-transient cycle
- Optimize combustion parameters for fuel efficiency and emissions



Automated Flow Reactor with feedback control and tandem catalysts

- Detailed characterization and screening of catalysts in simulated exhaust
- Investigation of alternative catalyst configurations and operating strategies
- Age and characterize selected catalyst formulations

Collaborations with modeling community and CLEERS



C-FOCAS Burner at SGS full scale catalysts aging

- Age selected TWC, SCR and CUC catalysts for engine and flow reactor evaluations
- Air-fuel ratio, temperature and flow rate control



Prototype Catalysts & Insights



Technical Guidance

Milestones

Quarterly Milestones

Complete

- **FY2019, Q3:** Complete evaluation of 5-function emissions control system with cleanup catalyst

Delayed

now FY21, Q4

- **FY2020, Q4:** Complete measurement of fuel economy benefit and emissions using transient drive cycle on the newly installed MAHLE Jet Ignition engine

Delayed

now FY22, Q1

- **FY2021, Q4:** Tier 3 Bin 30 level emissions with an advanced engine platform with less than 4 g Pt-equivalent per liter engine displacement

GO/NO-GO Decision

Complete

- **FY2019, Q4:** Install MAHLE Jet Ignition engine at ORNL with full controls which will expand lean operation map for higher fuel efficiency and lower engine out emissions

Collaborations and Partners

Primary Project Partners

(regular monthly teleconferences)

- **GM:** guidance and advice on lean gasoline systems
- **Umicore:** guidance and catalysts (commercial and prototype formulations)



Additional Collaborators/Partners on Project/Engine Platform (since project inception)

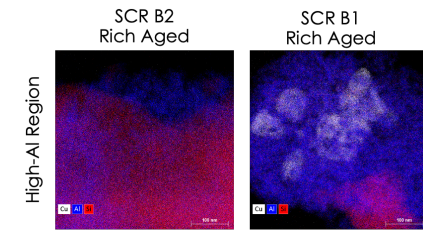
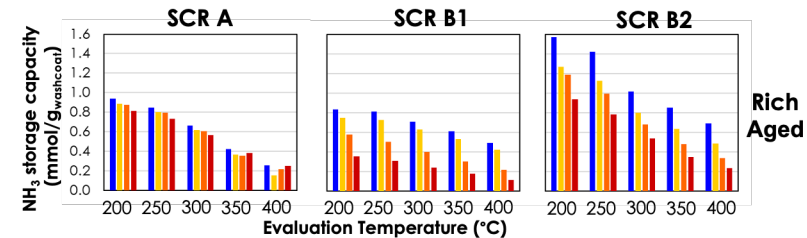
- CLEERS: share results/data and identify research needs
- AEC MOU: share results and receive feedback from the industry partners in the MOU
- LANL: engine platform used for NO_x/HC/NH₃ mixed-potential sensor research
- PNNL: detailed PM characterization from lean gasoline engines using SPLAT
- DOE Co-Optima: engine platform used for biofuel-based HC-SCR studies
- U. of Minnesota: collaboration on DOE funded project at U. of Minn. related to lean GDI PM
- U. of Kentucky: FOA project on HC/NO_x trap catalysts for gasoline applications
- Tennessee Tech U.: project data being used for lean gasoline emission control system modeling
- CDTi: catalysts for studies
- MECA: GPF studies via NTRC User-Facility contract
- CTS: FOA project on radio-frequency (RF) sensors for GPF, SCR, TWC diagnostics
- SGS: full scale catalyst aging
- Hyundai: engine platform used for Proprietary User Agreement Project
- MAHLE: new advanced pre-chamber ignition ultra lean gasoline engine

R&D Expanded Coverage via Collaborations:

- PM Emissions
- Sensors
- Modeling
- Fuels
- Aging

Summary of Technical Accomplishments

- Completed experimental investigation of aging effects on three Cu-zeolite SCR catalysts on synthetic exhaust flow reactor under relevant passive SCR operating conditions
- Completed material characterization of aged Cu-zeolite SCR catalysts to understand aging mechanisms
- Completed installation and commissioning of the new 400 hp AVL alternating current (AC) dynamometer in the test cell
- Installed and instrumented MAHLE Jet Ignition (MJI) engine in the test cell in preparation for commissioning

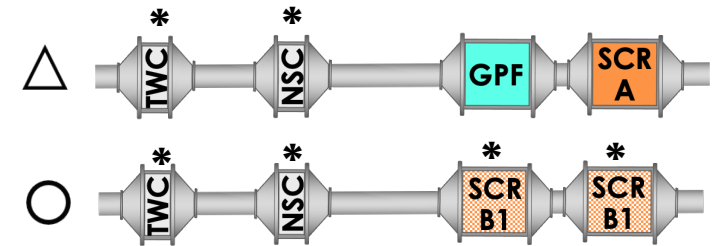


FY20 results: SCR activity degrades after aging, severity depends on catalyst formulation, temperature and air-fuel ratio

Sample ID	Description	Cell Density (cpsi)	Washcoat loading, g/l
SCR-A	early generation Cu SCR	400	150
SCR-B1	production Cu SCR	400	150

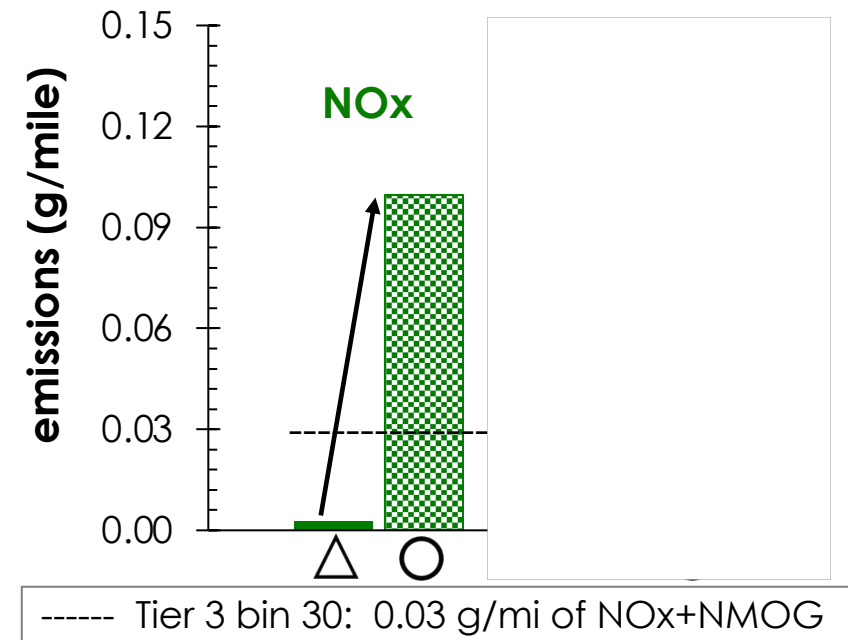
SCR catalysts designed for diesel applications, different zeolite structures
 SCR A had other durability issues, new formulations supplied by Umicore

- Increase in NOx emissions with aged SCR-B1 when using the same engine operating strategy as with SCR-A even with 2x the volume



* catalysts aged using ACEC aging protocol (see backup slides)

