NH_3 Adsorption and SCR Reactions over a Cu-CHA Catalyst – NH_3 Injected as a Pulse

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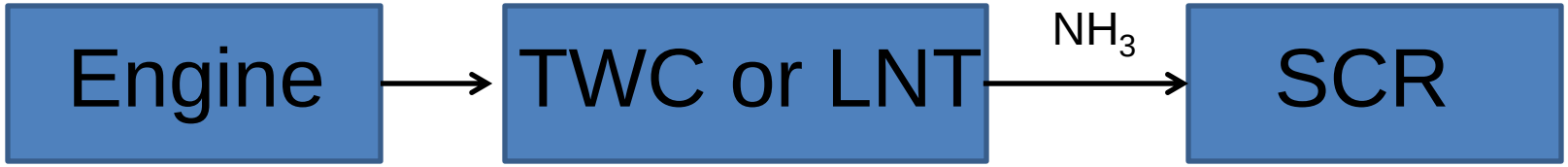
Background

- Passive SCR



  – Adsorbed NH_3 reacts with any NO_X slip past the LNT or TWC

- NH_3 to SCR is not continuous
  – From LNT during regen
  – From TWC during rich operation

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Objectives

- How do key parameters affect NH_3 adsorption profiles?
  - Temperature
  - Exposure time and concentration
- How do the evolved profiles affect the standard and fast SCR reactions?
- How does thermal aging impact these?

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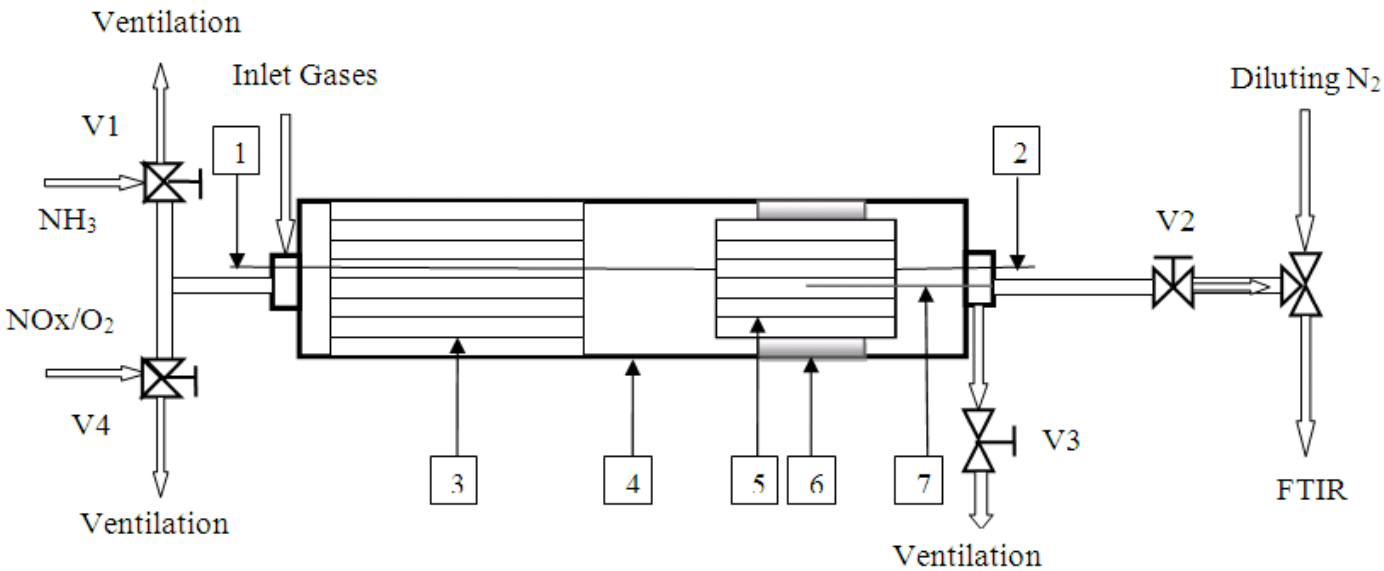
Experimental approach

- BASF-supplied Cu/CHA SCR catalyst
  - 16 hrs at 500°C or 72 hrs at 700°C
- Spaci-FTIR technique



(1) inlet thermocouple, (2) outlet thermocouple, (3) hollow quartz tubes, (4) quartz reactor tube, (5) catalyst monolith, (6) insulation/wrapping material, (7) silica capillary

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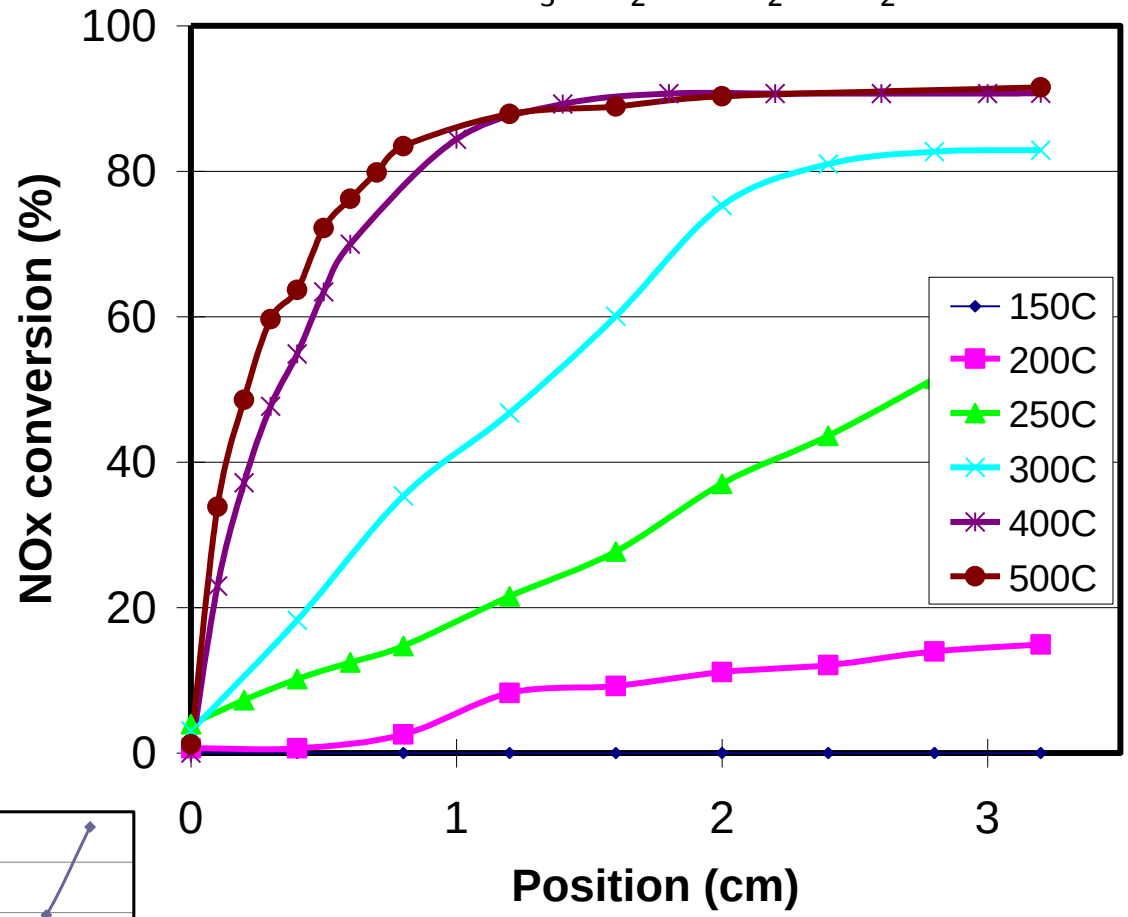
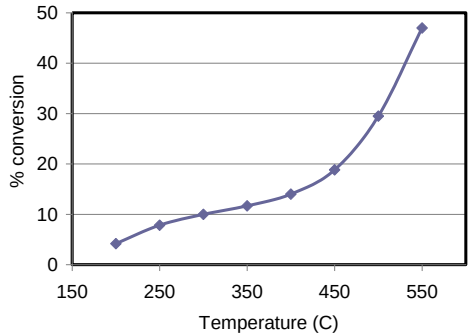
SS Results, standard SCR

