Distributed Transient Performance of a Model Cu-Beta SCR Catalyst :

for development of Self-Diagnosing Catalyst Systems

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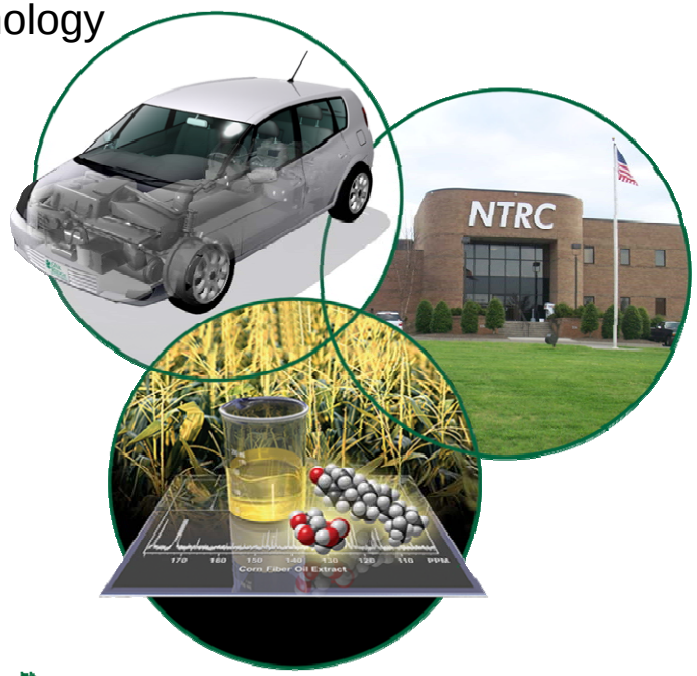

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U.S. DEPARTMENT OF ENERGY

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Background & Theme

Challenge: SCR catalyst are very difficult to control

- Realistic conditions very dynamic: SV, NO_x, NH_3:NO_x, Temp,….
- NH_3 storage complicates coordinating response to emissions transients
- NH_3 capacity is distributed & can change w/ conditions
- Reactions can change w/ location (e.g., parasitic vs. normal NH_3 oxy zones)
- No built-in periodic trigger like w/ LNT that may be used for OBD

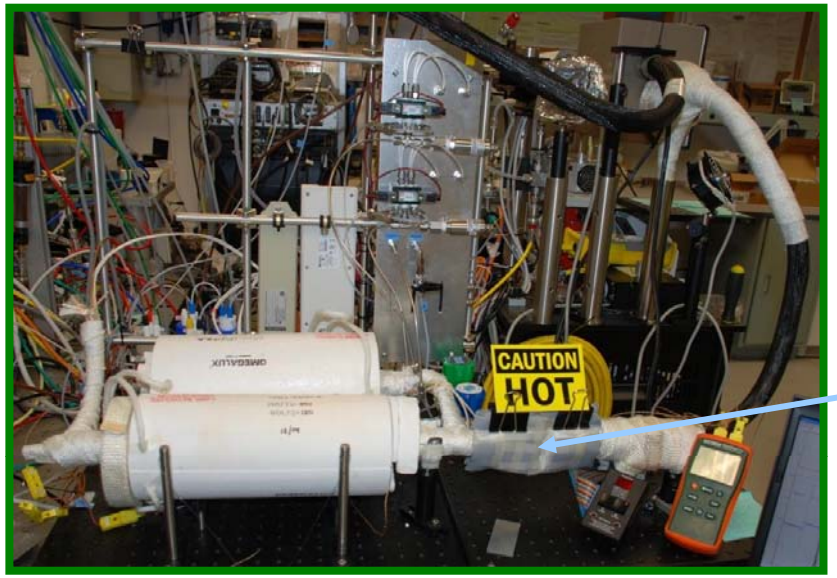
Approach: Need diagnostics to enable real-time catalyst control

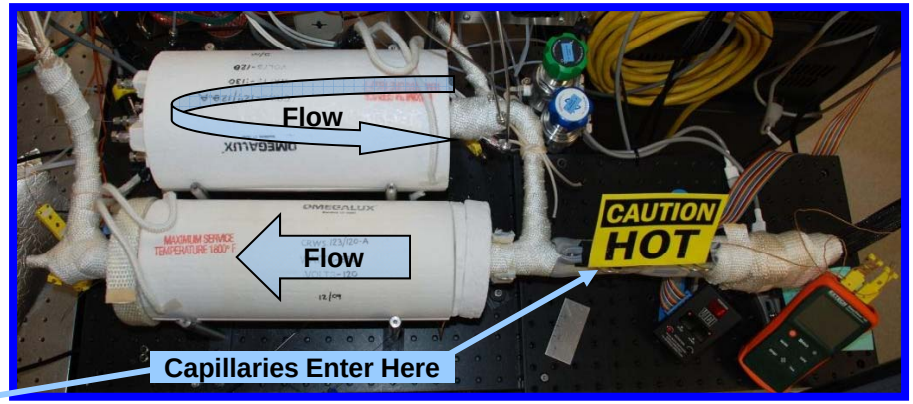
- Evaluate static & dynamic catalyst nature
- Understand chemical & spatiotemporal relationships
- Identify control parameters
- Approach is similar to that used for LNT development

