Innovative SCR Materials and Systems for Low Temperature Aftertreatment

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Project Overview

Timeline

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

Budget

- DOE funding:

  $500K/Year for a total of $1.5M
- FCA US LLC (in-kind):

  $500K as per CRADA agreement

Barriers

- 2.3.1.B Lack of cost-effective emission control
- 2.3.1.E Durability of emissions control devices
- Low temperature performances

Partners

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

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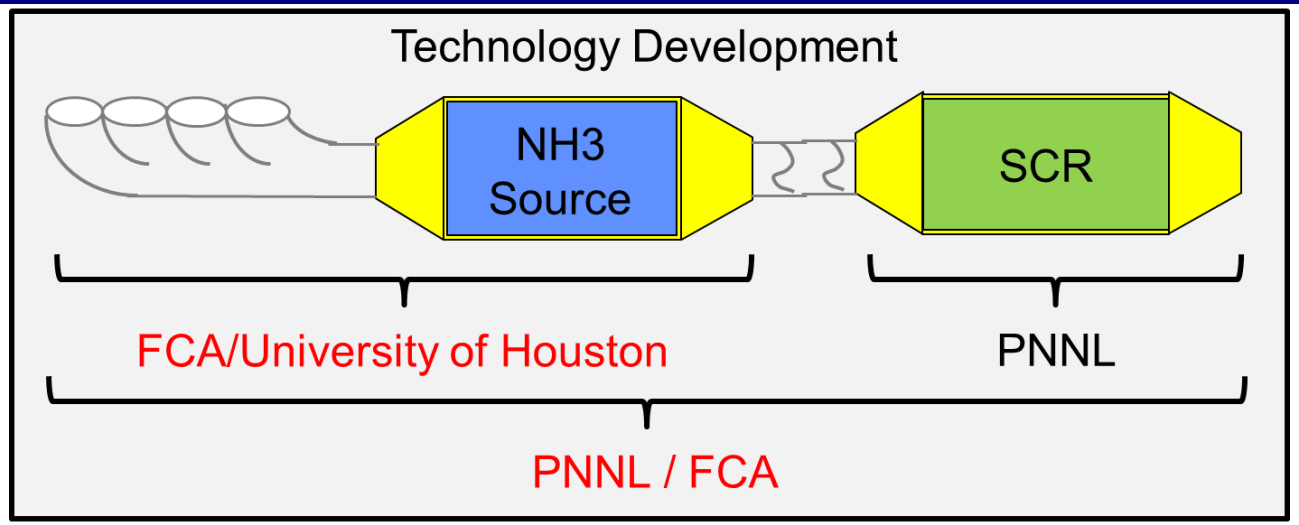
Relevance

- Address the 150°C Challenge identified from the 2012 USCAR workshop.
- Focus on providing a new 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 system development at FCA US LLC.

Milestones

- ✓ **Milestone 1 (1.1.1)**: Complete synthesis of small batches of various catalysts and a large batch of the best catalyst (Sept, 2015).
- ✓ **Milestone 2 (1.1.2)**: Complete initial performance tests (Dec., 2015).
- ✓ **Milestone 3 (1.1.3):** Determine optimized composition of the first generation low-temperature SCR catalyst (March, 2016)
- ✓ **Milestone 4 (1.1.4)**: Deliver a large batch of first generation SCR catalyst (April, 2016)
- **Milestone 5 (1.2.1):** Initiate the synthesis of second generation SCR catalyst (Sept., 2016) – on track
- **Milestone 6 (3.2):** Operational status of NH_3 generation - incorporated baseline NH_3 generation catalyst into engine dyno exhaust aftertreatment (June, 2016) – on track

Approach/Strategy



CRADA Partner Project Areas of Responsibility:

- FCA – Primary passive NH_3 generation & system integration, supplemental NOx control
- PNNL – Primary low temperature SCR development, supplemental system integration

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

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Approach/Strategy, cont'd

Adapt a newly developed SCR material to provide 90% conversion efficiency of NO_x at near 150˚C under conditions consistent with low temperature portions of drive cycles such as the FTP cycle in the US:

- Demonstrate selectivity toward N_2 formation of 90%
- Demonstrate the SCR catalyst, aged under realistic conditions, will continue to provide 90% conversion efficiency at near 150˚C
- Evaluate the SCR catalyst activity using a matrix of both passive and active NH_3 sources

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

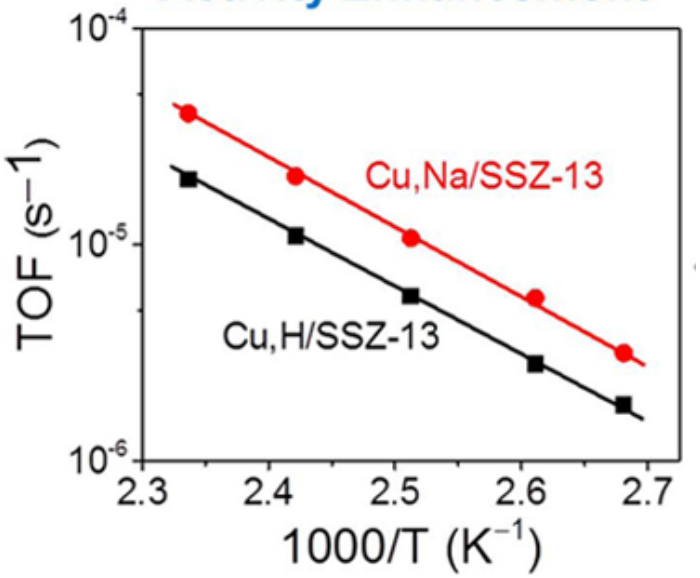
- Compare the NO_x reduction efficiency and selectivity toward N_2 formation of the SCR system using both active and passive NH_3 generation strategies
- Determine the fuel penalty associated with each strategy
- Estimate the control/OBD complexity and cost
- Estimate the component and system cost

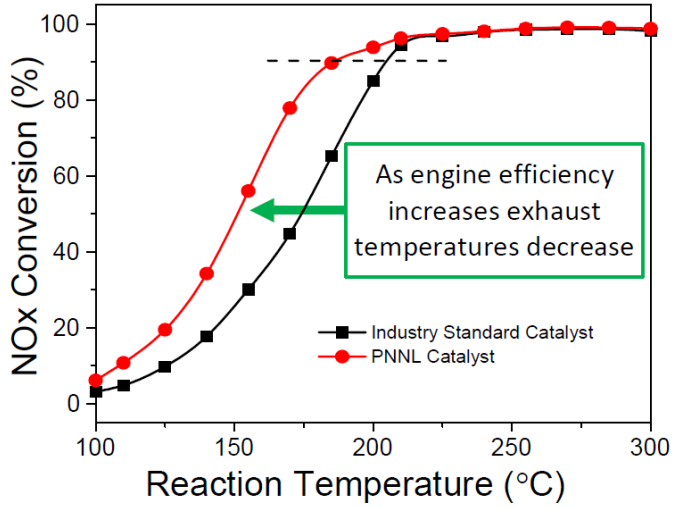
Technical Accomplishments

- Demonstrated >90% NO_x conversion efficiency at 175ºC with 1st generation catalyst, much improved as compared to the current commercial catalysts.
- Identified research direction for the development of 2nd generation catalysts.
- Synthesized a large batch of Cu/SSZ catalyst for the preparation of washcoat and hydrothermal aging testing of core samples.
- Downselected on a possible alternative (to urea) NH_3 generation strategy and identified the operation characteristics of NH_3 generation catalyst.

