Field-Ageing Impacts on a Commercial Automotive Cu/SAPO-34 SCR Catalyst: Focusing on NH_3 Capacity Utilization

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Objective, Approach & Applications

Objective

- Understand how Field Ageing impacts the performance of a commercial Cu/SAPO-34 NH_3 SCR Catalyst

Approach

- Use sample with real-world on-road exposure
  - Acquired from field with normal ageing profile
  - Sample should be generally representative of field-aged catalysts
- Assess aged sample vs. degreened
- Focus on spatially resolved intra-catalyst impact distributions
- Compare impacts on different catalyst functions
  - SCR, NH_3 capacity & oxidation reactions, inhibition limit

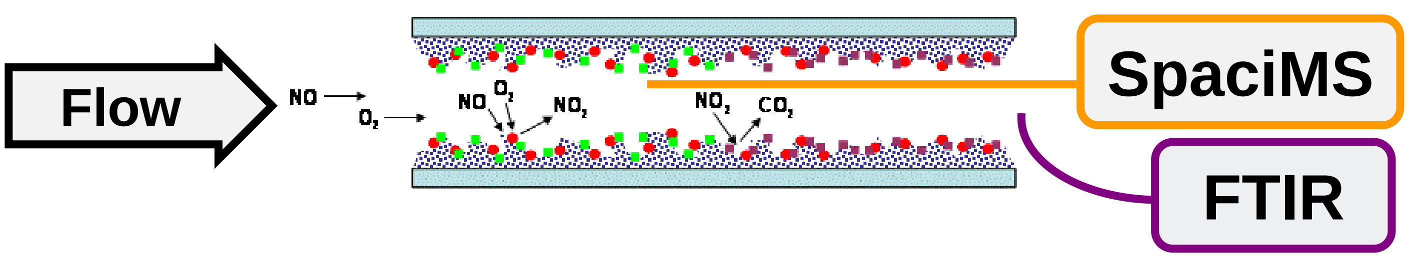
Applications

- Apply data to improve and critically assess catalyst models
- Identify strategies for catalyst-state assessment

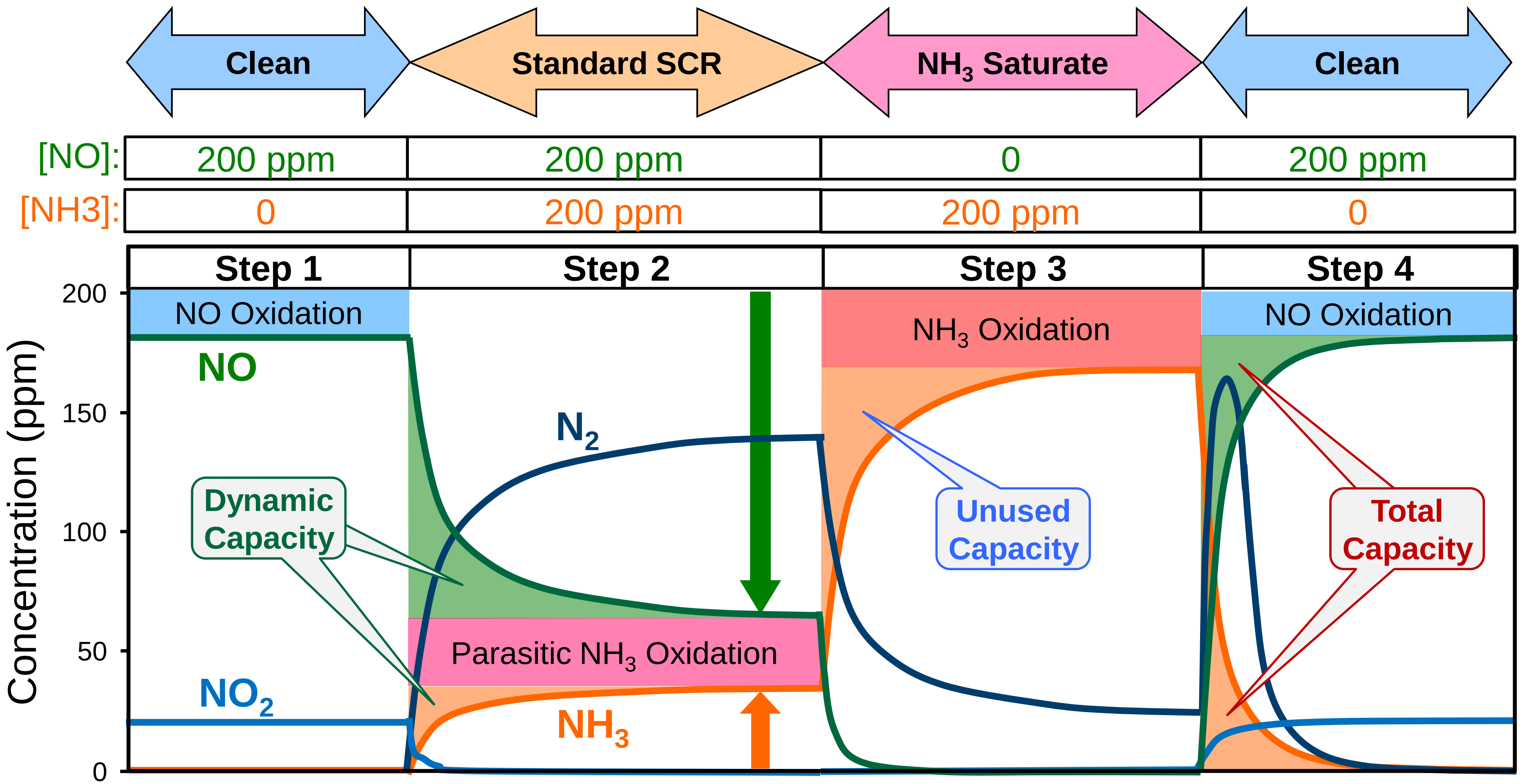
Experimental: Catalyst, Conditions, Methods & Approach

