2017 DOE AMR Review

Vehicle Technologies Office

Innovative SCR Materials and Systems for Low Temperature Aftertreatment

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Institute for Integrated Catalysis
Pacific Northwest National Laboratory

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PM066

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Project Overview

Timeline

- Project starting date:
  - 7/1/2015
- Project ending date:
  - 6/30/2018

Budget

- DOE funding:

  PNNL

  $500K/Year($1.5M total)
- FCA US LLC:

  $500K(total)

Barriers

- Low temperature performance
- Lack of cost-effective
  - emission control
- Durability of emissions
  - control devices

Partners

- Pacific Northwest National Laboratory
- FCA US LLC
  - w/U of Houston

  (FCA in-kind funding)

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Relevance

- Address the 150°C Challenge identified from the 2012 USCAR workshop.
- Focus on providing a low temperature enabling SCR catalyst aftertreatment system that will function at very high efficiency to attain the most demanding emissions regulations and thereby facilitate the market introduction of advanced powertrains that will support domestic energy independence and security.
- Strengthen and accelerate this technology transfer of innovative materials and processes from the laboratory environment to vehicle by coupling with system development at FCA US LLC.

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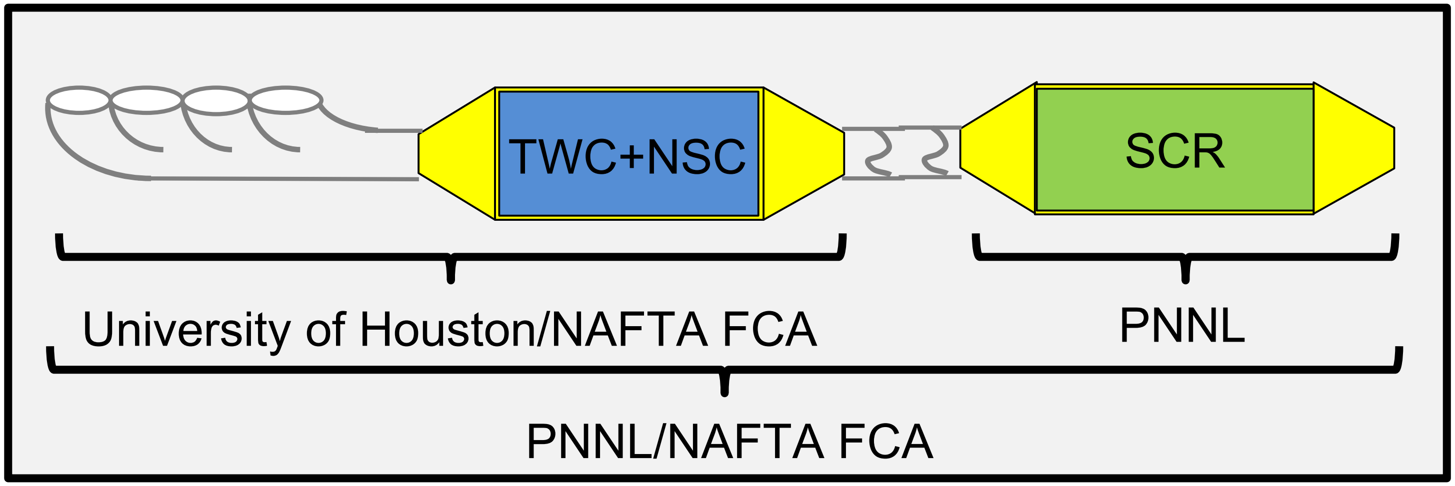
Approach/Strategy

Vehicle Technologies Office

CRADA Partner Project Areas of Responsibility:

- FCA – NH_3 generation, supplemental NOx control and system integration
- PNNL – Low temperature SCR development, supplemental system integration



Task	Year 1 (Q1 Q2 Q3 Q4)	Year 2 (Q1 Q2 Q3 Q4)	Year 3 (Q1 Q2 Q3 Q4)
Characterization/optimization of novel SCR materials	Q1–Q4	Q1–Q4	Q1–Q4
Laboratory aging studies of novel SCR materials		Q1–Q4	Q1–Q4
NH_3 generation and design	Q3–Q4	Q1–Q2	
System component aging		Q3–Q4	Q1–Q2
Dyno testing SCR NOx reduction strategies			Q1–Q4
SCR cost model			Q4

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Approach/Strategy

SCR

Adapt a newly developed SCR material to function with high efficiency under conditions consistent with low temperature portions of drive cycles.

- Demonstrate the SCR catalyst, aged under realistic conditions (lean or stoichiometric), will provide 90% conversion efficiency at/near 150˚C.

Aftertreatment System

Demonstrate that a SCR catalyst system will attain Tier III and SULEV30 emissions using an engine or simulated engine FTP cycle.

- Evaluate SCR catalyst system activity using alternate upstream NOx control and NH_3 generation strategies.
  - Tier 3 criteria emissions control and GHG minimization
  - Estimate:
    - The fuel penalty
    - Control/OBD complexity
    - Component/system cost

2017 Milestones

- ✓ Initiate realistic aging studies of the optimized first generation catalysts that have been washcoated onto a monolith substrate – 12/31/2016 (completed)
- ✓ Determine an optimized composition of the second generation LT-SCR catalyst – 3/31/2017 (completed)
- ✓ Verify sufficient hydrothermal stability of the first generation catalyst formulation – 9/31/2017 (completed)
- ✓ Go/No-Go: Downselect for each passive NH_3 dosing technology – 6/30/2017 (met)