Emissions at SCR-A (Δ) and aged SCR-B1 (○) over pseudo-transient cycle

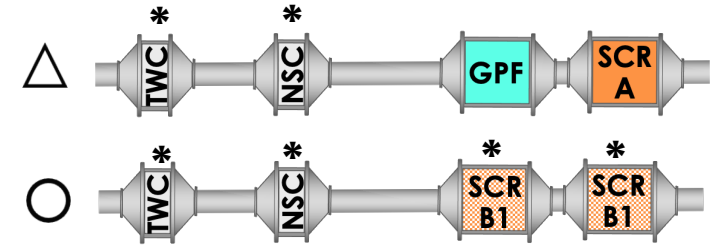


References: SAE2008-01-0811
 SAE2016-01-0954
 Catal. Sci. Technol., 2019, 9, 2152
 Catalysts 2019, 9, 929

FY20 results: SCR activity degrades after aging, severity depends on catalyst formulation, temperature and air-fuel ratio

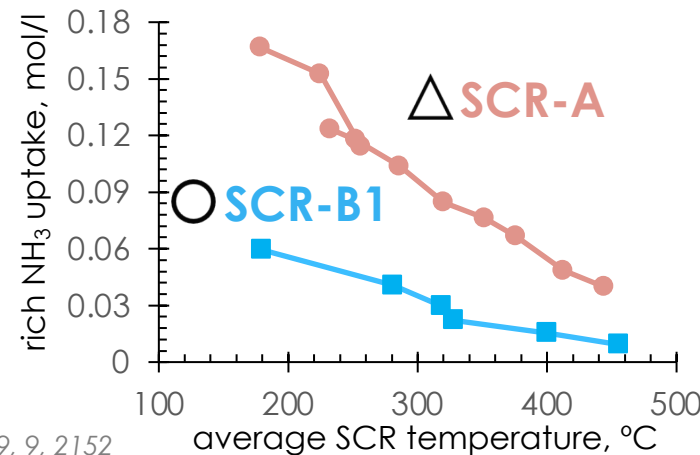
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SCR catalysts designed for diesel applications, different zeolite structures
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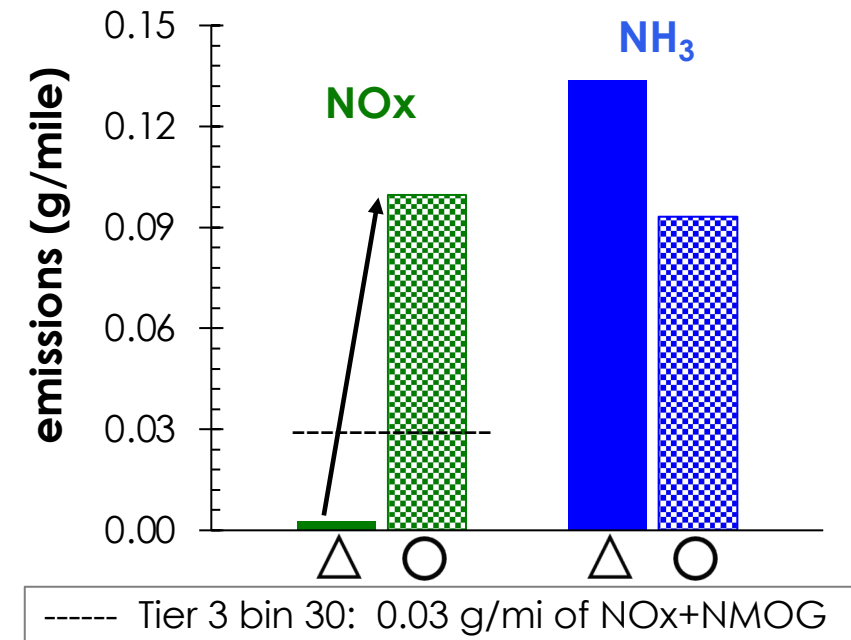
* catalysts aged using ACEC aging protocol (see backup slides)

- Increase in NOx emissions with aged SCR-B1 when using the same engine operating strategy as with SCR-A even with 2x the volume
- NOx and NH₃ slip indicative of lower NH₃ storage capacity of aged SCR-B1
- Significantly lower rich NH₃ storage capacity measured on aged SCR-B1
- SCR activity and/or NH₃ storage degrade after hydrothermal aging



References: SAE2008-01-0811
SAE2016-01-0954
Catal. Sci. Technol., 2019, 9, 2152
Catalysts 2019, 9, 929

Emissions at SCR-A (Δ) and aged SCR-B1 (○) over pseudo-transient cycle

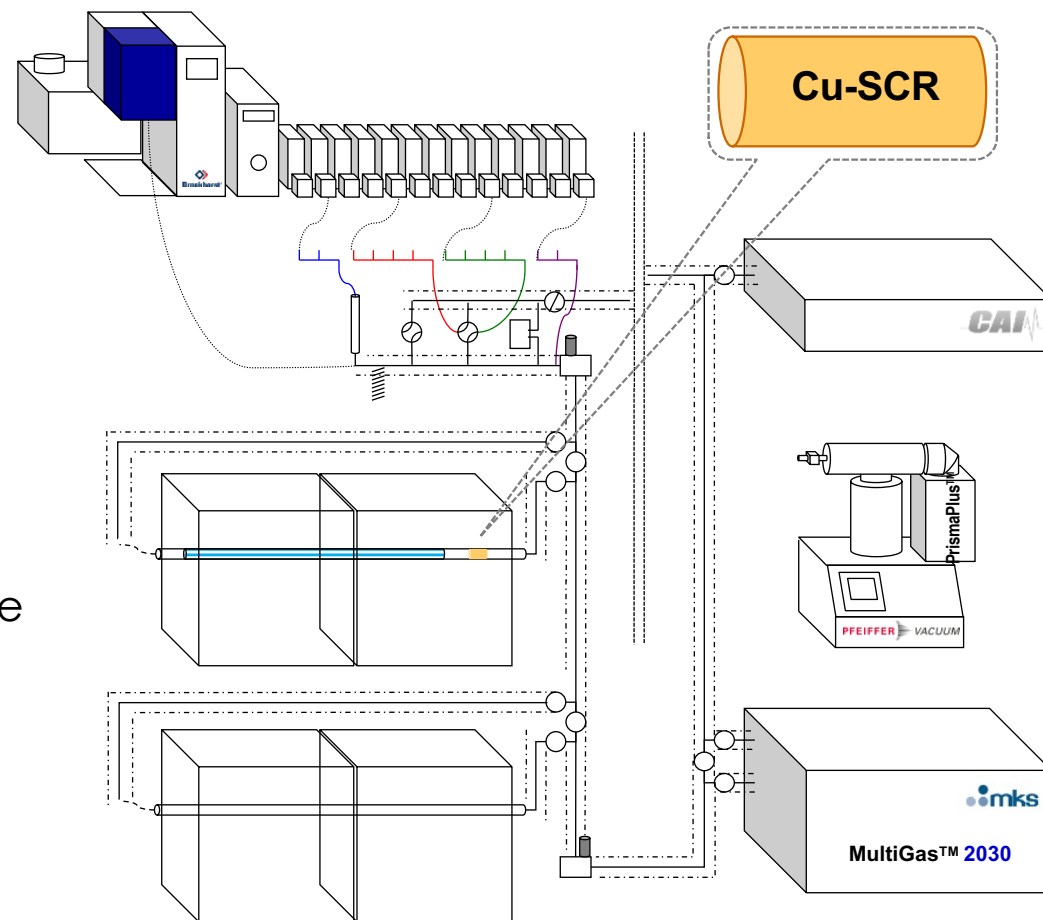


Effects of aging temperature and gas composition on the performance of SCRs evaluated on a synthetic exhaust flow reactor