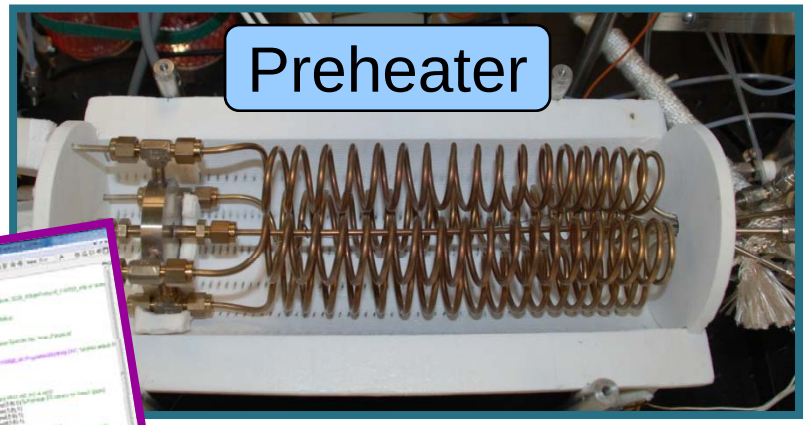
Applications: Broad practical development benefits

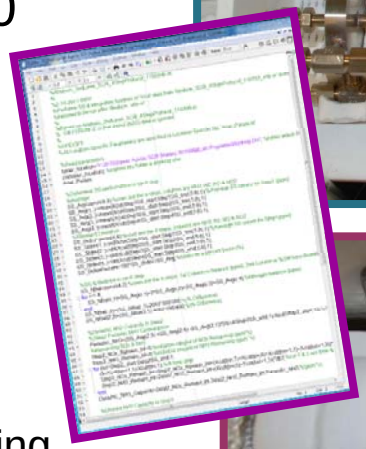
- Better models & design tools
- Self-diagnosing catalyst systems
- Improved efficiency, cost & durability

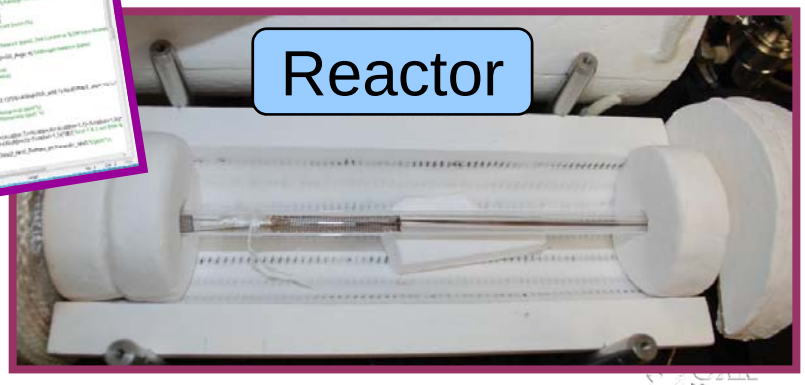
Experiment & Analysis has been Challenging!











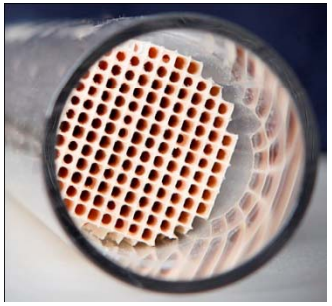
- MicroReactor redesigned mid 2010
  - Improved SpaciMS capillary access
  - Improved temperature control
    - Separate gas preheat before mixing
    - Catalyst T uniformity > 99%
    - Capillaries > 195°C
  - 2x independent gas switching feeds
  - LabView microreactor control & monitoring
- MatLab analysis:
  - Steady state, transient & integrated analysis