	Commercial
Catalyst	2010 CMI, Cu/SAPO-34
Mini-Core size	21 cells; ca. 2.45-cm long x 0.78 wide
Channel density	300 cpsi
Space Velocity	60,000 hr^{-1}
NH_3, NO_x	200ppm, 200ppm
Base O_2 & H_2O	10% & 5%
Temperatures	200, 300 & 400°C
Standard SCR	✓ focus of these slides
Fast SCR	✓
Diagnostic	SpaciMS & FTIR

State	Conditions
DeGreened (**DeG**)	700°C, 4hrs, 10%O_2 + 5%H_2O; • From front of sample B11-22
Hydrothermal Ageing (**HTA**)	800°C, 50hrs, 14%O_2 + 8%H_2O; • CMI ageing rig: 10-9-2013 • From front of sample B11-23
Field Ageing (**FA**)	Prepared by CMI; • CMI date: 7-1-2014 • Normal ageing profile • From front of larger sample; • Pretreatment at ORNL: • 500°C to remove HC & S • Cycling at 200, 300 & 400C to steady state



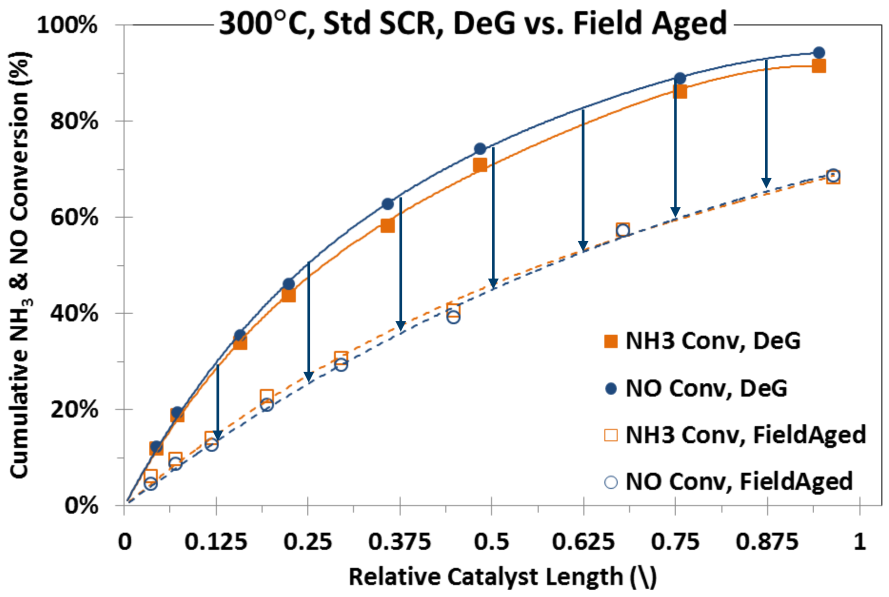
Cummins 4-Step Protocol Resolves Reaction Parameters