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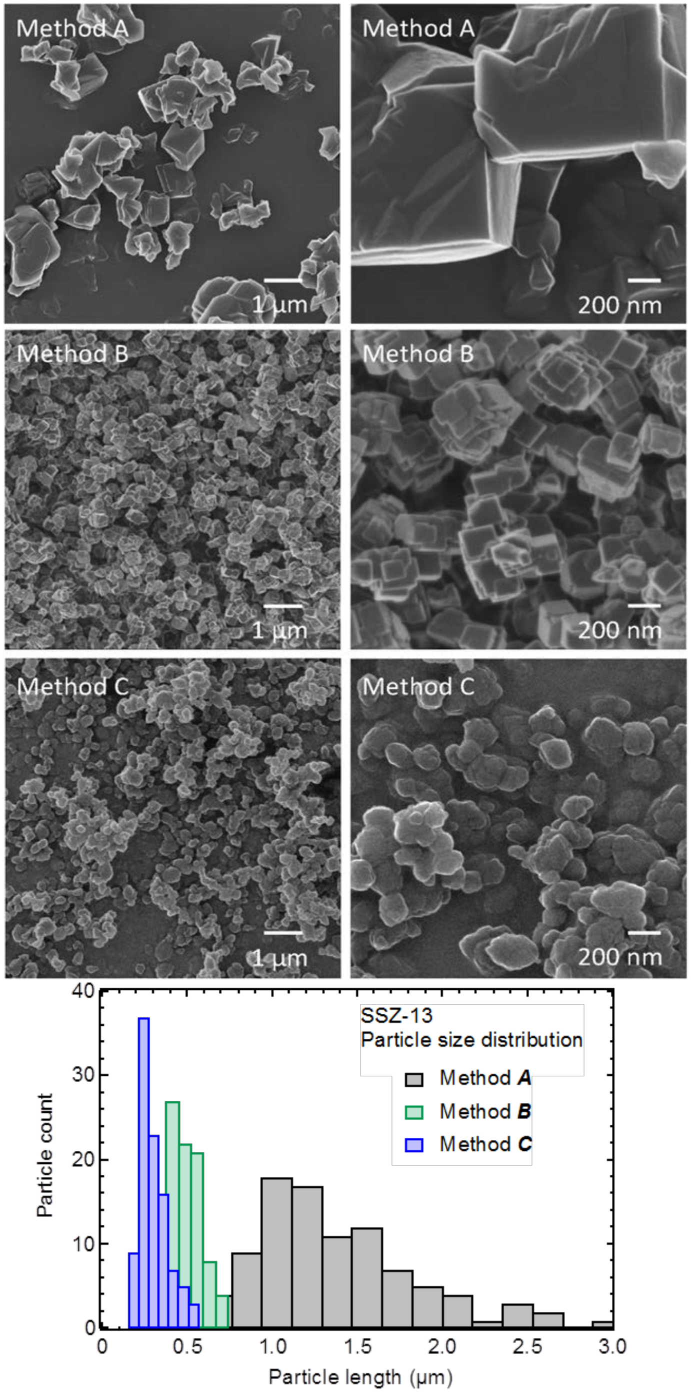
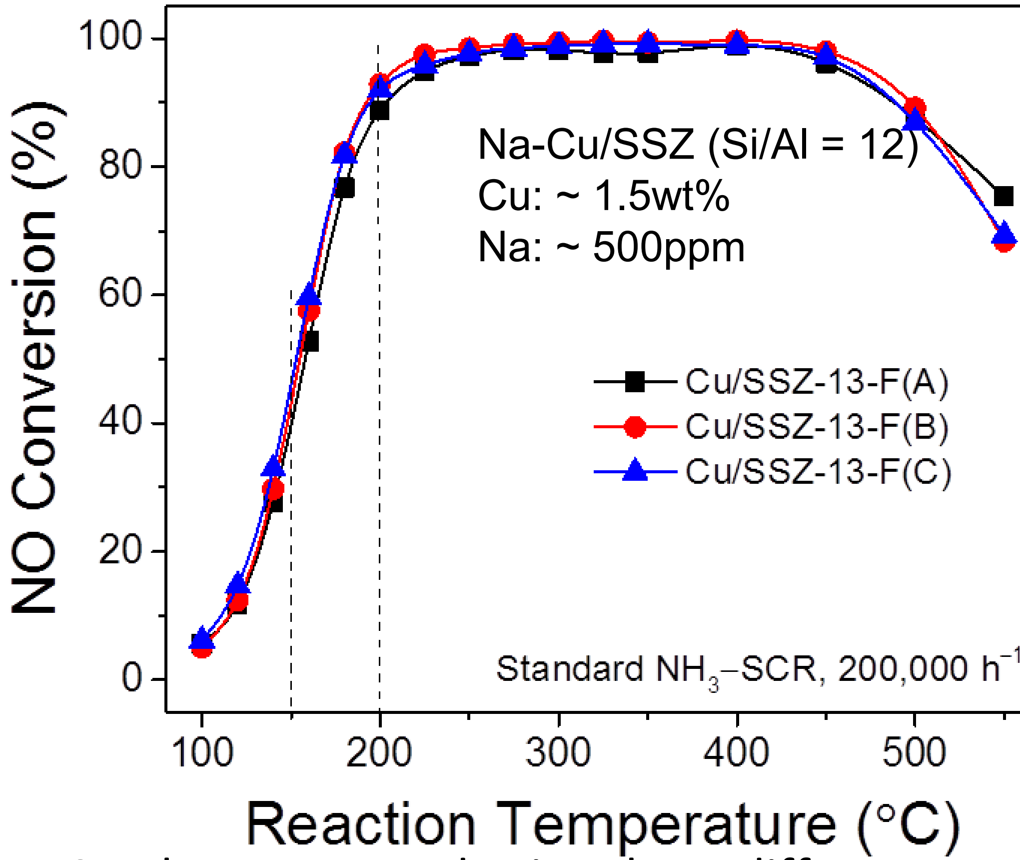
SCR Update (1st Gen. SCR Catalysts)





- Catalysts prepared using three different methods lead to different particle size of SSZ-13
- Similar SCR performances were obtained (~50% NO conversion at 150°C/75%@175°C)
- No particle size effect on NOx conv.(for both fresh and aged)

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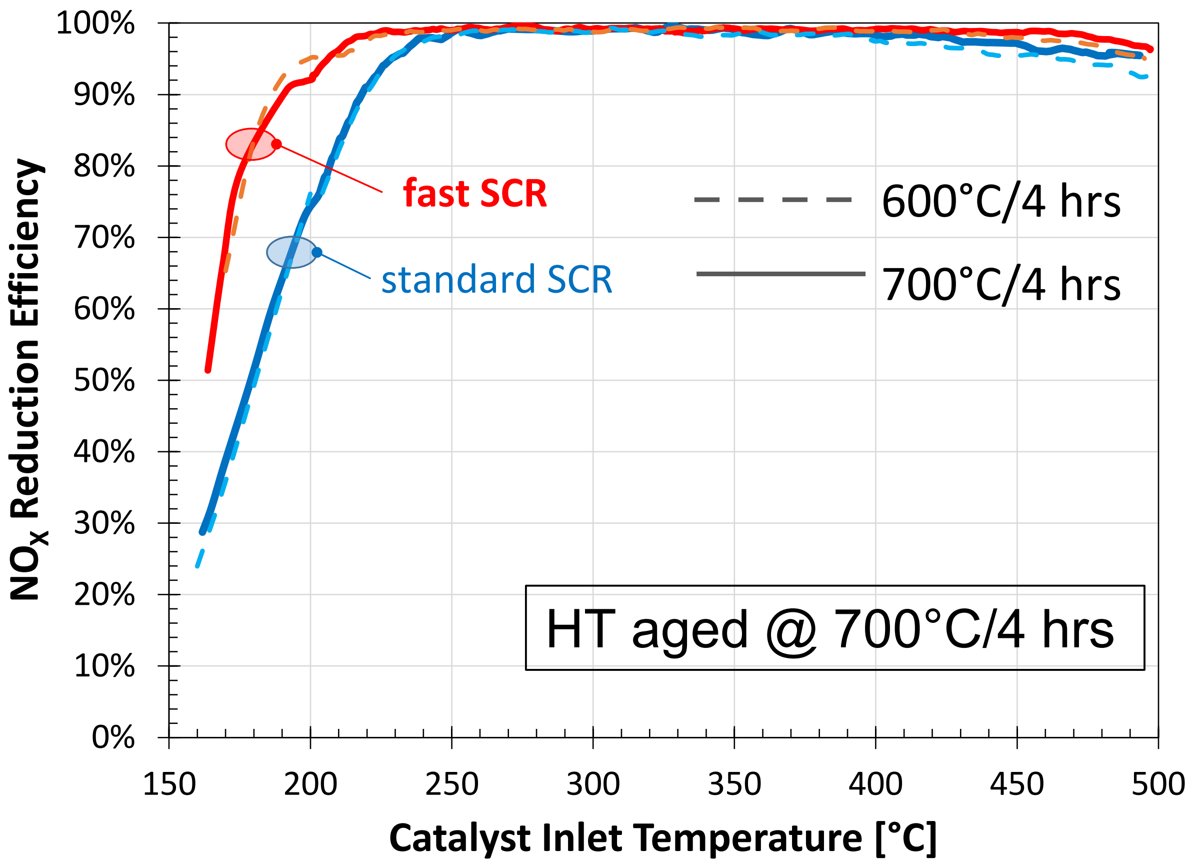
SCR Update (Monolith Bench Testing on 1st Gen. SCR)



12% O_2
6% CO_2
6% H_2O
300 ppm NO_x
300 ppm NH_3

35000 GHSV

Core size: 1-in OD, 2.4 in L

Sample Pretreatment
Core 1 – 600°C/4-hrs
Core 2 – 700°C/4-hrs

NH_4NO_3 poisoning observed at 170°C and below with both core samples

- Fast SCR shows 75-80% NOx conversion efficiency at 175°C.
- Successfully transferred formulation to monolith.
- 700°C aging shows little hydrothermal effect on NOx conversion.
- High temperature activity not compromised.