Catalyst & Conditions

- Washcoat: **Chalmers Model Cu-Beta zeolite**

  643mg sample; ca. 17.83% mass is Cu-Beta washcoat

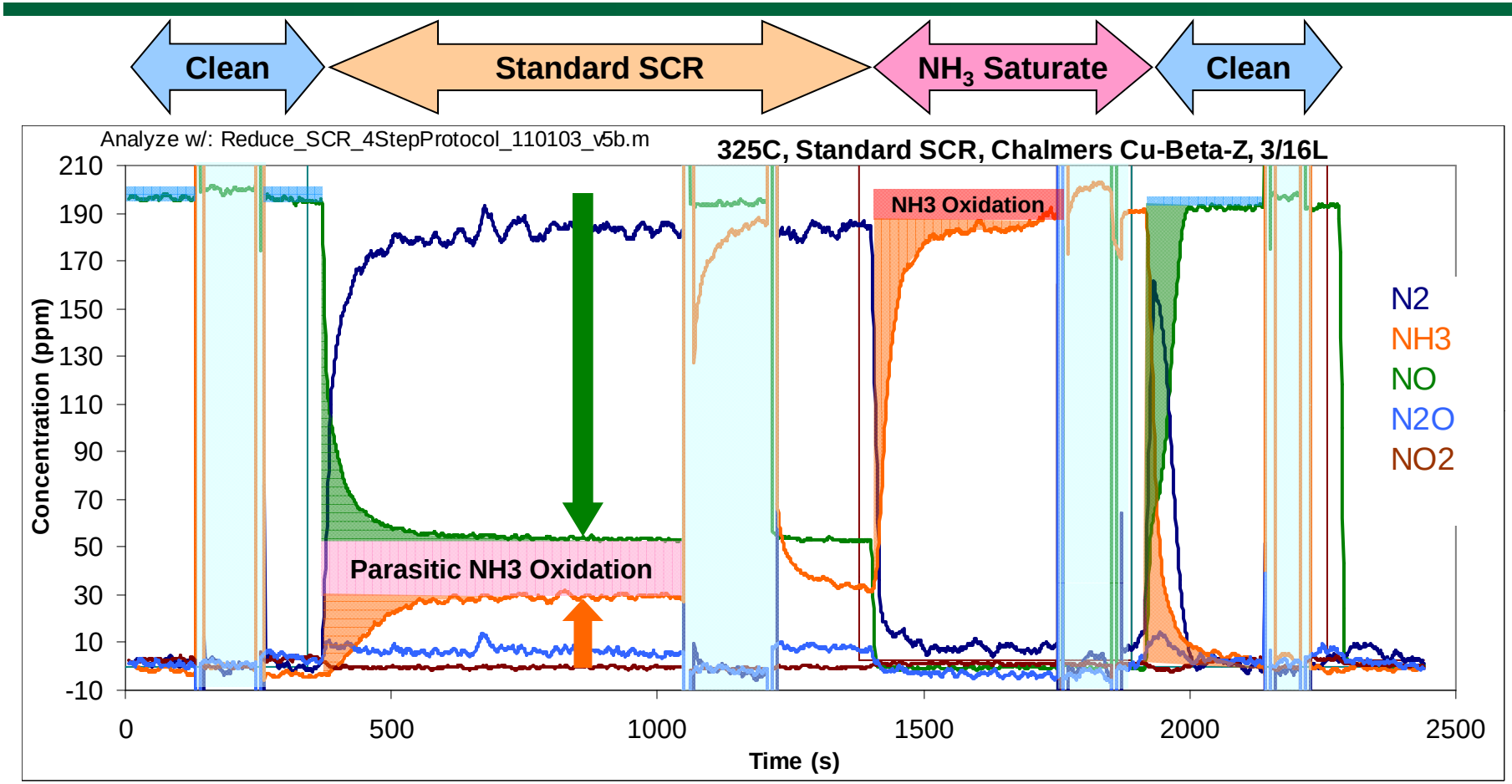
  Wilken et al., Catalysis Today 151 (2010) 237-243



- Channel density: **400cpsi**
- Monolith dimensions: **1" long x 0.28" OD**
- Total flow: **510mL/min**
- Space velocity: **30000h^{-1}**
- Temperature: **200, 325 & 400°C**
- Standard SCR: $\mathbf{4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O}$

	NO_X	NH_3	O_2	H_2O	Kr
Step1 (clean)	200ppm	0	10%	5%	100ppm
Step2 (SCR)	200ppm	200ppm	10%	5%	100ppm
Step3 (NH_3 saturate)	0	200ppm	10%	5%	100ppm
Step4 (clean)	200ppm	0	10%	5%	100ppm

