NO_x Control & Measurement Technology for Heavy-Duty Diesel Engines
Project ID: ACE032

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Cummins Inc.

H. Hess, H.-Y. Chen
Johnson Matthey Inc.

DOE Vehicle Technologies Office
Annual Merit Review & Peer Evaluation Meeting
June 23, 2021; Virtual Meeting

VTO Program & Technology Managers:
Gurpreet Singh, Siddiq Kahn, Ken Howden, Mike Weismiller

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Overview

Timeline

- Started in 2018 VTO AOP Lab Call
  - AOI-1E: Low Temperature Emissions Control (Heavy Duty)
- Year 3 of 3-year
  - Oct. 1, 2018 to Sept. 30, 2021
  - Percent Complete: 86%
- Planning renewal focused on ASC
  - Formalize in FY22 VTO AOP Lab Call
  - Start ASC work in Q4FY21 or Q1FY22

Budget

- 1:1 DOE:Cummins cost share
- FY21 DOE Funding: $450k
  - DOE share: $450k
  - Cummins share: $450k (in kind)

Barriers

- From **21st CTP Research Blueprint**:
  - Emission control cost
  - Low-temperature emission control
  - Robustness in real-world application
- From **U.S. DRIVE Roadmap**:
  - Low-temperature emission control
  - Compliance via Real Driving Emissions (RDE)
  - Emissions control durability

Partners

- ORNL & Cummins Inc.
- Johnson Matthey (participant)
- Collaborating with CLEERS – data & modeling

Milestones

FY	Qtr	Milestone & Objectives	Status
2021	2	Determine kinetic impact of field ageing on commercial SCR catalyst	complete
2021	4	Draft journal manuscript describing kinetic impact of field ageing	on track

Responses to 2020 Review Comments

- Consider impacts of lube-oil & PGM poisons
  - *Most lube-oil contaminants are trapped in upstream DPF and do not impact the SCR*
  - *PGM & lube-oil poisons confined to the front 3-4mm, and excluded from the samples studied*
  - *Additional ageing routes can be studied in follow-on work using the foundational CRADA studies*
- Consider thermal ageing, and defined field ageing (FA)
  - *Hydrothermal ageing is part of the Cummins model, & CRADA experimental plan*
  - *The field-aged sample has been desulfated, but significant amounts of S remain*
  - *Impact of lab-sulfation and desulfation will be studied in proposed future work*
  - *The field-aged sample is representative of 90% of >10k systems across different Cummins platforms*
  - *Separate ageing routes are being studied to understand component contribution to field ageing*
- Too much effort on reactor improvements & Expectation that one exists at ORNL or Cummins
  - *Replacement of the CRADA-dedicated reactor was necessary & many improvements were implemented*
  - *Changing to a new catalyst dictated the timing to preserve resources and not duplicate work*
  - *New programmable/unattended/overnight operation is enhancing project*
- Desire for faster progress
  - *Needed and CRADA-focused post doc, Dr. Dhruba Deka, onboarded May 2020, & onsite October 2020*
- Thank you for the many positive comments
  - *Well-designed, unique approach*
  - *Progress is good, noticeable and tangible*
  - *Work is highly relevant, and absolutely supports the overall DOE objective*

Collaborations and Coordination

- **ORNL:** Bill Partridge (ORNL PI)
- **Cummins:** Saurabh Joshi (Cummins PI)
- **Johnson Matthey:** Howard Hess (JM Lead)
  - Formally included in CRADA and Project documentation

Teamwork & Roles

ORNL	Cummins	Johnson Matthey
• Diagnostics • Measurements • Modeling	• Modeling • Field ageing	• Model catalyst samples

Joint
- Planning
- Results interpretation
- Monthly+ telecons

- **CLEERS**
  - Joint participation in monthly meetings
  - Using CLEERS model structure for CRADA open model
  - Sharing CRADA spatiotemporal data for CLEERS model
- **Broader ORNL ACERG DOE Projects**
  - Formal weekly and routine feedback & coordination meetings

ORNL ACERG Catalyst-Research Portfolio

Low Temperature Emissions Control (ACE085)
Discover new low T catalysts & traps

CLEERS (ACE022)
Model new trap materials and aging effects on SCR catalysts

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 & ASC catalysts

Key Challenge Addressed by Project

- Improving ***Durability*** of urea-SCR catalysts in Heavy Duty engine applications

- Project focuses on understanding ***Field-Ageing*** process and impacts
  - **Impact on SCR reaction network & kinetic parameters**
  - **Improved models**
    - Improved design & control models
    - Improved durability through better SCR through-life performance
  - **Methods for synthetic field ageing**
    - Hydrothermal ageing does not represent field ageing
  - Improve catalyst performance & durability under ***Real-World Driving Conditions***

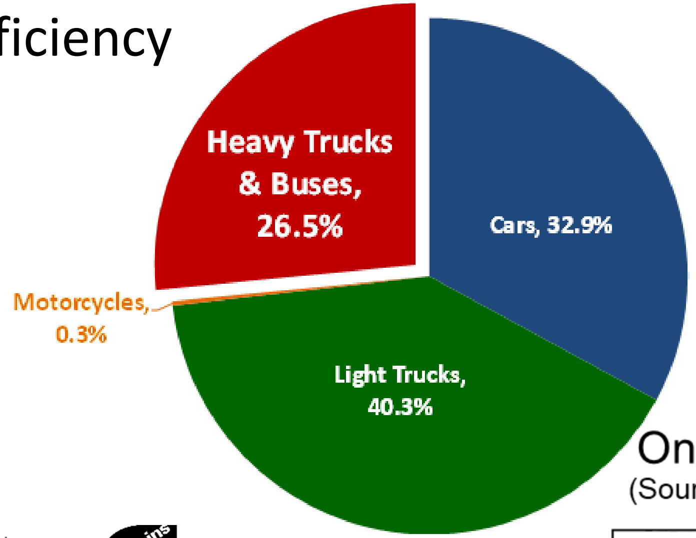
Relevance

- Improved Field-Ageing Models & Understanding critical to meeting increasing performance requirements

Heavy Heavy-Duty Emissions Regulations		
Current	**2027**	**2031**
CARB/EPA	CARB	CARB
Useful Life (miles,hr)	Useful Life (miles,hr)	Useful Life (miles,hr)
435,000 (10yr, 22k hr)	**600,000** (11yr, 30k hr)	**800,000** (12yr, 40k hr)

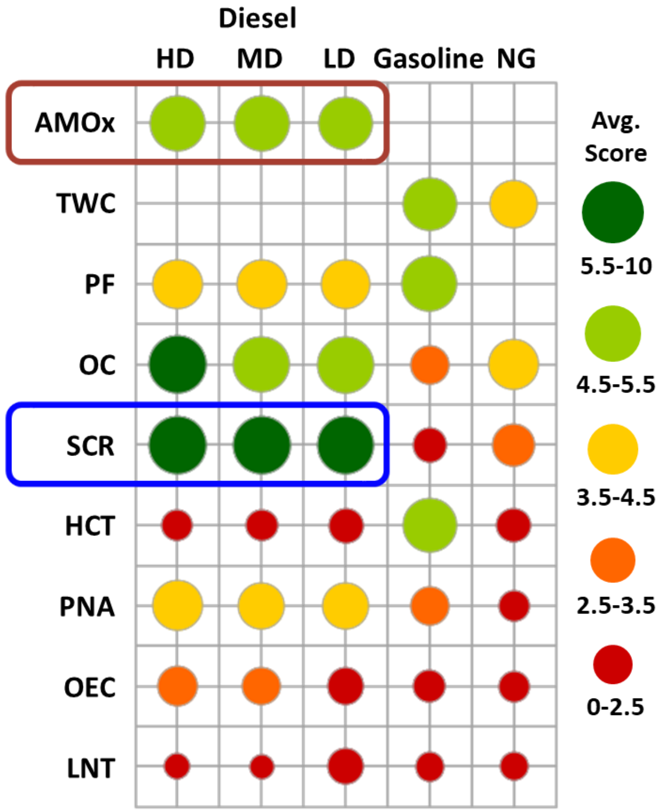
Rapidly Increasing Warranty & Useful-Life Demands

- Better catalyst performance allows engine to be optimized for fuel efficiency



On-Highway Petroleum Use
(Source: Transportation Energy Data Book)

2019 CLEERS Industry Priorities Survey



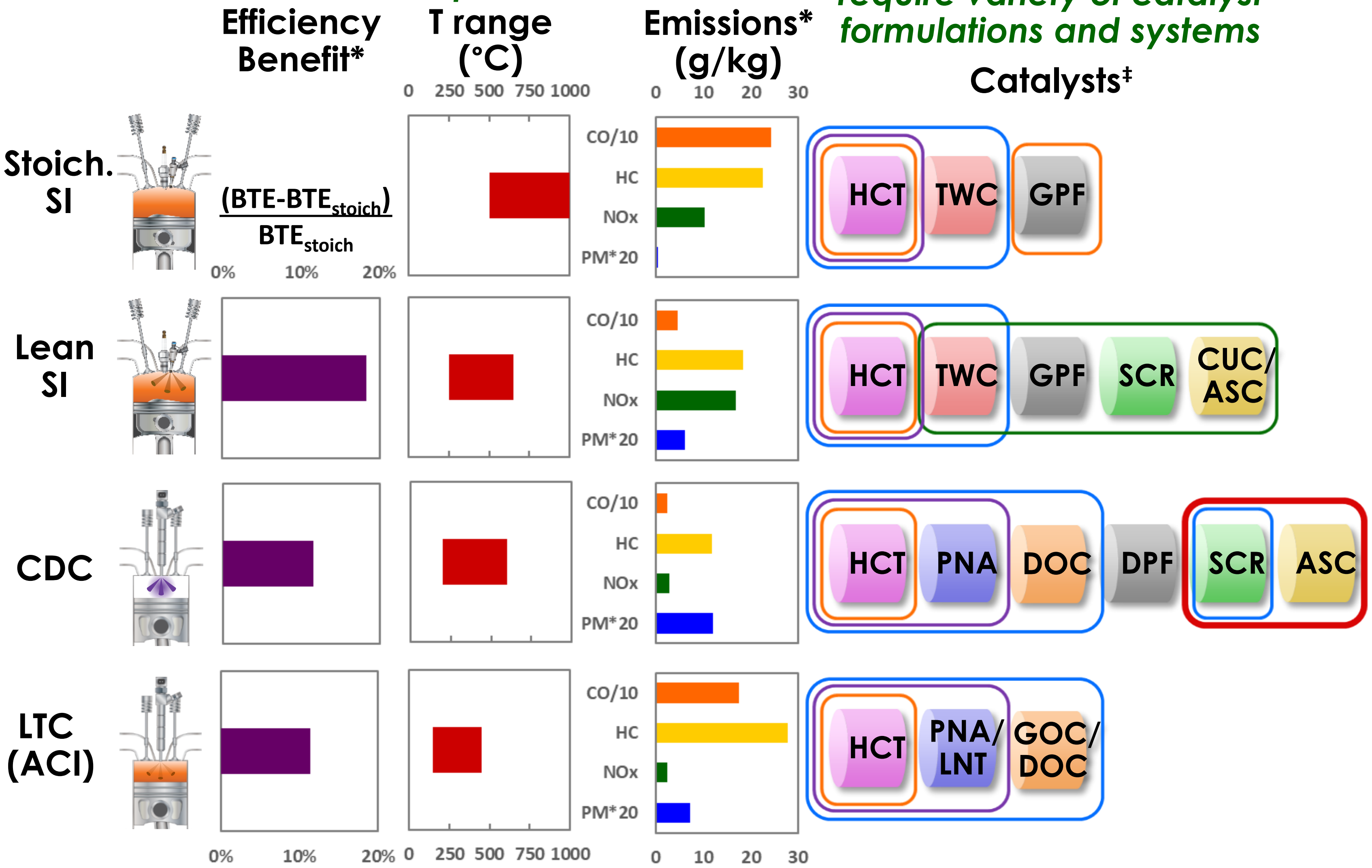
- **SCR** & **AMOx** top technology for Diesel
- **SCR Aging**: #3 for all HDD tech. & topics
- **AMOx** ageing & modeling high priority
  - Focus of Future Work

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



*(efficiency and emissions at 2000 rpm, ~2 bar BMEP)

‡Abbreviations in backup slides

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

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Understand how aging affects properties and performance of SCR catalysts

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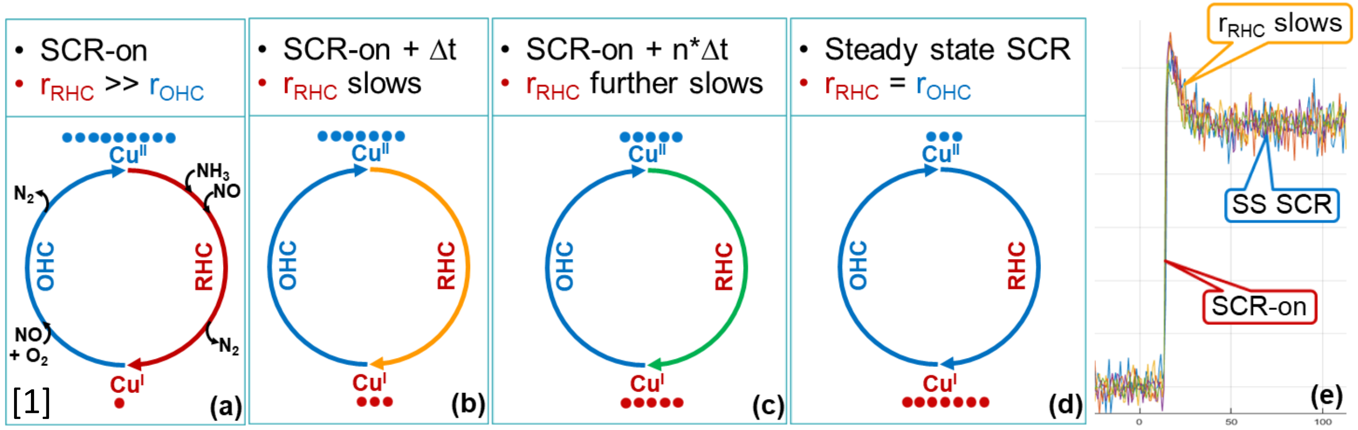
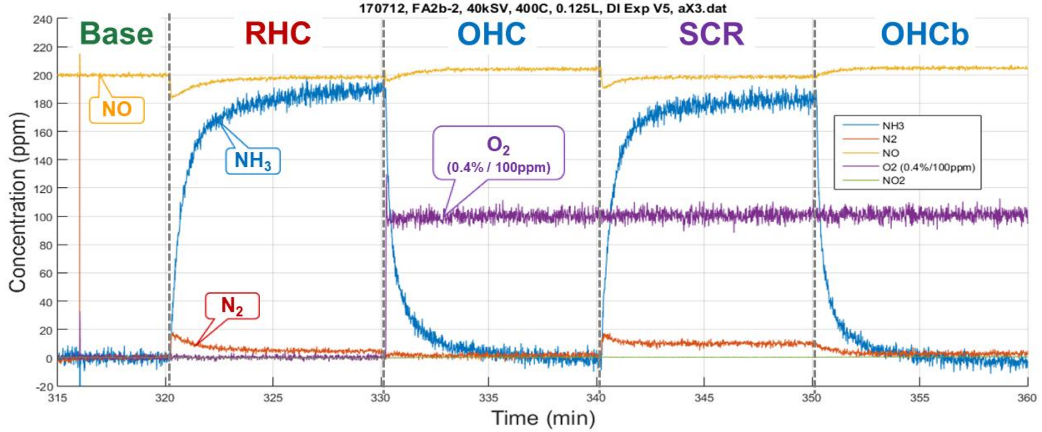
Background : Determine Kinetic Impacts of Field Ageing via Transient-Response Cu-Redox Half-Cycle Analysis