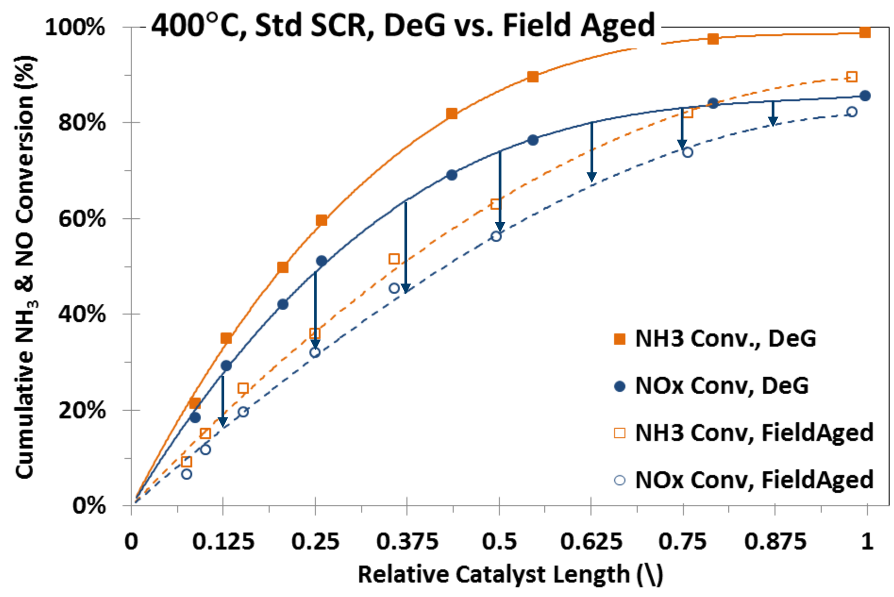


- Step1: NO oxidation
- Step2: SS NO_x & NH_3 conversions, Parasitic NH_3 oxidation, Dynamic NH_3 capacity
- Step3: NO_x-free NH_3 oxidation, Unused NH_3 capacity
- Step4: NO oxidation, Total NH_3 capacity

Total = Dynamic + Unused

Field Ageing Significantly Reduces SCR Conversion





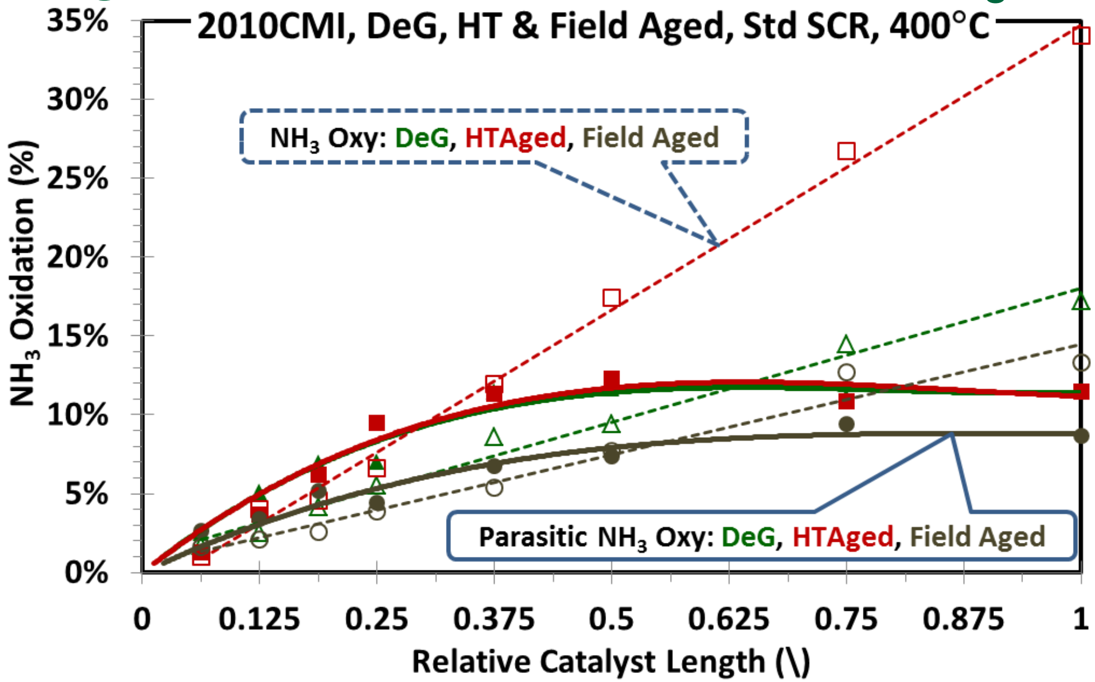
- Major SCR degradation with FA
  - Greatest in front 0-0.5L region:
  - ~40-55% lower conversion at 300°C
  - ~20-40% lower conversion at 400°C