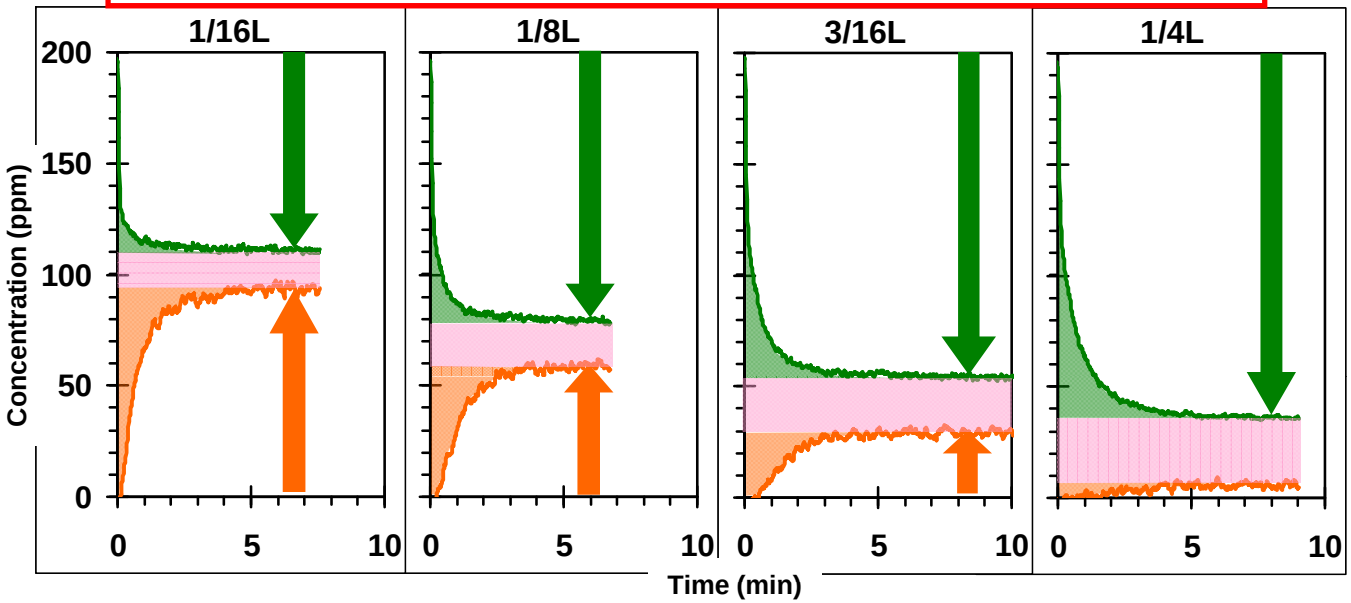
Typical 4-Step-Protocol Data

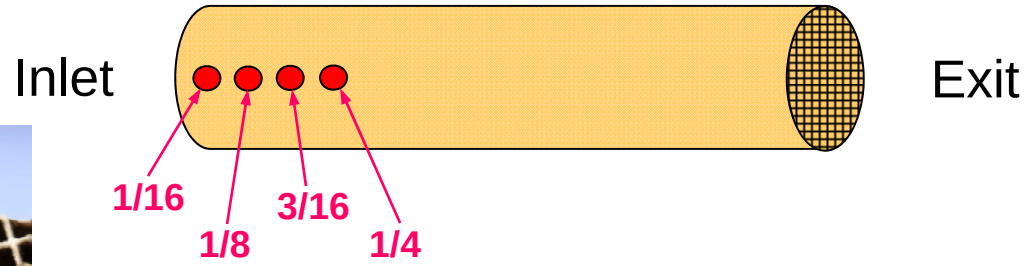


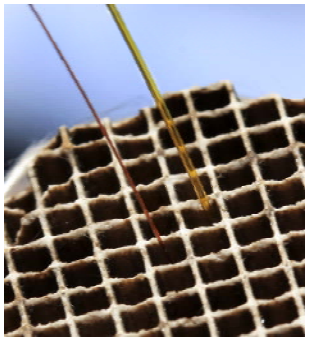
- Step1: NO oxidation
- Step2: SS NO_x & NH_3 conversions, parasitic NH_3 oxidation, dynamic NH_3 capacity
- Step3: Unused NH_3 capacity, NH_3 oxidation
- Step4: Total NH_3 capacity