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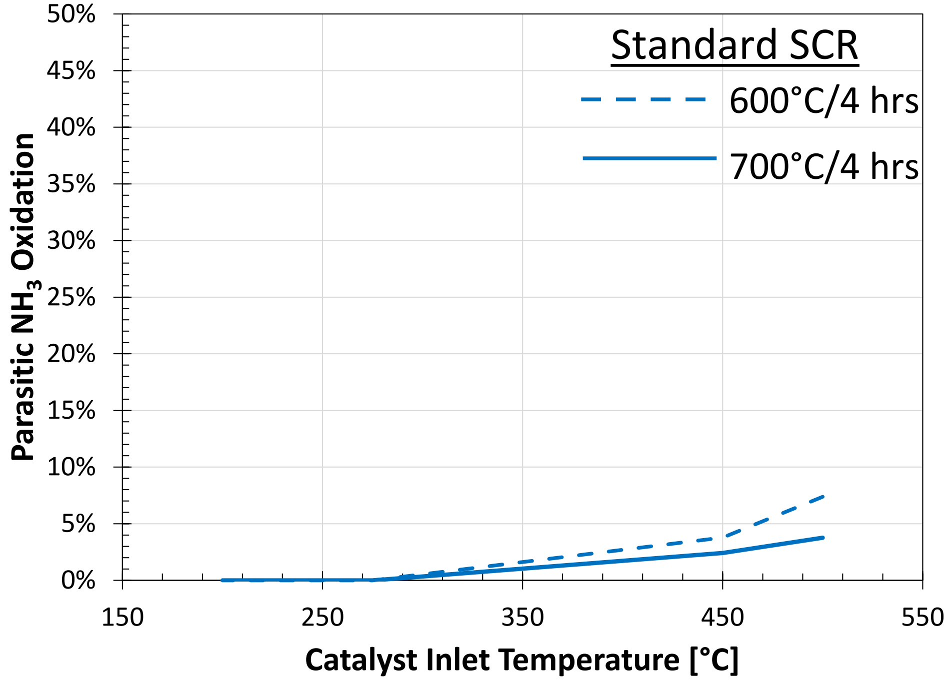
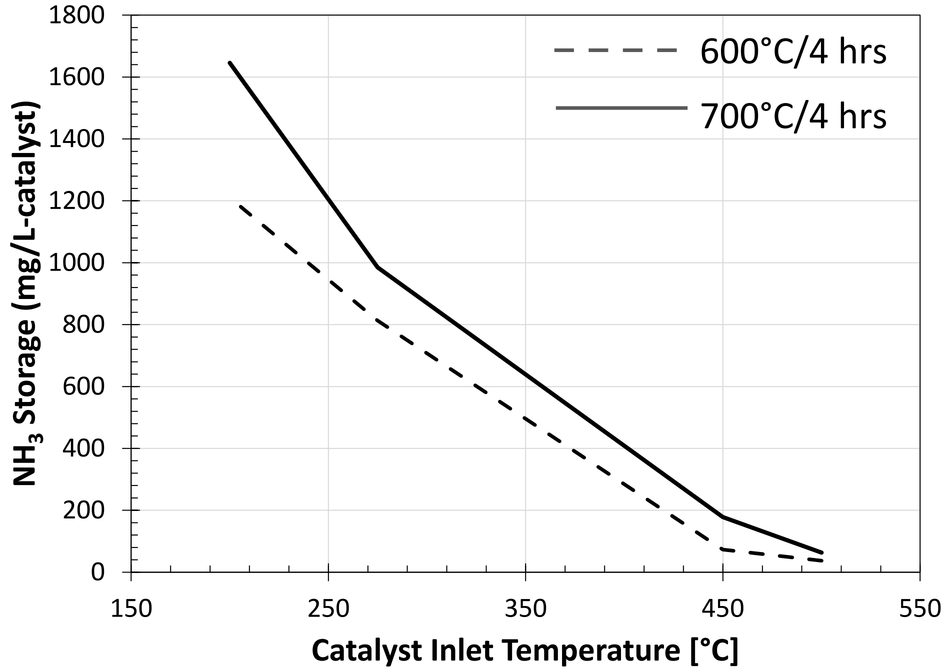
SCR Update (Monolith Bench Testing on 1st Gen. SCR)





Pretreatment (700°C versus 600°C):

- Increased NH_3 storage with temperature ($Cu(OH)^+ \rightarrow Cu^{+2}$).
  - 700°C aging not enough to damage Bronsted Acid sites quickly.
- Decreased NH_3 oxidation.
  - $Cu(OH)^+$ more active for NH_3 oxidation.
- Both desirable characteristics after aging.

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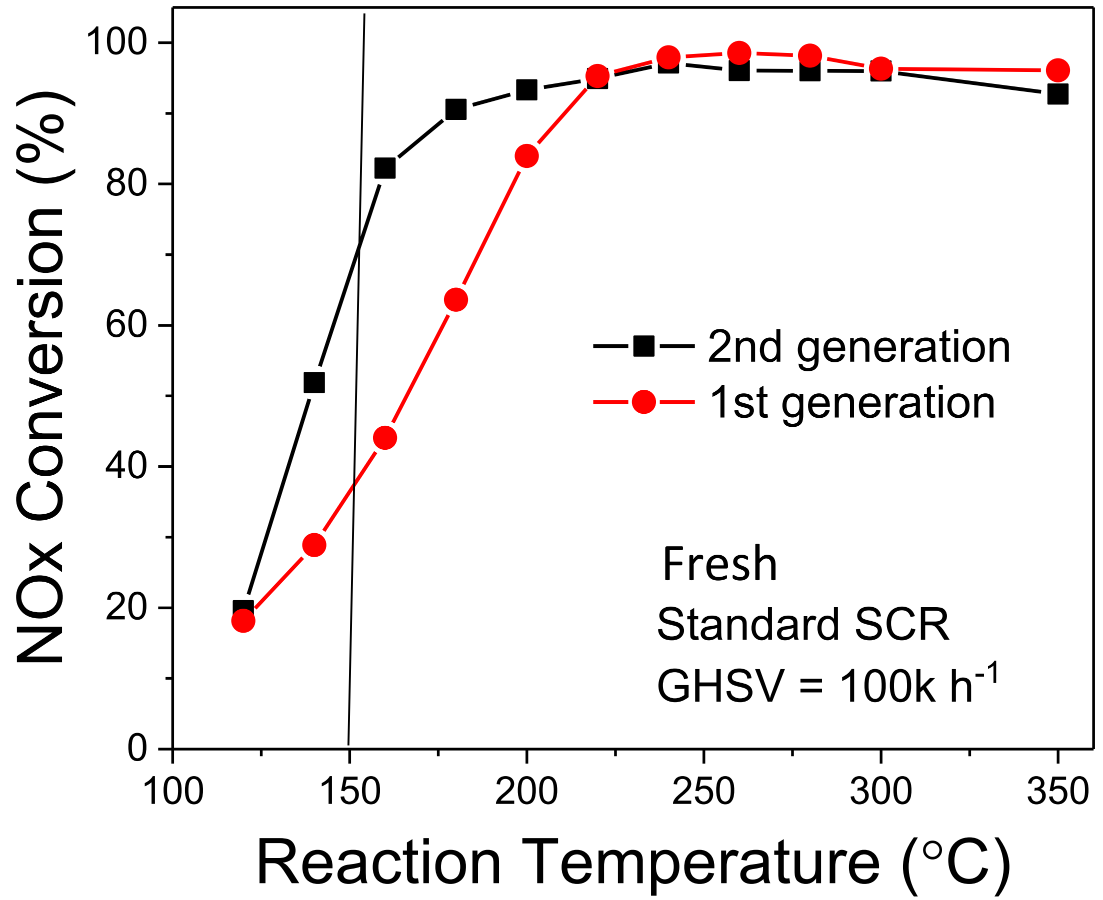
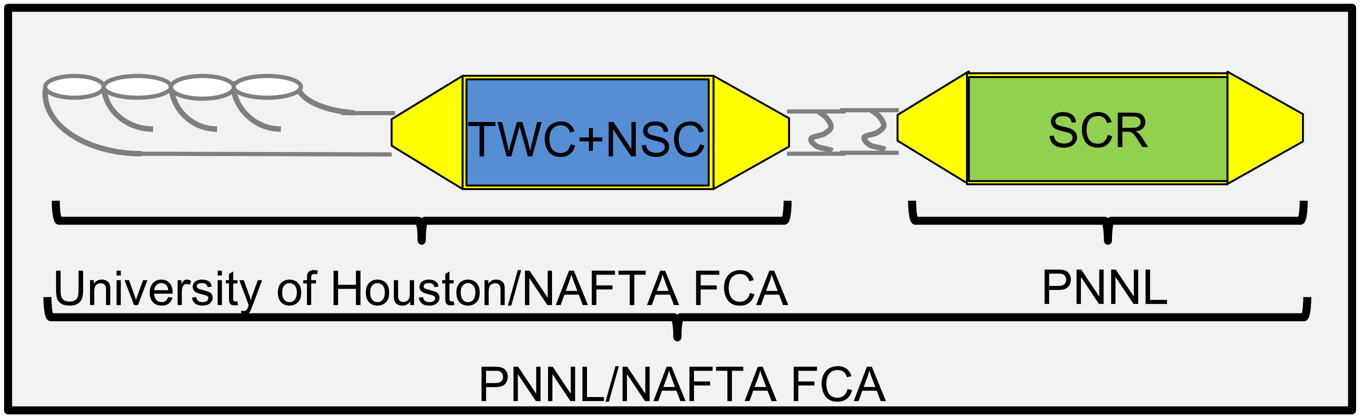
SCR Update (2nd Gen SCR Powder Catalysts)