- Increasing T, increasing conversion
- Increasing T, reaction zone moves closer to inlet
- At T ≥ 300°C, not all the catalyst is being used

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$





NO = 600 ppm, NH_3 = 600 ppm, 8% O_2, 5% CO_2, 2.5% H_2O

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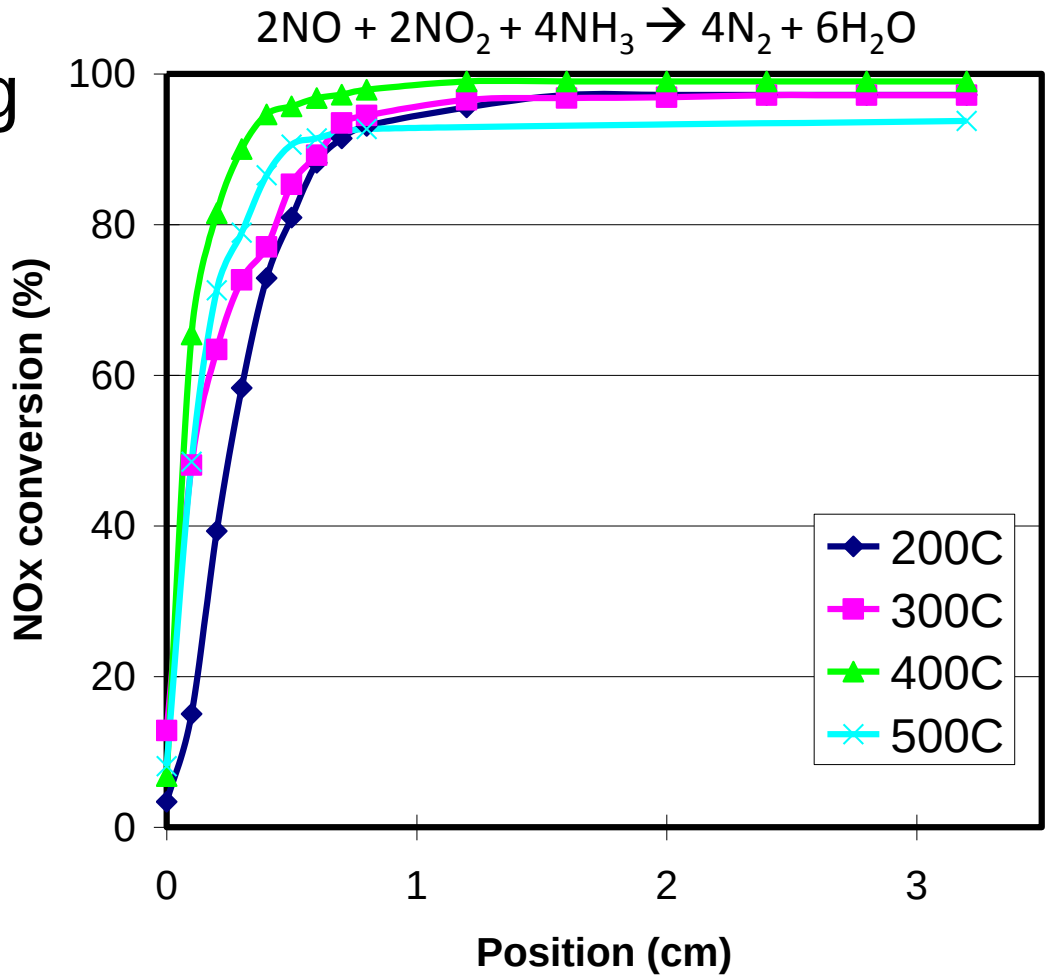
SS Results, fast SCR

1/3 of the catalyst being used, even at 200°C

Better conversion at 400°C than 500°C



NO = NO_2 = 300 ppm, NH_3 = 600 ppm, 8% O_2, 5% CO_2, 2.5% H_2O

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SS Results, fast SCR

Why is performance better at 400 than 500?

NO_2 Decomposition		
Temperature (ºC)	NO outlet (ppm)	NO_2 outlet (ppm)
200	298	310
300	283	330
400	295	315
500	449	146

300 ppm NO, 300 ppm NO_2, 8% O_2, 5% CO_2, 2.5% H_2O

With ~1:1 NO_2:NO in, NO_2 decomposition begins between 400 and 500°C (500°C conversion similar to standard SCR)

Therefore, above 400°C, fast SCR can be limited by NO_2 decomposing, but admittedly NH_3 oxidation light-off as well