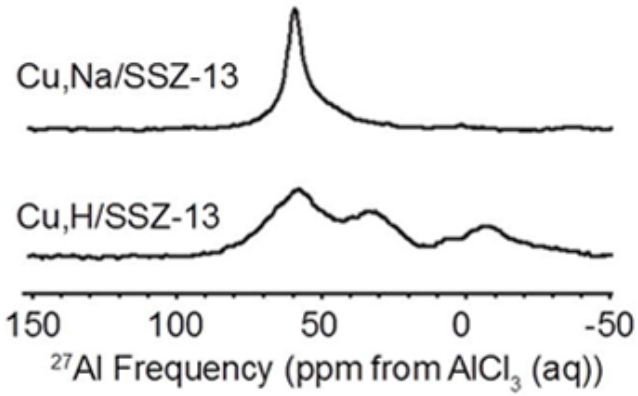
Co-cation Effects at Low Cu Loadings

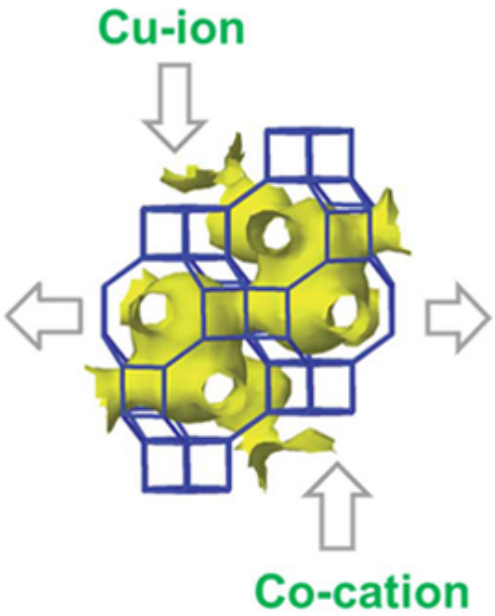
Activity Enhancement





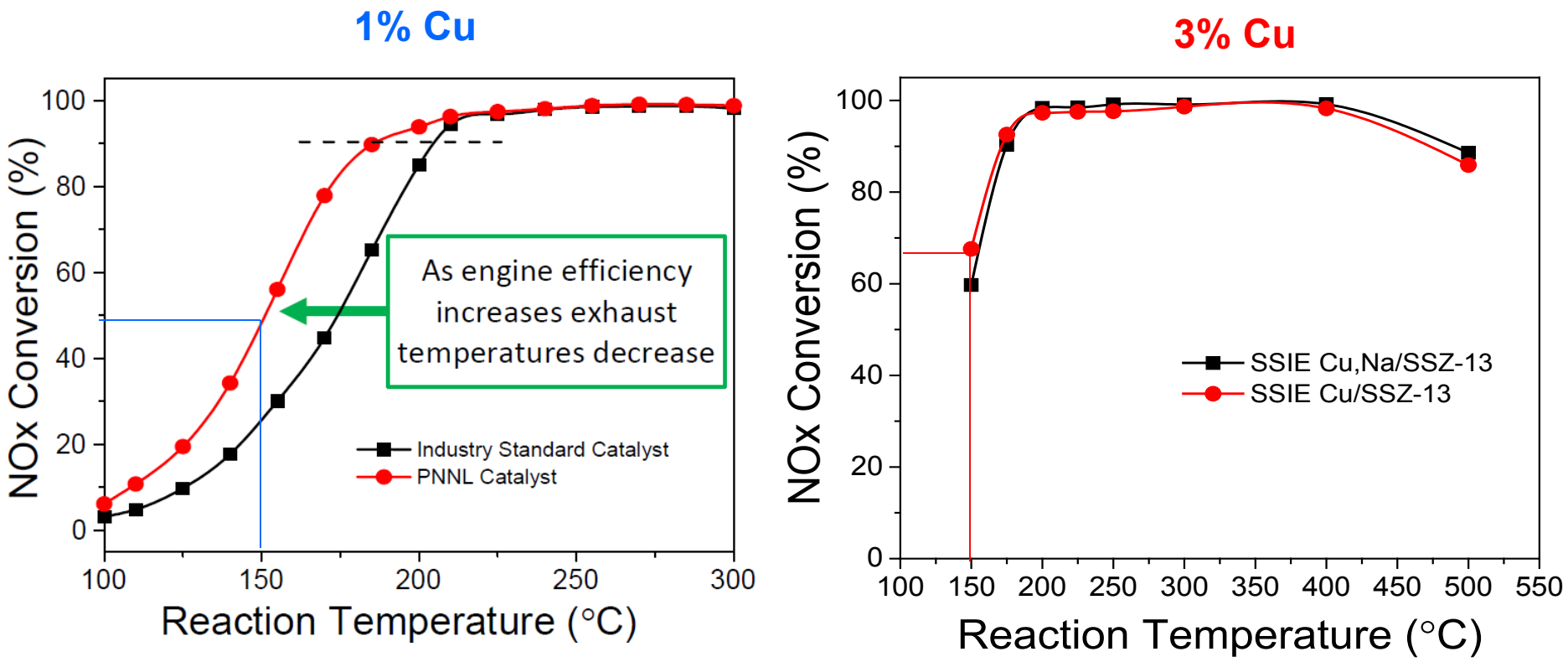
Stability Enhancement





- At Si/Al = 6 and low Cu loading (~1wt%) conditions, the addition of alkali and alkaline earth improves both low-temperature NO_x conversion and catalyst hydrothermal stability.

Co-cation Effects at High Cu Loadings



- High Cu loading (from ~1wt% to ~3wt%) favors NO_x conversion (from ~50% to ~66%).
- However, at high Cu loading, the presence of a cocation (e.g., Na) sacrifices the optimized Cu dispersion/location.

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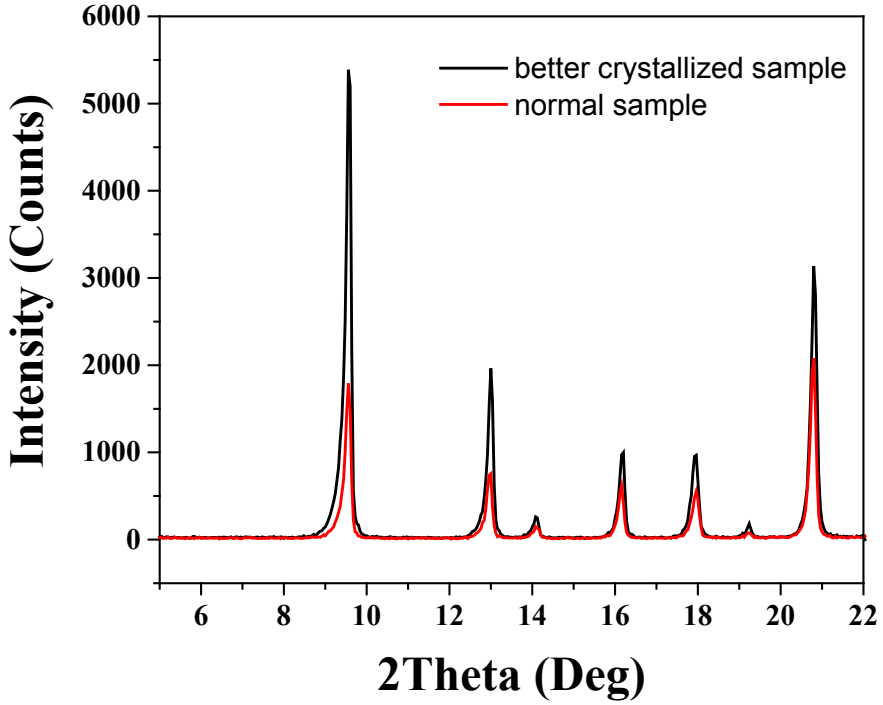
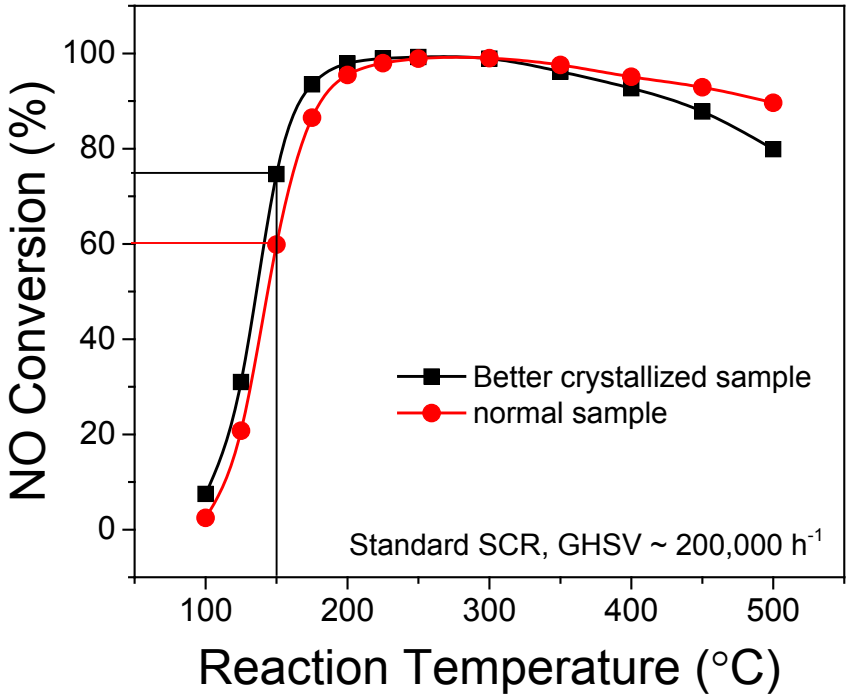
Improvement of SCR Activity by Crystallinity