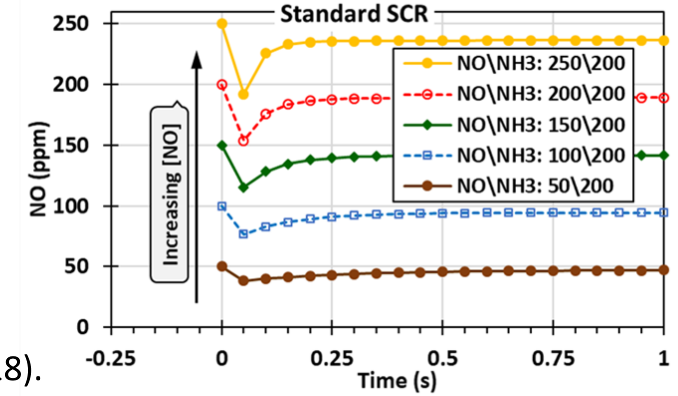




- Cu-redox half-cycle rate imbalances induce CI at SCR onset
  - **RHC: Reduction Half Cycle** – oxidized Cu (Cu^{II}) is reduced to Cu^{I}
  - **OHC: Oxidation Half Cycle** – $Cu^{I} \rightarrow Cu^{II}$ completing the cycle
  - ***Conversion Inflection (CI)*** indicates RHC-OHC rate imbalances
  - ***CI shape reflects on half-cycle kinetic parameters***

- ***Use transient analysis to study SCR Field-Ageing***
  - ***Quantify kinetic impact on individual RHC & OHC***
  - *Insights: ageing process, better lab ageing, models, …*

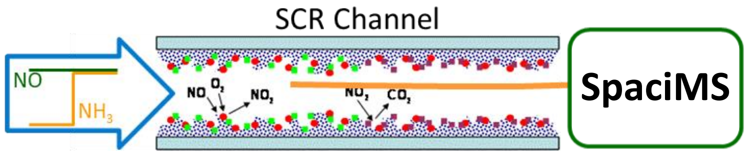
- Transient Cu-Redox Experimental Protocol
  - Individual & combined half cycles
- Simple Kinetic Model developed
  - Reproduces experimental CI trends



[1] Partridge et al., Appl. Catl. B, V236, p195(2018).

Technical Approach

Transient-Response Analysis
Spatial & Temporal Mapping



Gov. - National Lab – Industry CRADA Partnership
(DOE VTO – ORNL – Cummins – Johnson Matthey)

Technical Approach

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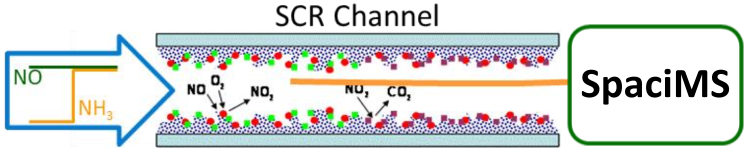
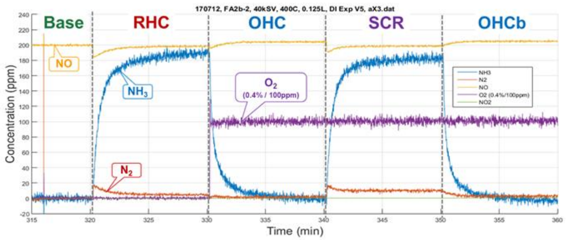
Transient-Response Analysis
Spatial & Temporal Mapping



Redox Protocols & Characterization



Kinetic Models

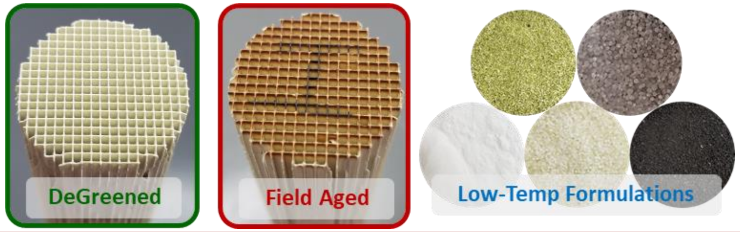
Standard-SCR Reduction Half Cycle, RHC

$ZCuOHNH_3 + NO \rightarrow ZCu + N_2 + 2H_2O$

$Z_2CuNH_3 + NO \rightarrow ZCu + ZH + N_2 + H_2O$

$Z_2Cu(NH_3)_2 + NO \rightarrow ZCuNH_3 + ZH + N_2 + H_2O$

Catalyst Age State & Formulation



Kinetic Impact of Ageing

- NH_3 capacity
- Active sites
- Reaction pathways
- Half-cycle rates
- …..

Development & Durability Advances

- Improved development models
- Rapid real-world-ageing protocols
- Catalyst formulation optimization
- Enhanced control procedures & models
- …..

Heavy Duty Emissions Regulations	
Current	**2031**
CARB/EPA	CARB
Useful Life	Useful Life
435,000	**800,000**

Advanced Durability Solution Pathway

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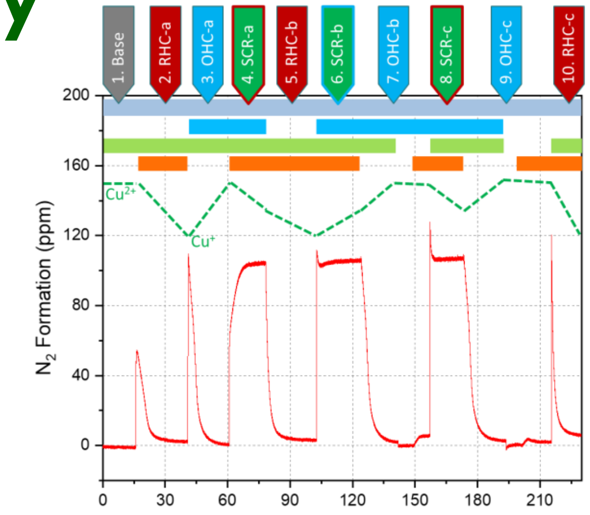
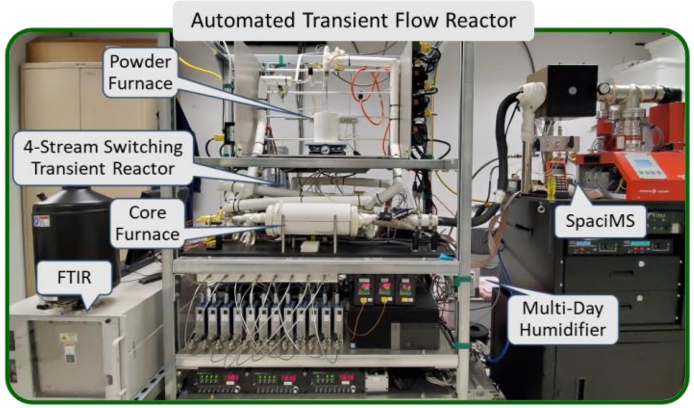
Technical Progress Summary

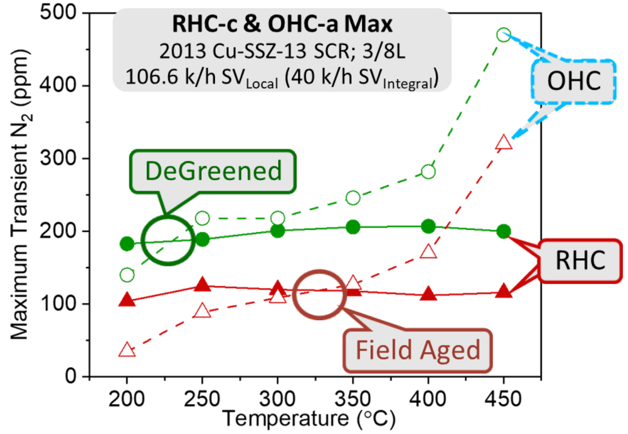
- Transient-Response Reactor is operating
  - Programed unattended operation increases efficiency



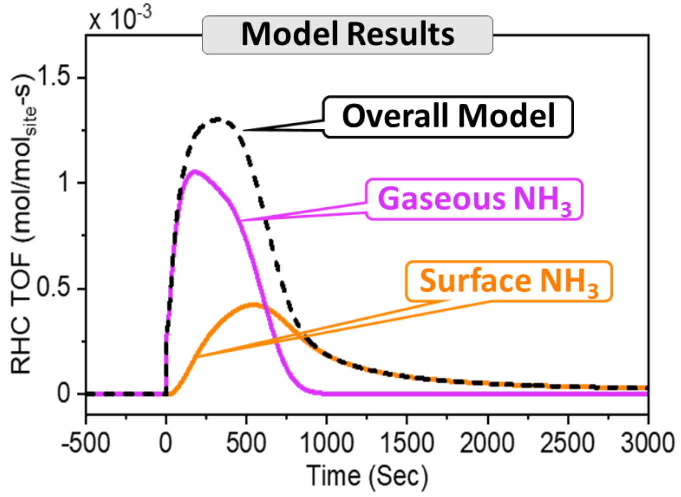


- Expanded Transient-Response SCR-Redox Protocol
  - Greater detail & needed for new Cu-SSZ-13 sample

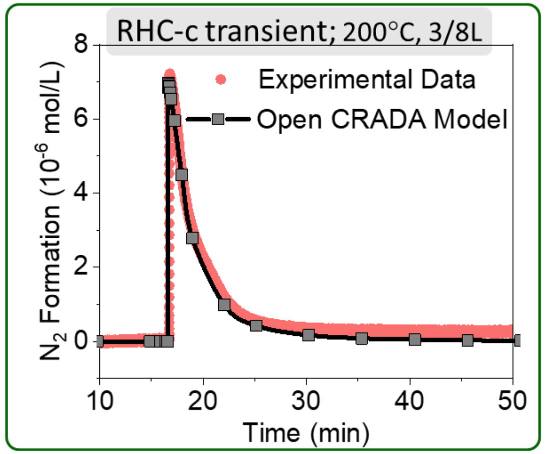
- Qualitative impact of Field Ageing on Cu-redox half cycles
  - Quantitative results to come from fitting kinetic parameters



- Cummins Internal SCR model
  - Predicts major RHC features over wide T range

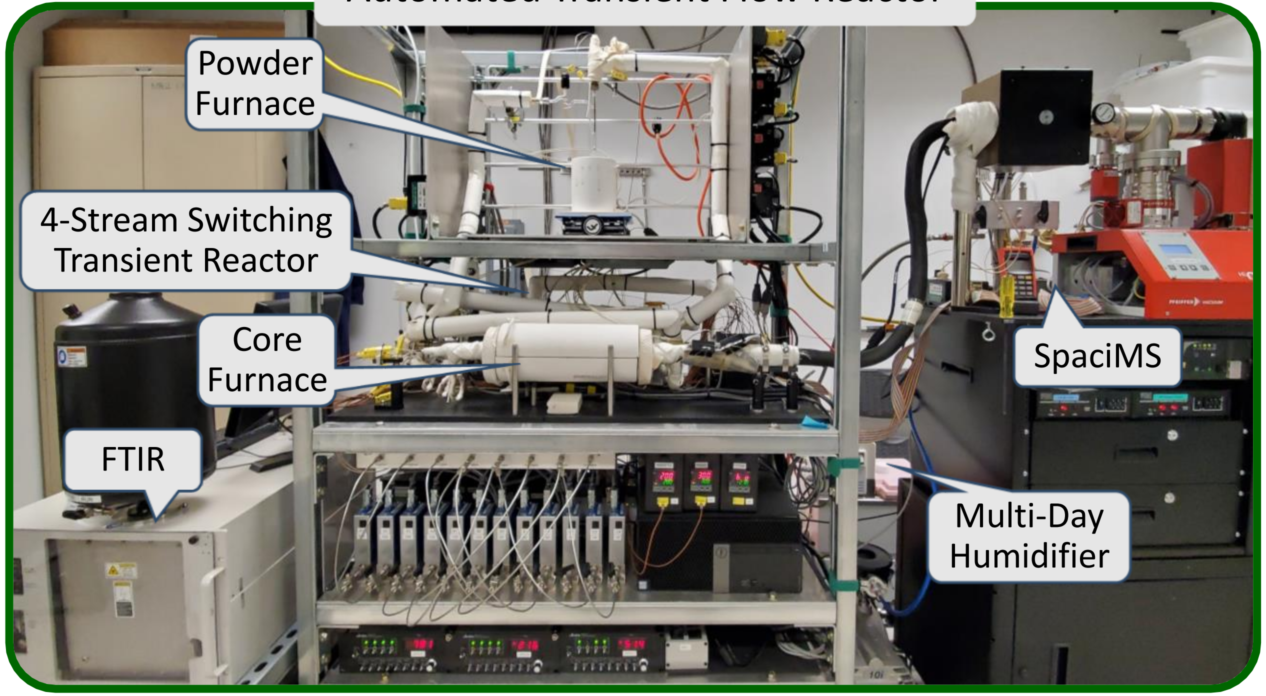


- CRADA Cu-redox Open Model
  - ***A model we can openly report to public***
  - ***Enhance CRADA value to broader community***
  - Initial fits of NH_3 adsorption/desorption & RHC