Distributed Intra-Catalyst SCR Evolution

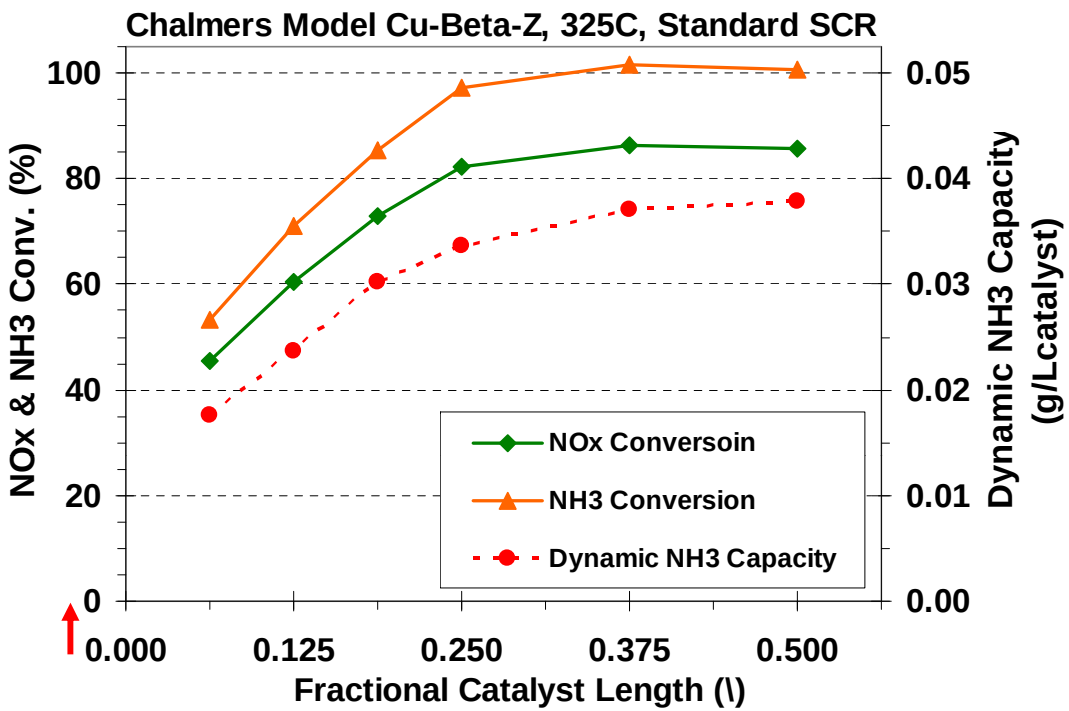
Protocol Step 2: 325ºC Standard SCR

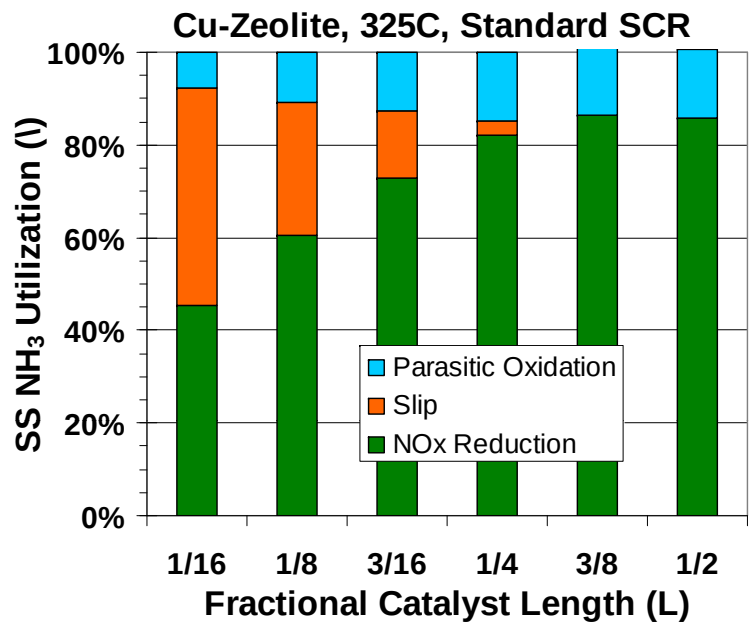






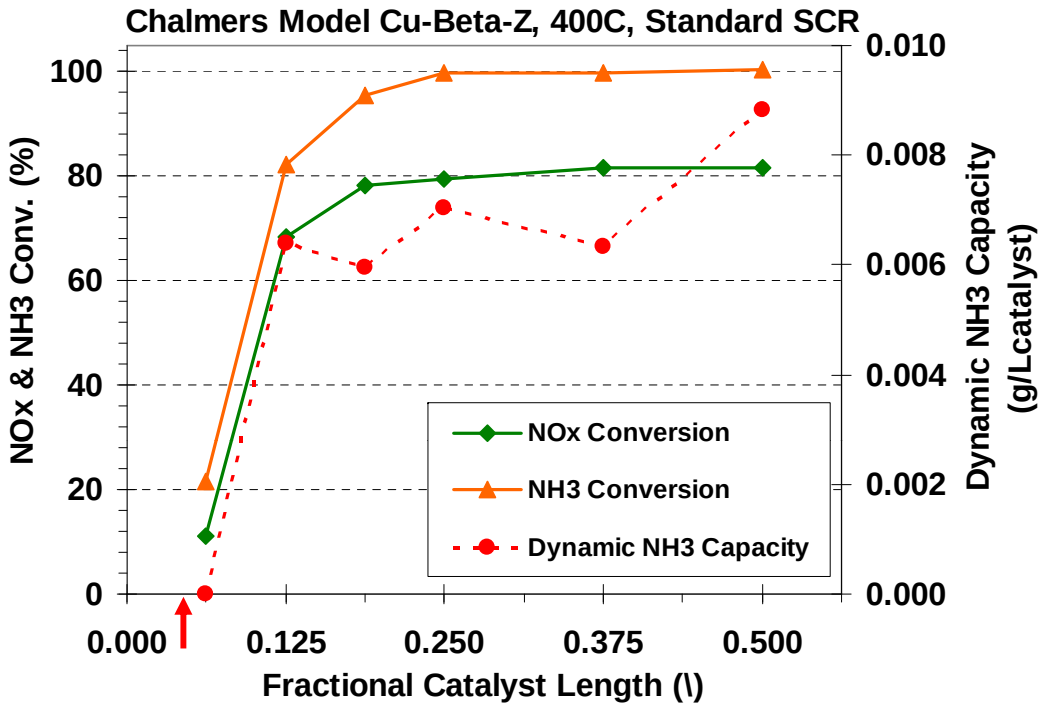
325ºC SCR Reaction Primarily in Catalyst Front Quarter