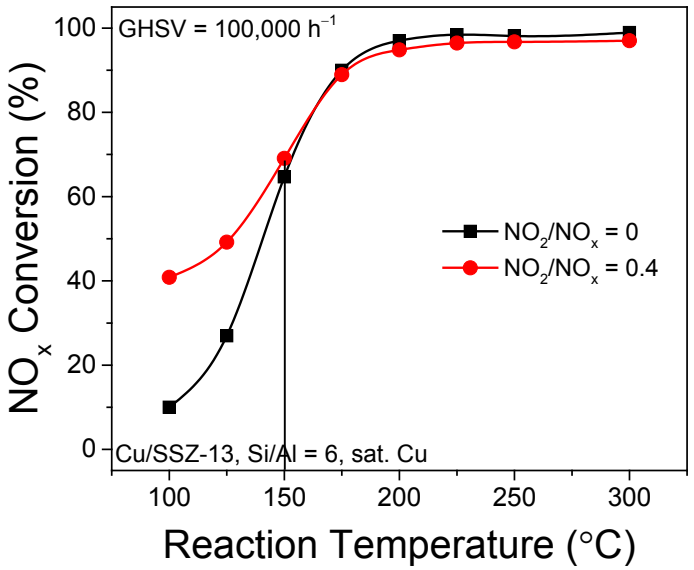




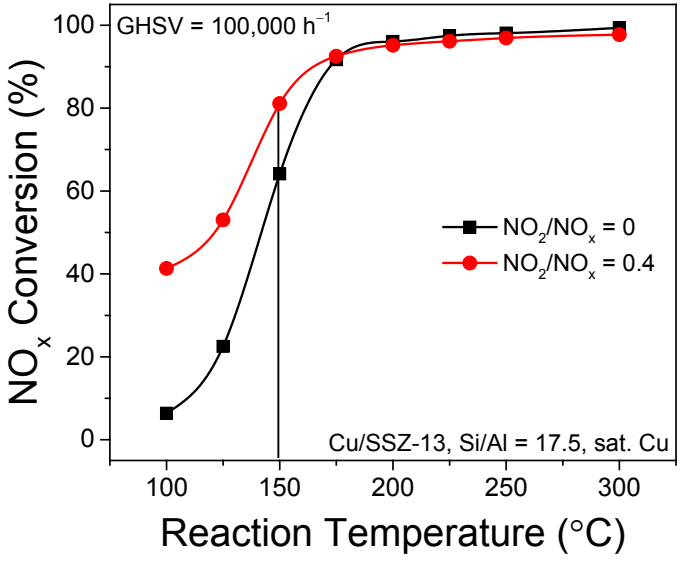
- Adjusting Si/Al ratio is limited by the hydrothermal stability.
- At Si/Al = 12, increase in crystallinity appears to be beneficial for the low-temperature activity, achieving ~75% NO conversion at 150ºC.

Improvement of SCR Activity by NO_2

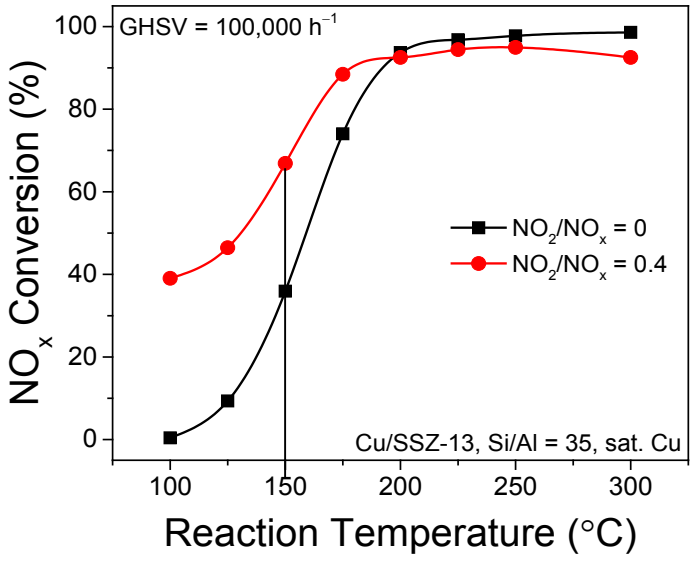
Si/Al = 6



Si/Al = 17.5



Si/Al = 35



- The presence of NO_2 promotes low-temperature NO_x conversion at high Si/Al ratio due to less poisoning by NH_4NO_3.
- At Si/Al = 17.5 and NO_2/NO_x = 0.4, ~80% NO conversion is achieved at 150ºC
- Requirement of NO_2 certainly will complicate NH_3 generation strategy.

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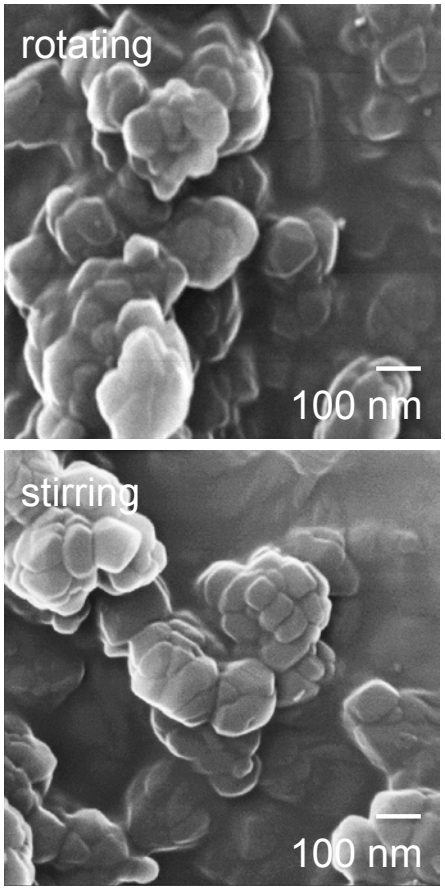
Large autoclave (0.7L)
(stirring, sampling)

Rotated autoclaves (0.12L)

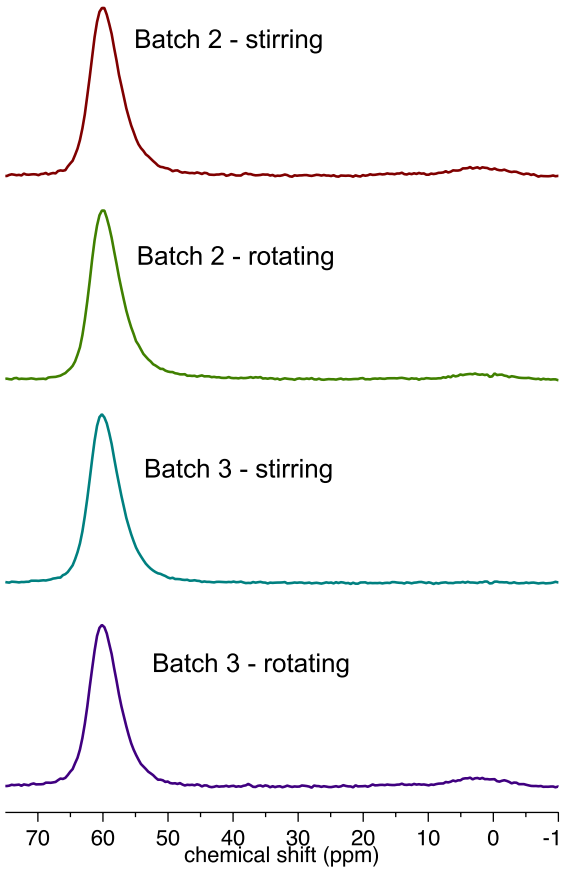
14 batches needed (~750 g)

- Existing capabilities at PNNL were used to synthesize >500g Cu/SSZ catalyst :
  - BET Surface Area 540 m^2/g;
  - t-plot micropore volume: 0.267 cm^3/g;
  - Element analysis from ICP: Cu~1.84 wt%.

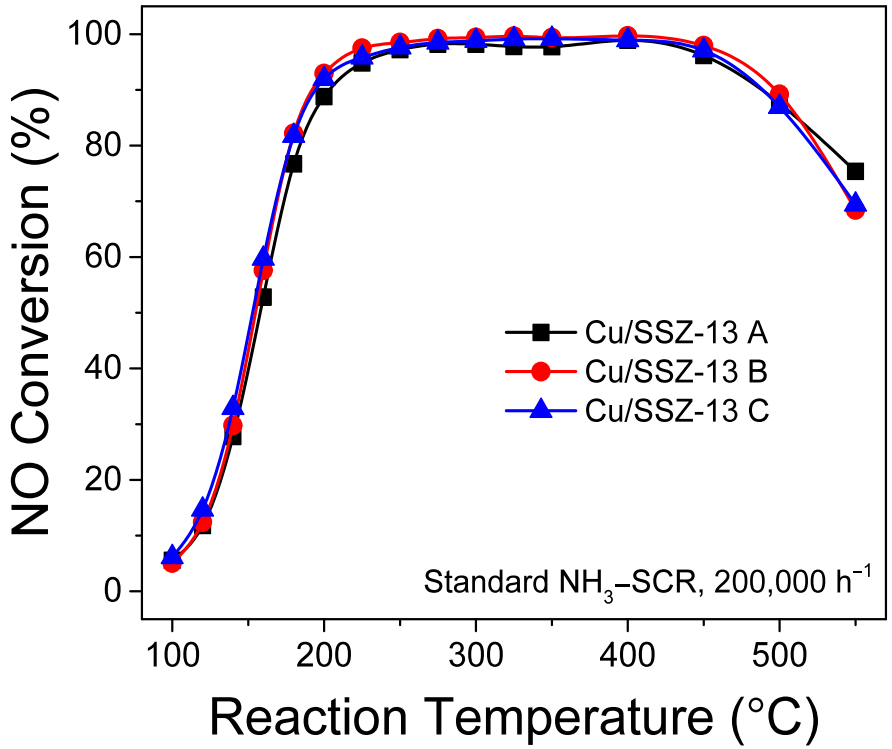
Helium Ion Microscopy (HIM)