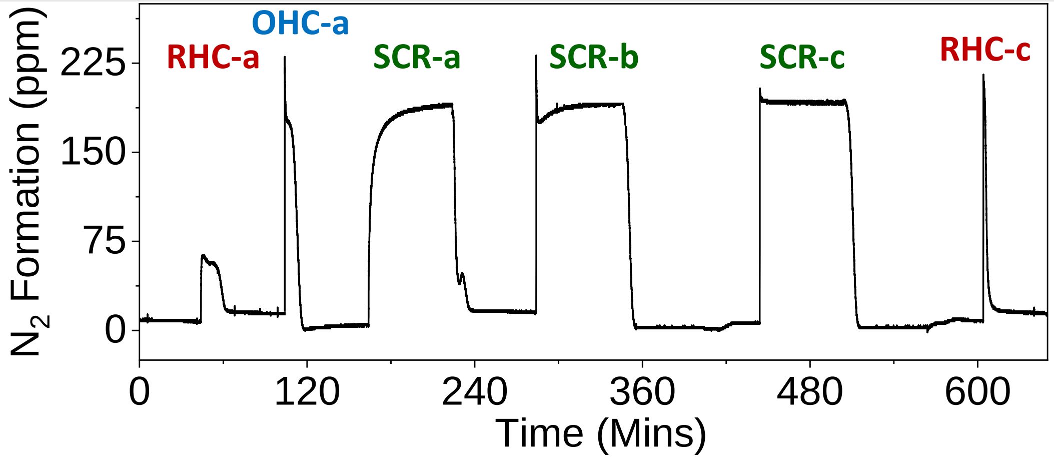


Transient-Response Reactor

- Reactor is operating:
  - 10-Step Redox Protocols
  - NH_3 TPD with Half-Cycle steps
  - DeGreened & Field-Aged samples
- Using in programed unattended operation
  - Overnight protocol runs
  - Increasing reactor productivity
- Longer 24-7 operation:
  - Implemented multi-day H_2O impinger
  - Designing Cal-gas switching system for unattended calibrations
  - Further reactor productivity
- New Redox & TPR protocols

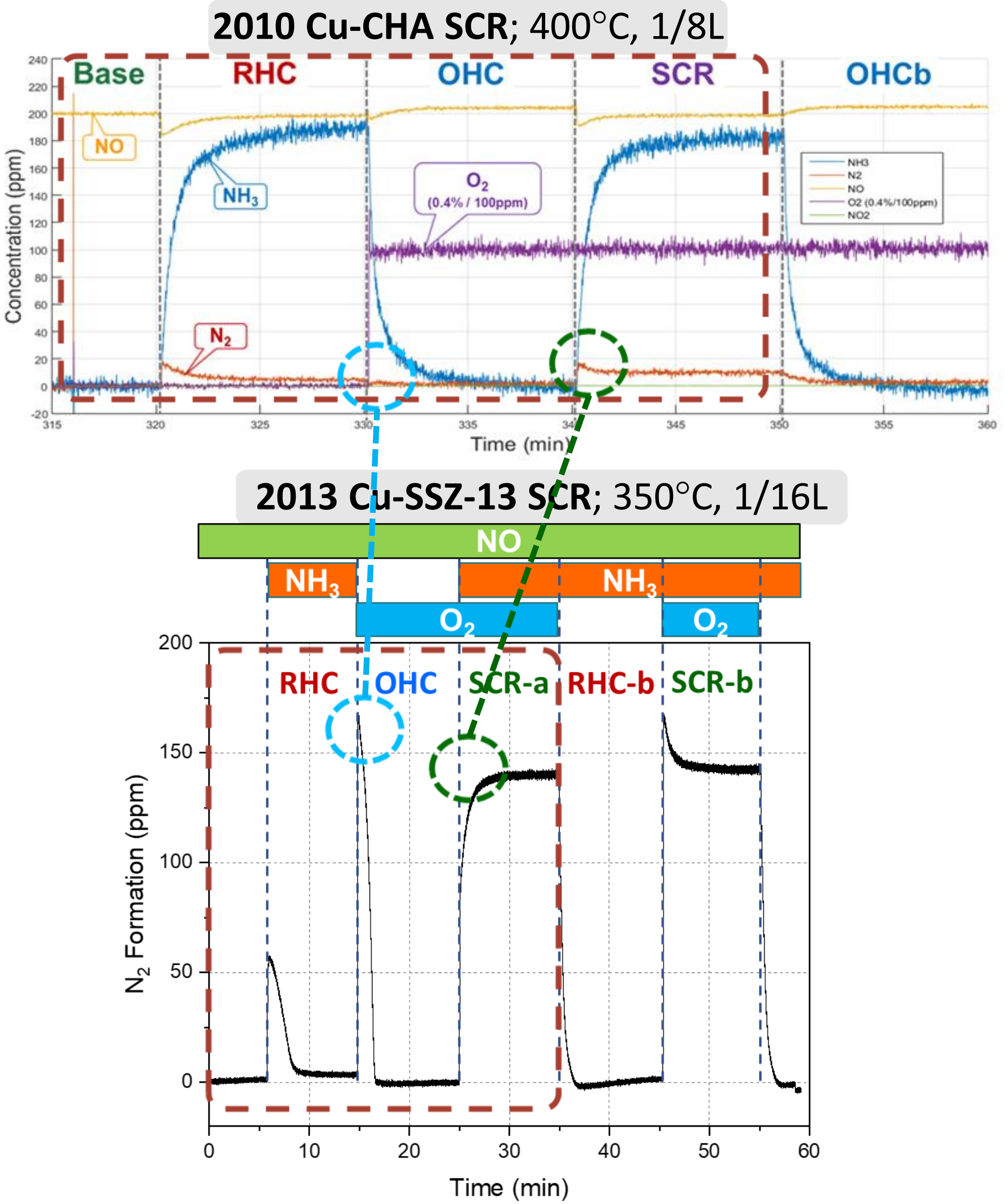


1st Programmed Unattended Protocol; Cu-SSZ-13; DG; 250°C; 1/2L

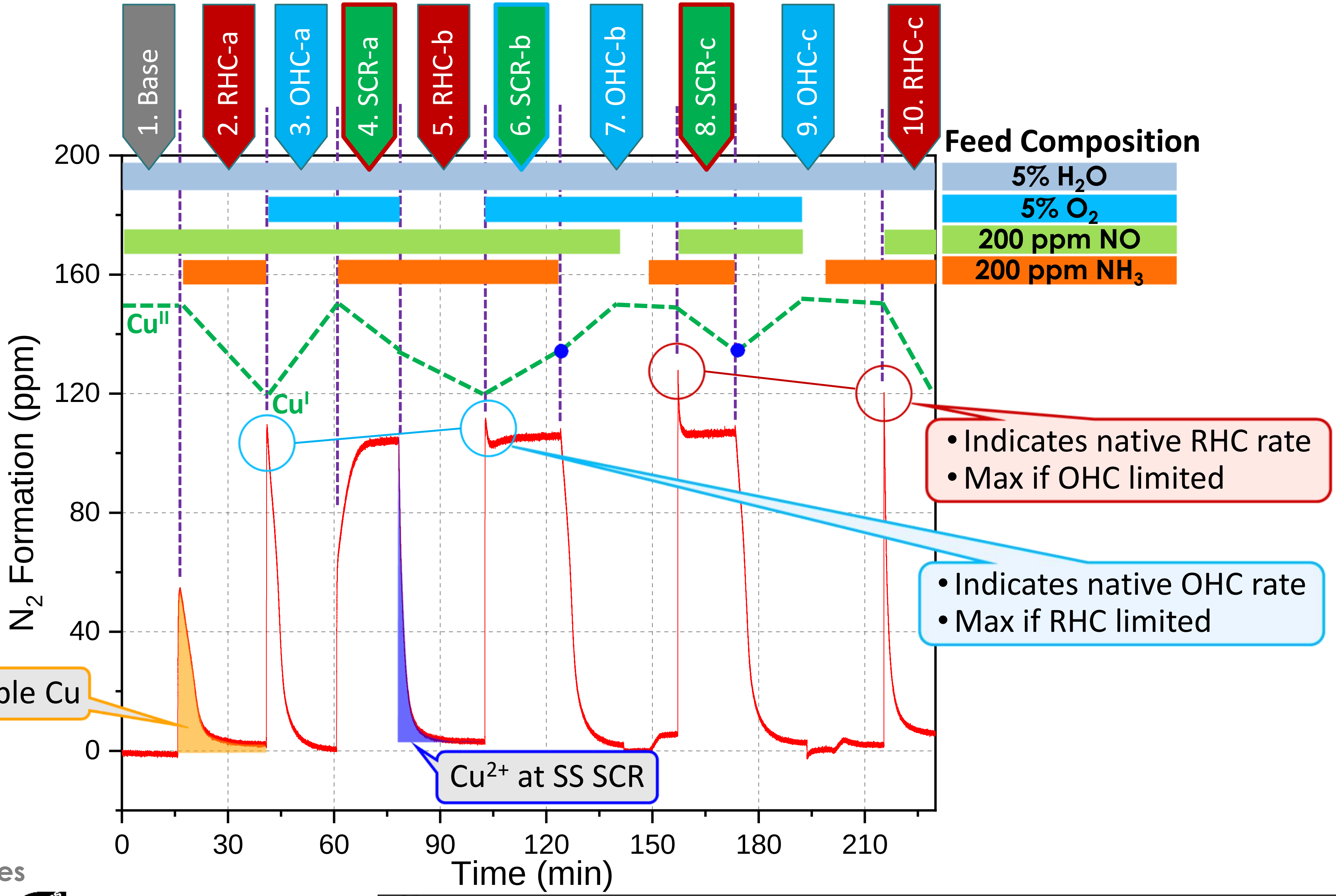


Expanded Transient-Response SCR-Redox Protocol

- New commercial Cu-SSZ-13 SCR catalyst is very different from previous commercial Cu-CHA
- New catalyst has significant CI in **OHC** step:
  - OHC is much faster
- New catalyst has no CI in NH_3-initiated **SCR** step
  - NH_3 loading capacity much more significant
- Differences mandated additional studies
  - Nature of new Cu-SSZ-13 catalyst
  - Development of a new Transient-Response Cu-Redox Protocol
  - Couldn't just implement FY20 plan based on studies of Cu-CHA Field Ageing

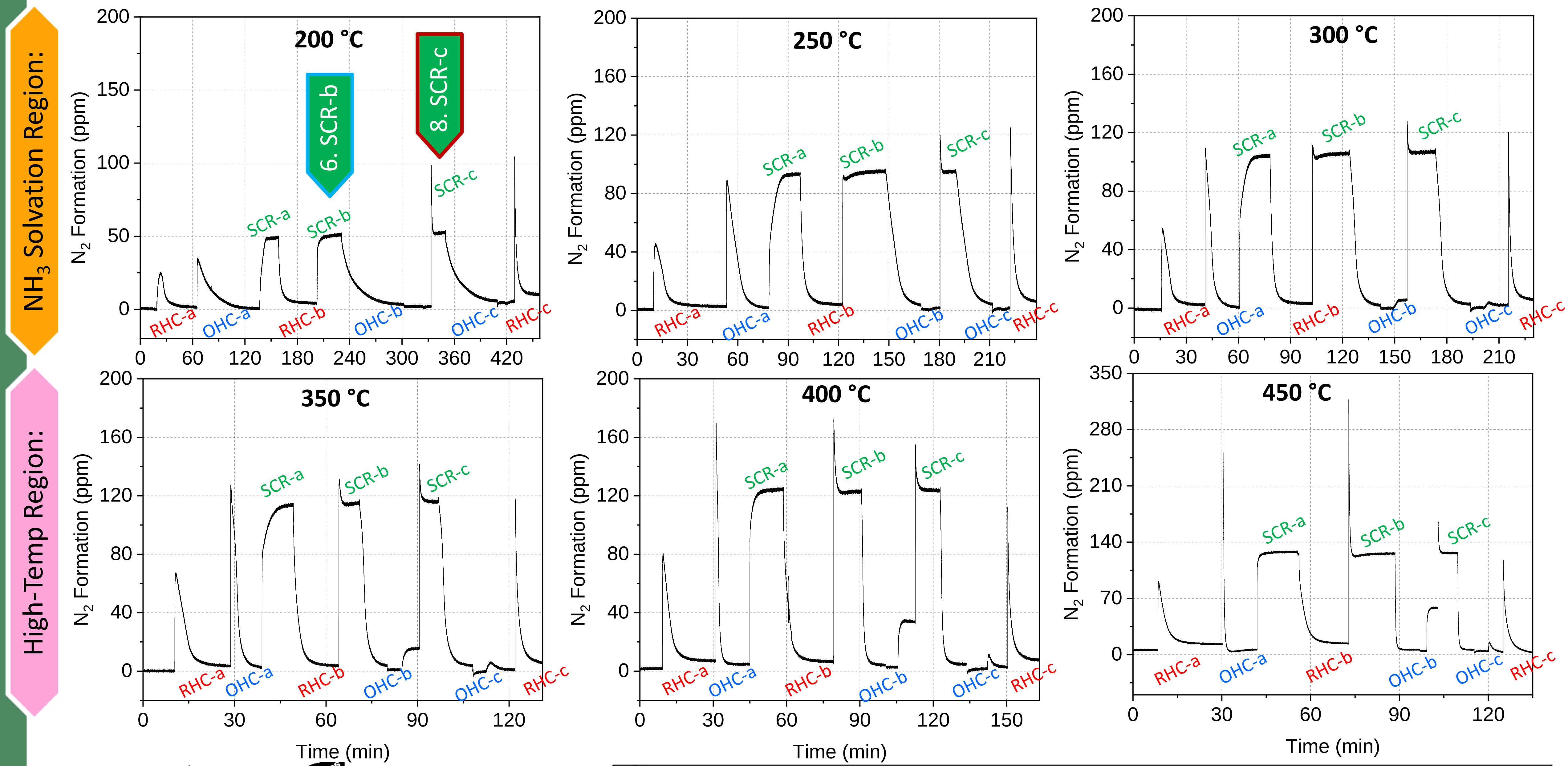


Expanded 10-Step Transient-Response SCR-Redox Protocol



Additional detail in Technical Backup Slides

T-Variation in Half-Cycle Rates (Field-Aged Cu-SSZ-13, 3/8L)