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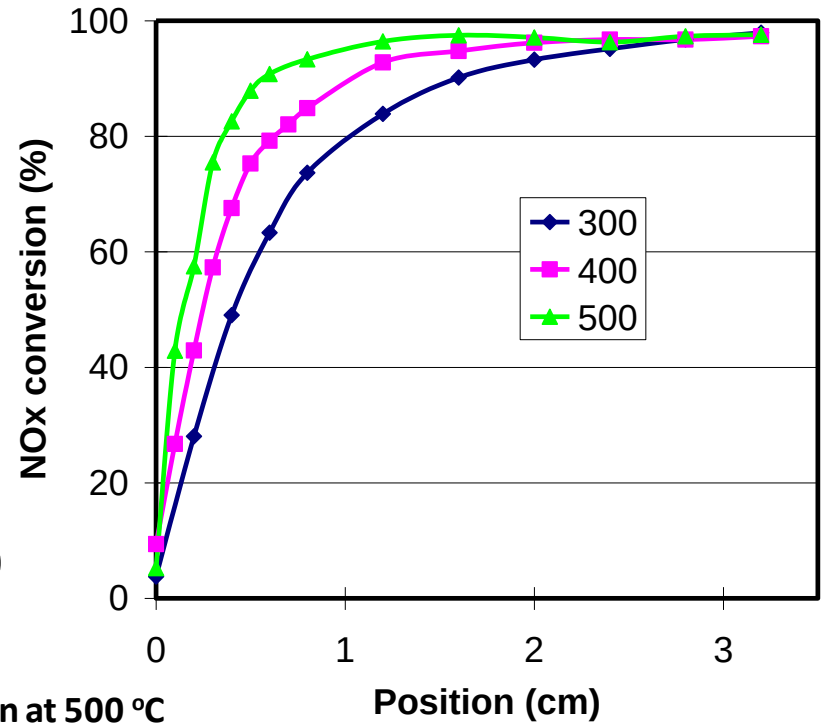
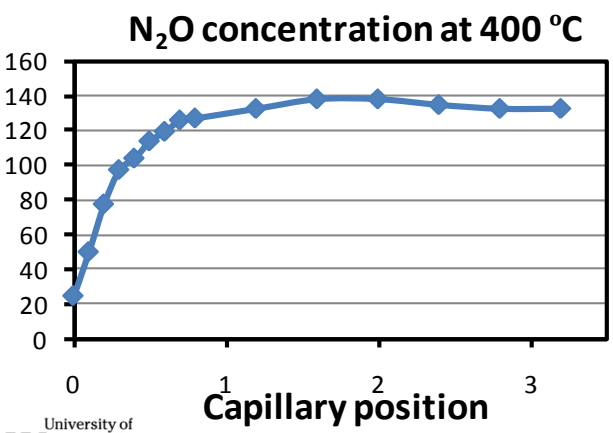
SS results, NO_2 SCR

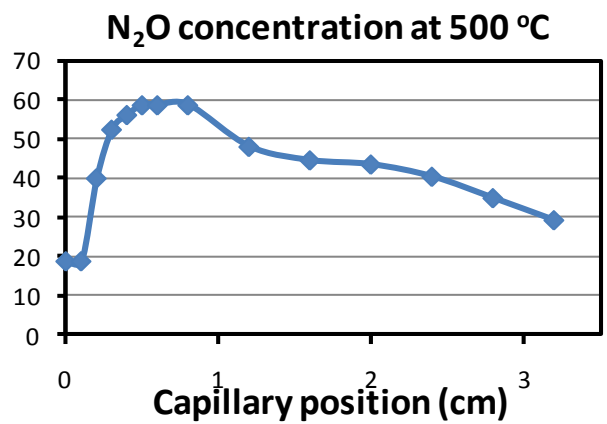
Increasing T, increasing conversion

N_2O

- At 400°C, follows conversion
- At 500°C, a max occurs near cat in – N_2O decomp after







NO_2 = 600 ppm, NH_3 = 600 ppm, 8% O_2, 5% CO_2, 2.5% H_2O

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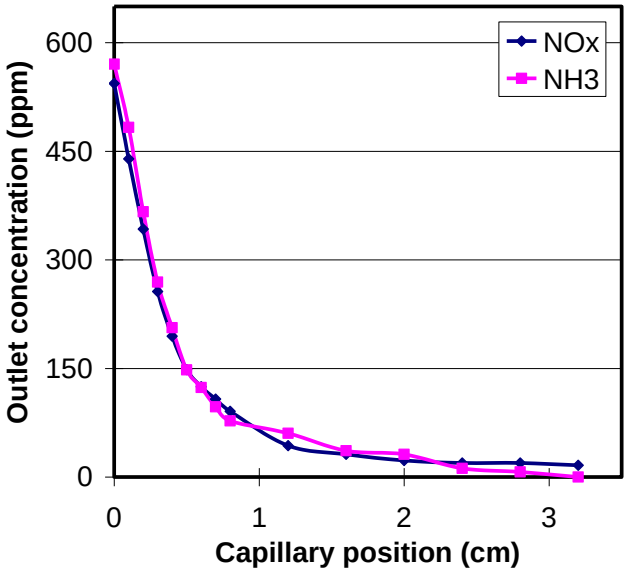
SS results, NO_2 SCR

Highly selective: NO_2 and NH_3 are consumed in a 1:1 ratio



Proposed NO_2 SCR:

$2NH_3 + 2NO_2 \rightarrow N_2 + N_2O + 3H_2O$ (1)

$4NH_3 + 3NO_2 \rightarrow 3.5N_2 + 6H_2O$ (2)

NO_2/NH_3 data indicate NO_2 SCR occurs via reaction (1) not (2)

But the outlet N_2O concentration is lower than would be predicted

- Example, 600 ppm NH_3, 600 ppm NO_2 → theoretically 300 ppm N_2O
- N_2O = 170 (300°C) and 130-140 ppm (400°C)
- Again, NO_2 decomp leads to fast SCR reaction so it is not only NO_2 SCR

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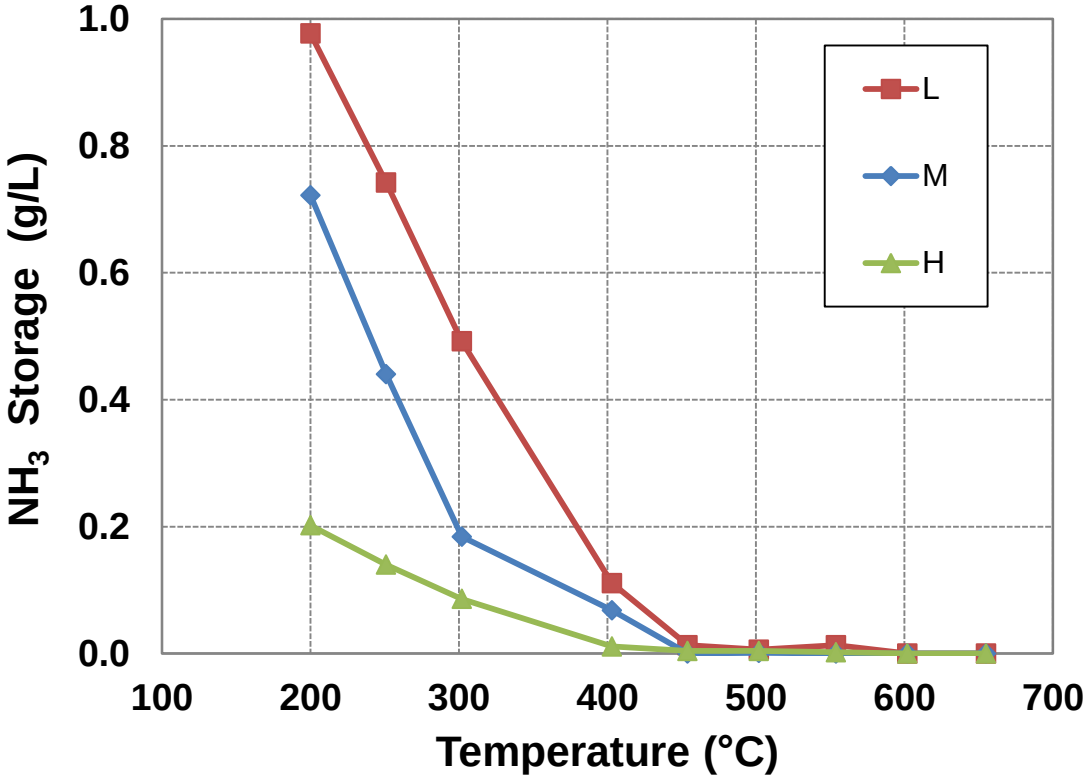
NH_3 adsorption