^{27}Al-MAS-NMR

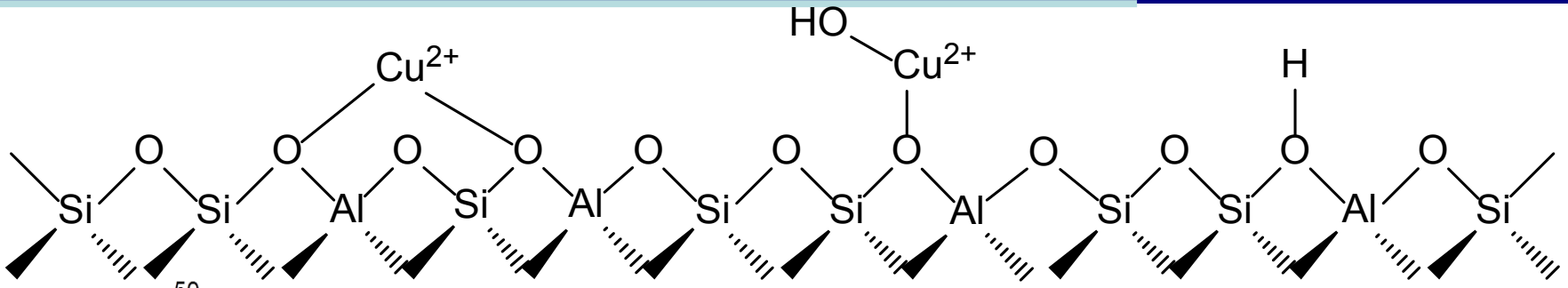


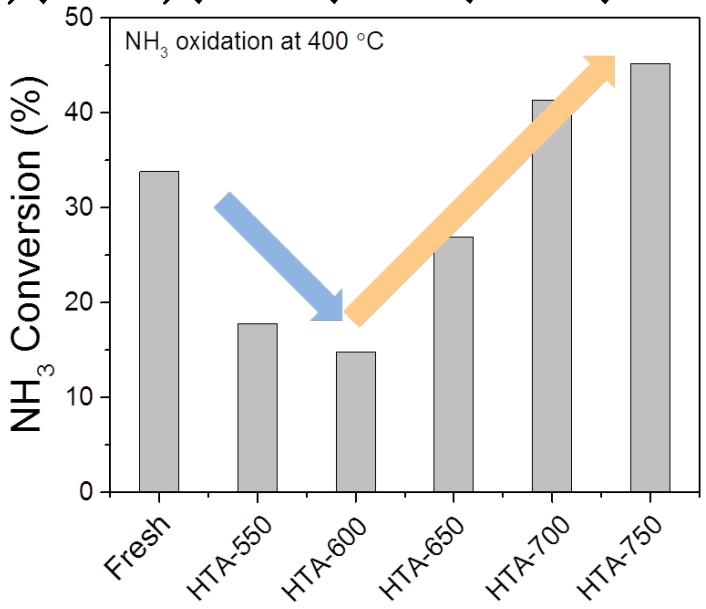
SCR Reaction

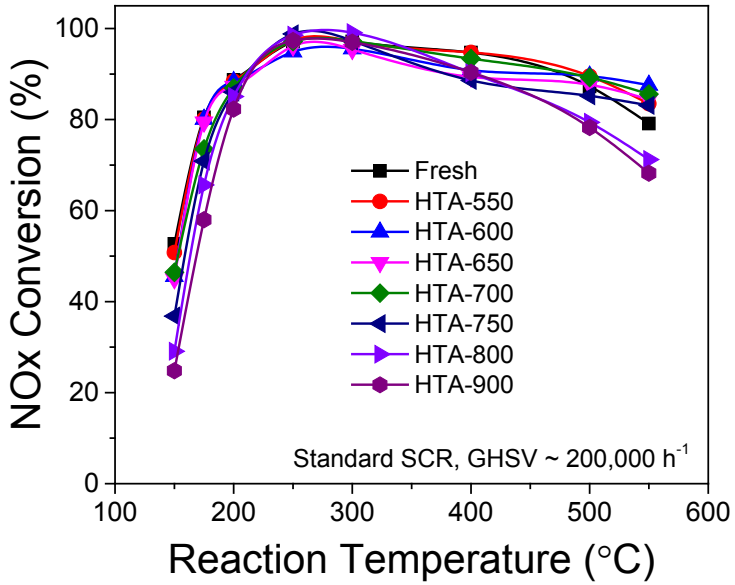


- Characterizations (HIM, N_2 physisorption, XRD, ^{27}Al-MAS-NMR etc) show similar crystallinity, morphology, phase purity, and structure among different batches with stirring or rotating.
- There is no difference in measured SCR activity.

Hydrothermal Aging of a Large Batch of Cu/SSZ Catalyst (1st generation)







- Si(OH)Al hydrolysis occurs as low as 550 ºC, leading to a lower NH_3 storage.
- At >600ºC, migration and agglomeration of Cu(OH) results in the formation of CuO_x, which is highly active in catalyzing NH_3 oxidation.
- Kinetic studies and characterizations (e.g., EPR) are being conducted to validate the stability of Cu^{2+} -2Al.

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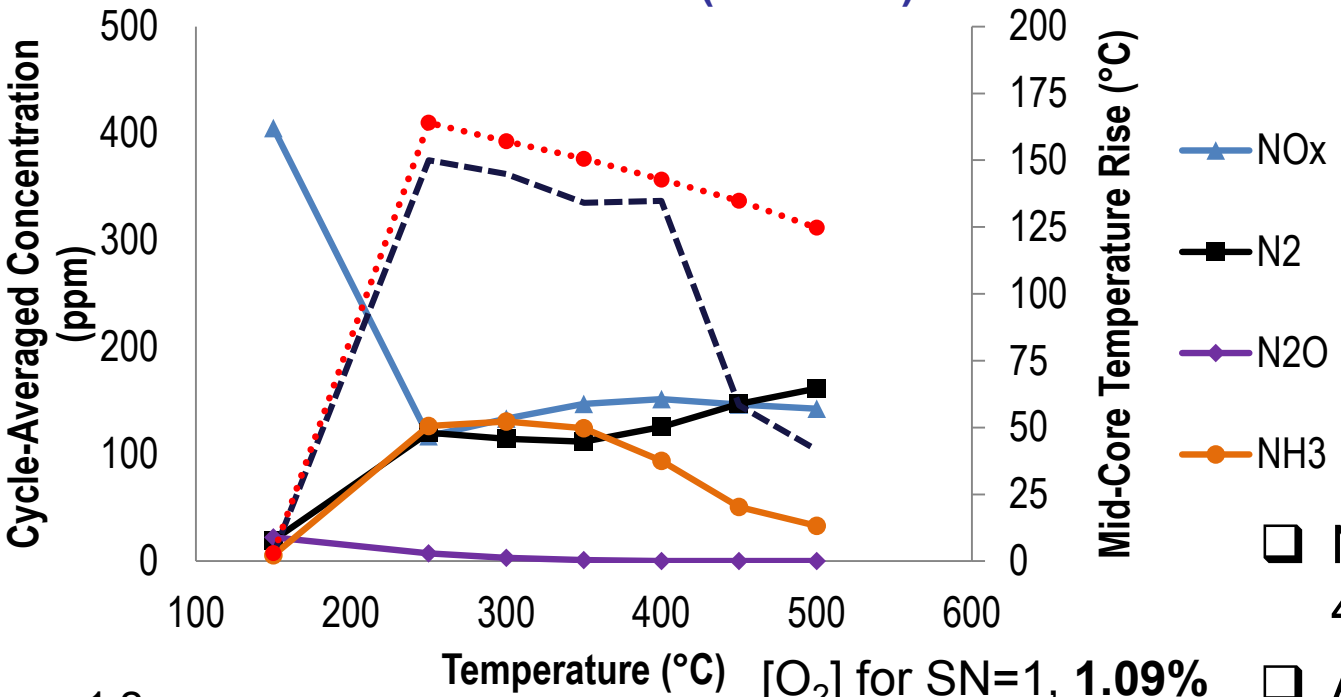
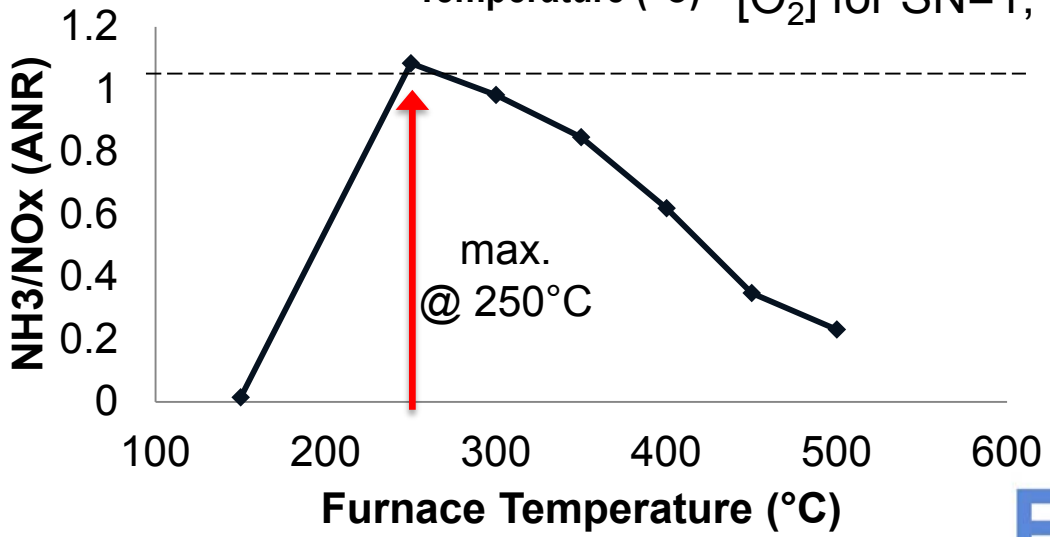
Technical Accomplishments: NH_3 Generation and NO_x Reduction