Sample ID	Description	Cell Density (cpsi)	Washcoat loading, g/l
SCR-A	early generation Cu SCR	400	150
SCR-B1	production Cu SCR	400	150
SCR-B2	latest generation Cu SCR	600	200

SCR catalysts designed for diesel applications, different zeolite structures
 SCR-A used in all prior engine studies, included here for a reference
 SCR-B2 represents advancements from SCR-B1

- 9 total samples: 3 formulations, 3 aging conditions
- Aging
 - Lean, rich and stoichiometric
 - 500, 600, 700 and 800 °C for 4 hours at each temperature
- Evaluation
 - NH₃ storage, SCR, passive SCR:
 - 200, 250, 300, 350, 400 °C
 - NH₃ TPD:
 - Desorption from 200 – 550 °C



Detailed experimental protocol in the backup slides

Loss of NH₃ storage depends on hydrothermal aging temperature, gas composition and catalyst formulation

λ	~
NO	0 ppm
NH ₃	600 ppm
O ₂	0.2%
CO ₂	6.6%
H ₂ O	6.6%
SV	45,000 h ⁻¹

Aging T(°C):

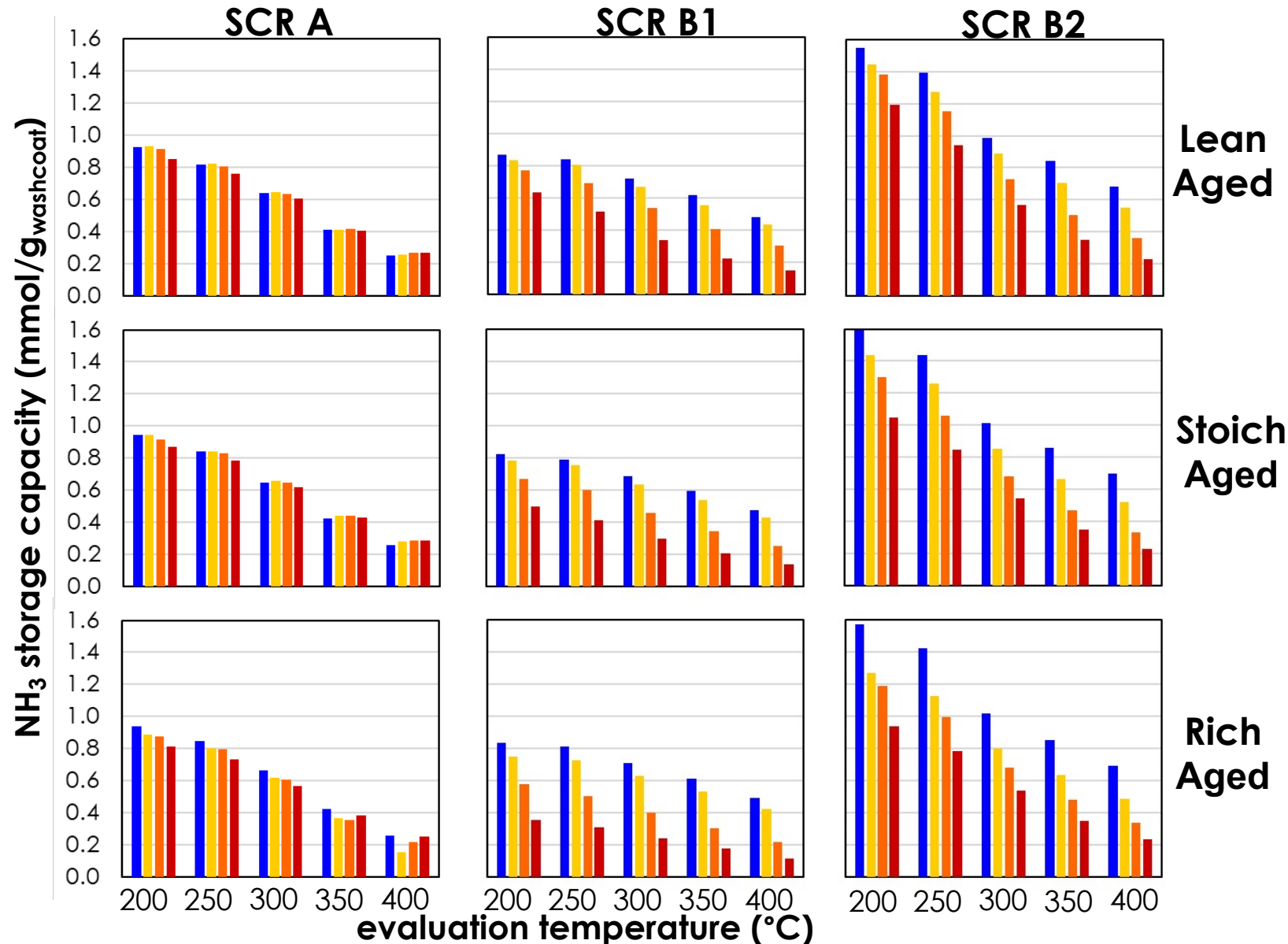
500

600

700

800

- SCR A: no aging conditions show significant effect
- SCR B1: shows significant degradation in storage after 700 and 800 °C aging
 - more severe aging from stoich and rich aging
- SCR B2: shows significant degradation, but maintains storage better than SCR A & B1



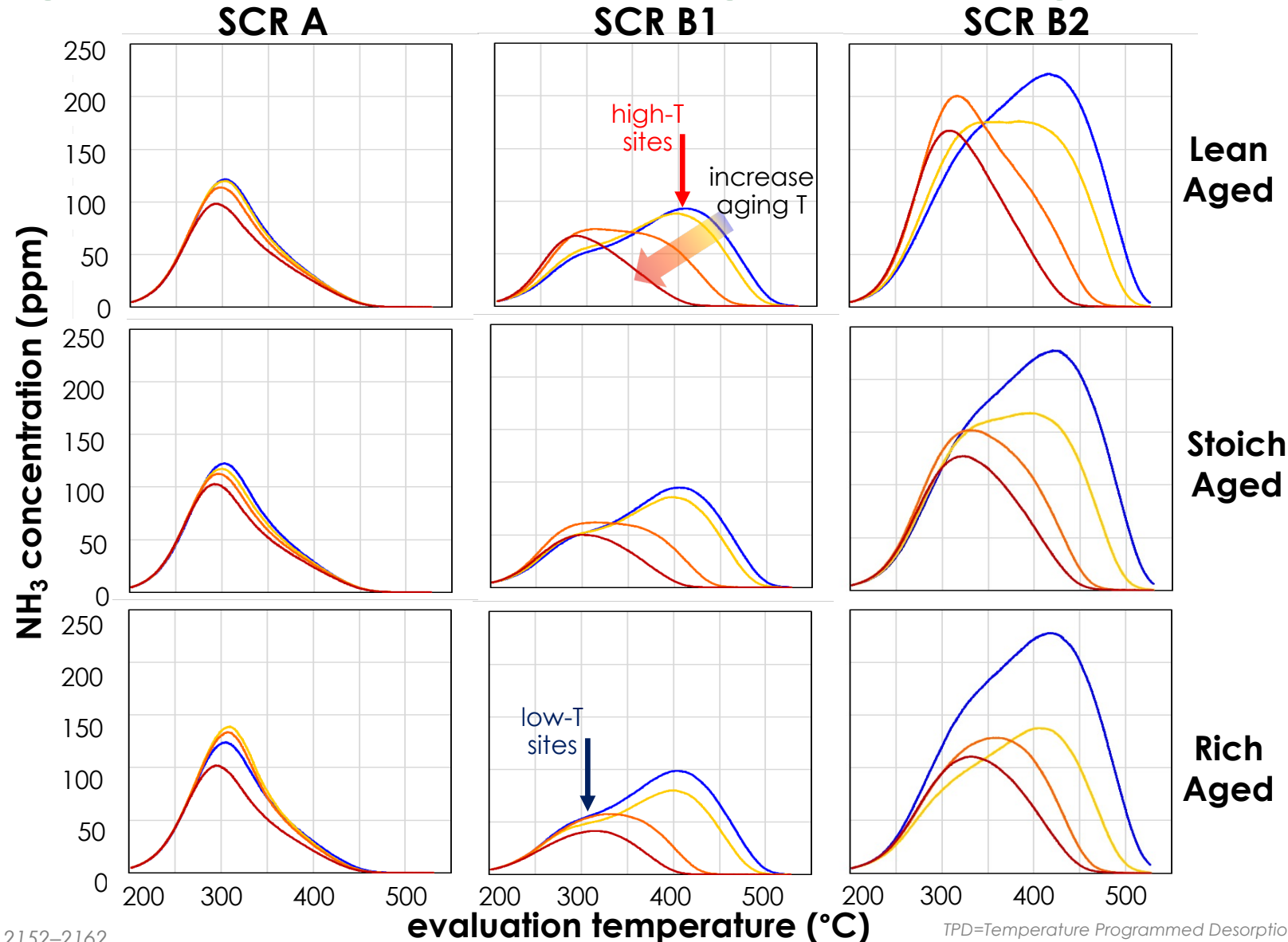
NH₃ TPD results indicate loss of high temperature storage sites in SCR B catalysts at ≥ 700 °C aging, SCR B2 still maintains high NH₃ storage