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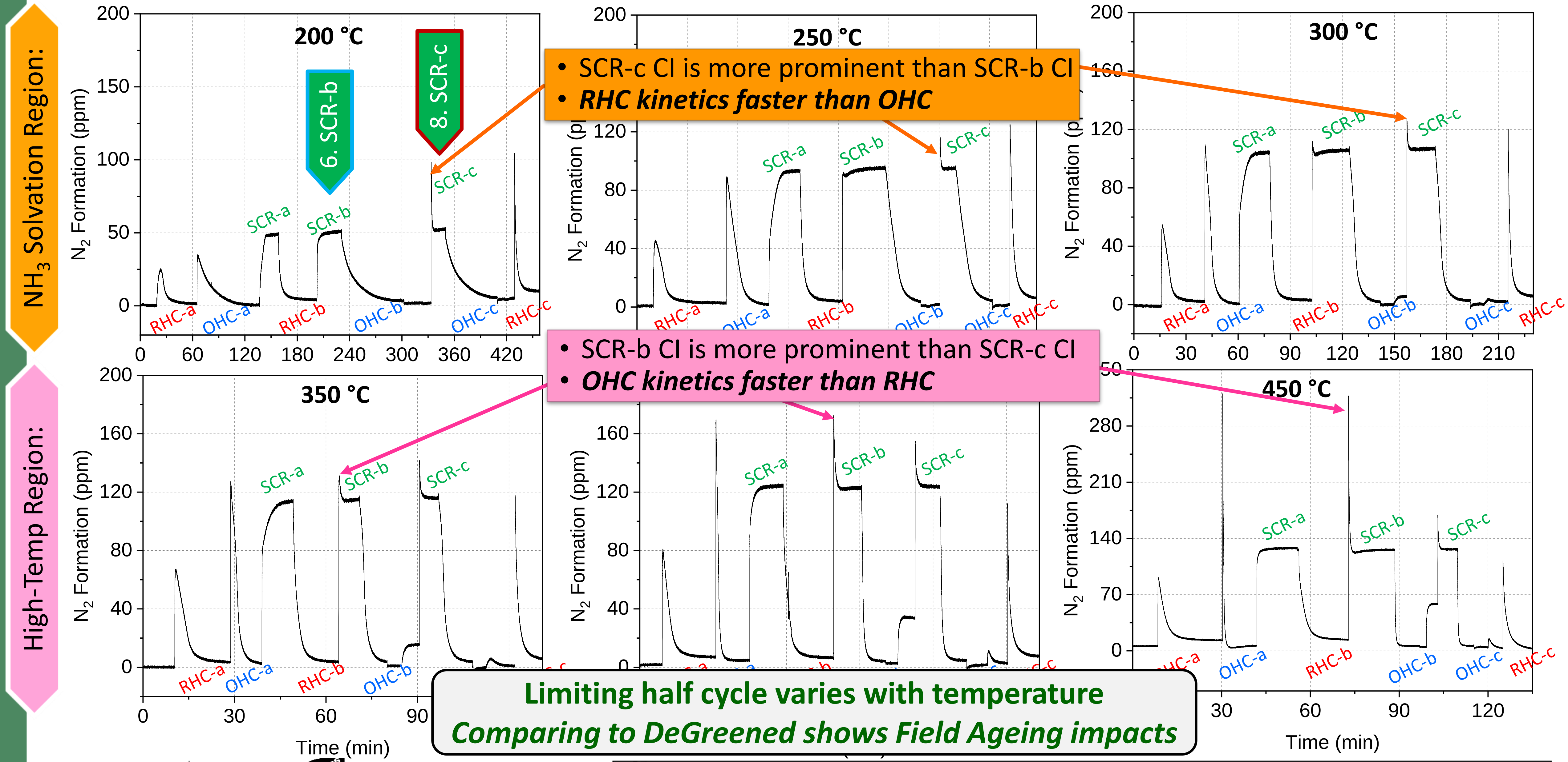


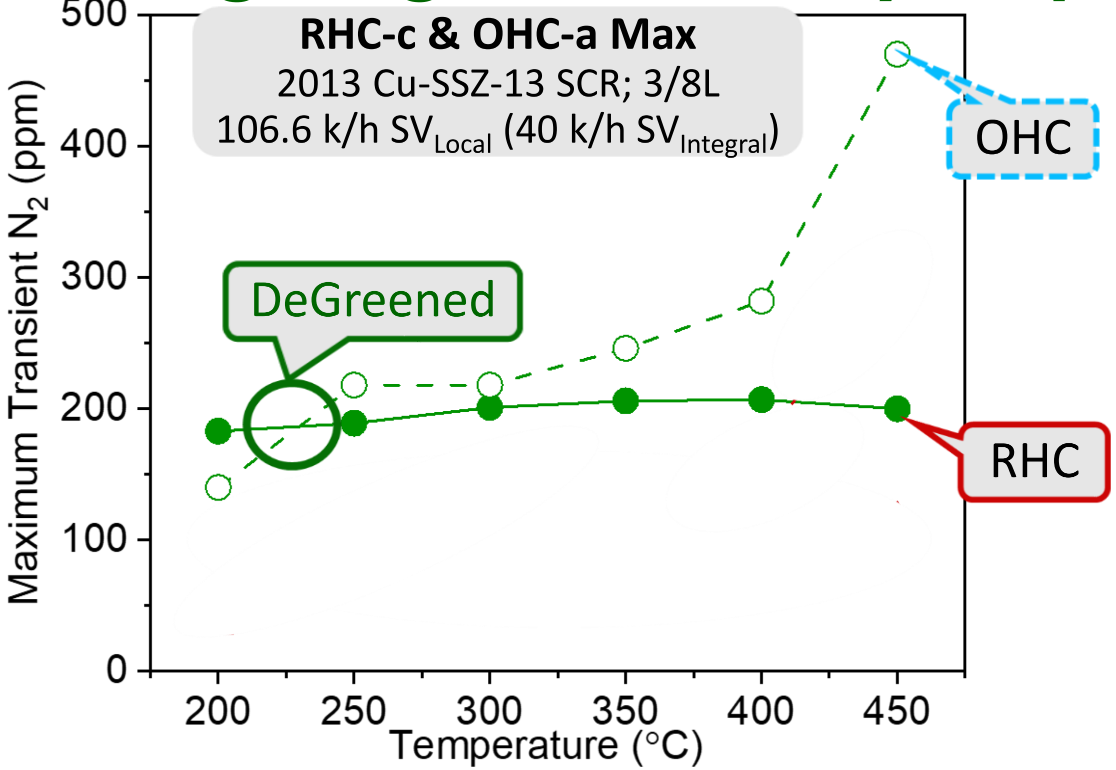
- SCR-c CI is more prominent than SCR-b CI
- ***RHC kinetics faster than OHC***

- SCR-b CI is more prominent than SCR-c CI
- ***OHC kinetics faster than RHC***

Limiting half cycle varies with temperature

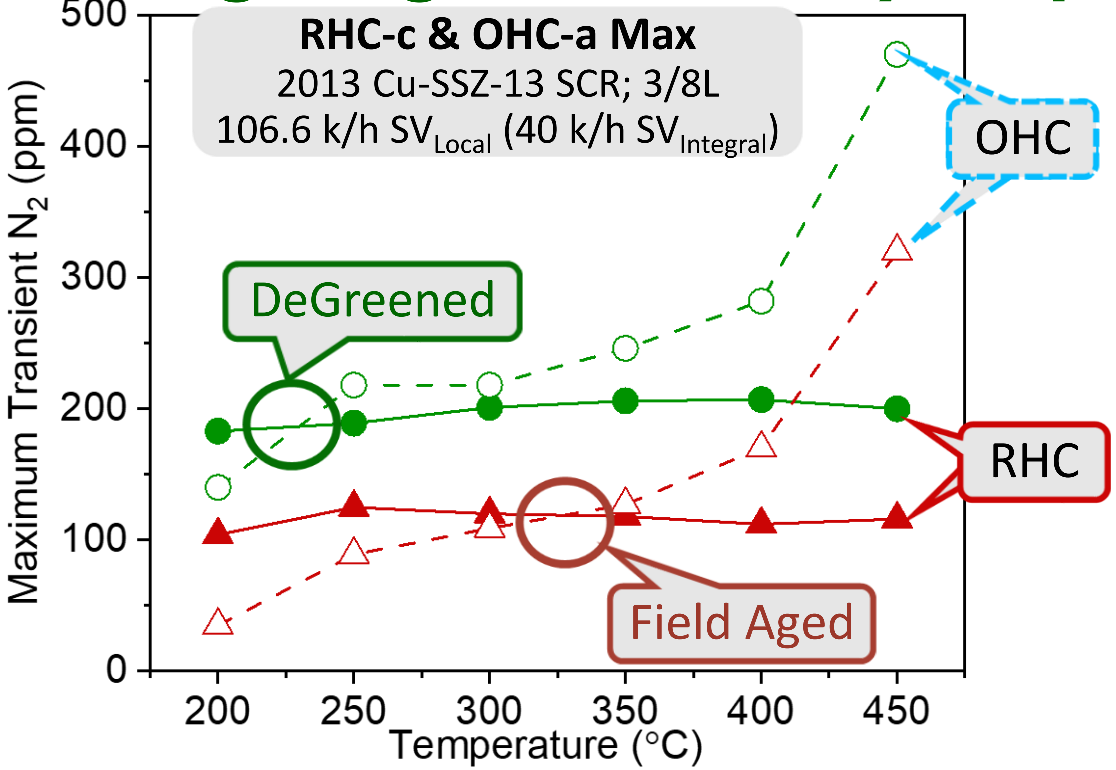
Comparing to DeGreened shows Field Ageing impacts

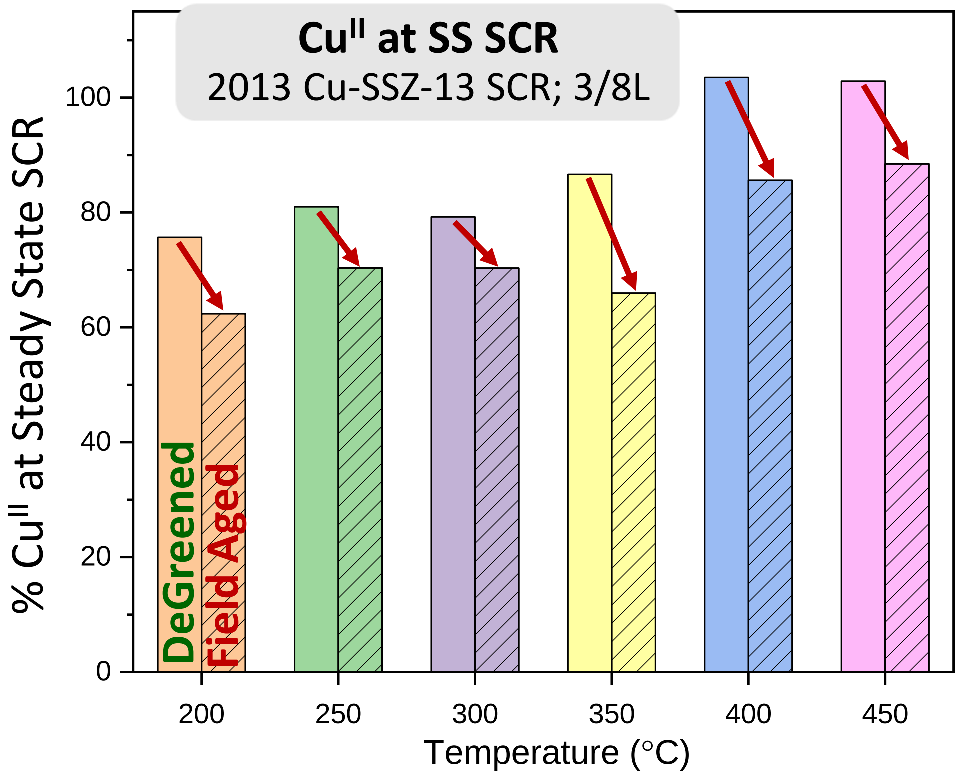
Field Ageing Selectively Impacts OHC over RHC



- Native RHC rate varies little with temperature
- Native OHC rate increase with temperature
  - Relatively flat at intermediate temperatures