Transient Behavior (20L-40R)



Lean Feed	Rich Feed
500 ppm NO	500 ppm NO
1K ppm C_3H_6	1K ppm C_3H_6
3.3K ppm H_2	3.3K ppm H2
1% CO	1% CO
7% H_2O	7% H_2O
10% CO_2	10% CO_2
1.3% O_2	**1% O_2**



[O_2] for SN=1, **1.09%**

- NH_3 is generated in the 250 – 400ºC window.
- ANR reaches max at 250ºC.
- Highest mid-core temperature rise is associated with max NH_3 formation.
- Very little N_2O formation.
- Max NO_x reduction is ~80%.

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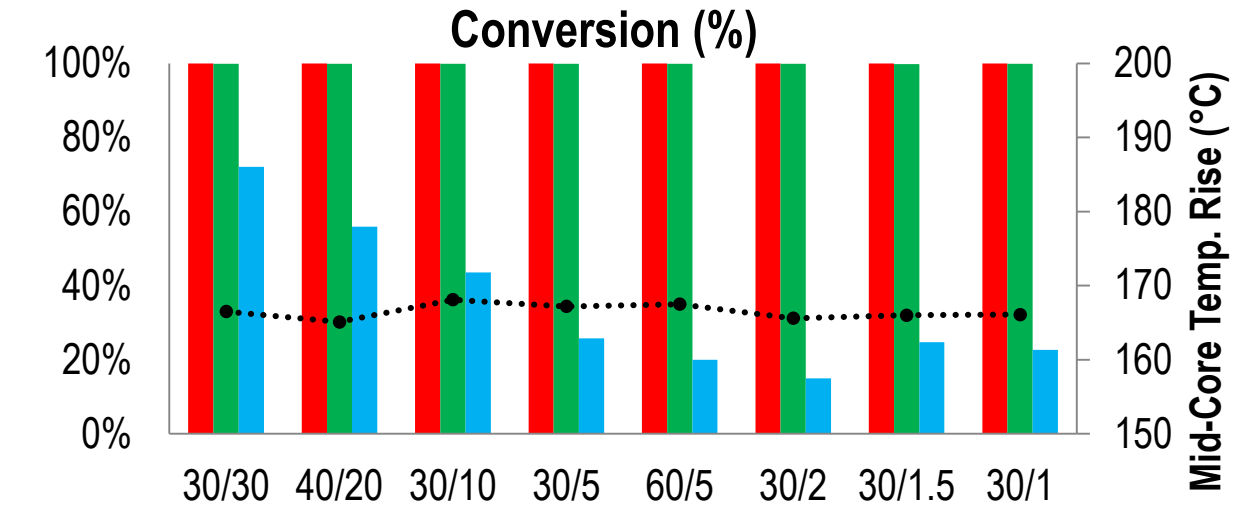
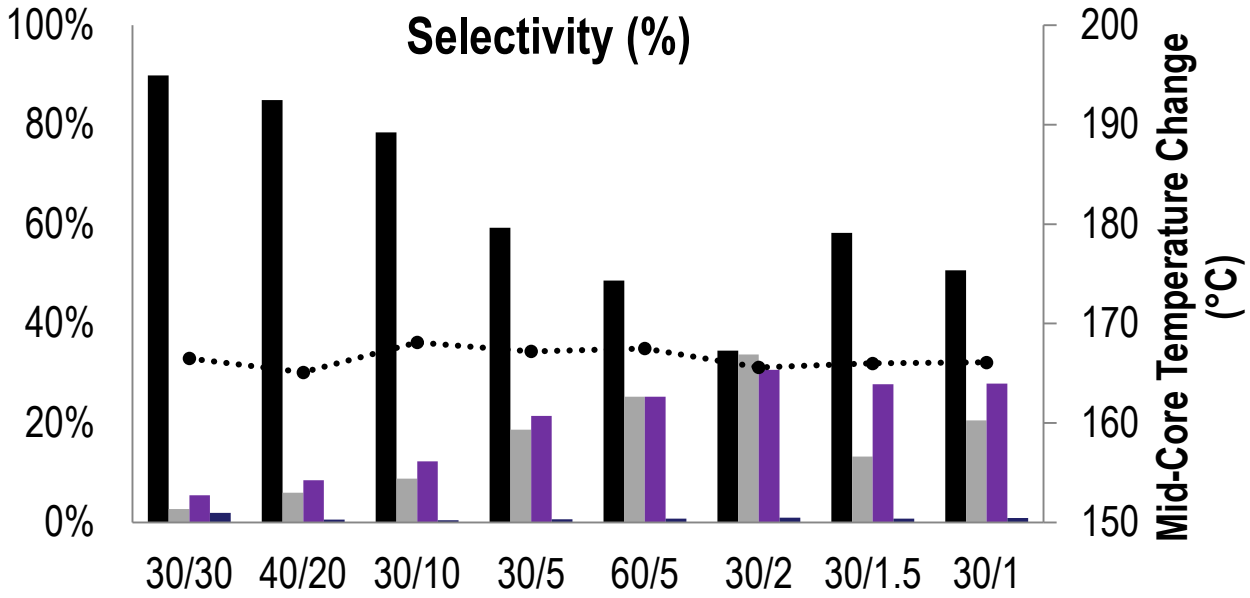
Technical Accomplishments: NH_3 Generation and NO_x Reduction at Various L-R Cycles (250ºC)





- Low L/R cycles favor NH_3 and N_2 yields.
- High L/R cycles produce more N_2O.
- No NH_3 is produced at high L/R ratios, and fuel economy needs to be considered.
- Tailor catalyst to minimize rich phase to produce NH_3 without significant N_2O formation.