- Parasitic NH_3 Oxidation: PO
  - negligible at 300°C
  - apparent at 400°C for both DG & FA

Does Field Ageing have similar impact on other catalyst functions?

Use FA impact correlations to infer contribution to significant SCR loss.

Field Ageing Reduces both Parasitic & NH_3 Oxidation

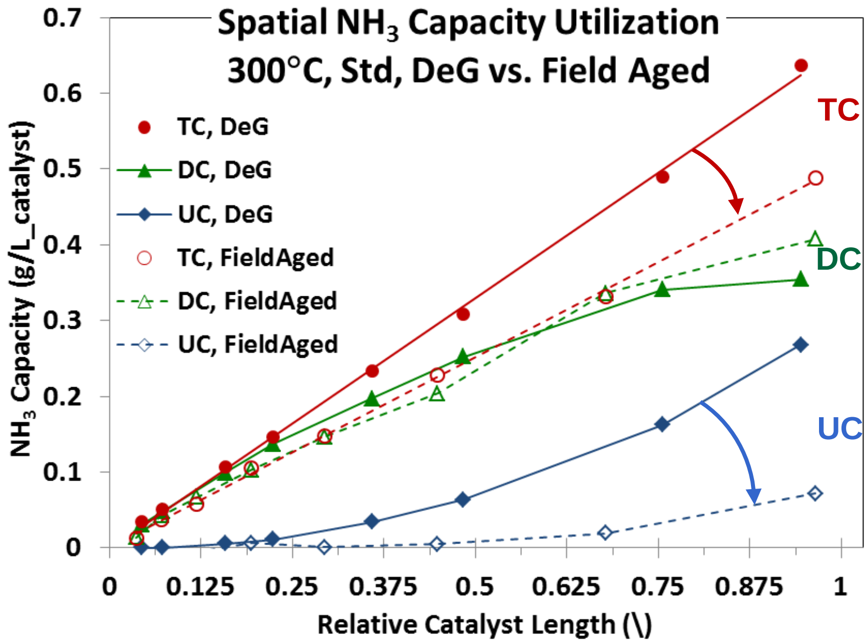


	Parasitic NH_3 Oxidation (PO: during SCR)	NH_3 Oxidation (in absence of NO_x)
FA vs. DeG	~20% lower	~20% lower
HTA vs. DeG	same	~100% greater

- **Reduced competition should cause greater SCR conversion if PO limits SCR**
- HTA impacts PO & NH_3 Oxy differ
  - PO & NH_3 Oxy are different reactions
  - Common FA results are unusual

- ***FA & HTA have different impacts***
  - ***Impacting different functions differently***
- ***FA SCR loss >> PO loss***
  - ***Significant PO change would cause opposite SCR trend***
- ***FA reduces both SCR & PO***
  - ***FA apparently impacts a common site***
  - ***SCR is more sensitive to this impact***
  - ***PO site competition not limiting SCR***