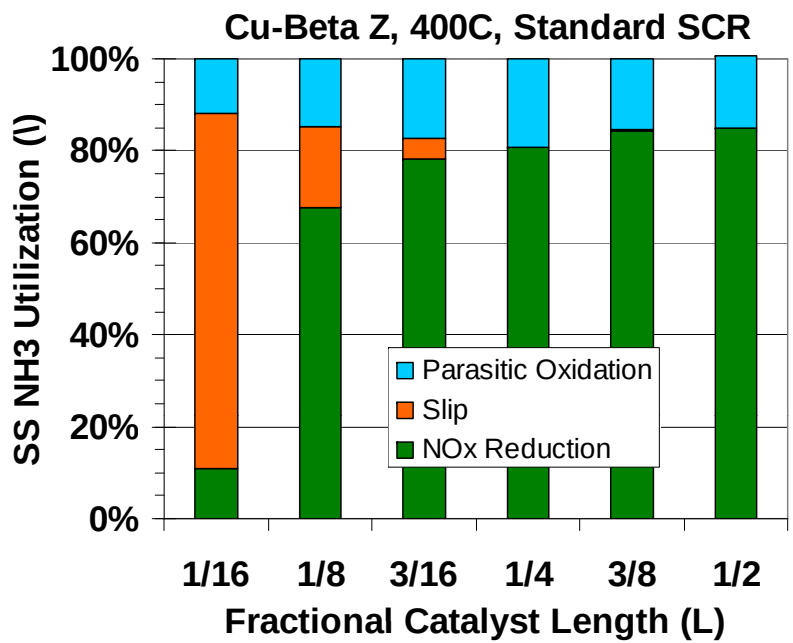




- Half of total NO_x conversion in very front section
  - Due to entrance effect?
  - Remaining conversion to 1/4-3/8L (where NH_3 fully consumed)
- Parasitic oxidation is difference between NH_3 & NO_x conversion curves
  - PO varies from ca. 5-15% total NH_3 utilization
- Dynamic (a.k.a. Active, Used) NH_3 capacity follows NO_x conversion
  - Half of total DC is in very front catalyst section (w/ major SCR)

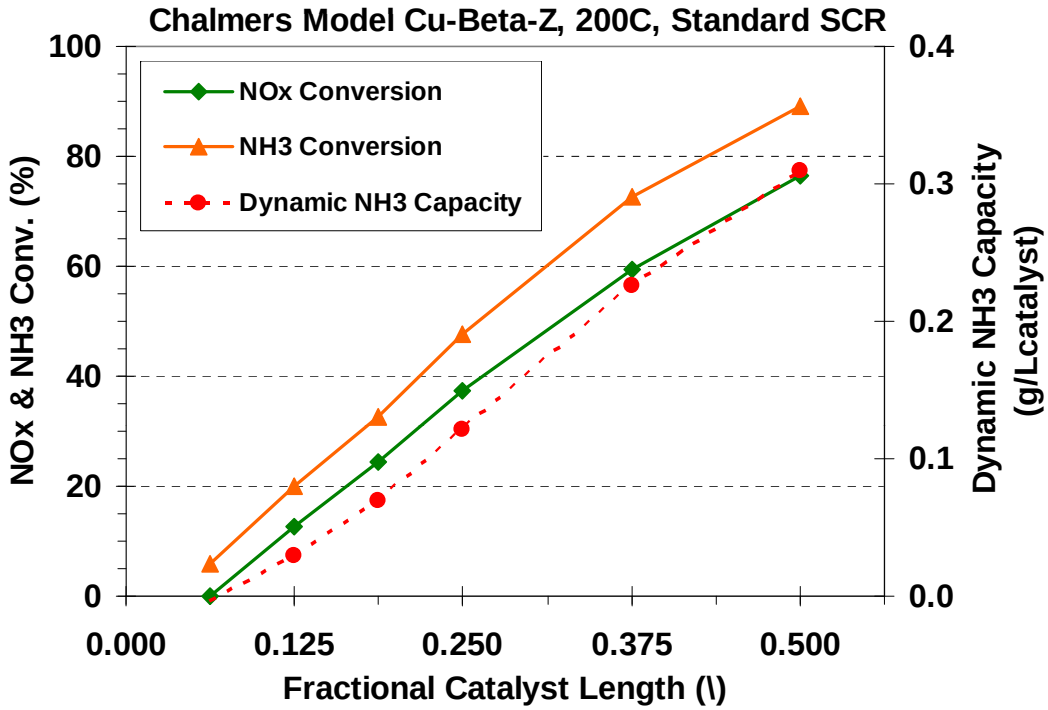
400ºC SCR Reaction Shifts to Catalyst Front