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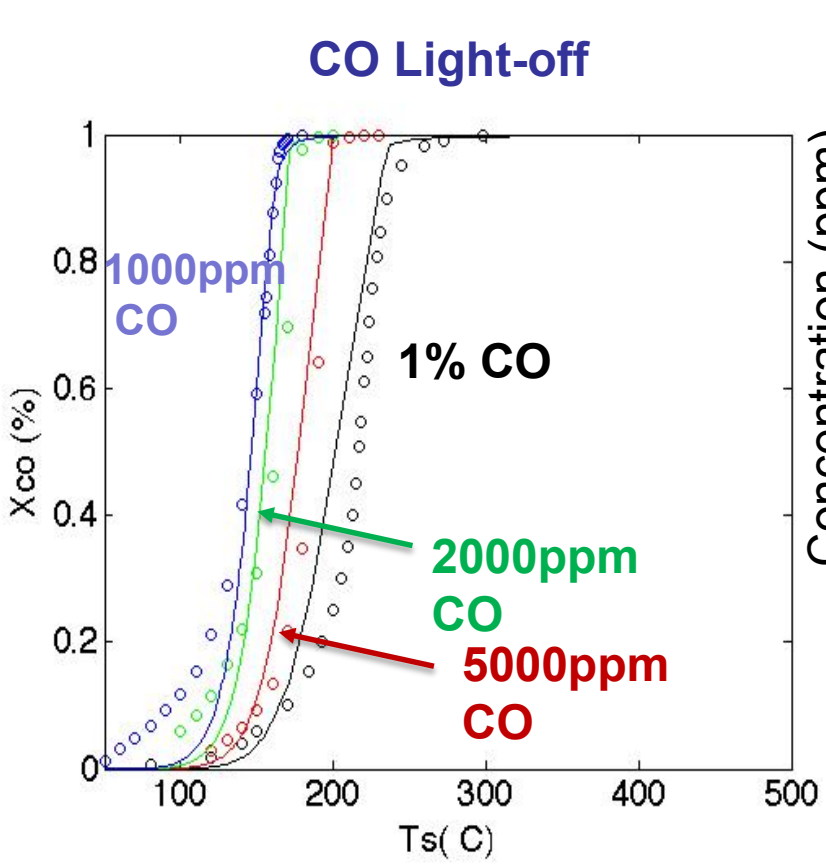
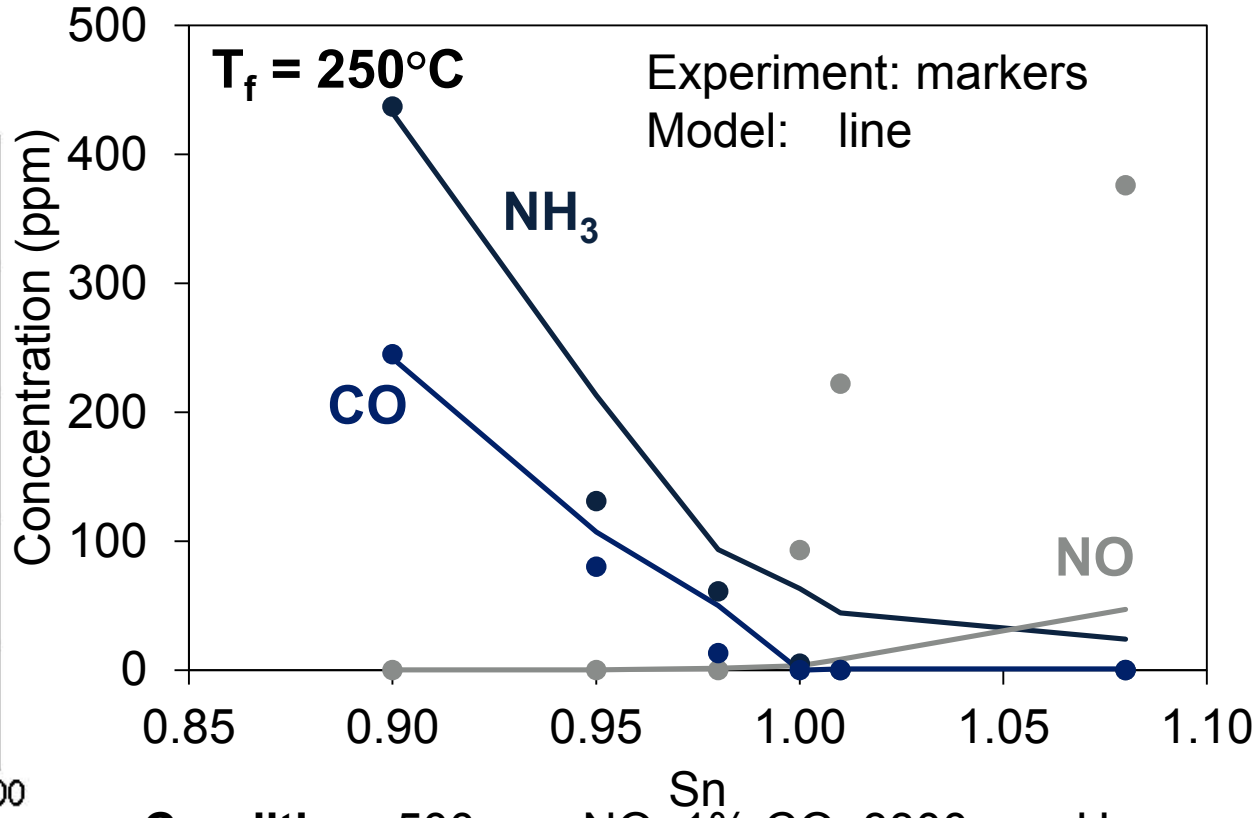
Kinetic and Reactor Model Development - NH_3 Generation Catalyst





Condition: 500ppm NO, 1% CO, 3300ppm H_2, 1000ppm C_3H_6, 7% H_2O, 10% CO_2, degreened

- High CO concentrations shift light-off to higher temperature.
- Current model cannot capture dynamics at lower Ts for CO light-off, need to incorporate oxygen storage sites.
- Current model cannot capture NOx behavior, must incorporate NOx storage site at Sn > 1

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Collaborations/Interactions

- PNNL
  - Low temperature SCR catalyst development
  - Advanced characterizations
- FCA US LLC
  - Primary passive NH_3 generation
  - Dyno engine control inputs
  - System integration
  - Coordinating U of Houston effort
- U of Houston (Epling/Harold)
  - Characterization of NH_3 generation catalysts and mechanistic study of catalyst degradation.
  - Kinetic and model development for NH_3 generation catalysts.

- Conference calls are held typically once every month to discuss the results.
- Bi-annual face-to-face meetings. The most recent annual face-to-face CRADA Review was held at PNNL (March 23, 2016).

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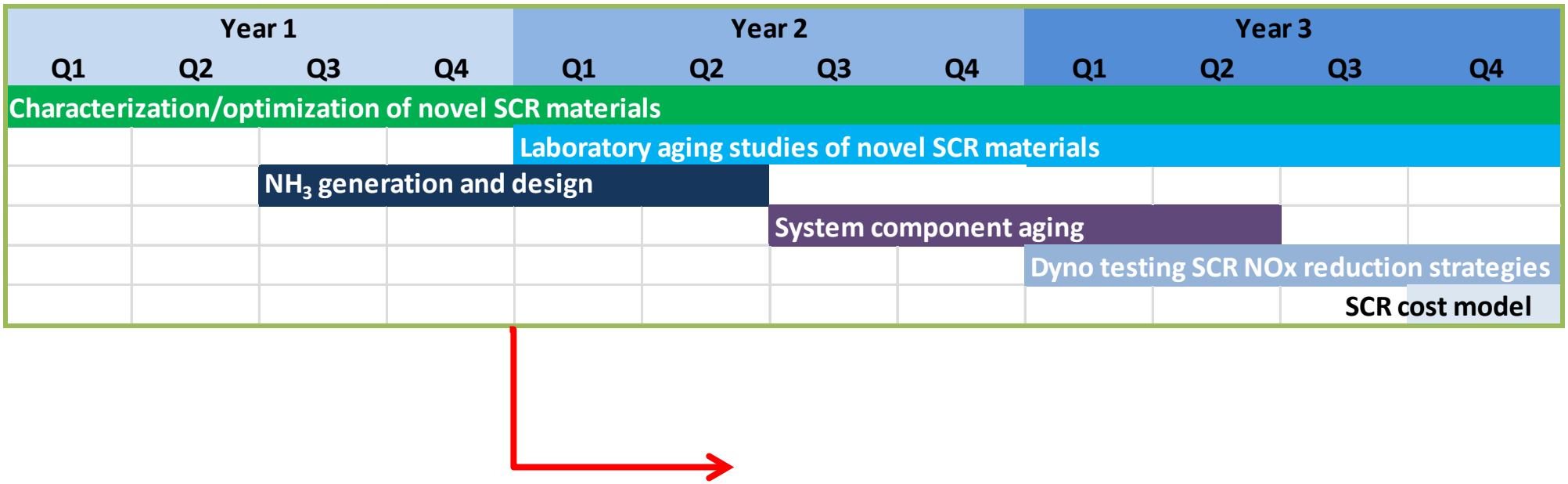
Planned Future Work

- Development of 2nd generation SCR catalysts to meet the conversion efficiency target
- Verify sufficient hydrothermal stability of 2nd generation SCR catalysts
- Design NH_3 generation
- System component aging