Field Ageing Changes TC & UC, but Little DC Impact



Total NH_3 Capacity: **TC**

Dynamic NH_3 Capacity: **DC**

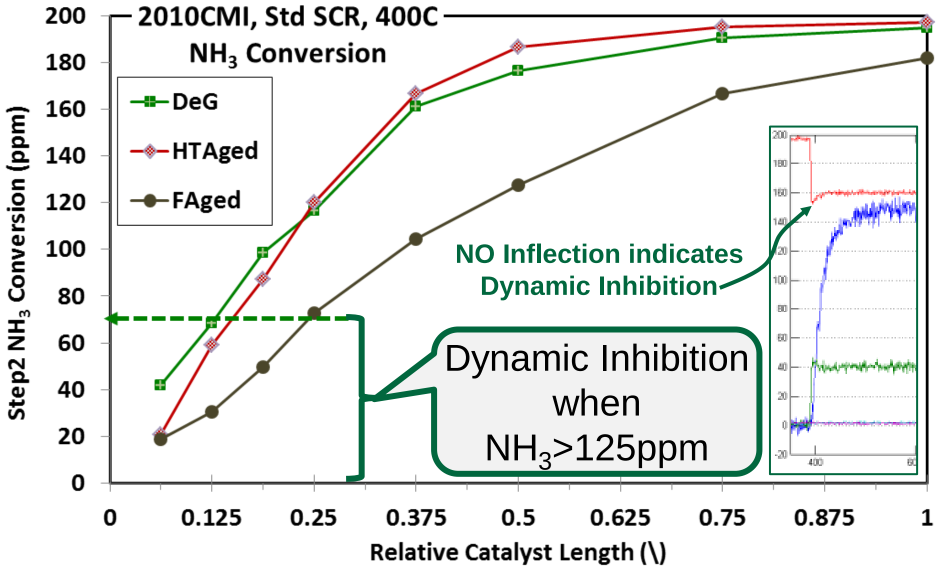
- **DC: fraction used during SCR**

Unused NH_3 Capacity: **UC**

DC + UC = TC

- **Total NH_3 Capacity: TC**
  - FA ~25% lower at both 300 & 400°C
  - Similar loss with HTA
- **Dynamic NH_3 Capacity: DC**
  - DC≈TC at catalyst front
  - FA causes DC≈TC deeper into catalyst
    - DC saturated deeper into catalyst
    - ***Overall very small DC change***
    - [NH_3] similar at DC-TC separation point
      - Suggests similar Adsorption Isotherm
- **Unused NH_3 Capacity: UC**
  - FA lowers UC (Due to TC & DC behavior)
    - May impact dosing control
    - Candidate for catalyst-state monitor
- Same general behavior at 400°C
- ***FA has little impact on DC quantity***
- ***FA SCR loss >> DC change***
  - ***Apparently not due to DC quantity loss***
  - ***But, is Field Aged DC less accessible?***