Field Ageing Selectively Impacts OHC over RHC





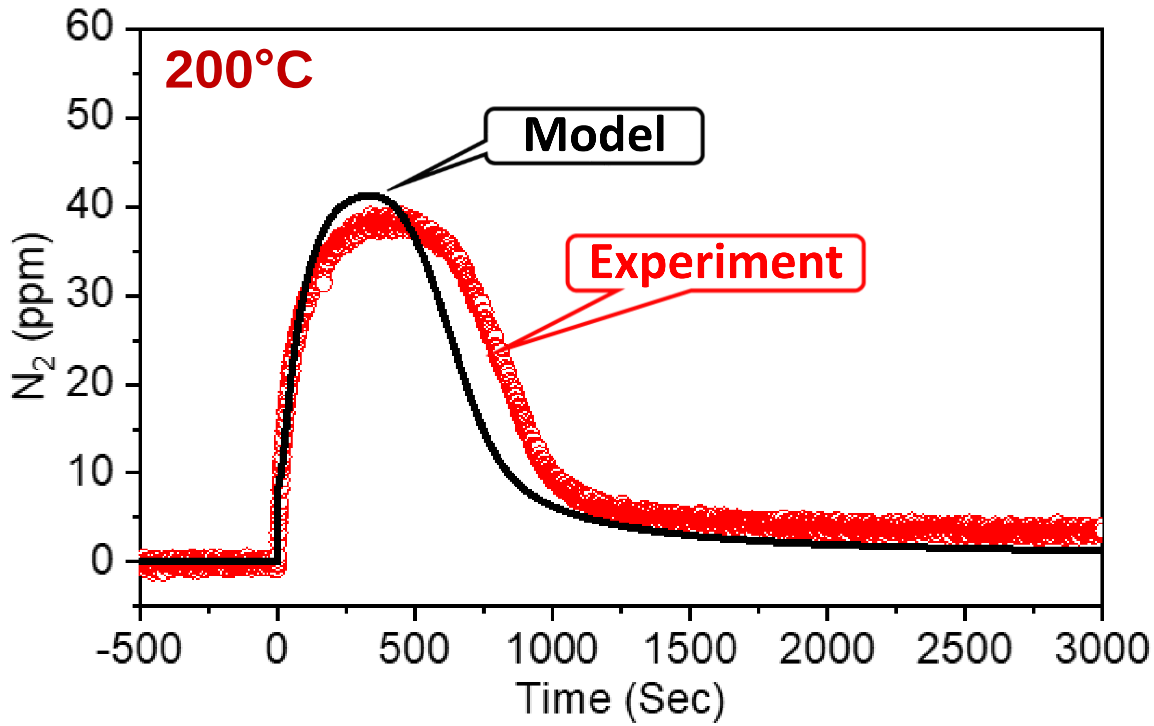
- Native RHC rate varies little with temperature
- Native OHC rate increase with temperature
  - Relatively flat at intermediate temperatures
- Field Ageing, FA, degrades both RHC and OHC
  - OHC degradation is greater
- RHC-OHC crossover shifts to higher T with FA

- Field Ageing reduces oxidized Cu at steady state
- ***Indicates OHC slowed more than RHC by FA***

Quantitative ageing impact from fitting kinetic half-cycle parameters with data & models

Validating Cummins Kinetic Model using RHC-a Transients

NH_3-Initiated RHC; DeGreened Cu-SSZ-13; $NO=NH_3=200$ppm; 106.6 k/h SV (3/8L, 40 k/h $SV_{Integral}$)



Pseudo Microkinetic Reaction Mechanism

NH_3 Storage in Oxidized State[1]

$ZH + NH_3 \leftrightarrow ZNH_4$
$ZNH_4 + NH_3 \leftrightarrow ZNH_4NH_3$
$P + NH_3 \leftrightarrow PNH_3$
$ZCuOH + NH_3 \leftrightarrow ZCuOHNH_3$
$Z_2Cu + NH_3 \leftrightarrow Z_2CuNH_3$
$Z_2CuNH_3 + NH_3 \leftrightarrow Z_2Cu(NH_3)_2$

Standard-SCR Reduction Half Cycle, RHC

$ZCuOHNH_3 + NO \rightarrow ZCu + N_2 + 2H_2O$
$Z_2CuNH_3 + NO \rightarrow ZCu + ZH + N_2 + H_2O$
$Z_2Cu(NH_3)_2 + NO \rightarrow ZCuNH_3 + ZH + N_2 + H_2O$
} NH_3-solvated Cu^{II} Sites

$ZCuOH + NH_3 + NO \rightarrow ZCu + N_2 + 2H_2O$
$Z_2Cu + NH_3 + NO \rightarrow ZCu + ZH + N_2 + H_2O$
} NH_3-free Cu^{II} Sites[2]

NH_3 Storage on ZCu Sites[1]

$ZCu + NH_3 \leftrightarrow ZCuNH_3$
$ZCuNH_3 + NH_3 \leftrightarrow ZCu(NH_3)_2$

Standard-SCR Oxidation Half Cycle, OHC

$2ZCu(NH_3)_2 + O_2 \leftrightarrow Z_2Cu_2(NH_3)_4O_2$
$Z_2Cu_2(NH_3)_4O_2 \leftrightarrow Z_2Cu_2O_2 + 4NH_3$
$Z_2Cu_2(NH_3)_4O_2 + 2NO \rightarrow 2ZCuOHNH_3 + 2N_2 + 2H_2O$
} Dimer formation, titration & NH_3 desorption

[1] Daya et al. (2021). *Applied Catalysis B: Environmental*, submitted.
[2] Daya et al. (2021). *Reaction Chemistry & Engineering*. (doi.org/10.1039/D1RE00041A)

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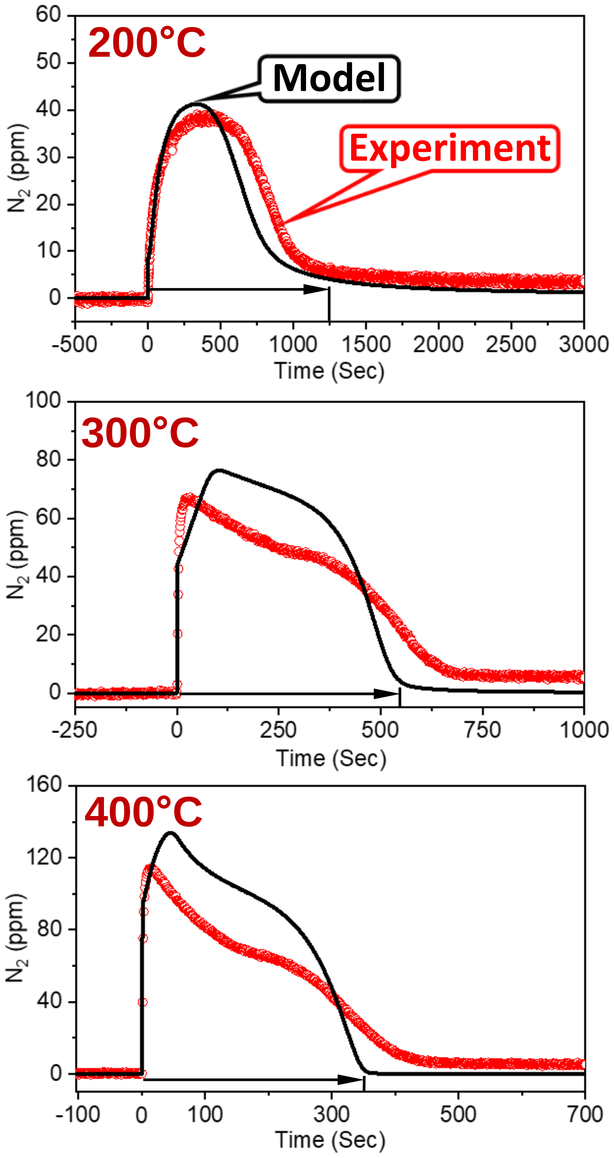

- Model captures variations with increasing T
  - Faster & multi-mode leading edge
  - Development of bimodal nature
  - Faster overall transient

Validating Cummins Kinetic Model using RHC-a Transients

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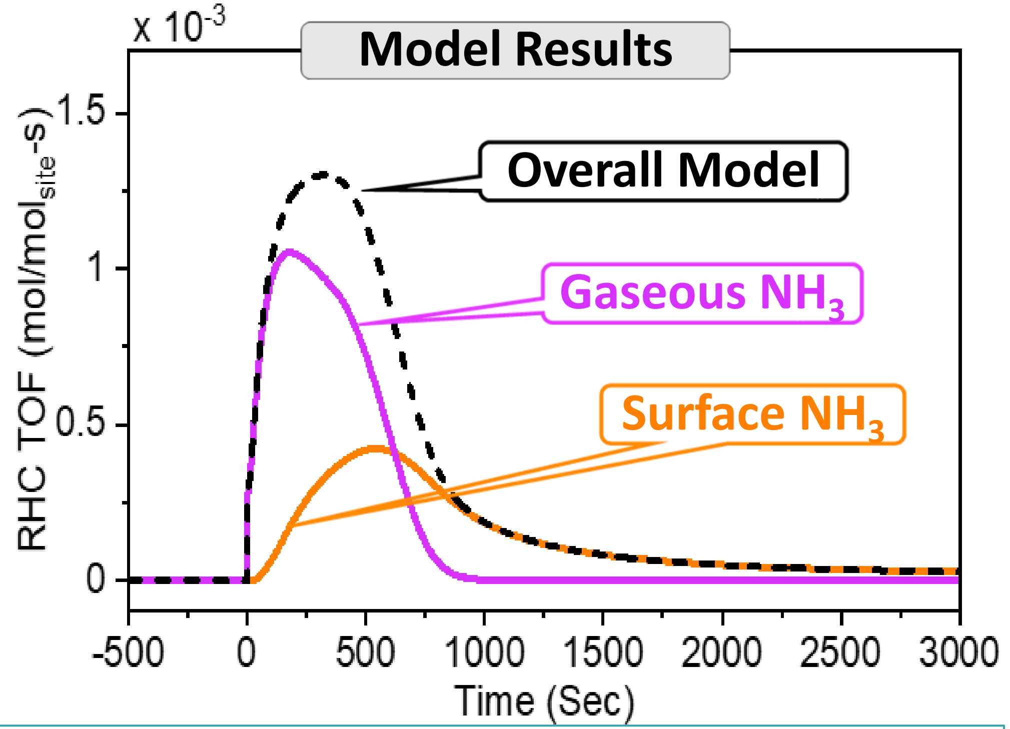

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- Model separates Gaseous- & Surface-NH_3 RHC routes

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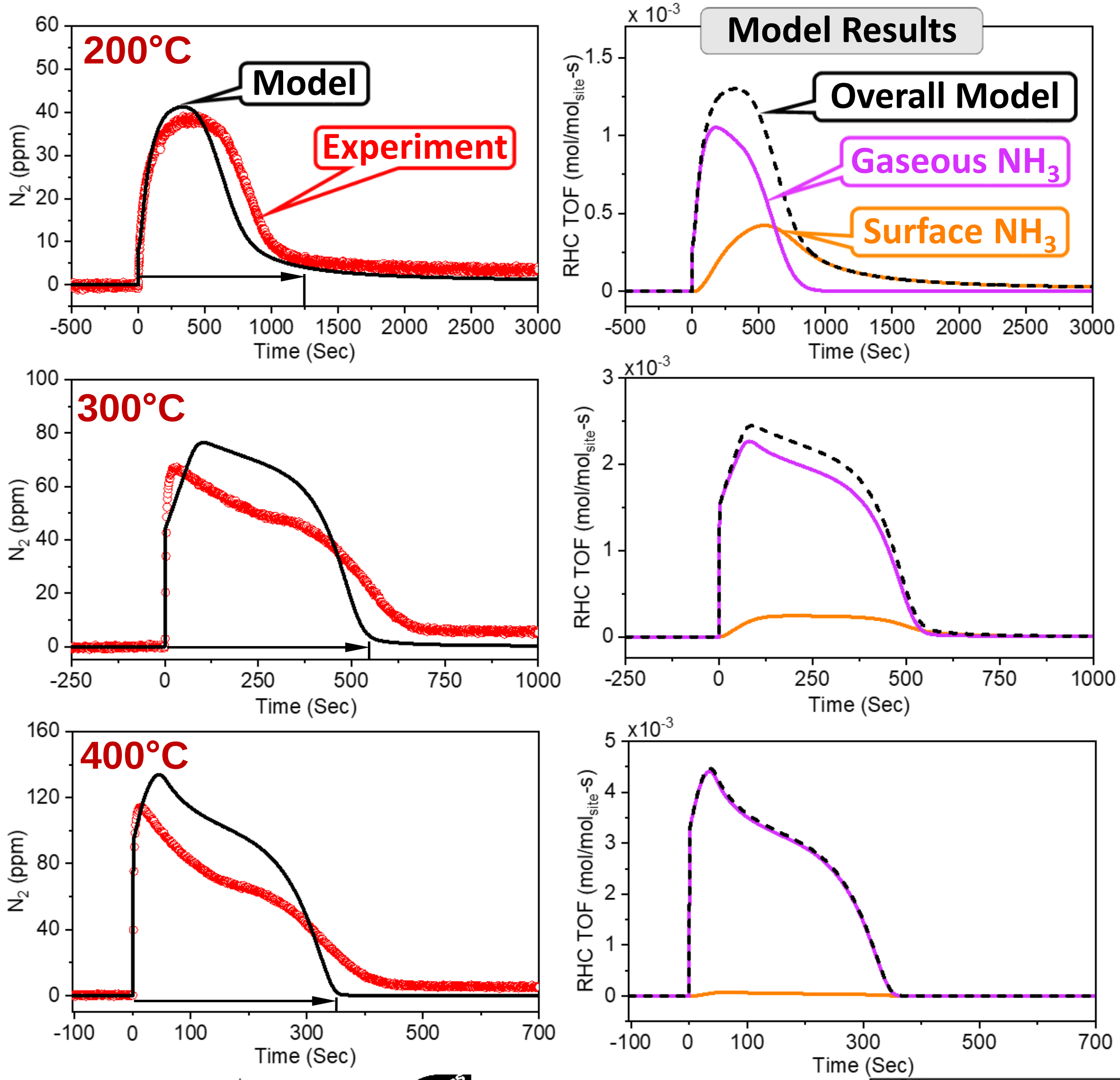
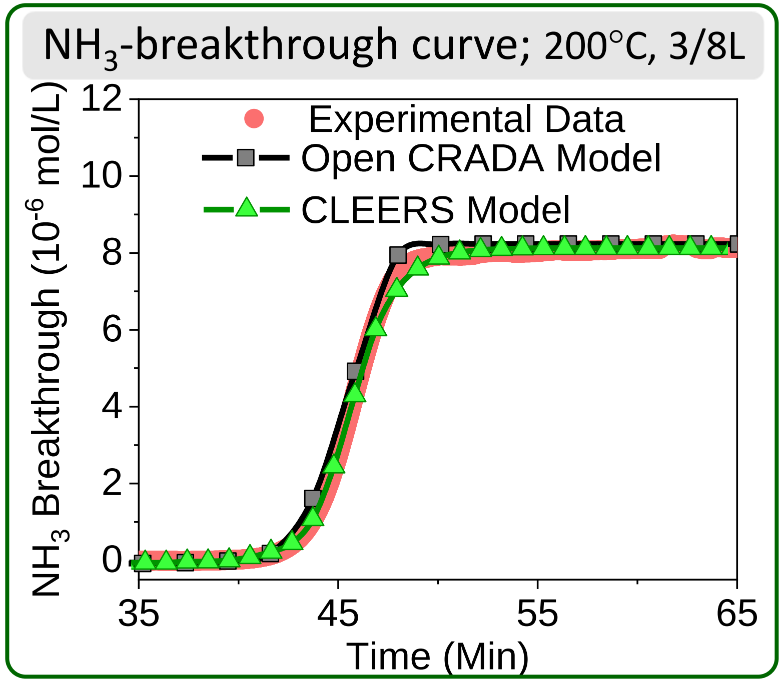
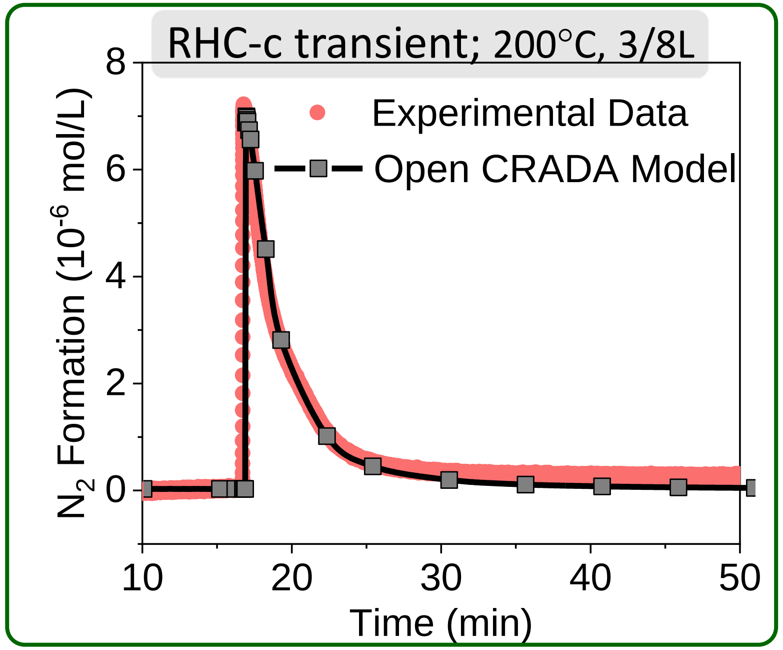