λ	~
NO	0 ppm
NH ₃	0 ppm
O ₂	0%
CO ₂	6.6%
H ₂ O	6.6%
SV	45,000 h ⁻¹

Aging T(°C):

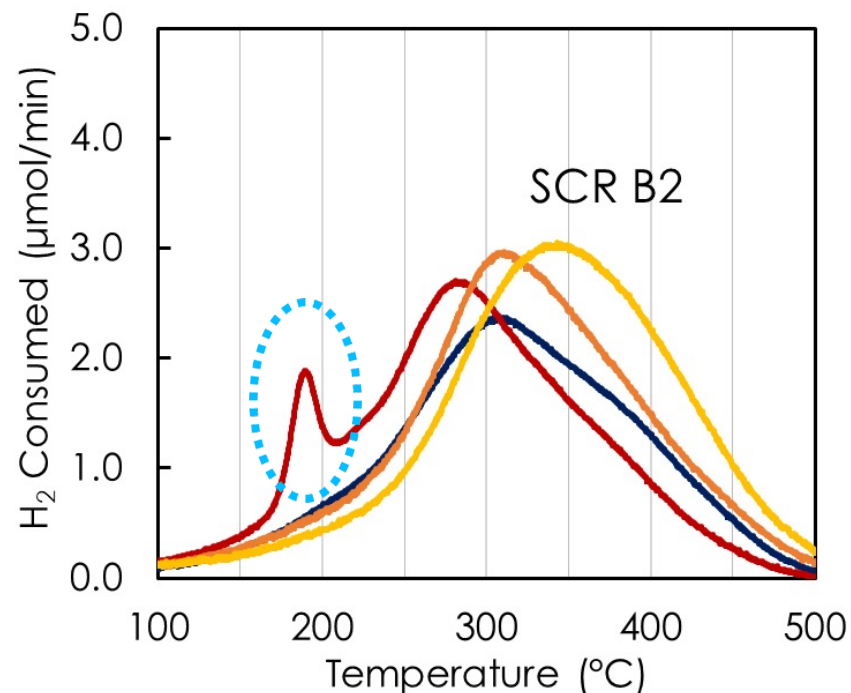
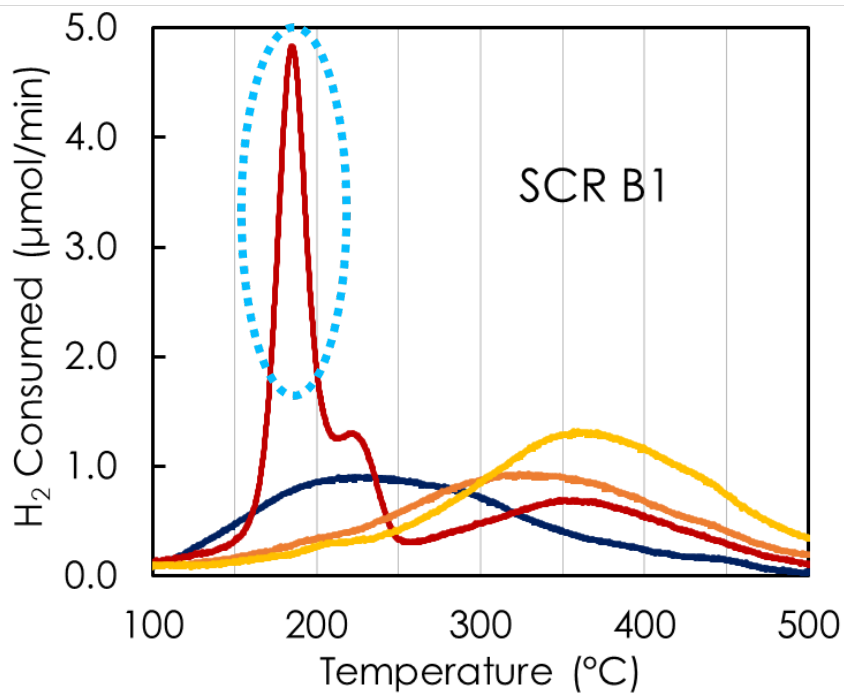
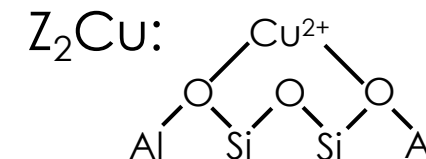
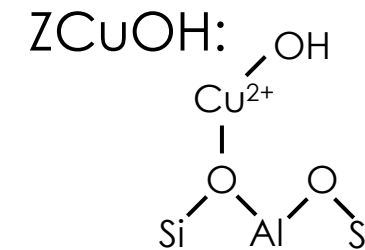
500
600
700
800

- SCR A: minor decrease in NH₃ storage for all aging conditions
- SCR B1: high temperature NH₃ storage (Bronsted acid sites) degraded at 700 °C, eliminated at 800 °C
 - stoich and rich accelerate degradation and reduce low temperature storage (Cu²⁺ sites)
- SCR B2: similar trends to B1, BUT
 - maintains high NH₃ storage
 - retains some high temperature NH₃ storage
- BET and XRD showed no noticeable structural degradation for all SCR samples, even after 800 °C aging (see backup slides)



H₂ TPR results show transitions between Cu species on SCR B, results indicate higher stability of SCR B2

- Transition from low temperature release to high temperature release on SCR B1:
 - ZCuOH to Z₂Cu
- Formation of sharp peak after rich aging:
 - CuO being reduced to Cu
- SCR B2 shows greater resistance to chemical changes