Field Ageing Does Not Change Dynamic NH_3 Inhibition



Tronconi, Cat.Today 105, p529; describes dynamic inhibition

- 'modified redox (MR) SCR rate law'
- Depends on T, C_{NO}, θ_{NH3} & C_{O2}

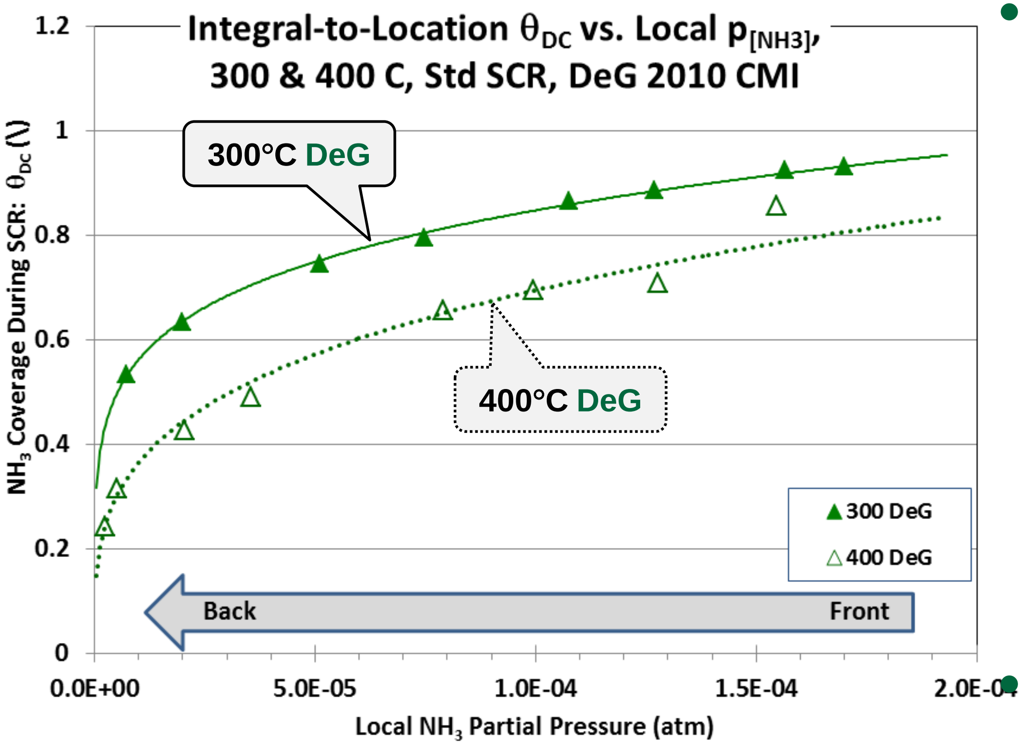
$$r_{NO} = \frac{k'_{NO} O' \exp\left(-\frac{E_{NO}}{RT}\right) C_{NO}\theta_{NH_3}}{1 + K'_{NH_3}\frac{\theta_{NH_3}}{1-\theta_{NH_3}}}\left(\frac{p_{O_2}}{0.02}\right)^{\beta} \qquad (12)$$

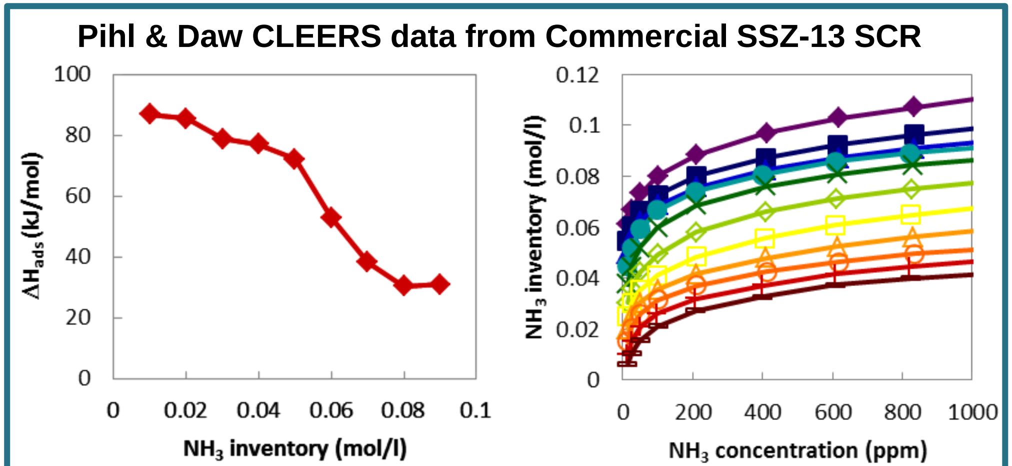
- r_{NO}: rate of DeNOx reaction
- E_{NO}: Activation energy for DeNOx reaction
- C_{NO}: gas phase concentration of NO
- θ_{NH3}: surface coverage of NH_3
- k_{NO}: pre-exponential factor for DeNOx reaction rate constant
- K_{NH3}: NH_3 rate parameter
- p_{O2}: O_2 partial pressure
- **S1: redox site for O_2 & NO adsorption/activation**
- **S2: acidic site for NH_3 adsorption**

- Dynamic inhibition at SCR start
  - Observed in catalyst front for all samples
  - ***Observed above consistent [NH_3] limit***
    - ≳ 165ppm [NH_3] at 300°C
    - ≳ 125ppm [NH_3] at 400°C
      - 400°C more sensitive
      - Due to faster reaction or less accessible DC?
      - More sensitive to spillover from Higher-E S2 sites, which are more dominant at high-T
  - Impacts NO & NH_3 adsorption parameters