NH_3 storage significantly impacted by adsorption temperature and thermal aging

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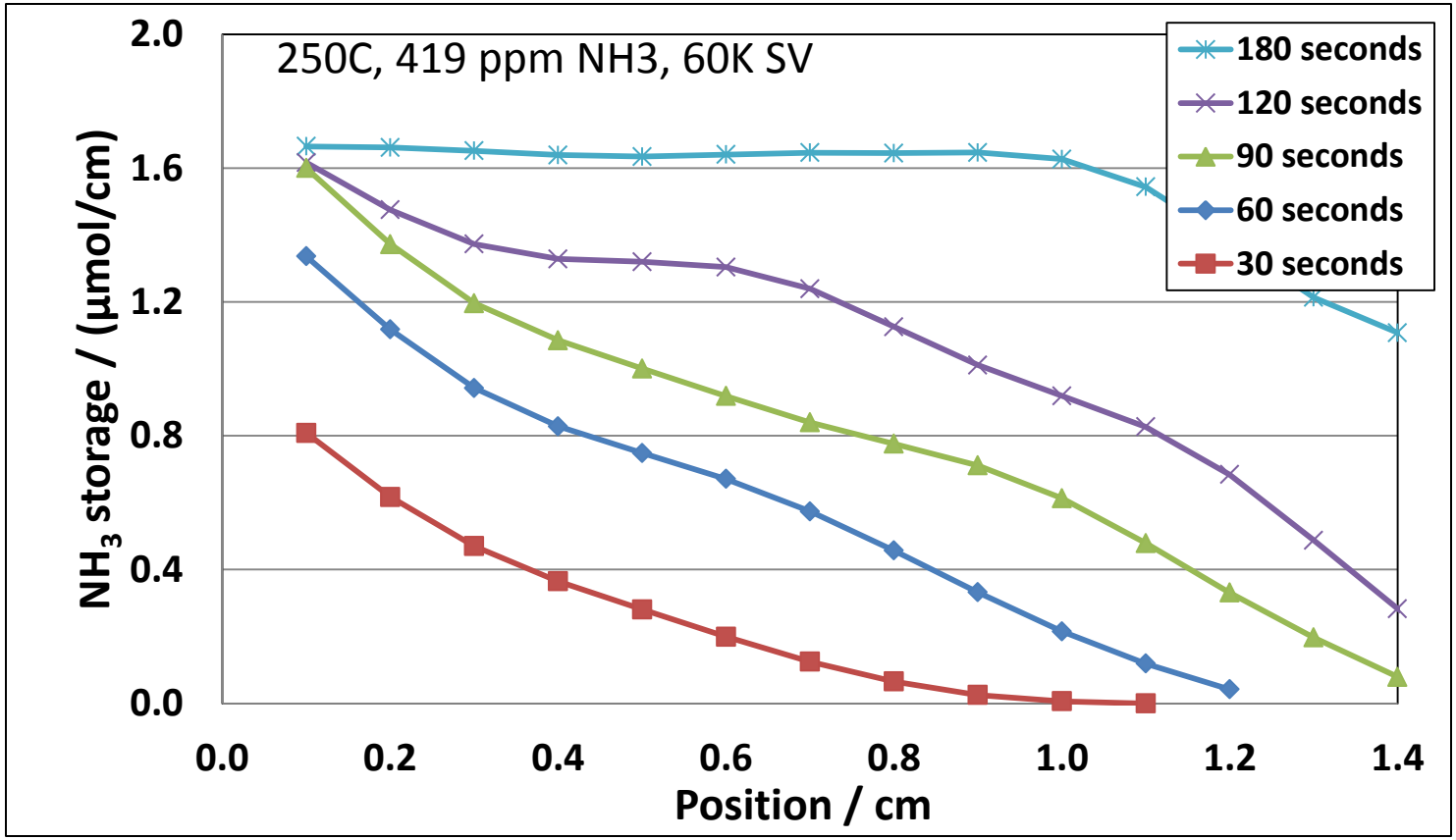
NH_3 adsorption profiles



- Far from saturation: not a step-change, f(exposure)
- Nearer saturation: f(exposure, coverage)