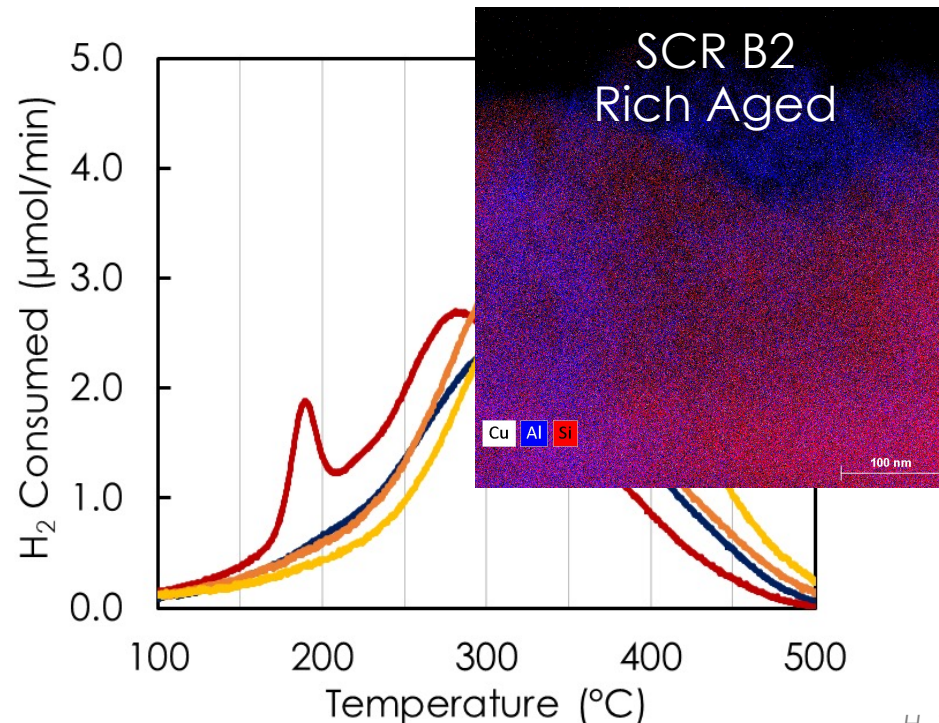
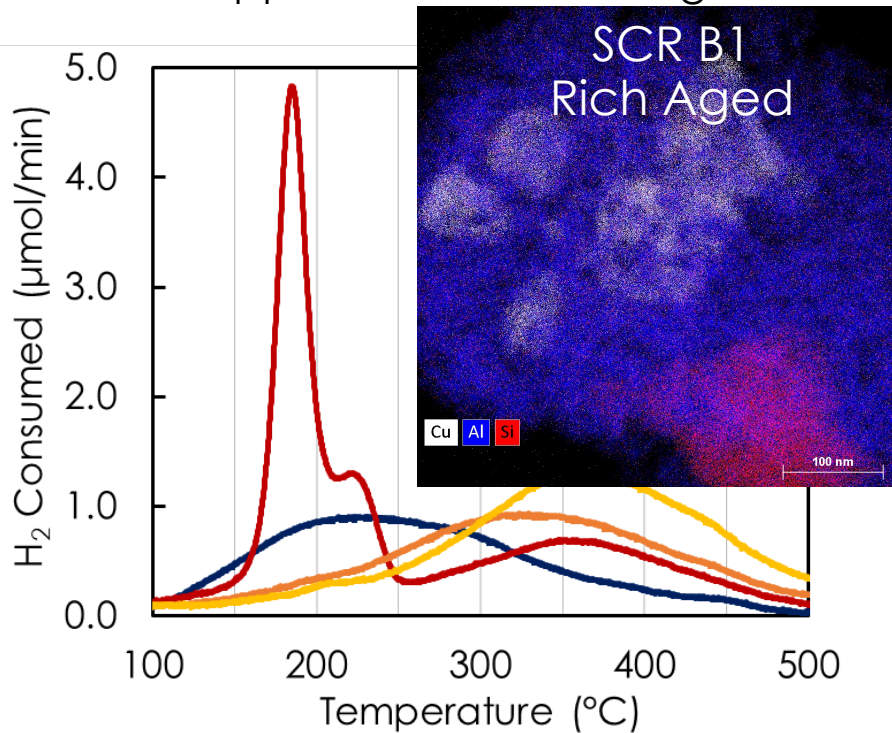
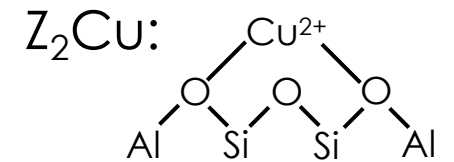
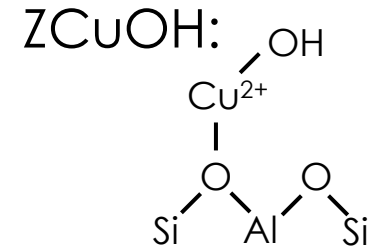
- Degreened at 500 °C
- Lean Aged at 800 °C
- Stoich Aged at 800 °C
- Rich Aged at 800 °C

J. Catal. 2015, 331, 25–38.
ACS Catal. 2018, 8, 1325–1337
Catal. Today 2016, 267, 3–9
J. Catal 330 (2015) 222–237

EDX=Energy-Dispersive X-Ray
 HAADF=High-Angle Annular Dark-Field
 TPR=Temperature Programmed Reduction
 H₂ TPR experimental protocol in the backup slides

H₂ TPR results show transitions between Cu species on SCR B, results indicate higher stability of SCR B2

- Transition from low temperature release to high temperature release on SCR B1:
 - ZCuOH to Z₂Cu
- Formation of sharp peak after rich aging:
 - CuO being reduced to Cu
- SCR B2 shows greater resistance to chemical changes
- HAADF and EDX imaging does not show noticeable Cu agglomeration on SCR B2
 - Supports TPR results of higher stability of SCR B2



- Degreened at 500 °C
- Lean Aged at 800 °C
- Stoich Aged at 800 °C
- Rich Aged at 800 °C