- ***Suggests inhibiting NH_3 & NO interactions not impacted by FA***
  - *Abundance of S2 vs S1 sites*
    - *i.e., NH_3 spillover from S2 to S1 is equivalent in DG & FA; even with lower FA TC*
    - *Consistent with lower NH_3 vs. NO capacity*
    - *Consistent with separate S1 & S2 sites*
    - *Can lose many S2 sites before change in NO-adsorption inhibition occurs*
    - *FA selectively impacts S2 sites over S1?*

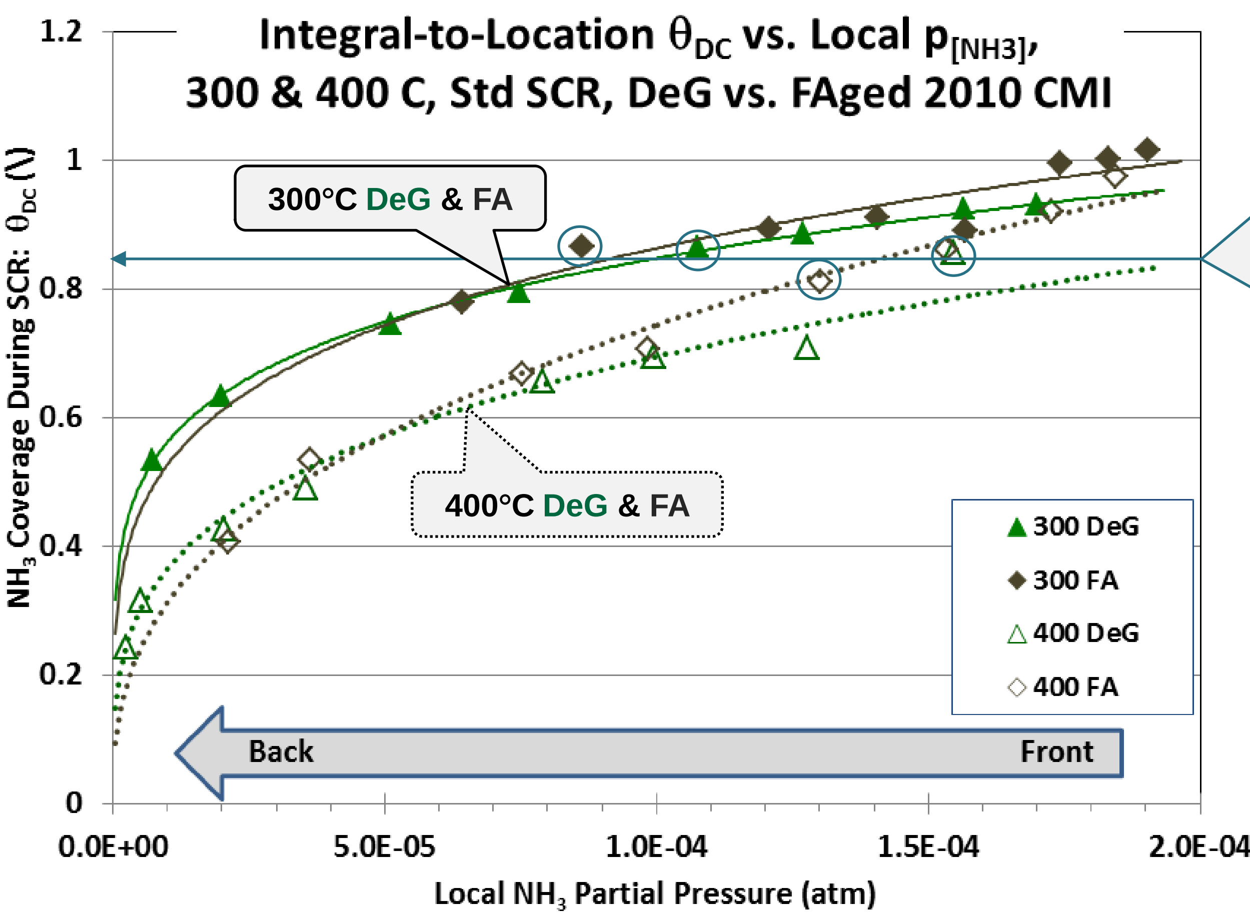
Adsorption Isotherm has Characteristics of 2-Site Langmuir