- New ion-exchange method and a different Cu precursor were used to improve a 2nd generation catalyst for low temperature NOx reduction.
- New Cu SCR Catalyst provides additional active sites and continues to maintain high Cu dispersion.
- 2nd generation catalysts with high Cu loading lead to **~80% NO conversion at 150°C**, while the 1st generation was ~40%.

Technical Accomplishments:

SCR System Integration – Upstream SCR NOx Control Requirements



TWC+NSC (Tri-functional):

- Low temperature lightoff of CO/HC oxidation
- NOx storage/release/reaction
- NH_3 generation for SCR

TWC+NSC (Considerations):

- Durability
- Low temperature selectivity toward N_2O
- Sulfur tolerance and effects
- Fuel penalty for regeneration and NH_3 regeneration

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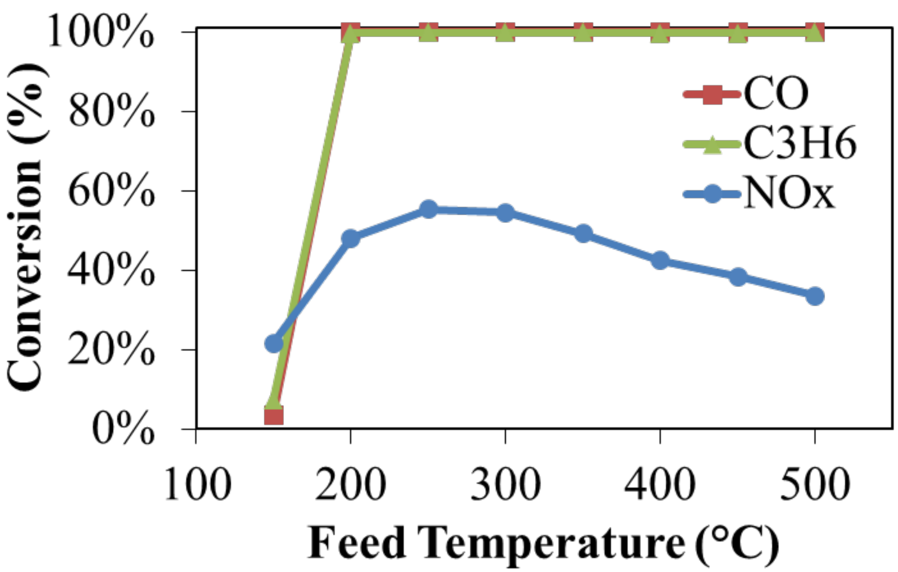
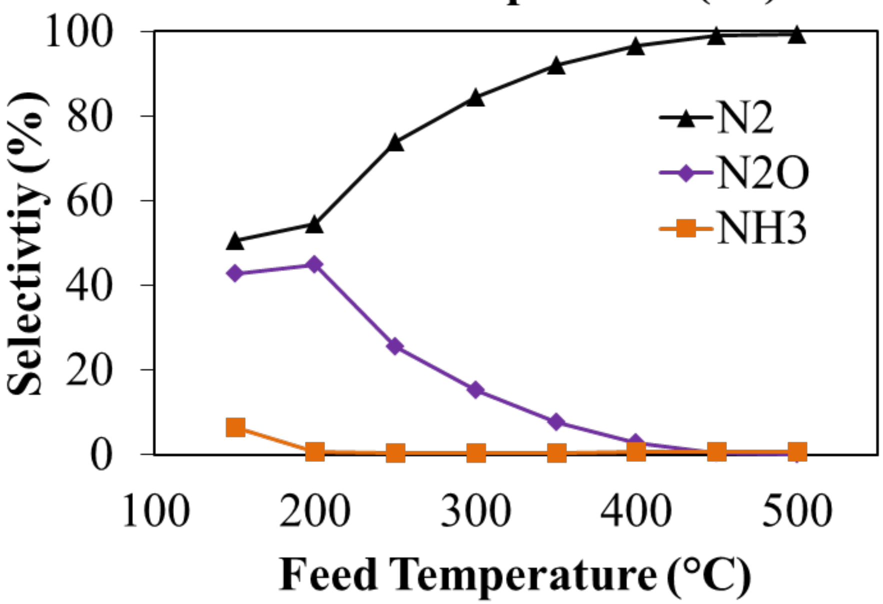
Technical Accomplishments:
TWC+NSC Characterization - (Kinetic Model Considerations (T))





Feed (S_N=1.01):

500ppm NO
1% CO
3300ppm H_2
1000ppm C_3H_6
7% H_2O
10% CO_2

- ~ Stoichiometric feed
- Low temp CO/HC lightoff
- NOx conversion maximum at 60%
- Window for NOx activity

NOx selectivity

- Selectivity to NH_3 minimal near λ≈1
  - Selectivity to NH_3 much higher under rich condition
- N_2O selectivity greatest below 300°C
- During regeneration conditions, GHG requirements were impacting the TWC+NSC catalyst selection