- Model captures variations with increasing T
  - Faster & multi-mode leading edge
  - Development of bimodal nature
  - Faster overall transient
- Model separates Gaseous- & Surface-NH_3 RHC routes
- Gaseous-NH_3 route accounts for fast onset
  - Captures bimodal onset
  - Dominates with increasing temperature
- ***Model describes broad NH_3-solvation & high-T range***
- Using SpaciMS Redox-Protocol data to validate model
  - Over high/wide SV range via intra-catalyst measurements
  - Oxidation of NH_3-solvated Cu^{I} sites
  - Oxidation of NH_3-free Cu^{I} sites
  - Redox under SCR on reduced & oxidized catalyst
  - Reduction of Cu^{II} sites by NH_3 only & NO only

CRADA SCR-Redox Open Model

- ***A public CRADA model we can openly report***
  - ***Further enhance CRADA value to broader catalysis community***
- Incorporates input from Cummins
- Collaboration with CLEERS
  - Using CLEERS base modeling tool developed by Austin Ladshaw
  - Demonstrates utility of this CLEERS tool
  - Mutually benefitting CRADA & CLEERS
- Models used to fit NH_3 adsorption/desorption parameters
  - Good fit, but need more data to identify unique parameters
  - More extensive CLEERS data from separate commercial SSZ-13 results in similar fit – *NH_3 ads/des kinetic parameters similar?*
- Initial RHC Modeling reasonably fits measured RHC-c transient
  - Captures bimodal nature of measured RHC transient
- Next steps
  - Expand detail, OHC modeling, identify RHC & OHC reaction pathways
  - Combine into an SCR model





Remaining Challenges & Future Work

Remaining Challenges:

- **Kinetic impact of Field Ageing**

	DeGreened		Field Aged	
	RHC	OHC	RHC	OHC
E_a				
A				

Future Work: *(subject to change based on funding)*

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- Fit RHC & OHC kinetic parameters using kinetic model
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- (Transitioning focus in FY22-24)

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- Characterization methodologies for Pt sites
- Impacts of Hydrothermal & Field ageing
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- **Improved SCR Real-World Durability**

Heavy Duty Emissions Regulations	
Current	**2031**
435,000 miles	800,000 miles

Solution Pathway

- **Integrate knowledge & results to advance Durability Solutions**
  - Improved catalyst-ageing models & experimental methods
  - Rapid ageing protocols
  - Tools for improved design, control and diagnosing

Summary

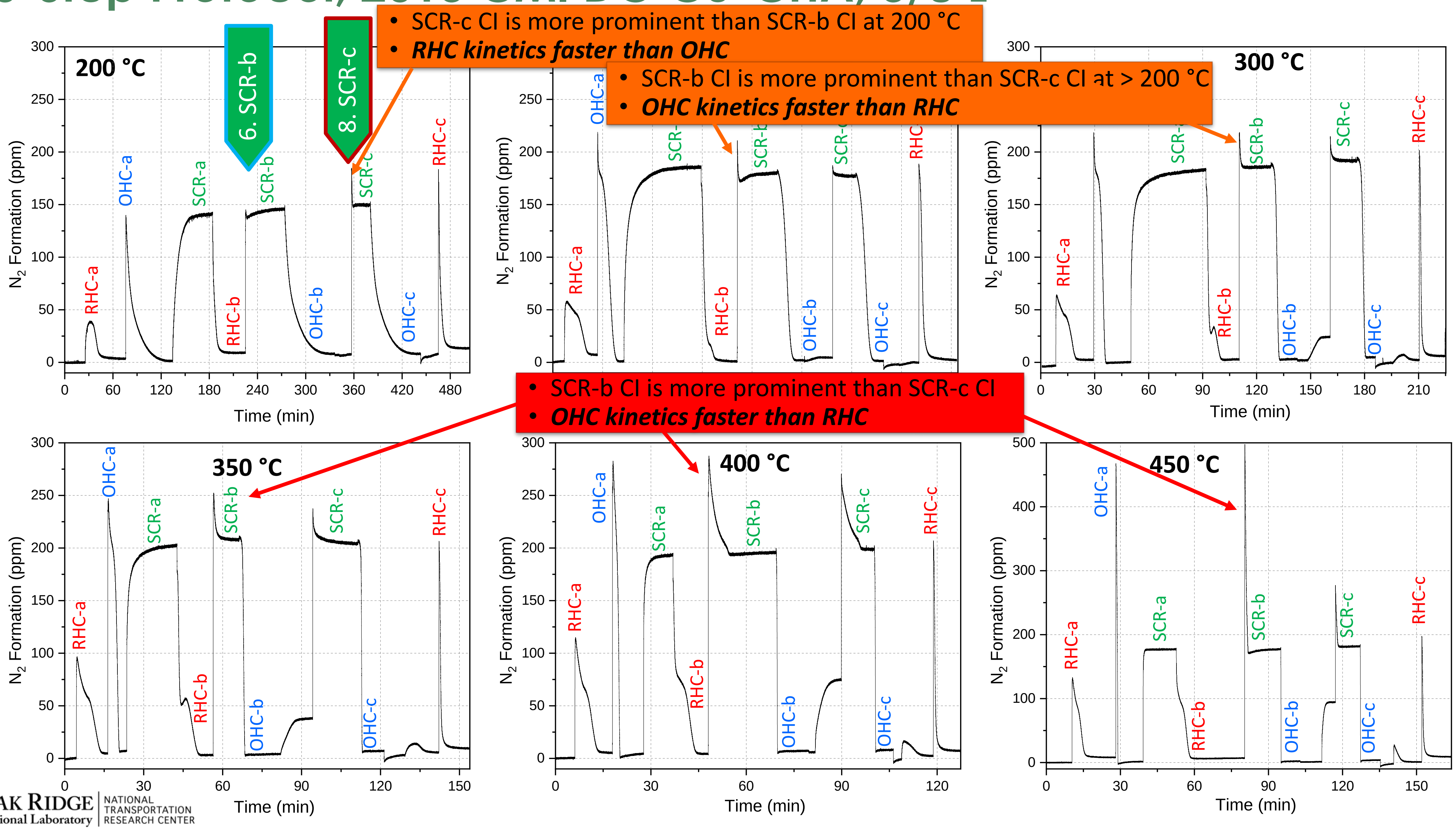
- **Relevance**
  - Focus is on kinetic origin of low-temperature performance and field aged SCR catalysts
  - Project work enables improved catalyst knowledge, models, design, OBD & control
  - Advances DOE goals for improved fuel economy, durability, & real-world emissions
- **Approach**
  - Apply experimental protocol to probe transient response of Cu-redox half-cycle steps
  - Develop and apply model to fit Cu-redox half-cycle kinetic parameters
  - Study kinetic impacts of low-temperature formulations and field-aged catalysts
- **Technical Accomplishments**
  - Improved programmable transient reactor performing unattended overnight experiments
  - New Cu-Redox and TPD protocols developed to study ageing impact on SCR redox cycle
  - Impact of Field Ageing on limiting redox half cycle experimentally characterized
  - Cummins-Internal and Open-CRADA kinetic models developed and demonstrated
- **Collaborations**
  - Johnson Matthey incorporated as project and CRADA participant
  - Communicate with community via presentations & publications
- **Future Work** (Any proposed future work is subject to change based on funding levels)
  - Determine impact of field-ageing on kinetics of commercial Cu-SSZ-13 SCR catalyst
  - Determine kinetic origins of performance for low-temperature formulations

Technical Back-Up Slides

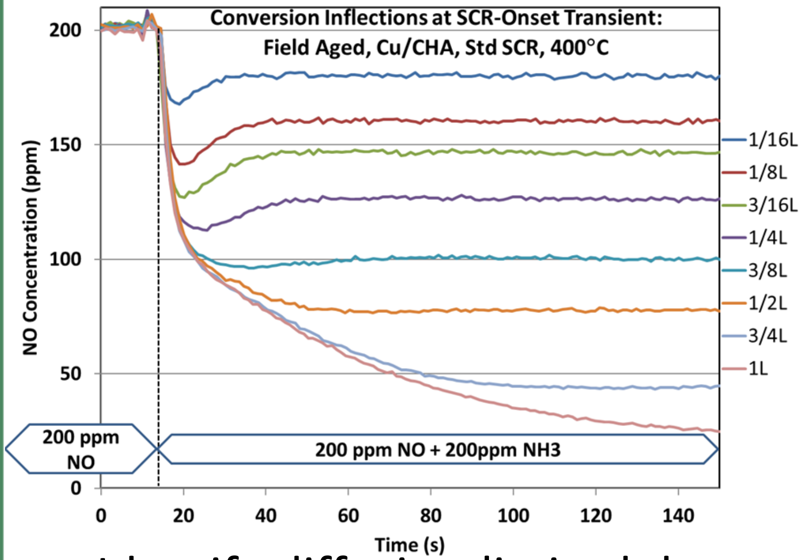
10-Step Protocol, 2013 CMI DG Cu-CHA, 3/8 L

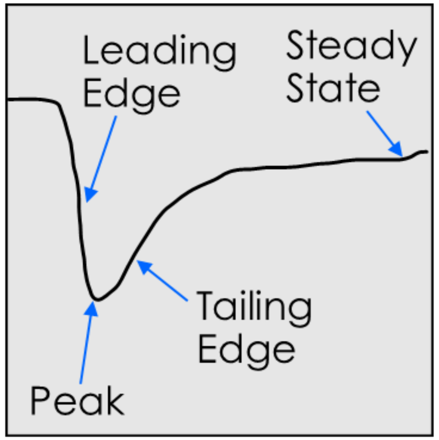
NH_3 Solvation Region:

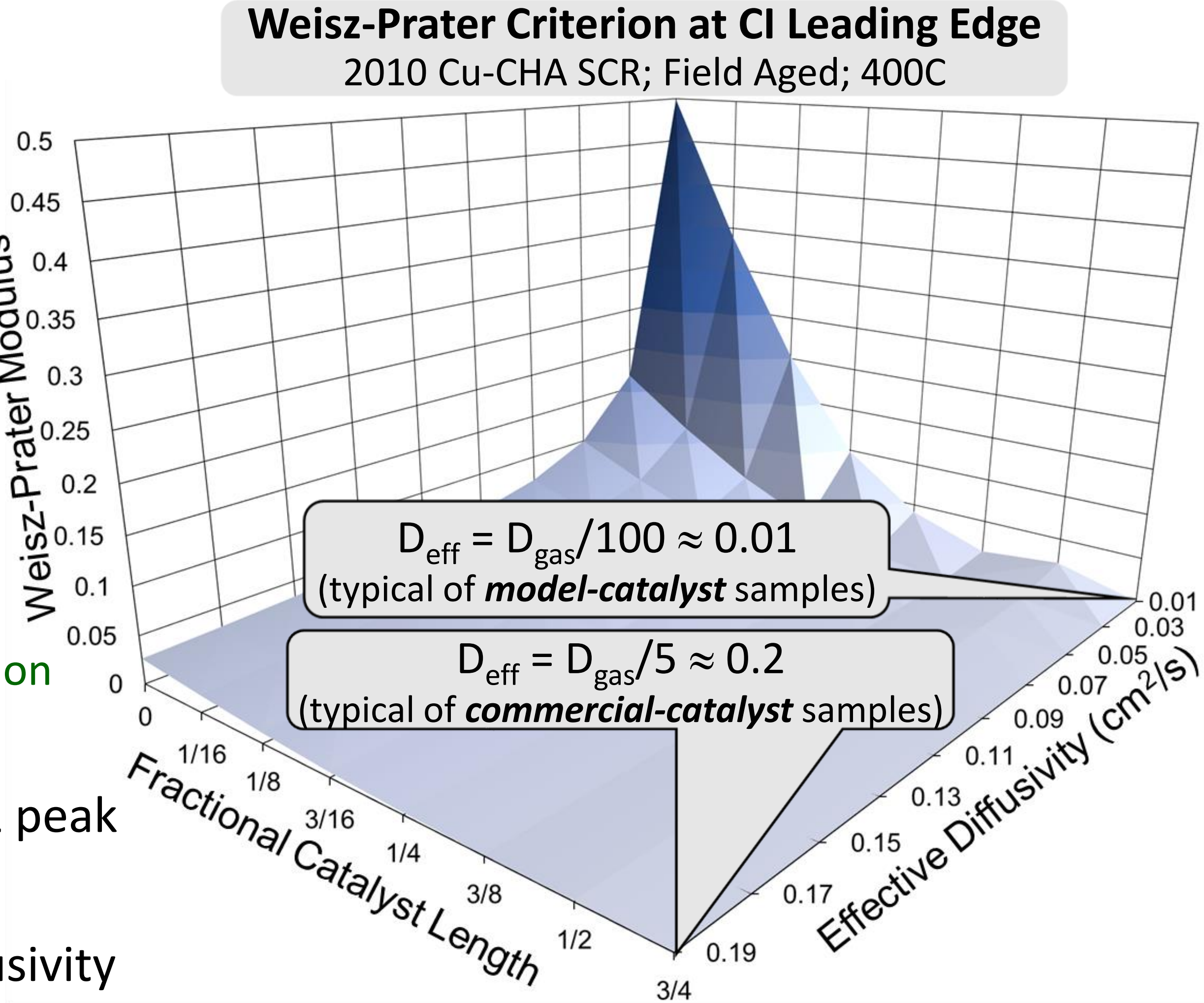
High-Temp Region:



Down Selecting Kinetically Limited SpaciMS Data Sets





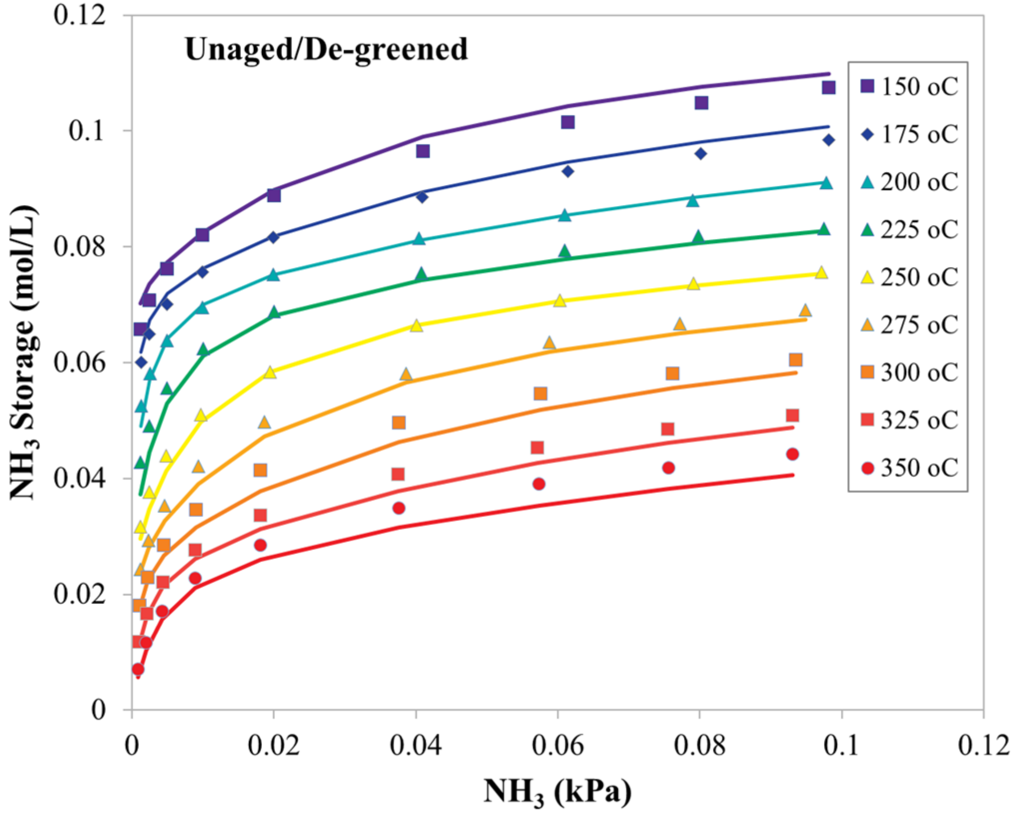


- Identify diffusion-limited data
  - **Weisz-Prater < 0.6** for negligible internal diffusion
  - **Mears < 0.15** for negligible external mass transfer limitation
  - Characterize criteria parameters at different regions
- Criteria parameter values greatest at CI leading edge & peak
  - Characterized throughout CI transient
- WP Criteria values greatest at catalyst front & low diffusivity
- WP & Mears Criterion << limits for diffusivity typical of commercial catalysts
- ***All SpaciMS CI data is kinetically limited for the Field Aged 2010 Cu-CHA SCR catalyst***

Open-CRADA SCR-Redox and CLEERS SCR Models

CLEERS Model

Ammonia inventory data and model comparisons



- Data analysis tool developed with Pyomo.DAE
- Implements a 1D-0D catalyst model
- Used to simulate and parameterize reactions

Open CRADA and CLEERS NH_3-Storage Model:

- CRADA model makes no differentiation in Cu-sites at present
- CLEERS model assumes formation of $Z_1CuOH\text{-}NH_3$, $Z_2Cu\text{-}NH_3$ and $Z_2Cu\text{-}(NH_3)_2$ surface species upon adsorption of NH_3

RHC Model

(Uses NH_3 adsorption kinetics from CLEERS model):

- **Reaction 1:** $Z_1Cu^{2+}OH\text{-}NH_3 + NO \rightarrow (ZCu^{+1}) + N_2 + 2H_2O$
  - $r_1 = k_1 (Z_1Cu^{2+}OH\text{-}NH_3)^2 {}_*NO$
- **Reaction 2:** $Z_2Cu^{2+}\text{-}NH_3 + NO \rightarrow (ZCu^{+1}) + ZH + N_2 + H_2O$
  - $r_2 = k_2 (Z_2Cu^{2+}NH_3)^2 {}_*NO$
- **Reaction 3:** $Z_2Cu^{2+}\text{-}(NH_3)_2 + NO \rightarrow (ZCu^{+1}NH_3) + ZH + N_2 + H_2O$
  - $r_3 = k_3 (Z_2Cu^{2+}NH_3)\ {}^2{}_*NO$

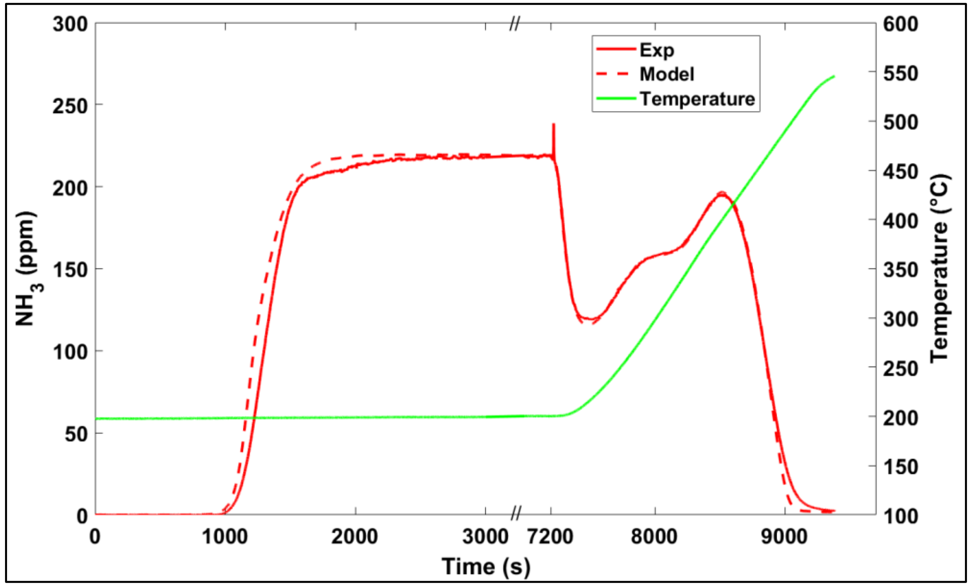
NH_3 storage kinetics on individual active sites

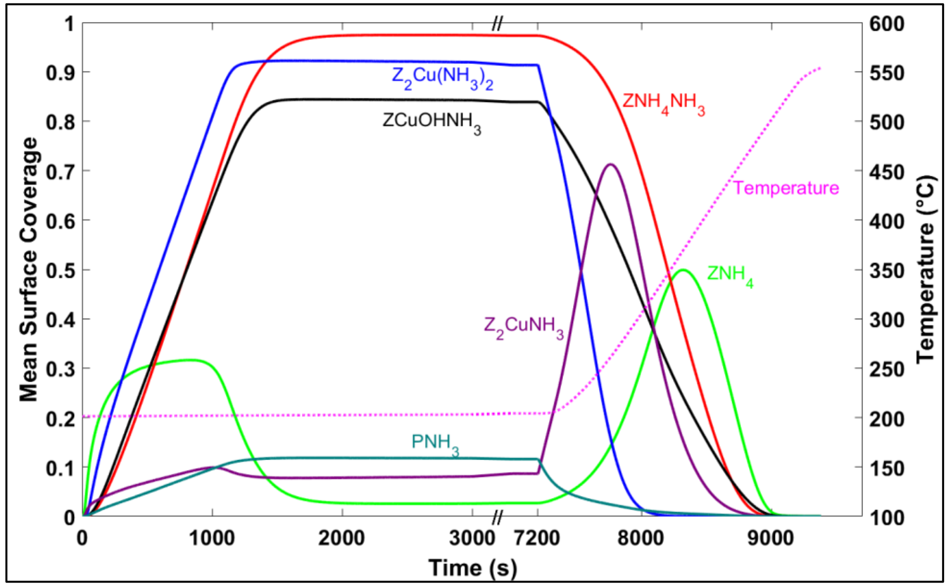
NH_3 Adsorption-Desorption Thermodynamics and Kinetics

Reaction	K_{eq}. at 200°C	$\Delta_{ads}H^0$ (kJ/mol)	$\Delta_{ads}S^0$ (J/mol-K)	A_{ads} (1/s)	A_{des} (1/s)
$NH_3 + ZH \leftrightarrow ZNH_4$	2.47e+10	-169.6 ($\alpha = 0.1$)	-158.7	5.14e+04	1e+13
$NH_3 + ZNH_4 \leftrightarrow ZNH_4NH_3$	1.97e+05	-73 ($\alpha = 0.09$)	-39.2	2.82e+01	3.14e+03
$NH_3 + P \leftrightarrow PNH_3$	6.58e+02	-48.6 ($\alpha = 0.65$)	-41	4.43e+01	6.05e+03
$NH_3 + ZCuOH \leftrightarrow ZCuOHNH_3$	2.77e+04	-117.8 ($\alpha = 0.28$)	-103.7	3.62e+01	9.51e+06
$NH_3 + Z_2Cu \leftrightarrow Z_2CuNH_3$	2.71e+07	-139.2 ($\alpha = 0.08$)	-150.2	2.76e+02	1.93e+10
$NH_3 + Z_2CuNH_3 \leftrightarrow Z_2Cu(NH_3)_2$	6.83e+04	-141.3 ($\alpha = 0.04$)	-194.4	9.63e+02	1.37e+13

Notation used for Cu-amine complexes and attribution of Physisorbed NH_3

Surface Species	Notation
$Z[(O_f)_y Cu^{II}(OH)(NH_3)(H_2O)_x]$	$ZCuOHNH_3$
$Z_2[(O_f)_{y2}Cu^{II}(NH_3)_2(H_2O)_{x2}]$	$Z_2Cu(NH_3)_2$
$Z_2[(O_f)_{y3}Cu^{II}(NH_3)(H_2O)_{x3}]$	Z_2CuNH_3
$ZNH_4(NH_3)_l$ for $l \geq 2$ EFAl. NH_3 $Z[(O_f)_{y4} Cu^{II}(OH)(NH_3)_m(H_2O)_{x4}]$ for $m \geq 2$ $Z_2[(O_f)_{y5}Cu^{II}(NH_3)_n(H_2O)_{x5}]$ for $n \geq 3$	PNH_3
$Z[Cu^{I}(NH_3)_2(H_2O)_{x6}]$	$ZCu(NH_3)_2$
$Z[(O_f)_{y7}Cu^{I}(NH_3)(H_2O)_{x7}]$	$ZCuNH_3$





Age : 550°C-4h
NH_3 : 200 ppm; H_2O : 7%; O_2 : 10%
Adsorption temperature : 200°C
Isothermal desorption time : 0s
Ramp Rate : 10°C/min
SV : 40k/h