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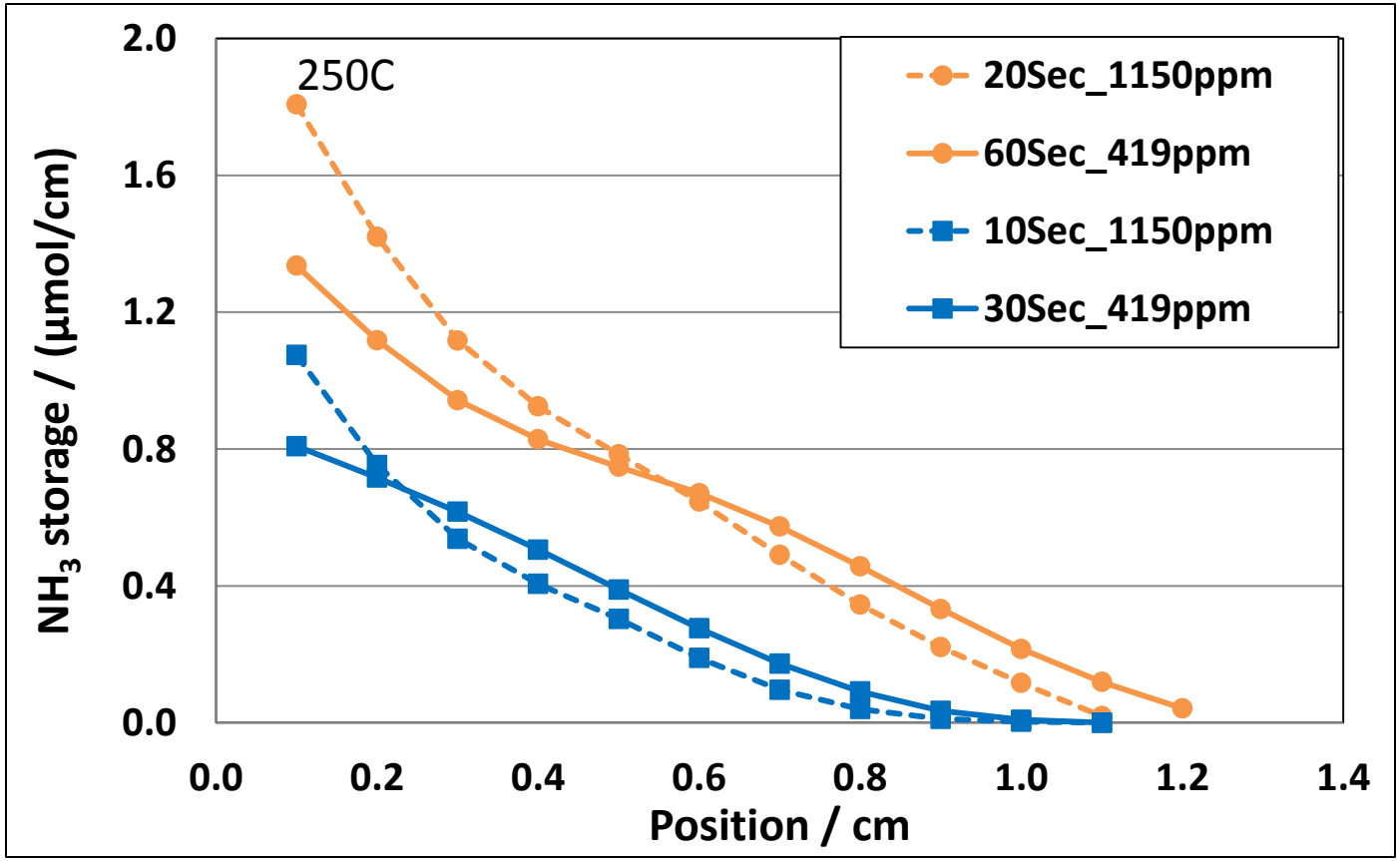
Effect of concentration



Same total dose of NH_3

- Sharper gradient with higher concentration → more at front, less at back of catalyst
- Definite dependence on inlet concentration

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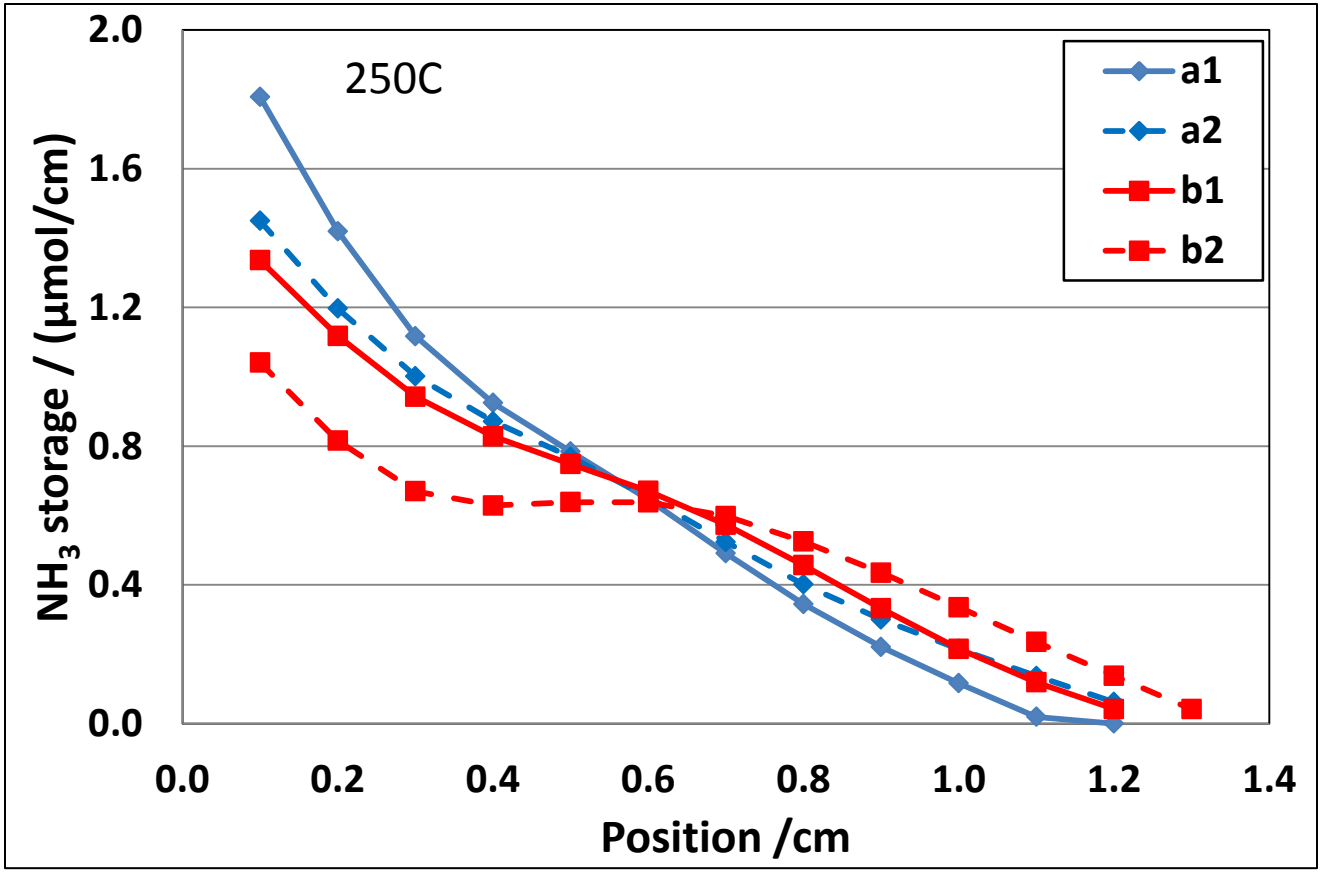
Effect of aging



a1:20×1150, lightly aged;

a2: 20×1150 highly aged;

b1: 60×419 lightly aged;

b2: 60×419 highly aged.