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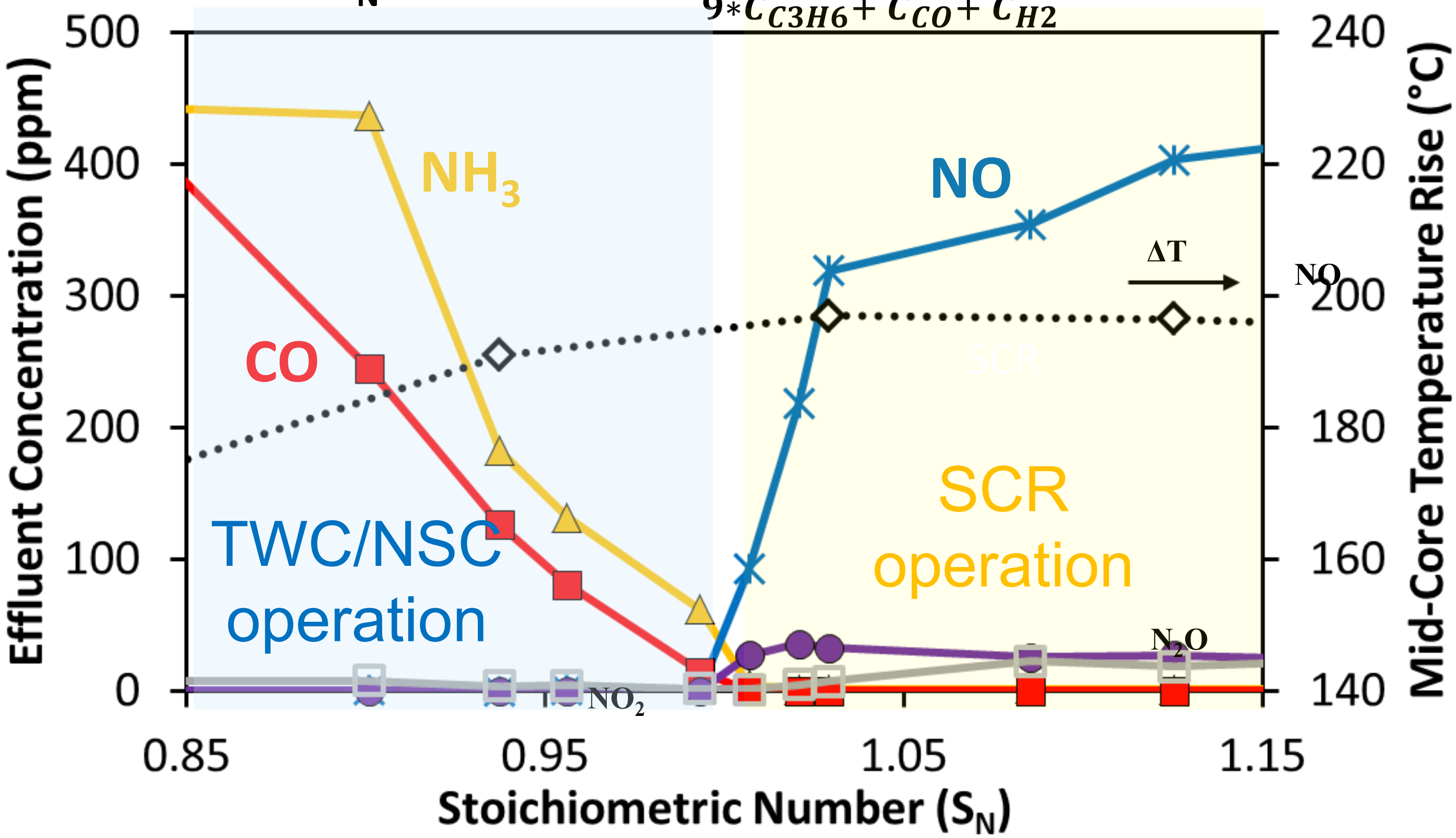
Technical Accomplishments:

TWC+NSC Characterization - (Kinetic Model Considerations (λ))

$$S_N = 0.85\text{—}1.15 = \frac{2*C_{O2}+C_{NO}}{9*C_{C3H6}+C_{CO}+C_{H2}}$$



T_{inlet} = 270°C

Feed:

500ppm NO
1% CO
3300ppm H_2
1000ppm C_3H_6
7% H_2O
10% CO_2
Var. O_2

TWC+NSC Functional Window

- Must complement SCR window of operation
- Provide CO/HC oxidation at low temperature and high efficiency
- Switch to NH_3 generation quickly (manage OSC content)
- Minimize N_2O generation

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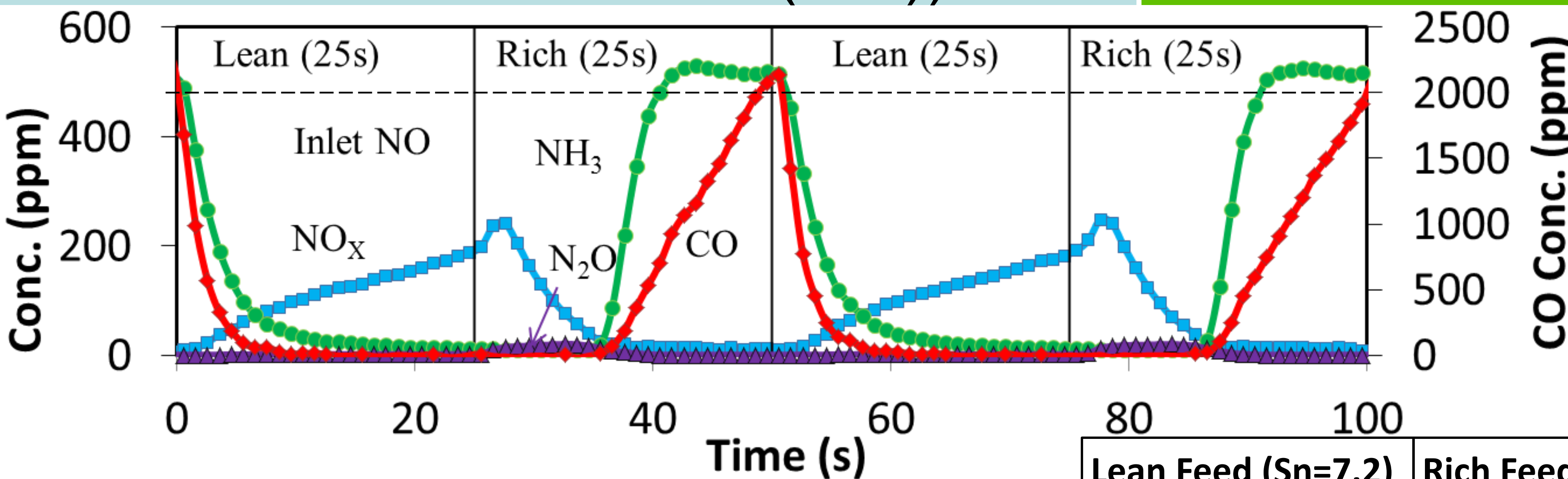
Technical Accomplishments:
TWC+NSC Characterization - (Kinetic Model Considerations(R/L))



Lean Feed (Sn=7.2)	Rich Feed (Sn=0.49)
7% H_2O, 10% CO_2	7% H_2O, 10% CO_2
500ppm NO	500ppm NO
5% O_2	**0.3% O_2**
1% CO, 0.33% H_2	1% CO, 0.33% H_2

Feed temperature = 270°C
Total Cycle Time = 50s
Lean Time = Rich Time = 25s

Example of cyclic operation:

- 81% Lean NOx Storage eff. measured as:
  $$\frac{C_{NO,in} * \tau_L - \int C_{NO,out}\, d\tau_L}{C_{NO,in} * \tau_L}$$
- ANR ~2
- Cycle averaged NO_X conversion ~83%
- NH_3 yield ~44%

Rich/Lean Cyclic Operation →

- Maximize lean duty time
- Minimize rich duty time (fuel penalty)
- Minimize N_2O generation
- Match OSC content to desired