- NH_3 Isotherm from SpaciMS data
  - ***Under SCR reaction conditions***
    - Isotherm has extra loss term: reaction
  - Normalized coverage shown
    - DC / (DC + UC)
  - Adsorption is faster than even Fast SCR
    - Implied by DC-TC separation at a common $[NH_3]$ for Standard & Fast SCR (previously shown)
  - Can interpret isotherm classically
- Shape is like 2-site Langmuir
  - See Pihl & Daw CLEERS data
    - From commercial SSZ-13 SCR
    - Model fit with uniform partitioning between the ca. 80 & 30kJ/mol sites
  - Distinct knee at low NH_3 partial pressure
- Isotherm flattens at higher temperature
  - Typical nature for Langmuir isotherm

Field Ageing Does Not Change NH_3 Adsorption Energetics



Circled points indicate where DC-TC separation occurs.

DC-TC separation occurs at common ca. 85% coverage for all cases (DG & FA, 300 & 400C).

Not at isotherm 'knee' as imagined.

- Isotherm is same at a give temperature
  - 400°C data overlay despite fit
    - 400°C DG 1.3E-4atm point looks low
  - Shape would change with energetics
    - e.g., if selective adsorption site ageing
- Simplifies modeling of aged samples
  - ***Field ageing reduces number of sites***
  - ***But adsorption occurs in same way***
  - ***Use same model with scaling factor***

Summary of Field-Ageing Impacts on SCR Functions

Function	Field-Ageing Impact vs. DeGreened	
	300°C	400°C
SCR	**40-55% lower**	**20-40% lower**
Parasitic NH_3 Oxidation	**NA; same**	**20% lower (opposite trend)**
NH_3 Oxidation	NA; same	20% lower
NH_3 Inhibition limit	same	same
Total NH_3 Capacity	25% lower	25% lower
Dynamic NH_3 Capacity	**ca. same**	**ca. same**
Unused NH_3 Capacity	lower	lower
NH_3 Adsorption Energetics	same	same

- Results generally consistent with
  - FA & HTA have different impacts
  - PO competition not limiting FA SCR
  - FA impacts common site related to SCR & PO
    - Common site more active for SCR than PO
  - FA reduces TC
  - DC quantity not limiting FA SCR
  - FA may make DC less accessible, causing longer\slower SCR
  - Practically nonselective FA impact on NH_3 adsorption-site energetics

Multiple Sites with Varying Functional Selectivity

- Olsson's group has discussed how **a range of exchanged Cu-BEA sites exist**
  - with a corresponding range of selectivity to different functions
  - Selective ageing could cause the SCR & oxidation results observed here

Supriyanto, Olsson, et al. (2015). Applied Catalysis B, V163, 382-392

Site	NO & NH_3 Oxidation	SCR
Low-exchanged Cu-BEA	**Low**	**High**
Medium-exchanged Cu-BEA	**Low**	**High**
Over-exchanged Cu-BEA	**High**	**Low**

Losing these sites would selectively degrade SCR vs. oxidation

The FA impact is likely similar for the Cu/SAPO-34 catalyst studied here

- Different sites with functions, selectivity and sensitivity to ageing
- FA degrades site(s) with higher SCR activity & lower oxidation activity
  - Large impact on SCR (selective loss of high-efficiency SCR sites)
  - Small impact on PO (PO competition not limiting SCR)
- FA does not significantly impact major NH_3-adsorption 'reservoir' energetics
  - Reduces Total Capacity
  - Capacity loss is not selective (adsorption energetics \ isotherm remain the same)
  - Dynamic Capacity practically unchanged (may be less accessible to remaining SCR sites)

Next Steps

- Additional catalyst characterization needed
  - Cu sintering
  - Poisoning; e.g., by lube components (S, Zn, P, Ca)
  - Number & nature of surface sites
  - Zeolite structure & dopant changes

- Comparison to Cummins catalyst models is ongoing

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