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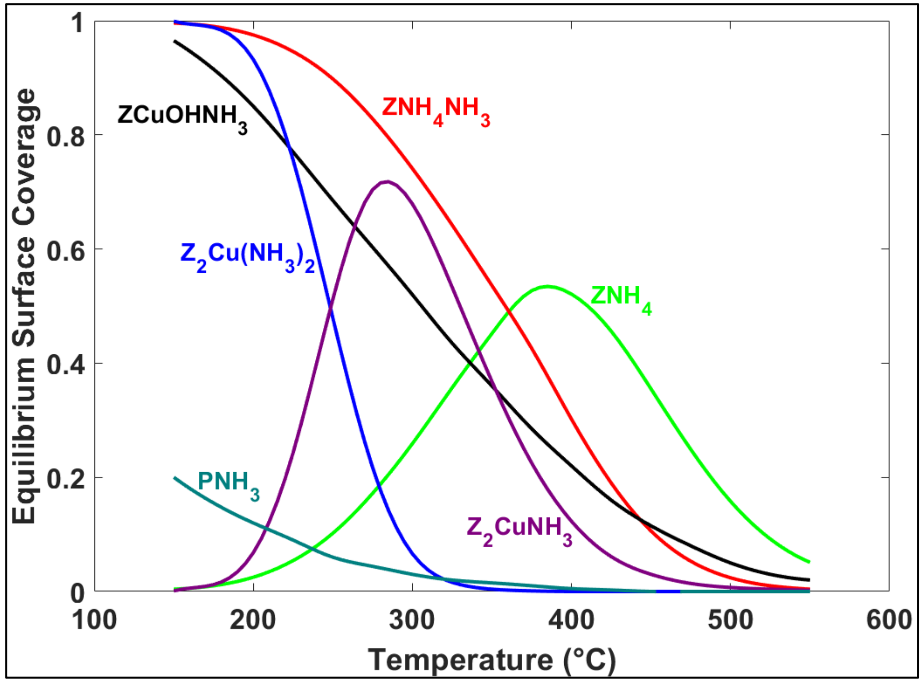
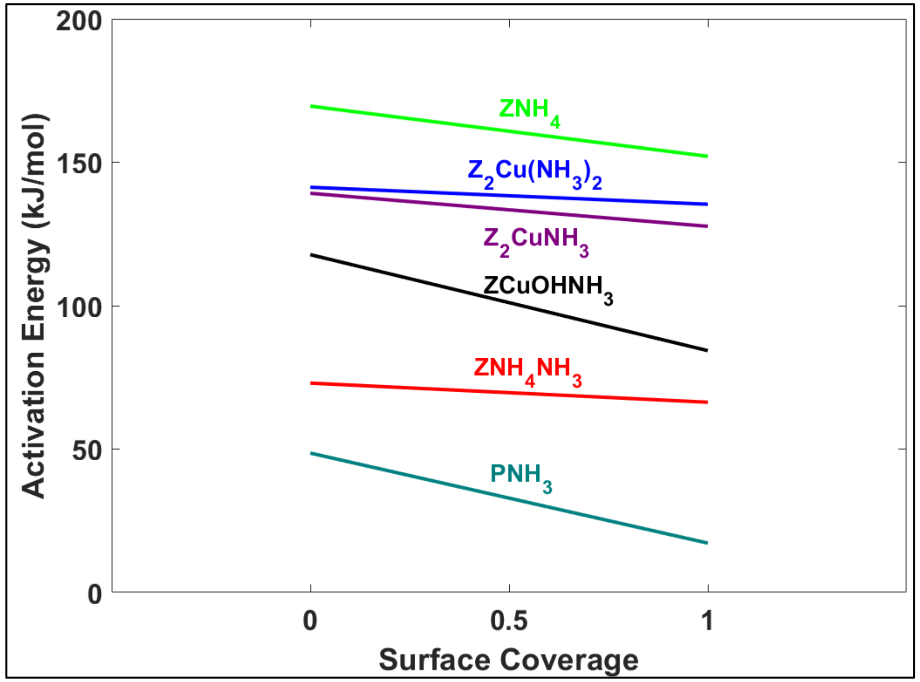
Mean surface coverage and activation energies





Adsorption strength

$ZNH_4 > Z_2CuNH_3 > ZNH_4NH_3 > Z_2Cu(NH_3)_2 > ZCuOHNH_3 > PNH_3$

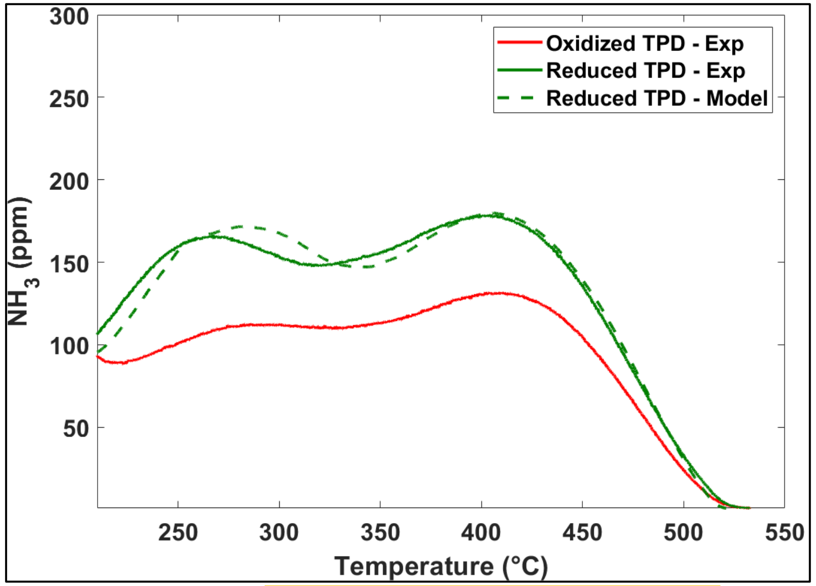
- Model predicts stronger adsorption of NH_3 on Z_2Cu sites relative to ZCuOH sites, as indicated by earlier approach to saturation upon decreasing temperature
- In addition, increased heterogeneity and/or higher repulsive lateral interactions predicted for ZCuOH sites, leading to slower loss of coverage vs. temperature

NH_3 storage kinetics on reduced copper sites

NH_3 Adsorption-Desorption Thermodynamics and Kinetics on ZCu Sites

Reaction	$K_{eq.}$ at 200°C	$\Delta_{ads}H^0$ (kJ/mol)	$\Delta_{ads}S^0$ (J/mol-K)	A_{ads} (1/s)	A_{des} (1/s)
$NH_3 + ZCu \leftrightarrow ZCuNH_3$	5.19e+05	-146.6 (α = 0.45)	-131.8	1.38e+02	4.82e+06
$NH_3 + ZCuNH_3 \leftrightarrow ZCu(NH_3)_2$	5.07e+03	-131 (α = 0.32)	-162	1.15e+03	2.46e+09

$ZNH_4 > Z_2CuNH_3 > ZNH_4NH_3 > ZCuNH_3 > Z_2Cu(NH_3)_2 > ZCuOHNH_3 > ZCu(NH_3)_2 > PNH_3$



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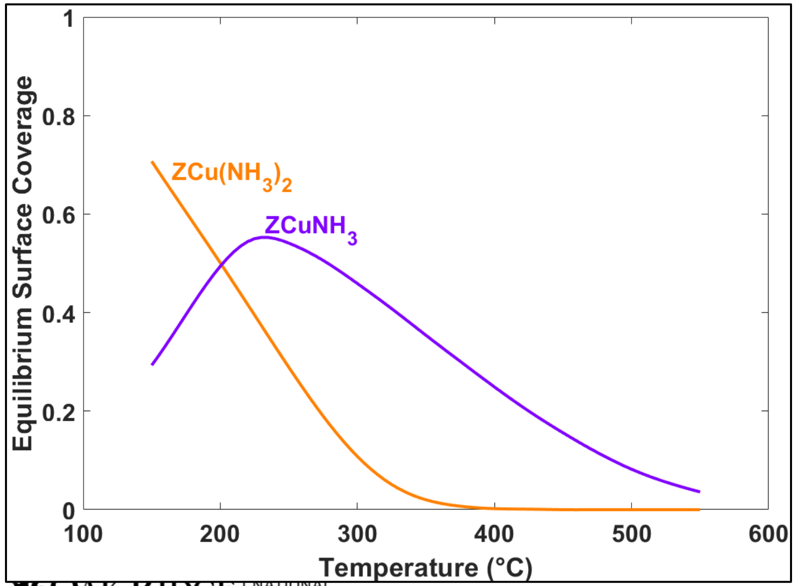
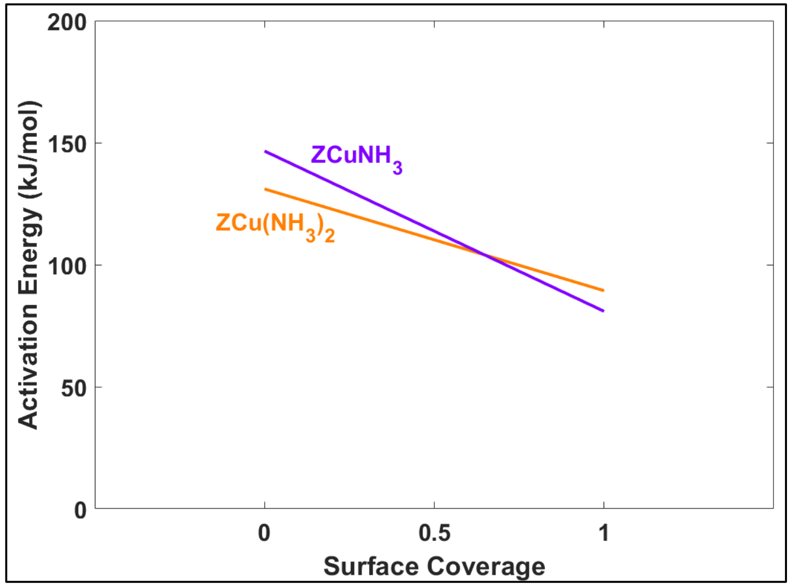




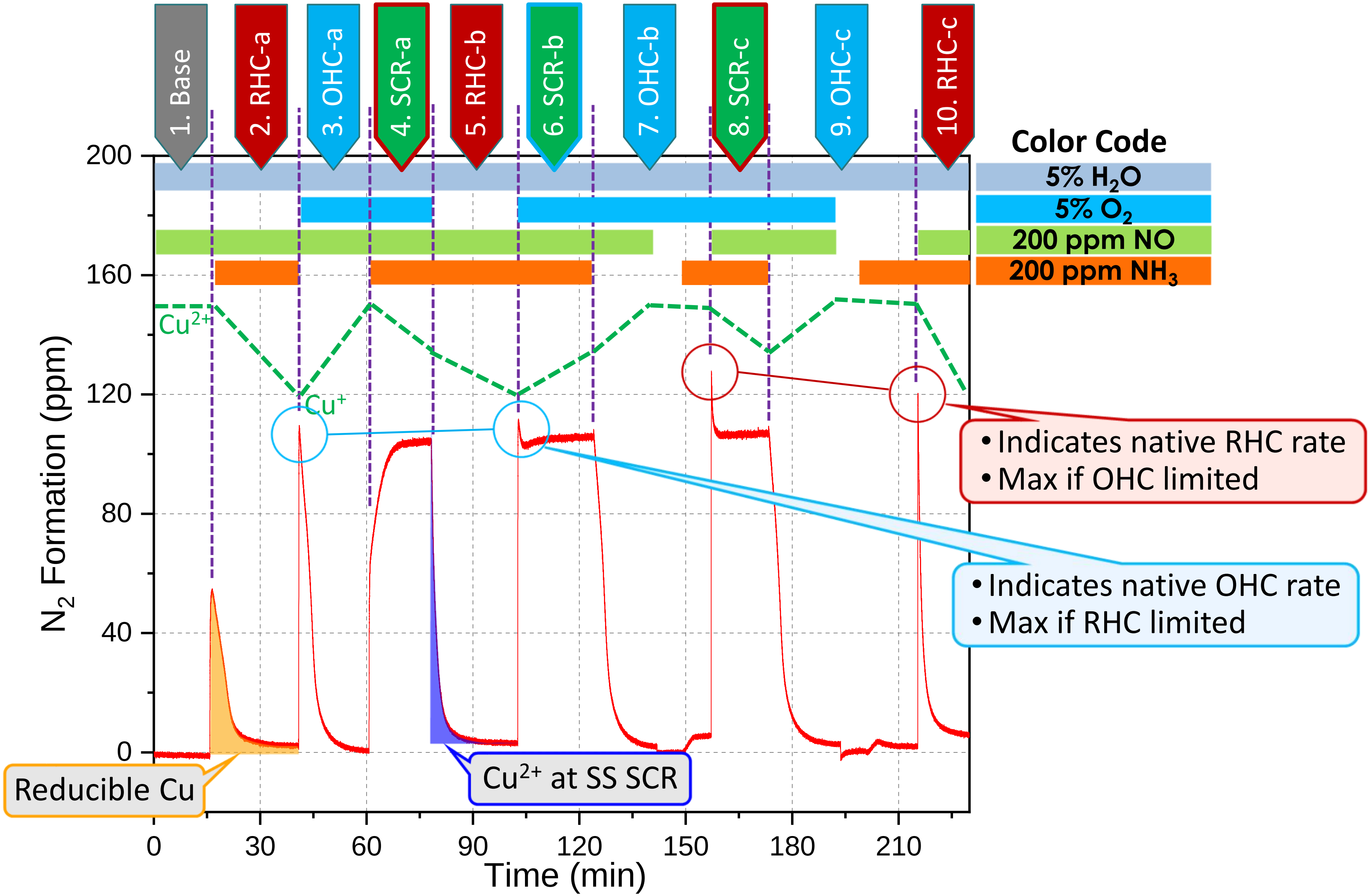
- Model predicts a mix of $ZCu(NH_3)_2$ (50%) and $ZCuNH_3$ (50%) species at 200°C, with progressive desorption $ZCu(NH_3)_2$ and $ZCuNH_3$ at high temperatures

Expanded 10-Step Transient-Response SCR-Redox Protocol

10-Step protocol:

5% H_2O flow throughout

1. Base: 200 ppm NO
2. **RHC-a**: NH_3-initiated RHC
3. **OHC-a**
4. **SCR-a**: NH_3-initiated SCR following OHC
5. **RHC-b**: Reduce the catalyst
6. **SCR-b**: O_2-initiated SCR following RHC, (***native OHC rate***)
7. **OHC-b**: Oxidize the catalyst, Turn NO off and NH_3 on, preparation for NO initiated SCR
8. **SCR-c**: NO-initiated SCR following OHC, (***native RHC rate***)
9. **OHC-c**: Oxidize the catalyst, Turn NO & O_2 off, and NH_3 on, preparation for NO initiated RHC
10. **RHC-c**: NO-initiated RHC



Abbreviations

AMOx	Ammonia oxidation catalyst
ASC	Ammonia slip catalyst
CUC	Clean-up catalyst
DOC	Diesel oxidation catalyst
DPF	Diesel particulate filter
GOC	Gasoline oxidation catalyst
GPF	Gasoline particulate filter
HCT	Hydrocarbon trap
LNT	Lean NOx trap
MOC	Methane oxidation catalyst
OC	Oxidation catalyst
OEC	Other emissions control catalysts
PF	Particulate filter
PNA	Passive NOx adsorber
SCR	Selective catalytic reduction
TWC	Three-way catalyst

ACI	Advanced compression ignition
BTE	Break thermal efficiency
CDC	Conventional diesel combustion
HD	Heavy duty
LD	Light duty
LTAT	Low temperature aftertreatment
LTC	Low temperature combustion
MD	Medium duty
NG	Natural gas
SI	Spark ignition