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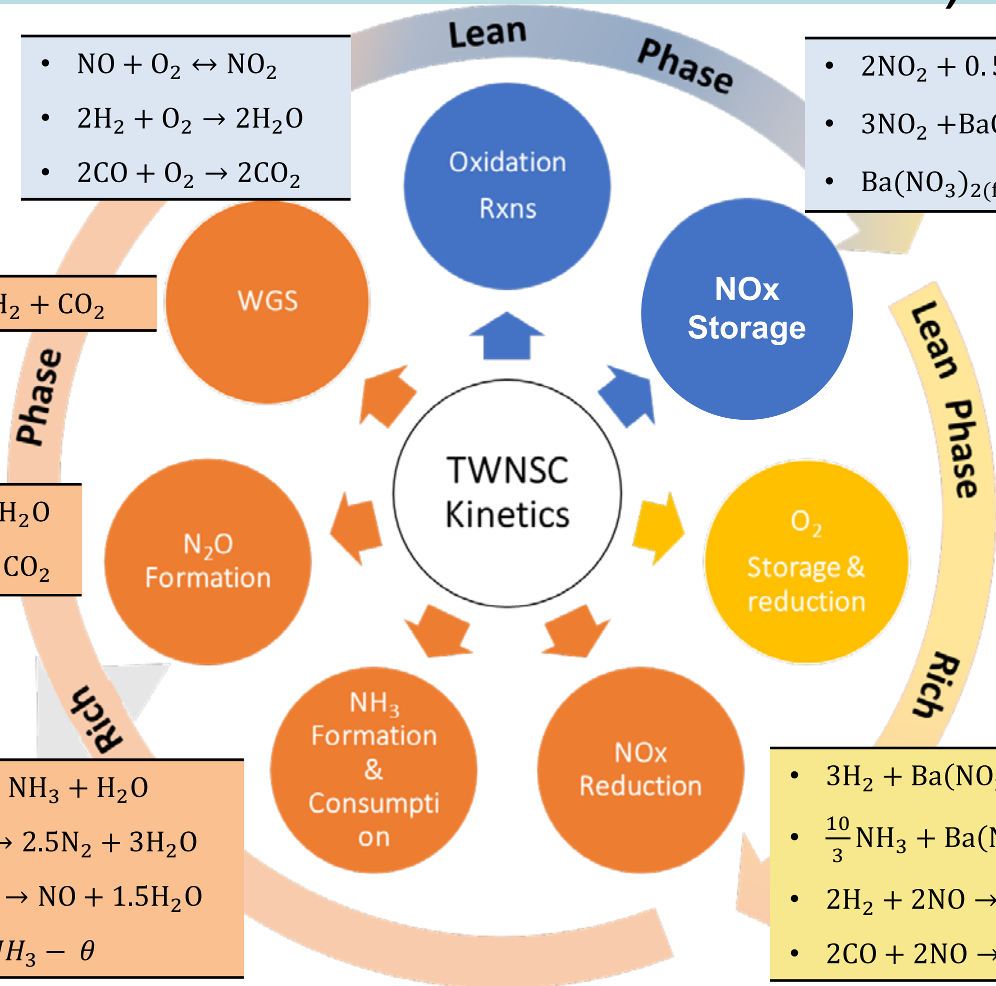
Technical Accomplishments:

TWC+NSC Characterization - (Kinetic Model Rxn Network Addressed)

- $NO + O_2 \leftrightarrow NO_2$
- $2H_2 + O_2 \rightarrow 2H_2O$
- $2CO + O_2 \rightarrow 2CO_2$

- $2NO_2 + 0.5O_2 + BaO_{(f)} \rightarrow Ba(NO_3)_{2(f)}$
- $3NO_2 + BaO_{(s)} \rightarrow Ba(NO_3)_{2(s)} + NO$
- $Ba(NO_3)_{2(f)} \rightarrow 2NO + 1.5O_2 + BaO_{(s)}$

- $CO + H_2O \leftrightarrow H_2 + CO_2$



- $O_2 + 2Ce_2O_3 \rightarrow 4CeO_2$
- $2NO + 2Ce_2O_3 \rightarrow 4CeO_2 + N_2$
- $H_2 + 2CeO_2 \rightarrow Ce_2O_3 + H_2O$
- $CO + 2CeO_2 \rightarrow Ce_2O_3 + CO_2$

- $2NO + H_2 \rightarrow N_2O + H_2O$
- $2NO + CO \rightarrow N_2O + CO_2$

- $NO + 2.5H_2 \rightarrow NH_3 + H_2O$
- $3NO + 2NH_3 \rightarrow 2.5N_2 + 3H_2O$
- $NH_3 + 1.25O_2 \rightarrow NO + 1.5H_2O$
- $NH_3 + \theta \leftrightarrow NH_3 - \theta$

- $3H_2 + Ba(NO_3)_2(f,s) \rightarrow 3H_2O + BaO(f,s) + 2NO$
- $\frac{10}{3}NH_3 + Ba(NO_3)_2(f,s) \rightarrow 5H_2O + BaO(f,s) + \frac{8}{3}N_2$
- $2H_2 + 2NO \rightarrow 2H_2O + N_2$
- $2CO + 2NO \rightarrow 2CO_2 + N_2$

TWC+NSC kinetic model incorporates:

- Rich/lean operation
- Aging effects
- Details of the CO/HC oxidation reactions as well as NOx reduction

NOx Storage: Dual-site construct (fast & slow sites) approximates Pt + BaO proximity and associated stored NOx diffusion limitations

[1] Bhatia et al., J. Catal. (2009)
[2] B.M. Shakya et al. , Chemical Engineering Journal (2014)
[3] K. Ramanathan et al., Ind. Eng. Chem. Res. (2011)

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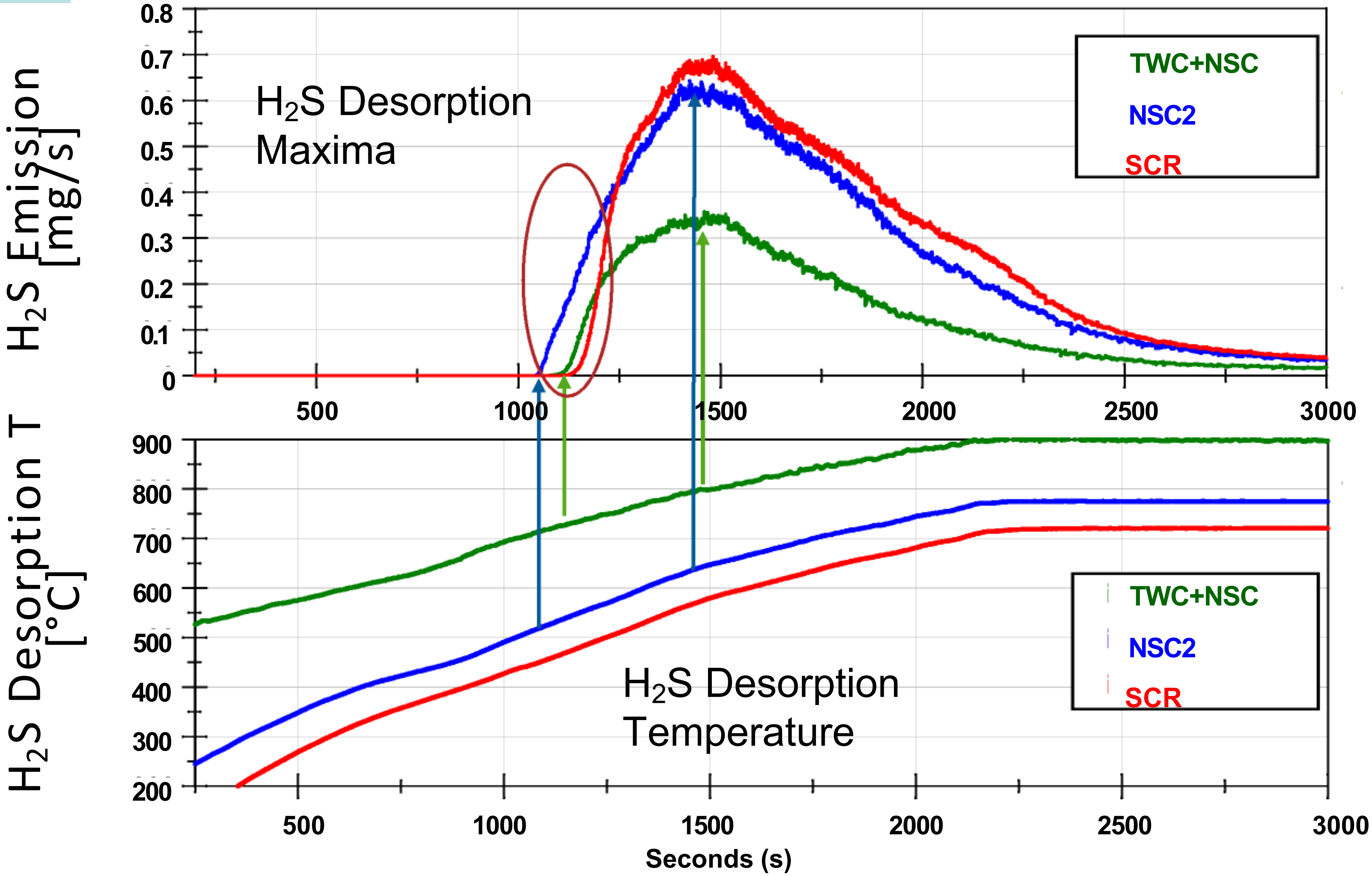
Technical Accomplishments:
System Integration Consideration – TWC/NSC/SCR DeSox Strategy