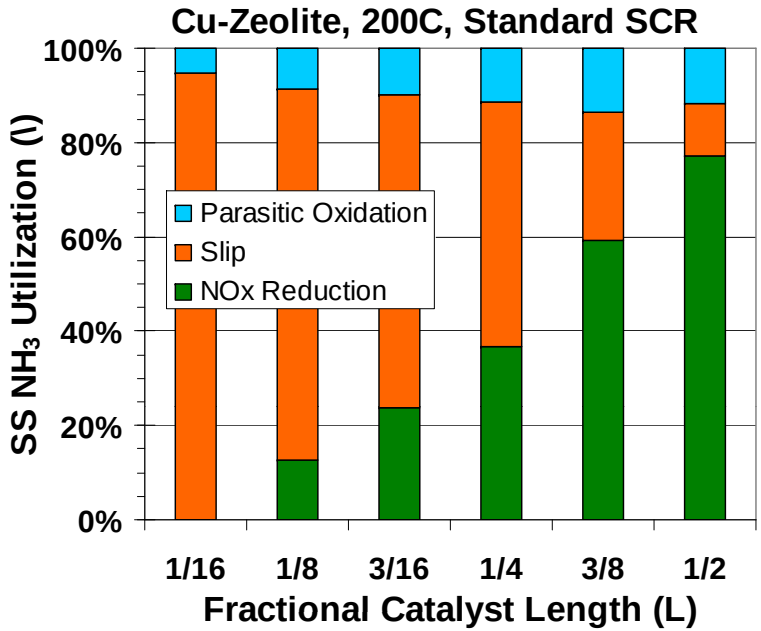




- More NO oxidation in Step1 (not shown here)
- 84% of total NO_x conversion in very front catalyst section (<1/8L)
  - First point is actually at ca. 1/64L (0.4mm) and not 1/16L (1.6mm) as displayed
- Parasitic NH_3 Oxidation ca. 12-19%
- Dynamic NH_3 capacity mirrors NO_x conversion distribution
  - ~1/10th capacity at 325ºC

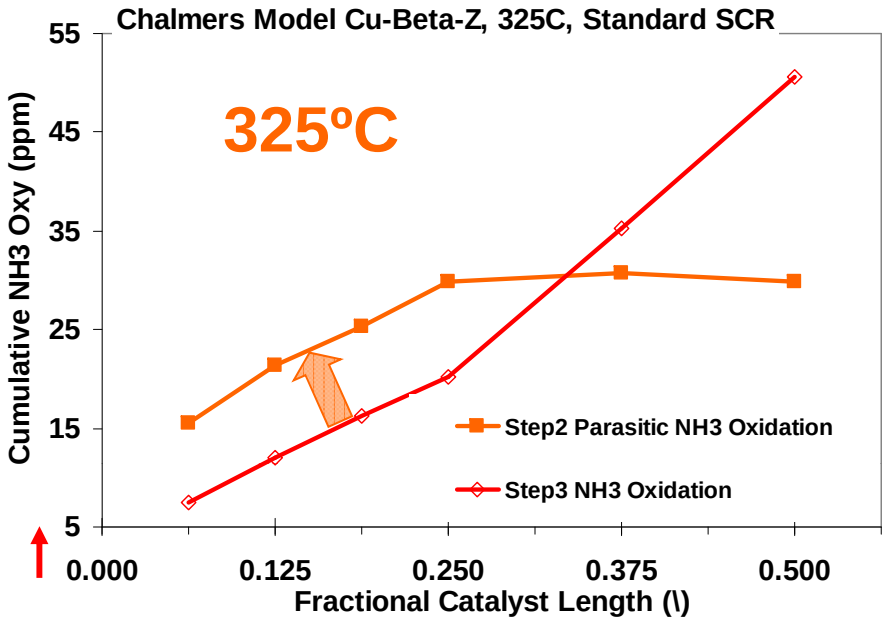
200ºC SCR Reaction Uniformly Distributed Along Catalyst