Sec x ppm

Aging leads to less total NH_3 adsorption

- therefore the NH_3 gradient is decreased → and spread across catalyst

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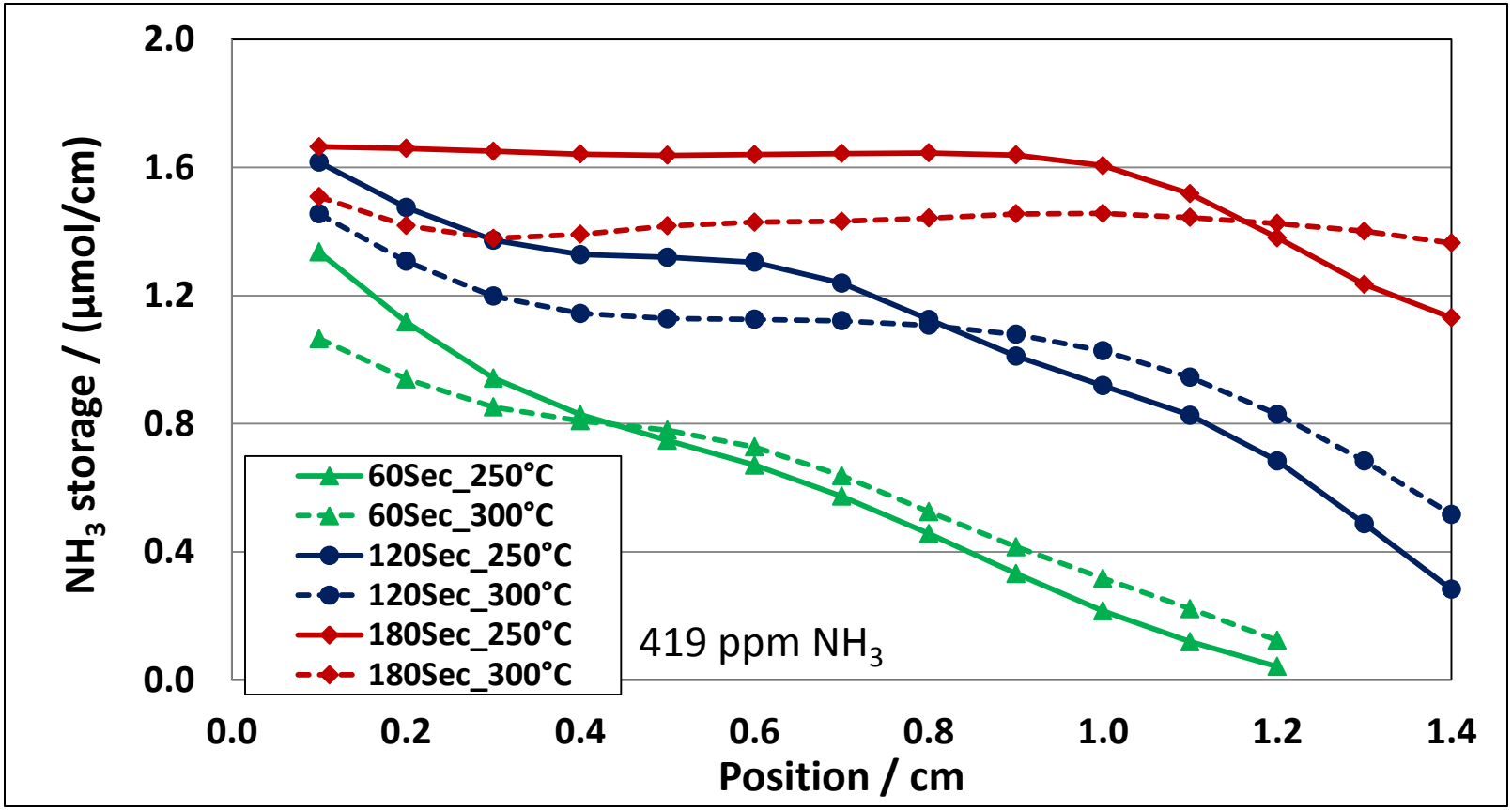
Effect of T



In general as T increases, less NH_3 adsorbs

- Results in a more even distribution along the catalyst
- Except near saturation, same total amount adsorbed though

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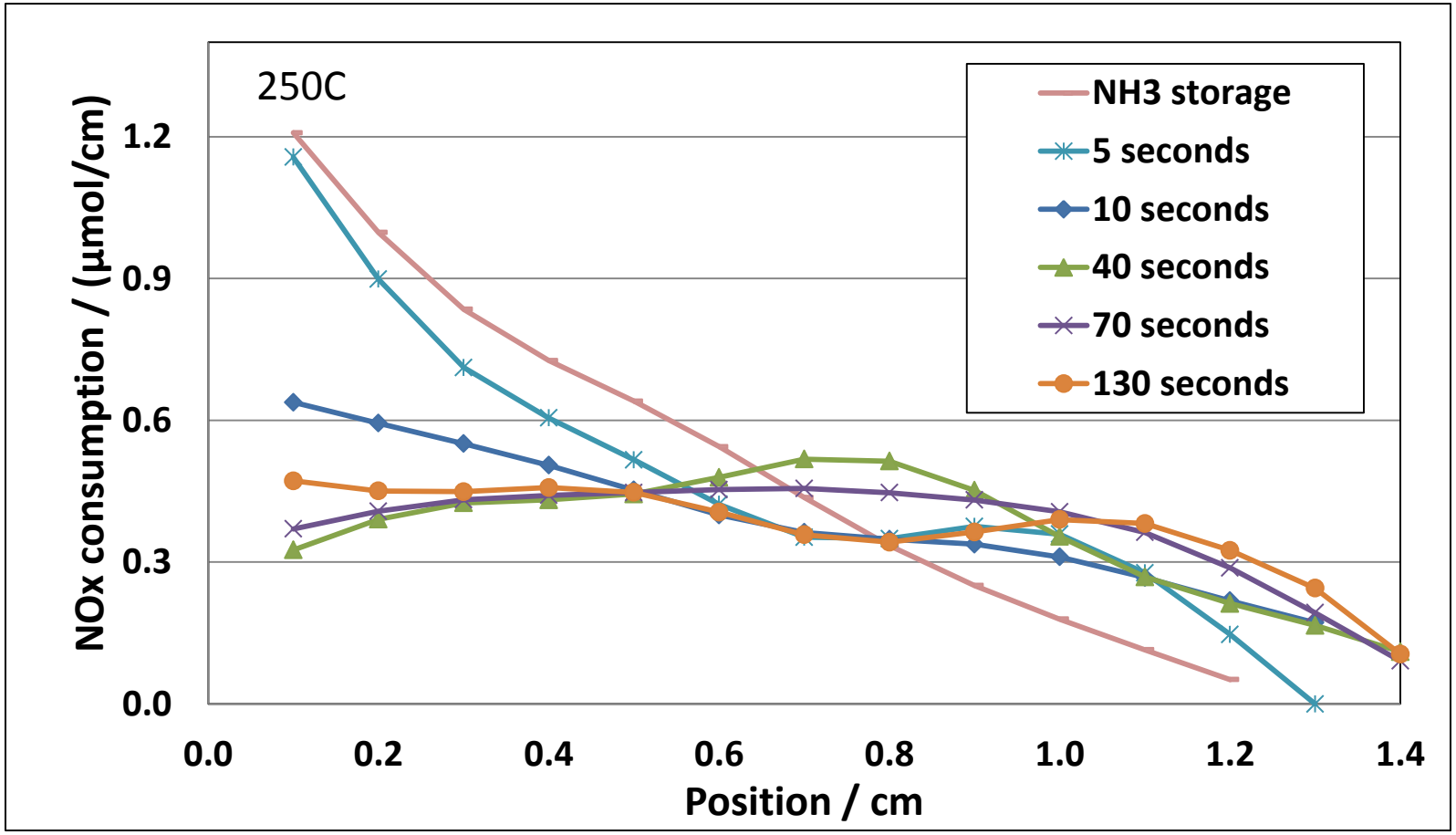
Stored NH_3 redistribution (migration)