- Greatest system efficiency requires the simultaneous DeSOx of components
- Formulations manipulated to perform temperature programmed DeSOx

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Technical Accomplishments:

System Integration Consideration – SCR Aging Environment

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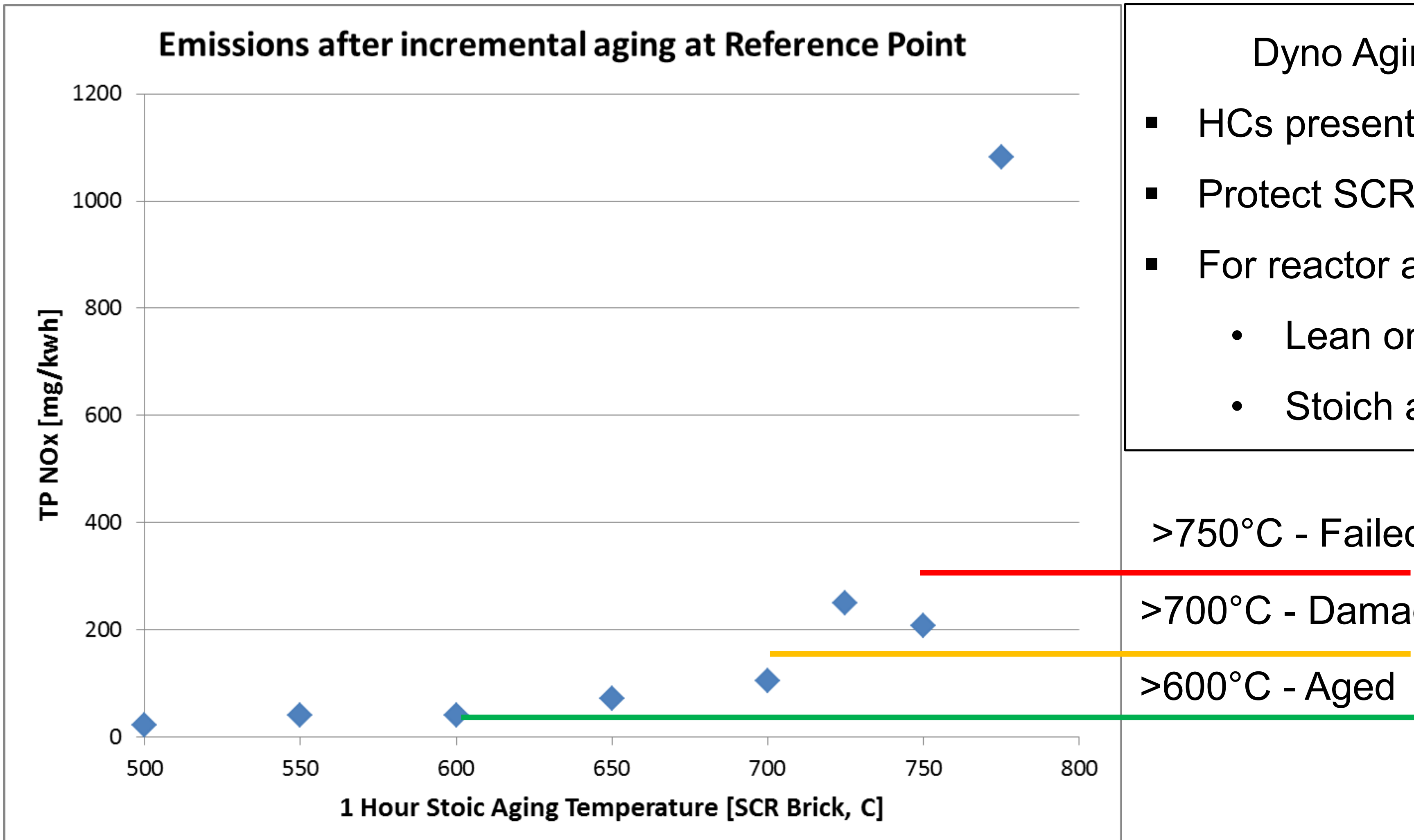

Dyno Aging

- HCs present (stoich)
- Protect SCR @ 700°C
- For reactor aging:
  - Lean only first
  - Stoich after testing

- $\Lambda = 1$ aging reduces time/temperature at which SCR performance degrades
- Standard HT aging not appropriate for passive NOx control systems