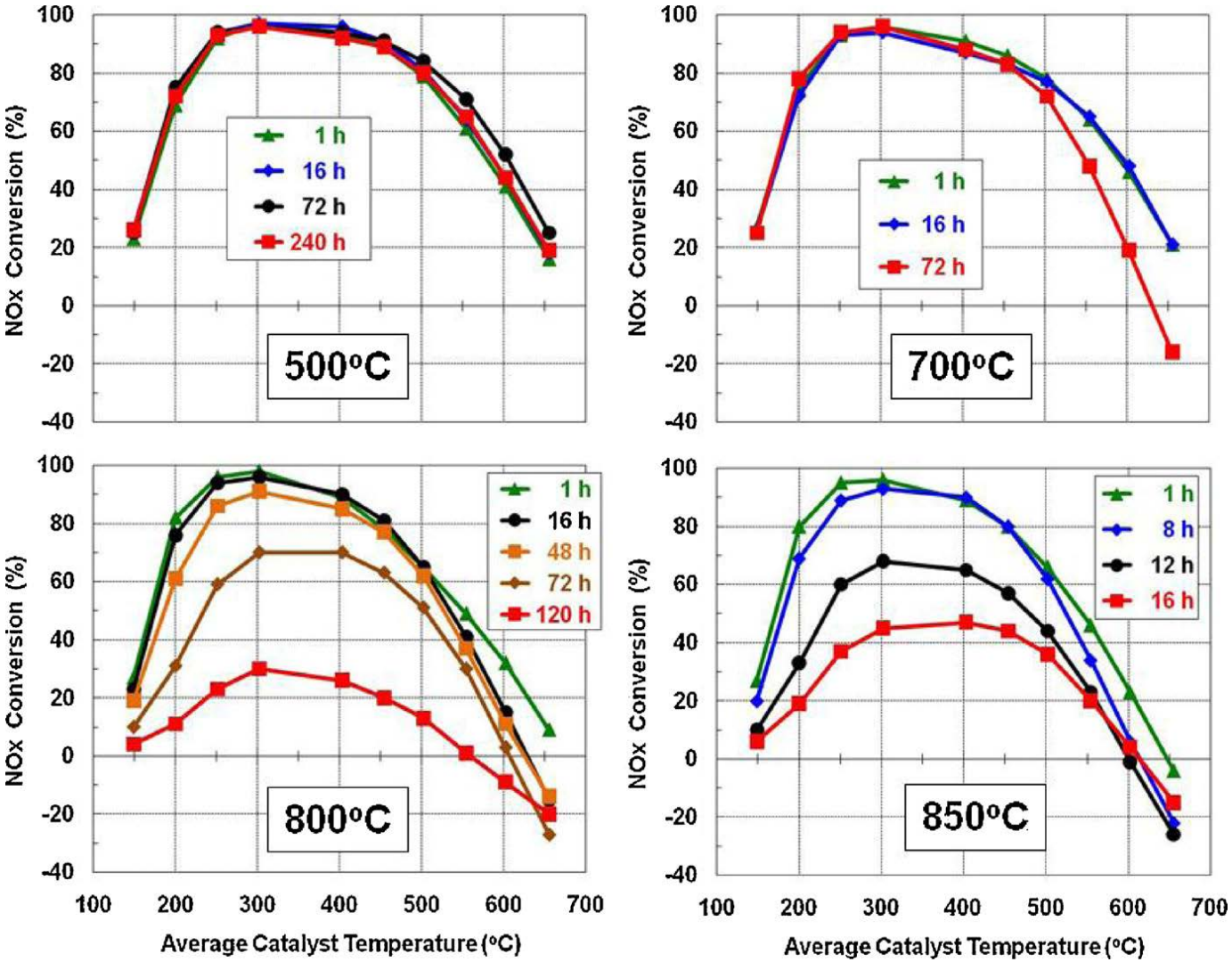


Summary

- Key milestones have been met.
- Identified research direction for the development of 2nd generation SCR catalysts that will meet target conversion efficiency.
- Synthesized a large batch of 1st generation Cu/SSZ catalyst (>500g) which will be used to identify key issues that may exist in the preparation of washcoat and to conduct HTA studies of core samples.
- Downselected on a possible NH_3 generation strategy and screened the conditions of NH_3 generation catalyst and identified areas for improving modeling accuracy.

Technical Back-Up Slides

Current Commercial SCR Catalysts



- BASF Catalysts: Si/Al = 17, Cu content 2.8%.
- GHSV ~ 30,000 h^{-1} for washcoated catalysts, corresponding to ~120,000 h^{-1} for powder catalysts.

Schmieg, et al., Catalysis Today 184 (2012) 252– 261

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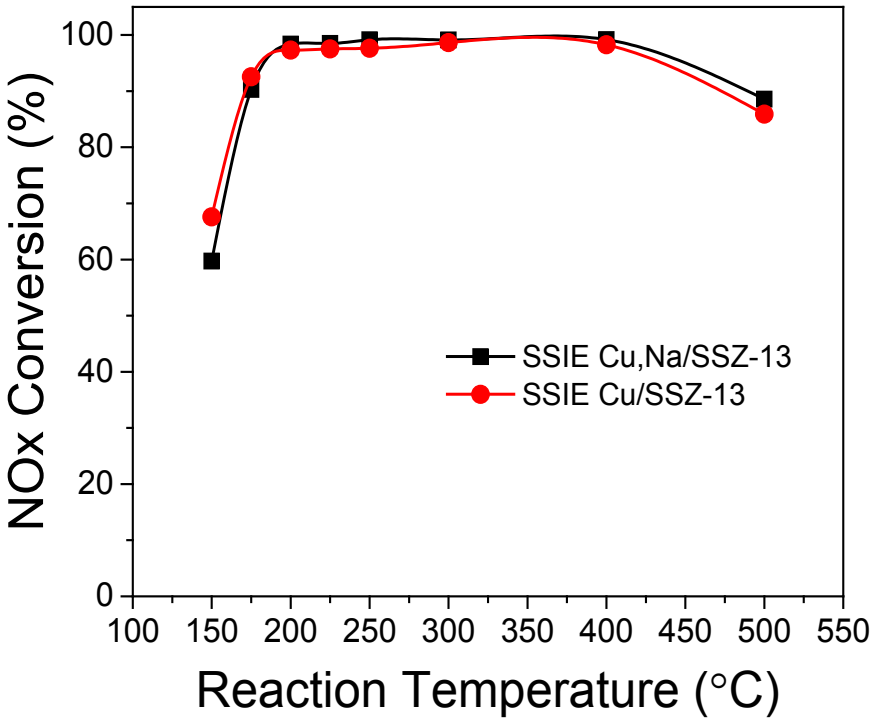
SSIE with and without Na^+

Method 3: thoroughly mix Na/SSZ-13 or NH_4/SSZ-13 powder and CuO powder, calcine in static air at 800 °C for 16 h. (method developed by us for Cu/SAPO-34 synthesis)*

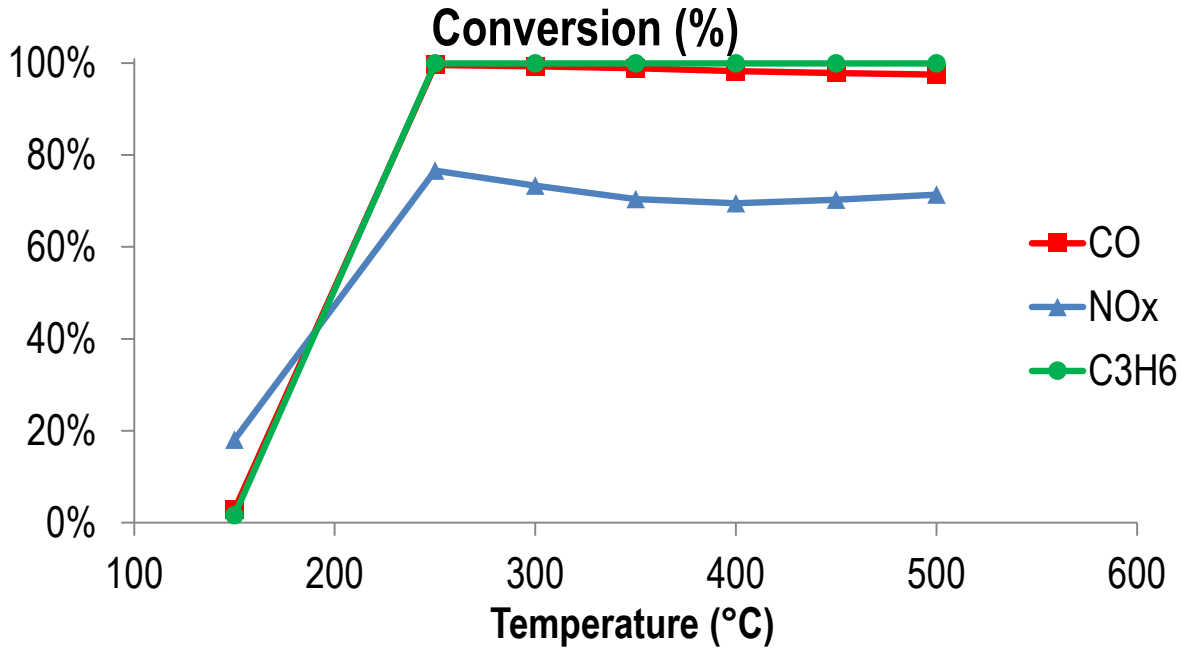
- 2 g Na/SSZ-13 powder + 0.075 g CuO, 800 °C, 16 h. ~3% Cu and ~1.5% Na in product.
- 2 g NH_4/SSZ-13 powder + 0.075 g CuO, 800 °C, 16 h. ~3% Cu in product.