Once the pulse ends, there will be a delay before NO_X reaches the catalyst



Fast SCR reaction used to probe where NH_3 is adsorbed

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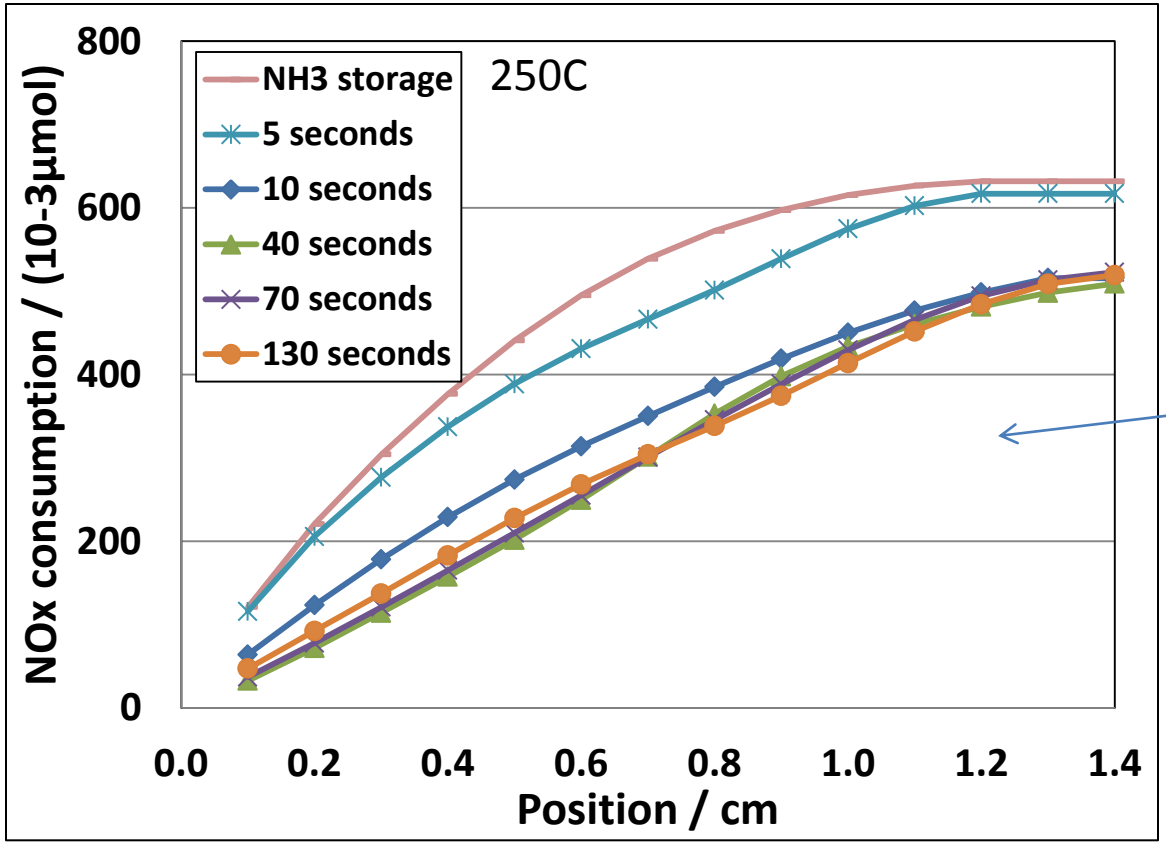
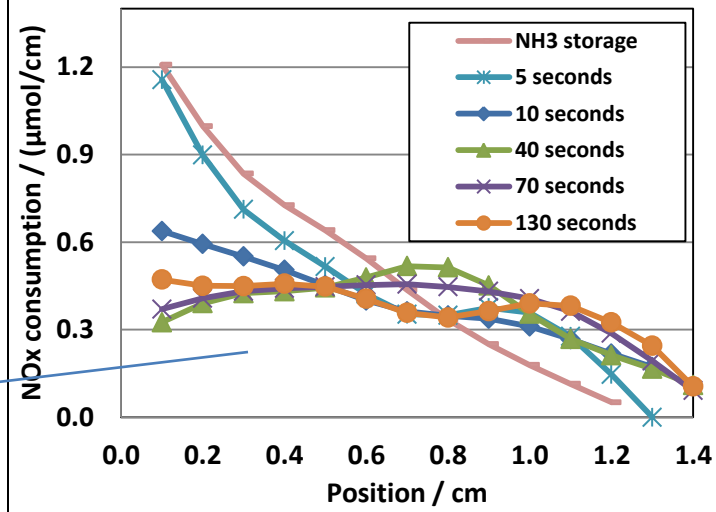
Effect on total adsorbed (i.e. “escaped”)