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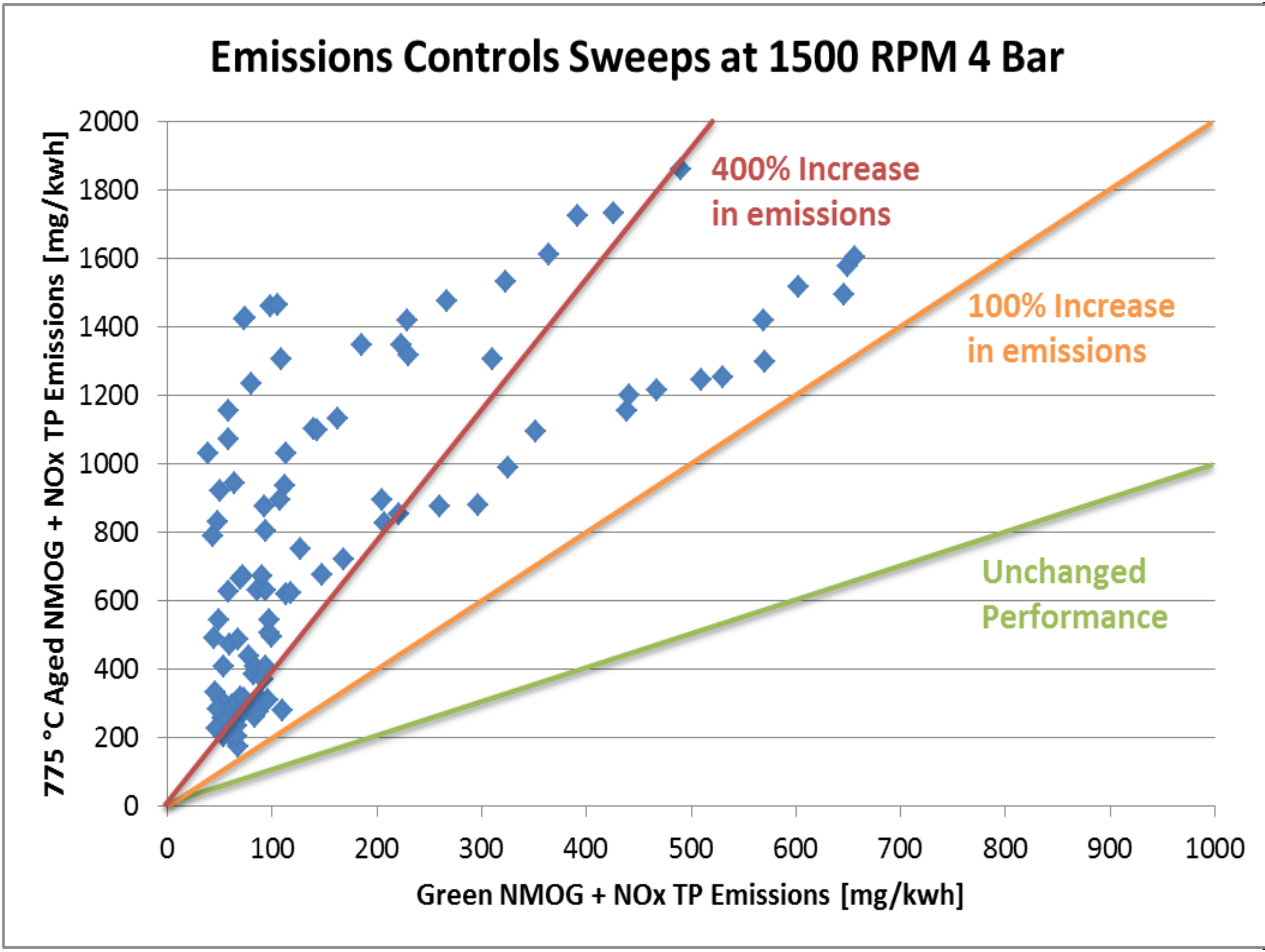
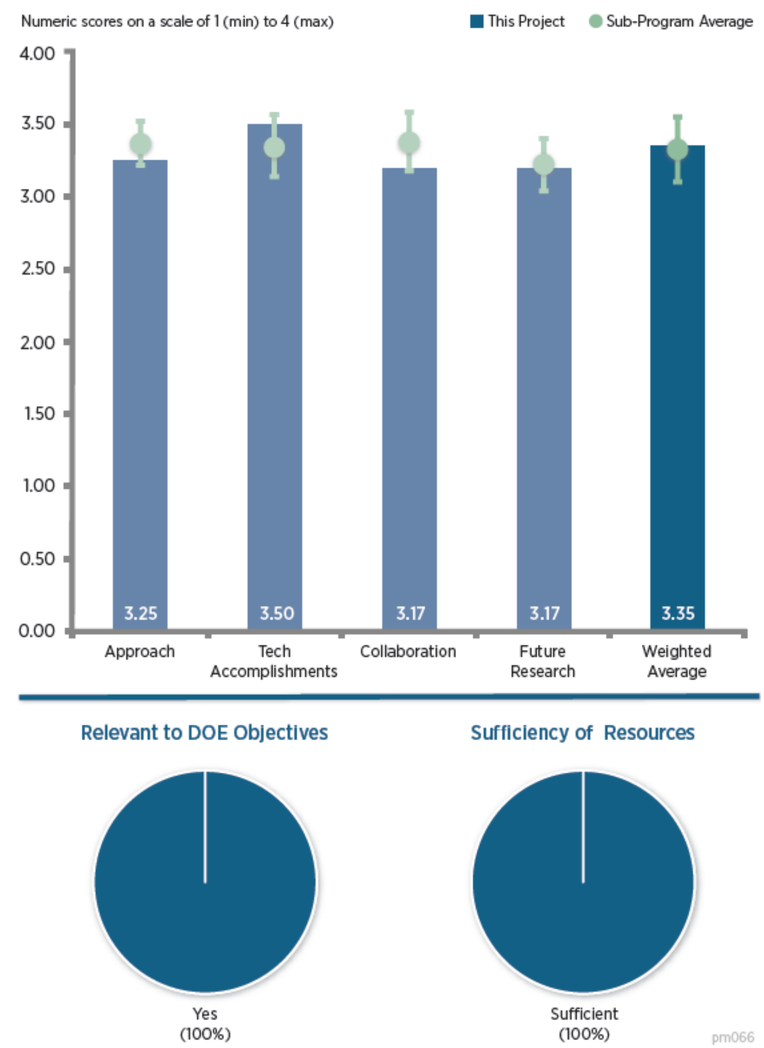
System Integration Consideration – SCR Aging Effects on System Efficiency



- System performance severely damaged at previous best operating point
- Minimum emissions during sweep increases from 38 mg/kWh to 172 mg/kWh
- Majority of degradation from decrease in NOx conversion
- SCR must be protected from high temp under engine operating conditions

Response to Previous Year Reviewers' Comments

- Nearly all the comments from the reviewers last year were very supportive and complimentary.
- Some comments/recommendations included:
  - .. Why a major catalyst supplier is not involved…
  - ...need to add the effect of sulfur on the new formulations…
  - ...washcoat loading of SCR catalyst is very important and should be included in future work…
- Our response:
  - A catalyst supplier is now involved in transitioning SCR catalyst to monolith form and related consultations.
  - Effect of sulfur is being included in the evaluation and development of 2nd generation SCR catalysts.
  - A catalyst supplier is indeed involved in this important area .



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Collaborations/Interactions

PNNL

- Low temperature SCR catalyst development
- Advanced characterizations

FCA US LLC

- Primary upstream NOx control and passive NH_3 generation
- Dyno engine control inputs
- System integration
- Coordinating U of Houston TWC+NSC characterization/kinetic model

U of Houston (Mike Harold)

- Characterization and kinetic model development of TWC+NSC catalyst
- NOx control, NH_3 generation catalyst, regeneration strategies, aging effects

Catalyst supplier (FCA in-kind)

- SCR material transfer to monolith
- Technology consultation

- Conference calls are held typically once every month to discuss progress and direction.
- Bi-annual face-to-face meetings. Latest group review (12/16).

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Planned Future Work

- Development of 2nd generation SCR catalysts to meet the conversion efficiency target.
- Investigate aging stability and sulfur tolerance of 2nd generation SCR catalysts.
- Alternatives to the initial TWC/NSC+SCR catalyst for NOx control and NH_3 generation.
- Optimize system integration efforts and durability.

Summary

- Demonstrated lightoff of the 1st generation SCR catalyst is improved over industry standard (>75% NO_x @ 175°C).
- Successfully synthesized a large batch of Cu/SSZ catalyst and transferred the material to a monolith for pre-vehicle evaluation.
- Bench reactor testing of SCR monolith confirmed performance.
- Identified and successfully applied a research direction for development of a 2^{nd} generation SCR catalyst (80% conv. @150°C).
- Down selected alternatives to urea NH_3 generation.
- Derived a kinetic model to predictively control the function of a TWC+NSC catalyst technology for NOx control & NH_3 generation.
- Established dyno test baseline system (TWC/NSC + SCR).