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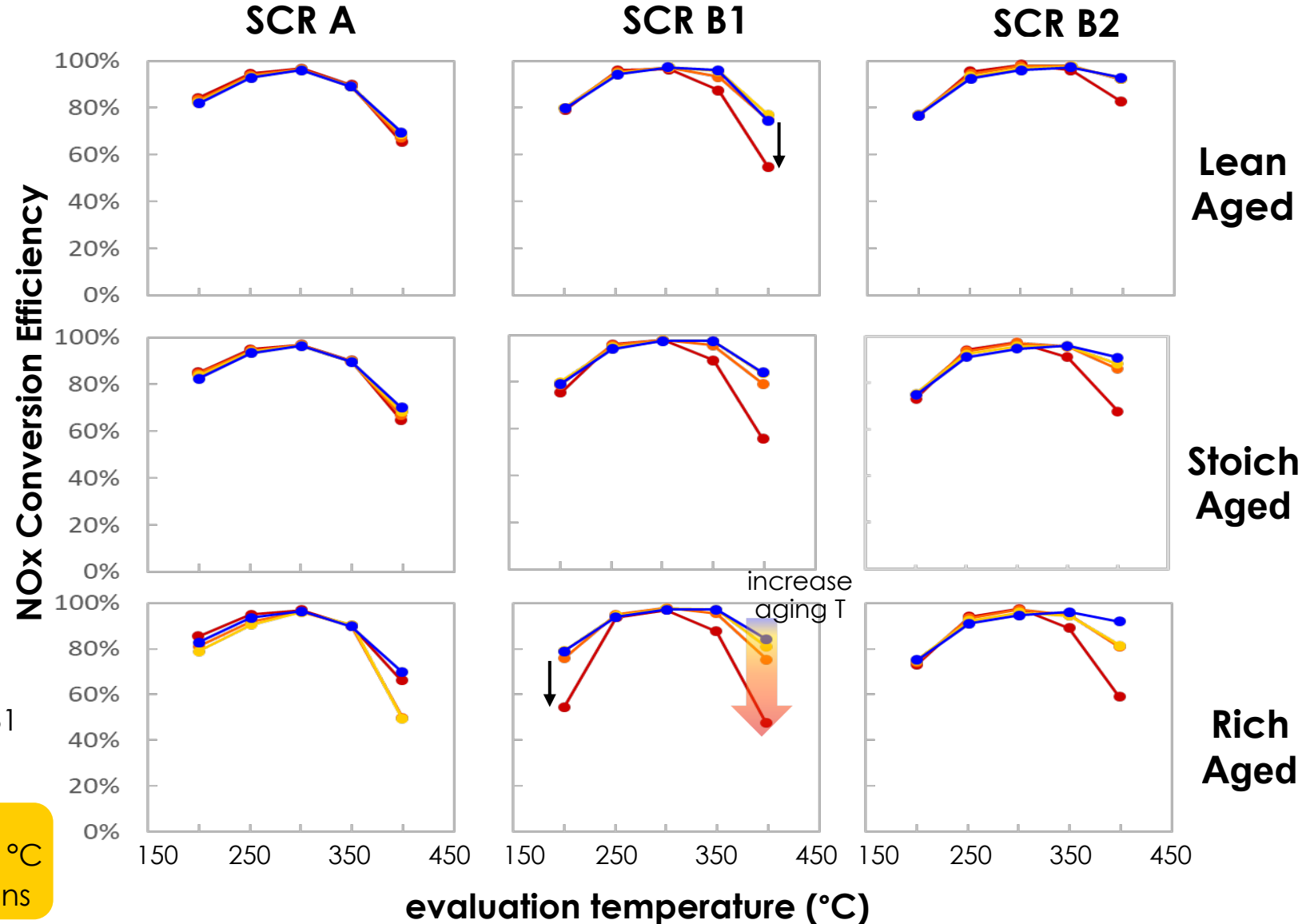
Commercial Cu SCR are still active for passive SCR NOx conversion even after 800 °C rich aging for 4 hours

λ	2.0	0.97
NO	360 ppm	0
NH ₃	0	600 ppm
O ₂	10%	0
CO	0	0.8%
H ₂	0	0.4%
CO ₂	6.6%	11%
H ₂ O	6.6%	11%
SV	45,000 h ⁻¹	27,000 h ⁻¹

Aging T(°C):

500
600
700
800

- SCR A: no aging conditions show significant effect
- SCR B1:
 - high temperature NOx conversion
 - degrades under 800 °C lean aging
 - progressively degrades under rich
 - low temperature NOx conversion
 - degrades after 800 °C rich aging
- SCR B2:
 - shows some high temperature degradation, not as significant as SCR B1
 - maintains initial low temperature NOx conversion
- Commercial (diesel) SCRs are still active for NOx conversion even after rich aging at 800 °C
 - promising for gasoline-based applications



Advanced pre-chamber ignition system enables ultra-lean combustion for emissions controls research at ORNL

- ORNL procured MAHLE pre-chamber turbulent jet ignition combustion system for lean gasoline emission control research
 - installed and instrumented in the test cell with full controls
- Platform enables wider range of ultra lean operation
- Capable of better control over exhaust composition and temperatures than conventional lean systems
- Based on a 2.3L Ford EcoBoost engine platform, provides relevant turbo-boosted stoichiometric baseline for comparison

MAHLE Jet Ignition (MJI) engine coupled to the new AVL dynamometer in test cell at ORNL



Remaining Challenges

- SCR durability under relevant passive SCR conditions
- Maximize fuel efficiency while maintaining or further reducing emissions
- CO control during rich conditions

Future Work*

- Continue flow reactor and engine aging evaluations of new SCR catalysts supplied by Umicore focusing on more long-term degradation mechanisms
- Utilize MAHLE Jet Ignition engine to expand lean operation map for higher fuel efficiency and lower engine out emissions
- Flow reactor and engine evaluations of additional catalyst technologies and architectures
- Improve control strategies and control emissions during engine mode transitions
- Experiments planned on flow reactor and engine platform to evaluate impact of new clean-up catalysts supplied by Umicore
- Optimize engine control strategies to minimize rich time operation
- Potential addition of secondary air

* - subject to change based on funding levels

Responses to FY20 reviewer comments

Summary of Reviewer's Feedback:

- "...system's inherent fuel penalty signals lack of fuel efficiency..."
- "...various challenges that this project needs to overcome...novel SCR technology, solutions to CO emission, cold-start and fuel penalty..."
- "It is imperative that future research be aimed at simplifying the packaging and the control strategies and addressing durability"

Project Responses:

- Demonstrated 8.3% fuel economy benefit and NO_x+NMOG emissions consistent with Tier 3 Bin 30 over pseudo-transient cycle, which translated to 1.3% fuel penalty relative to the maximum fuel economy benefit of 9.6%. The expanded lean operation map of MAHLE Jet Ignition engine will further enable higher fuel efficiency benefits.
- Demonstrated higher NH₃ storage capacity with the latest generation SCR catalyst that also retains high temperature NH₃ storage even after 4 hours rich aging at 800 °C. Flow reactor and engine evaluations of the latest generation SCR catalysts supplied by Umicore are ongoing.
- Demonstrated CO reduction with a clean-up catalyst; new clean up catalyst evaluations are planned on flow reactor and engine
- We continue to refine control strategies and investigate different aftertreatment technologies and architectures to maximize fuel economy and minimize emissions. Up-to-date, we demonstrated 8.3% fuel economy benefit relative to stoichiometric only operation as a result of improved system architecture.
- Durability to aging and sulfur is one of the key principles considered in this project. TWC hydrothermal aging and sulfur studied in the past. Currently focusing on SCR durability for gasoline applications.

Summary

- **Relevance**
 - Lean GDI engine emission control enables potential 10-15% fuel efficiency gain for gasoline-dominant U.S. light-duty fleet
- **Approach**
 - Engine, flow reactor, and aging studies are combined to study fuel efficiency and emissions relative to Tier 3 standard
- **Technical Accomplishments**
 - Completed experimental investigation of aging effects on three Cu-zeolite SCR catalysts on synthetic exhaust flow reactor under relevant passive SCR operating conditions
 - Completed material characterization of aged Cu-zeolite SCR catalysts to understand aging mechanisms
 - Completed installation and commissioning of the new 400 hp AVL alternating current (AC) dynamometer in the test cell
 - Installed and instrumented MAHLE Jet Ignition (MJI) engine in the test cell in preparation for commissioning
- **Collaborations**
 - GM and Umicore are primary partners
- **Future Work** (*subject to change based on funding levels*)
 - Evaluate effects of long-term aging on latest generation Cu SCR catalysts under passive SCR conditions
 - Measure fuel economy benefits and emissions on the MJI engine
 - Flow reactor and engine evaluation of impacts of clean-up catalysts
 - Evaluate additional catalyst technologies and architectures