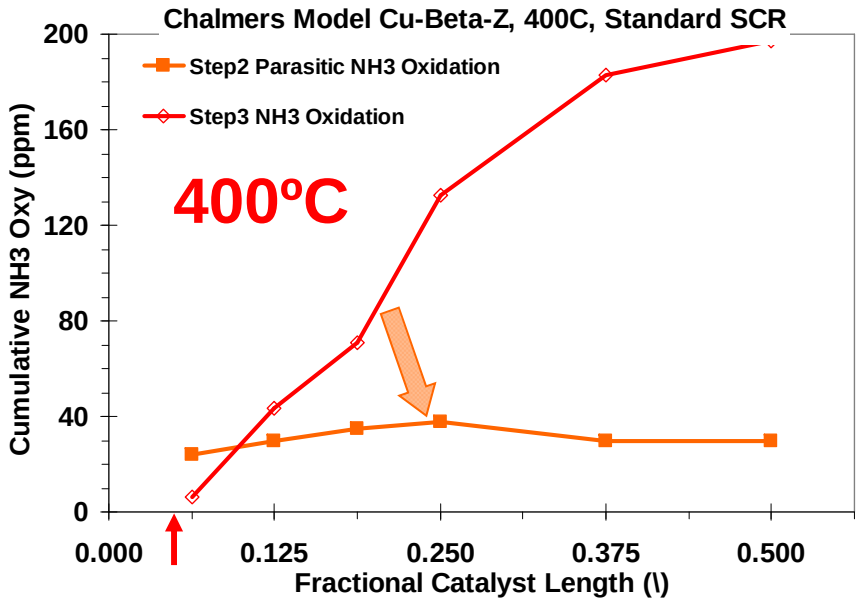




- NO_x conversion distributed along catalyst
- Parasitic NH_3 Oxidation ca. 10-25%
- Dynamic NH_3 capacity mirrors NO_x conversion distribution
  - ~10x capacity at 325ºC

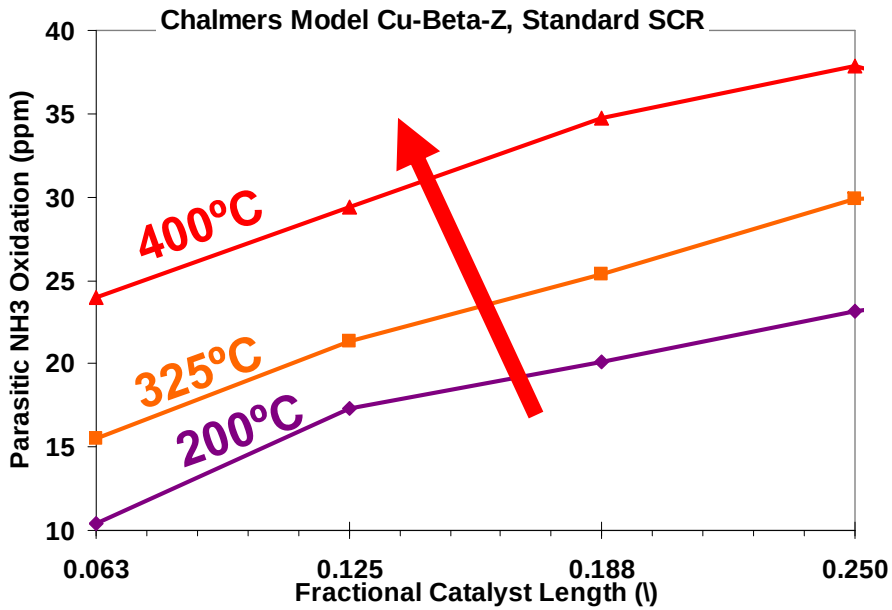
NH_3 Oxidation Changes as Move Out of SCR Zone





Parasitic NH_3 Oxidation:

- Different in SCR & non-SCR zones
- 400ºC > 325ºC > 200ºC



Observations

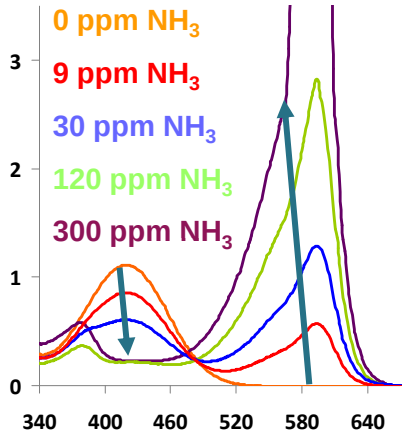
- Fraction of catalyst used for SCR
  - 0.5-1L @ 200ºC; ~3/8L @ 325ºC; <1/4L @ 400ºC
  - Gradient increases w/ Temp
  - ~ half or more of total SCR occurs in very front section at 325 & 400ºC
  - Need higher space velocity to spread out reaction gradients

- Parasitic NH_3 Oxidation varies w/ catalyst T & Position\Time
  - Consumes 5-25% of NH_3 (w/ model catalyst & cases studied)
  - Increased w/ temperature
  - Different than outside SCR zone (> @ 200 & 325ºC; <> @ 400ºC)

- Dynamic NH_3 capacity distribution mirrors SCR
  - Half or more in very front section at 325 & 400ºC
  - Progressive DC through remaining SCR zone
  - DC_{200C} ~ 10x DC_{325C} ~ 100x DC_{400C}

Next Steps

- Improve transient instrument response model for NH_3, NO_2 & other species
  - Improved capacity calculations (Dynamic, Unused & Total)
  - Also needed for Fast SCR analysis
- Impact of hydrothermal ageing on distributed performance
- Pursue goal of "Self-Diagnosing Catalyst Systems"
  - Other conditions (e.g., SV, NH_3:NO_x, NO:NO_2) to study performance impact
  - Inhibitor impact on SCR catalyst reaction and storage distributions
  - Correlate control relationships w/ performance parameters to identify strategies for SCR-catalyst OBD
  - Developing & applying catalyst diagnostics



Acknowledgments

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Thank You

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