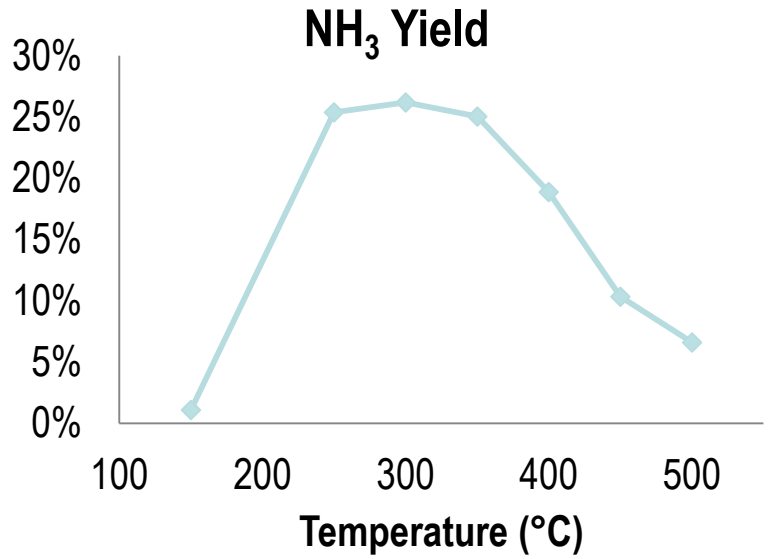


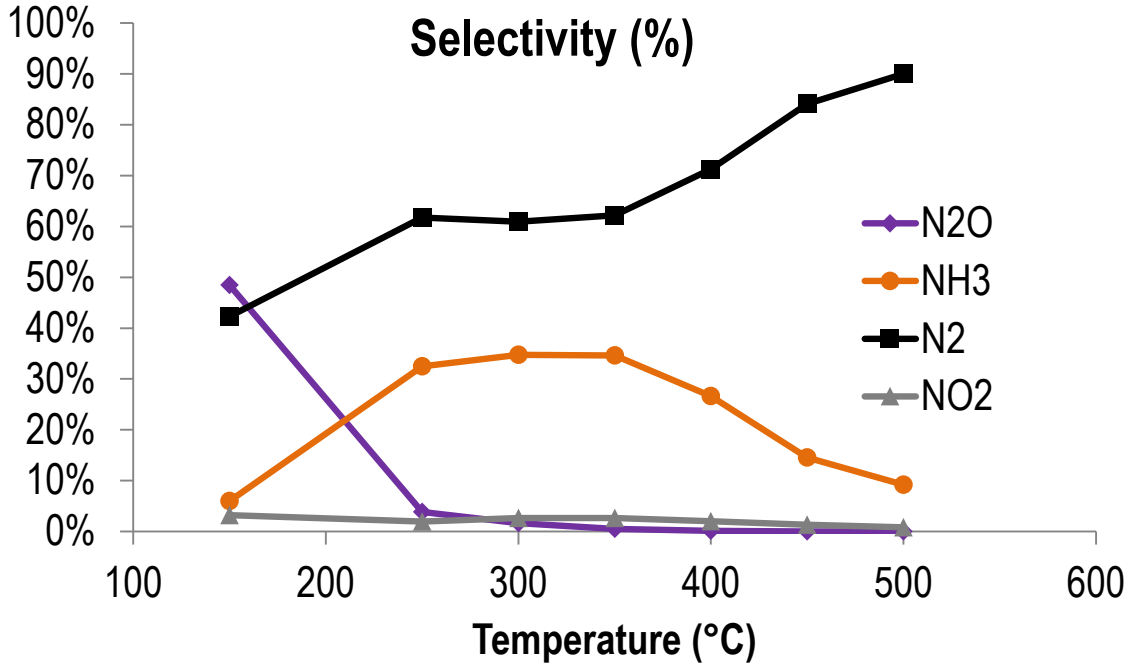
- Even at the same (high) Cu loading, the presence of a cocation sacrifices the optimized Cu dispersion/location.

* F. Gao, E.D. Walter, N.M. Washton, J. Szanyi, C.H.F. Peden, Appl. Catal. B 162 (2015) 501–514

Transient Behavior (20L-40R, 150-500°C): Conversion Eff., Selectivity, NH_3 Yield



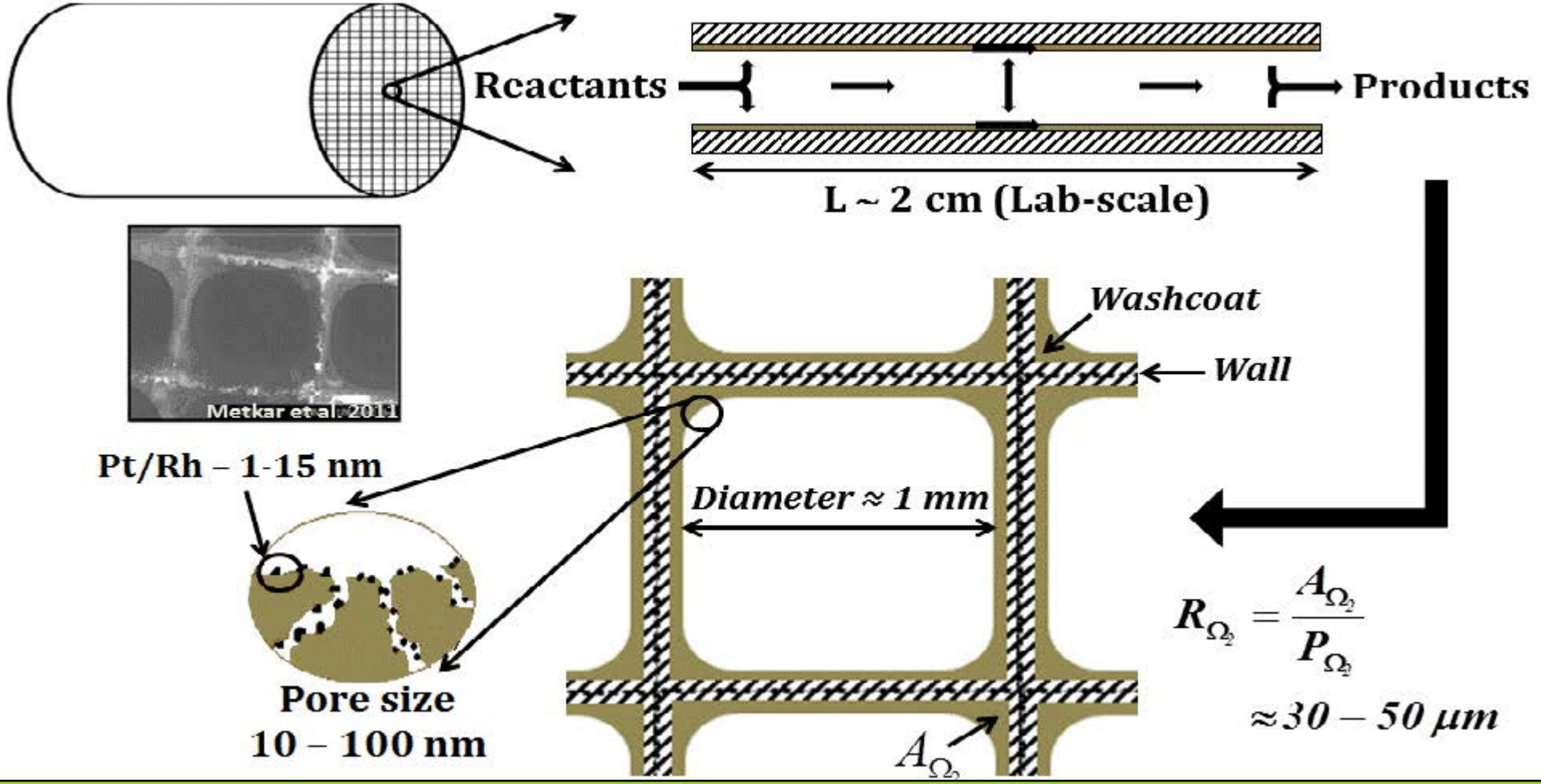




ANR and N conc.

- Max. NH_3 yield ~30%
- CO and HC 100% conv.
- Higher temps shift selectivity toward N_2
- N_2O only at very low T.

Reaction Model: Washcoated Monolith Considerations



Model assumptions:

- Laminar flow in the monolith channel
- Axial diffusion and conduction in the fluid phase is neglected as compared to convection
- Average values for physical properties may be used

Main Reactions in TWC Model

Oxidation Reaction
$2CO + O_2 \leftrightarrow 2CO_2$
$2C_3H_6 + 9O_2 \leftrightarrow 6CO_2 + 6H_2O$
$2H_2 + O_2 \leftrightarrow 2H_2O$
NO Reduction Reaction
$2CO + 2NO \leftrightarrow 2CO_2 + N_2$
$2C_3H_6 + 18NO \leftrightarrow 6CO_2 + 6H_2O + 9N_2$
$2H_2 + 2NO \leftrightarrow 2H_2O + N_2$
Water-gas and steam reforming
$CO + H_2O \leftrightarrow CO_2 + H_2$
$C_3H_6 + 3H_2O \rightarrow 3CO + 6H_2$

Reactions over Ceria
$O_2 + 2Ce_2O_3 \rightarrow 4CeO_3$
$2NO + 2Ce_2O_3 \rightarrow 4CeO_3 + N_2$
$CO + 2CeO_2 \rightarrow Ce_2O_3 + CO_2$
$C_3H_6 + 12CeO_2 \rightarrow 6Ce_2O_3 + 3CO + 3H_2O$
$H_2 + 2CeO_2 \rightarrow Ce_2O_3 + H_2O$
NH_3 generation and reduction
$5H_2 + 2NO \rightarrow 2H_2O + 2NH_3$
$2NH_3 + 2.5O_2 \rightarrow 2NO + 3H_2O$
$2NH_3 + 3NO \rightarrow 2.5N_2 + 3H_2O$

[1] Ramanathan, K., Sharma, C., *Ind. Eng Ind. Eng. Chem. Res.*, **2011**, *50* (17), pp 9960–9979

[2] Ramanathan, K., Sharma, C., Kim, C., *Ind. Eng. Chem. Res.*, **2012**, *51* (3), pp 1198–1208

TW+NSC can be modeled using:

- TWC reactions
- NSC storage and reactions (NOx)