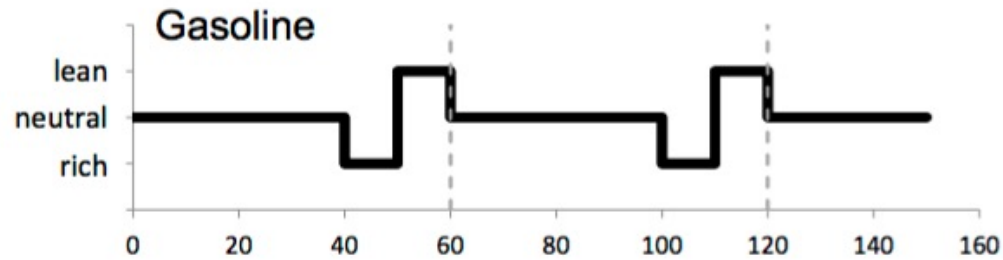
Technical back-up slides



Abbreviations

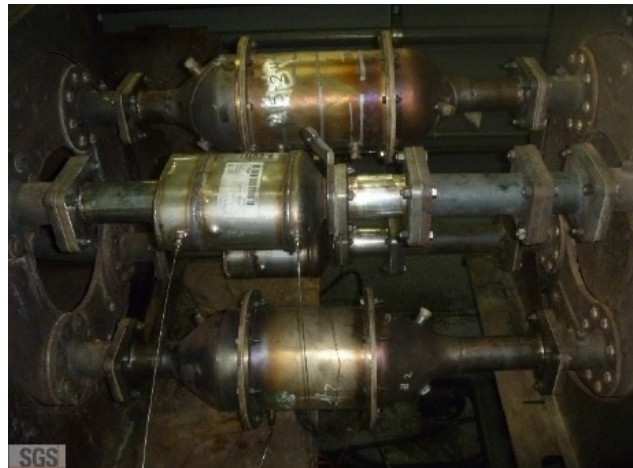
AMOX	Ammonia oxidation catalyst	ACI	Advanced compression ignition
ASC	Ammonia slip catalyst	BTE	Break thermal efficiency
CUC	Clean-up catalyst	CDC	Conventional diesel combustion
DOC	Diesel oxidation catalyst	HD	Heavy duty
DPF	Diesel particulate filter	LD	Light duty
GOC	Gasoline oxidation catalyst	LTAT	Low temperature aftertreatment
GPF	Gasoline particulate filter	LTC	Low temperature combustion
HCT	Hydrocarbon trap	MD	Medium duty
LNT	Lean NOx trap	NG	Natural gas
MOC	Methane oxidation catalyst	SI	Spark ignition
OC	Oxidation catalyst		
OEC	Other emissions control catalysts		
PF	Particulate filter		
PNA	Passive NOx adsorber		
SCR	Selective catalytic reduction		
TWC	Three-way catalyst		

SCR-B1 aged at SGS using LTAT aging protocol for 50 hours at 700 °C inlet temperature



Thermally aged at SGS using LTAT aging protocol

- Aging Cycle
 - Stoich: 40 seconds, $\lambda=1$
 - Rich: 10 seconds, $\lambda=0.91$
 - Lean: 10 seconds, $\lambda=1.33$
- Aging inlet temperature
 - **700 °C for underfloor**
- Aging time
 - 50 hours
- Catalyst space velocity
 - 30K hr⁻¹



Aftertreatment Protocols for Catalyst Characterization and Performance Evaluation: Low-Temperature Oxidation Catalyst Test Protocol

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

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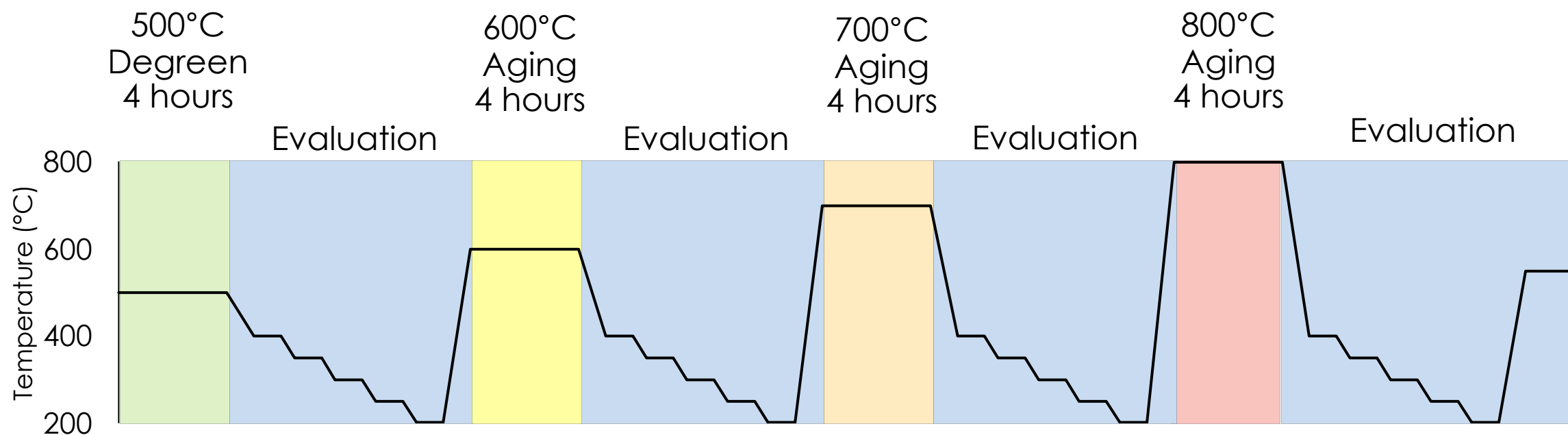
https://cleers.org/wp-content/uploads/2015_LTAT-Oxidation-Catalyst-Characterization-Protocol.pdf

Catalyst samples aged under lean, stoich and rich conditions in bench flow reactor

Evaluation:

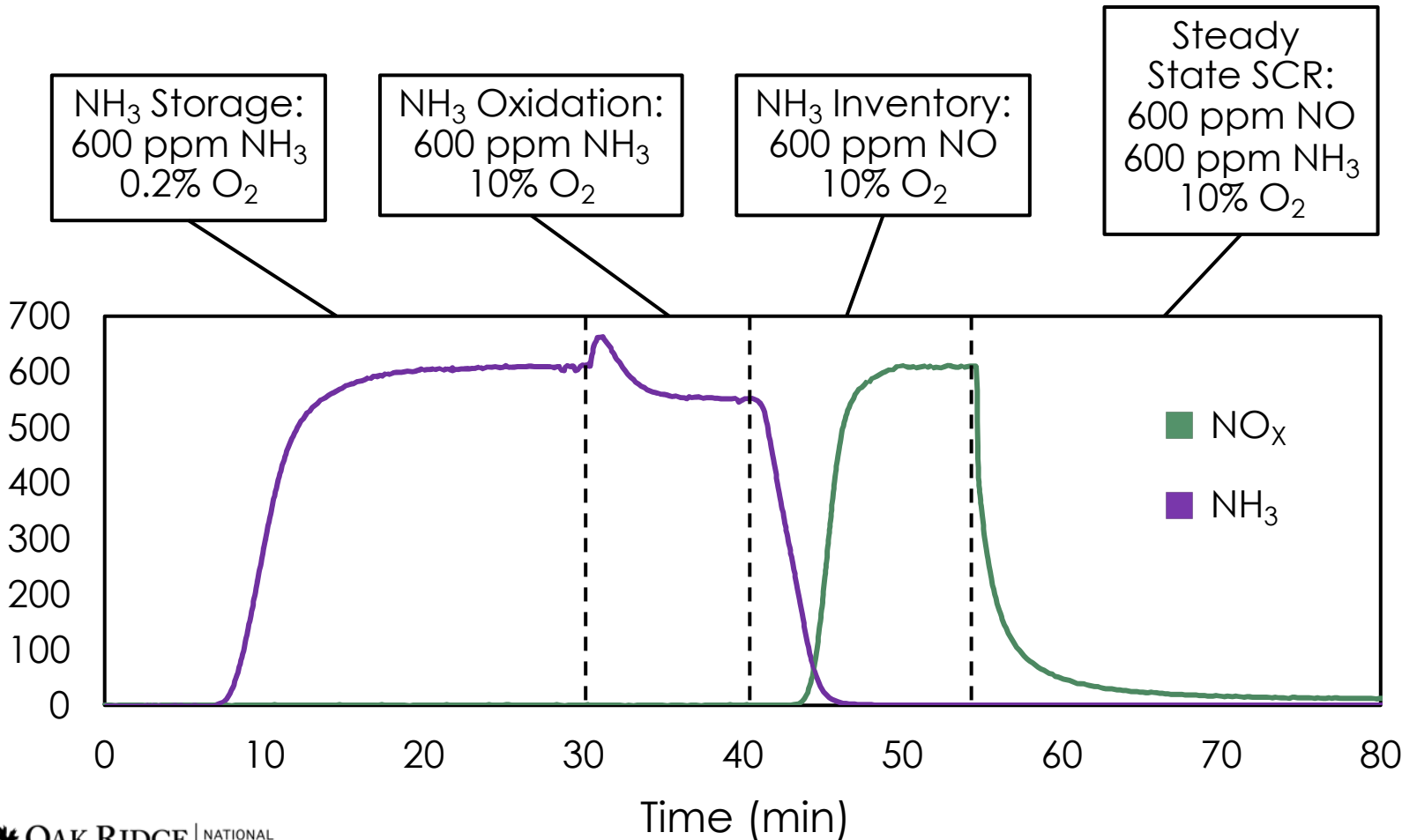
- NH₃ storage and passive SCR cycling activity:
 - 200 – 400°C
- NH₃ TPD: Adsorbed at 200°C, ramp to 550°C

Aging Conditions	Lean & Degreeen	Stoich	Rich
O ₂ (%)	10	~	~
CO (%)	~	~	0.8
H ₂ (%)	~	~	0.4
H ₂ O (%)	6.6	6.6	6.6
CO ₂ (%)	6.6	6.6	6.6

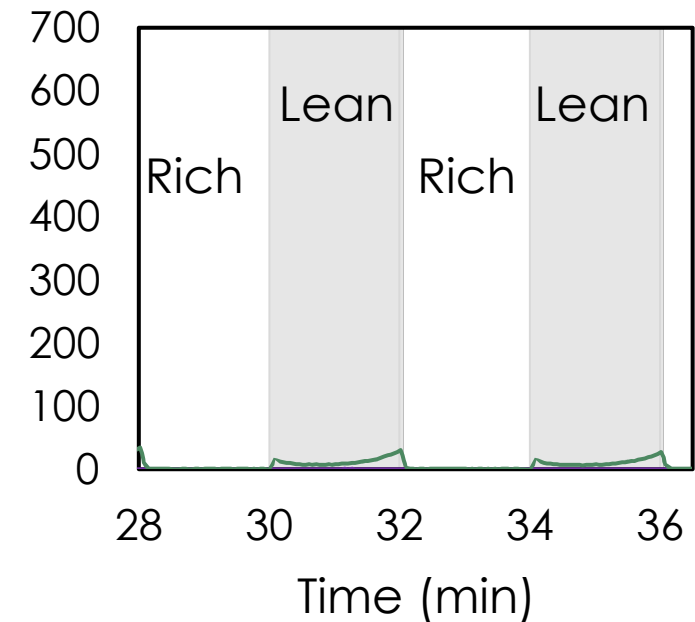


Each evaluation composed of several steps

- Steady state evaluations conducted with:
 - 45,000 h⁻¹ SV, 6.6% CO₂, 6.6% H₂O
- Example data from SCR A, 300°C evaluation

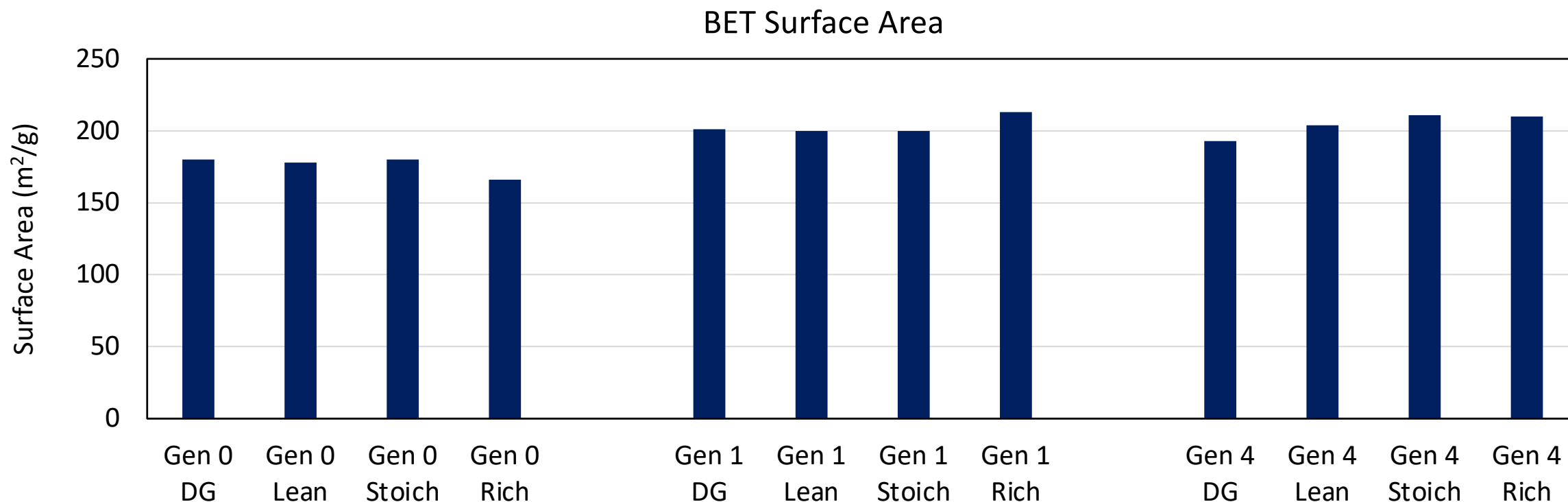


Cycling Evaluations		
	Lean	Rich
λ	2.0	0.97
NO	360 ppm	0
NH₃	0	600 ppm
O₂	10%	0
CO	0	0.8%
H₂	0	0.4%
CO₂	6.6%	11%
H₂O	6.6%	11%
SV	45000	27000



Characterization to determine degradation mechanisms

- Characterization conducted on fully aged catalyst samples
 - Degreened for 4 h at 500°C
 - Aged for 4 h at 600°C, 4 h at 700°C, and 4 h at 800°C
- BET and XRD were conducted on degreened and aged SCR samples
 - Showed no noticeable structural degradation



H₂ TPR was conducted to track changes in Cu speciation

- ~500 mg of catalyst core after aging (washcoat + monolith) cut and crushed
- Pretreatment under air at 550 °C for 30 mins
- TPR under 5% H₂/Ar up to 550 °C