Cumulative stored amount initially drops → weakly and strongly adsorbed NH_3

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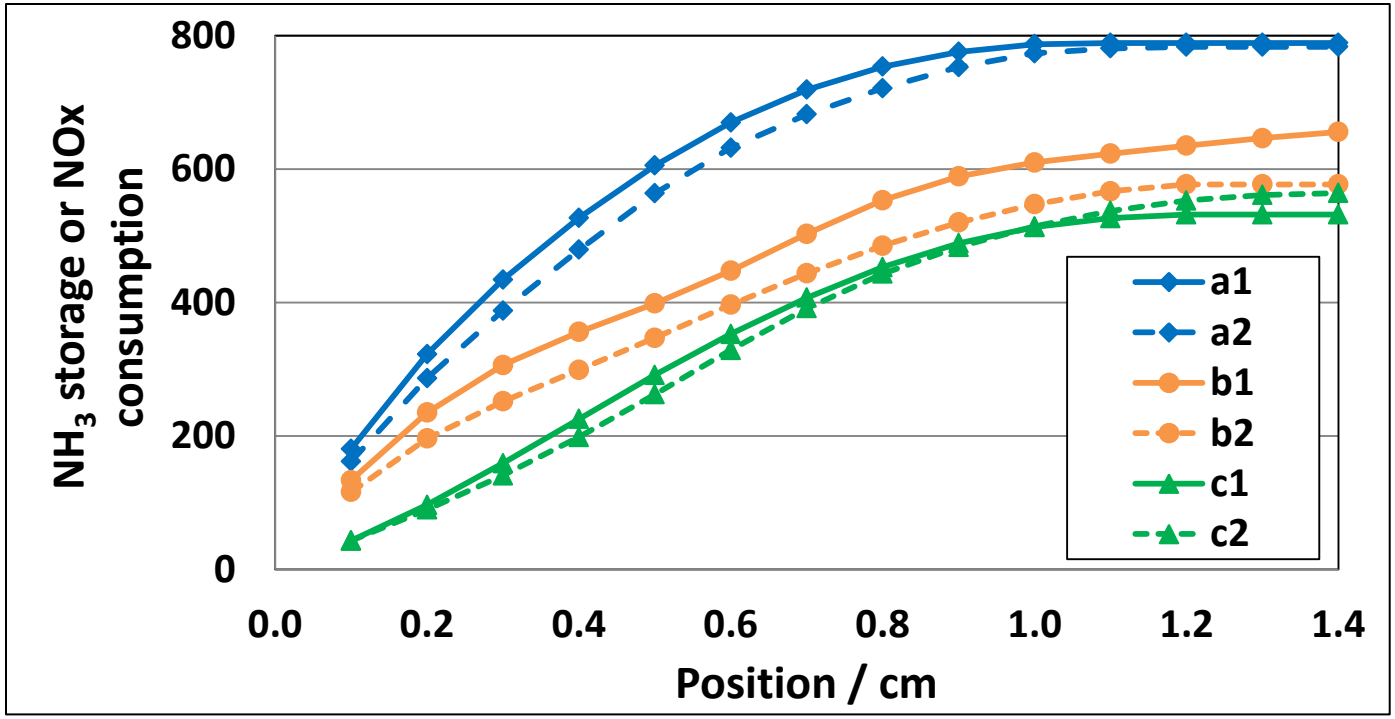
Effect of T on migration



a1: NH_3 storage at 250°C;
a2: NH_3 storage at 300°C;
b1: time gap 10 s at 250°C;
b2: time gap 10 s at 300°C;
c1: time gap 70 s at 250°C;
c2: time gap 70 s at 300°C

An effect of T is noted for short times

At longer times, T has little effect

Again related to weakly and strongly adsorbed NH_3

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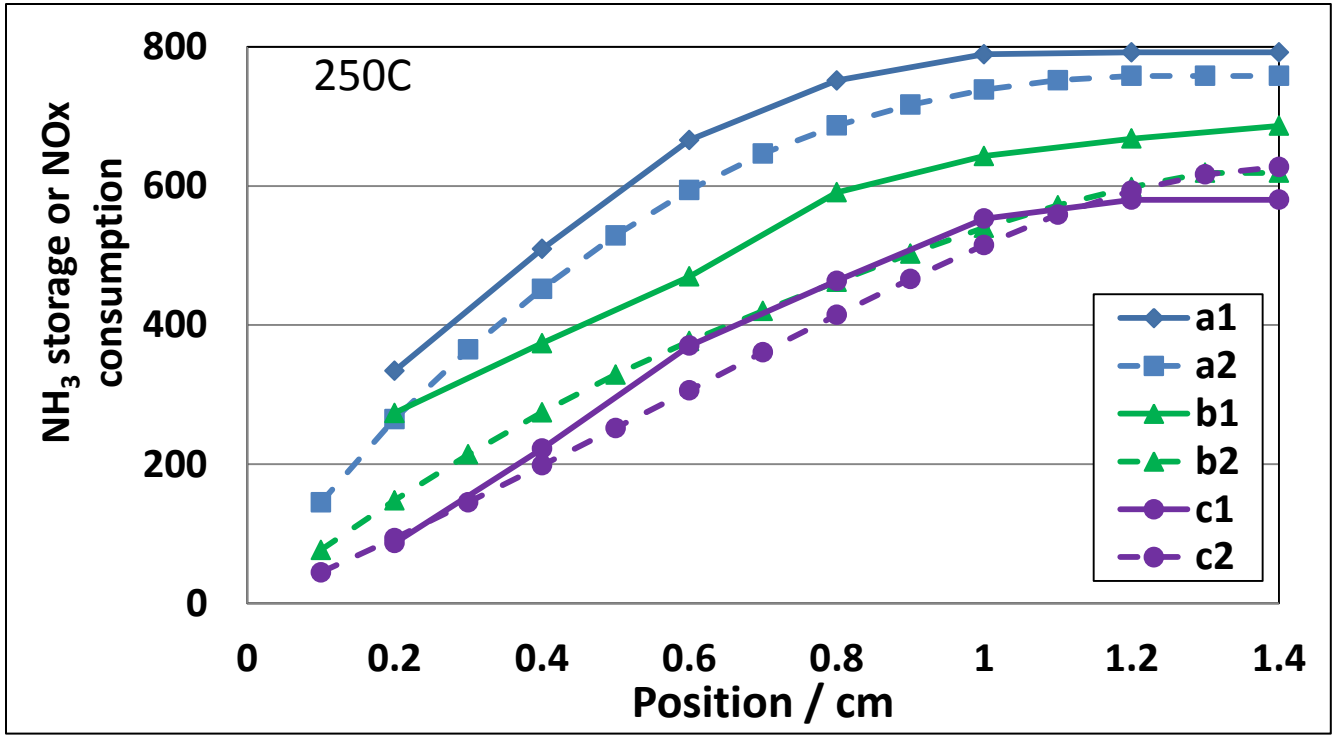
Effect of aging on migration



a1: NH_3 storage on lightly aged catalyst;
a2: NH_3 storage on highly aged catalyst;
b1: time gap 10 s on lightly aged catalyst;
b2: time gap 10 s on highly aged catalyst;
c1: time gap 70 s on lightly aged catalyst;
c2: time gap 70 s on highly aged catalyst.

Again, there is a more significant effect for short time gaps, but this effect decreased with longer times (weakly adsorbed NH_3 affected by aging, strongly not)

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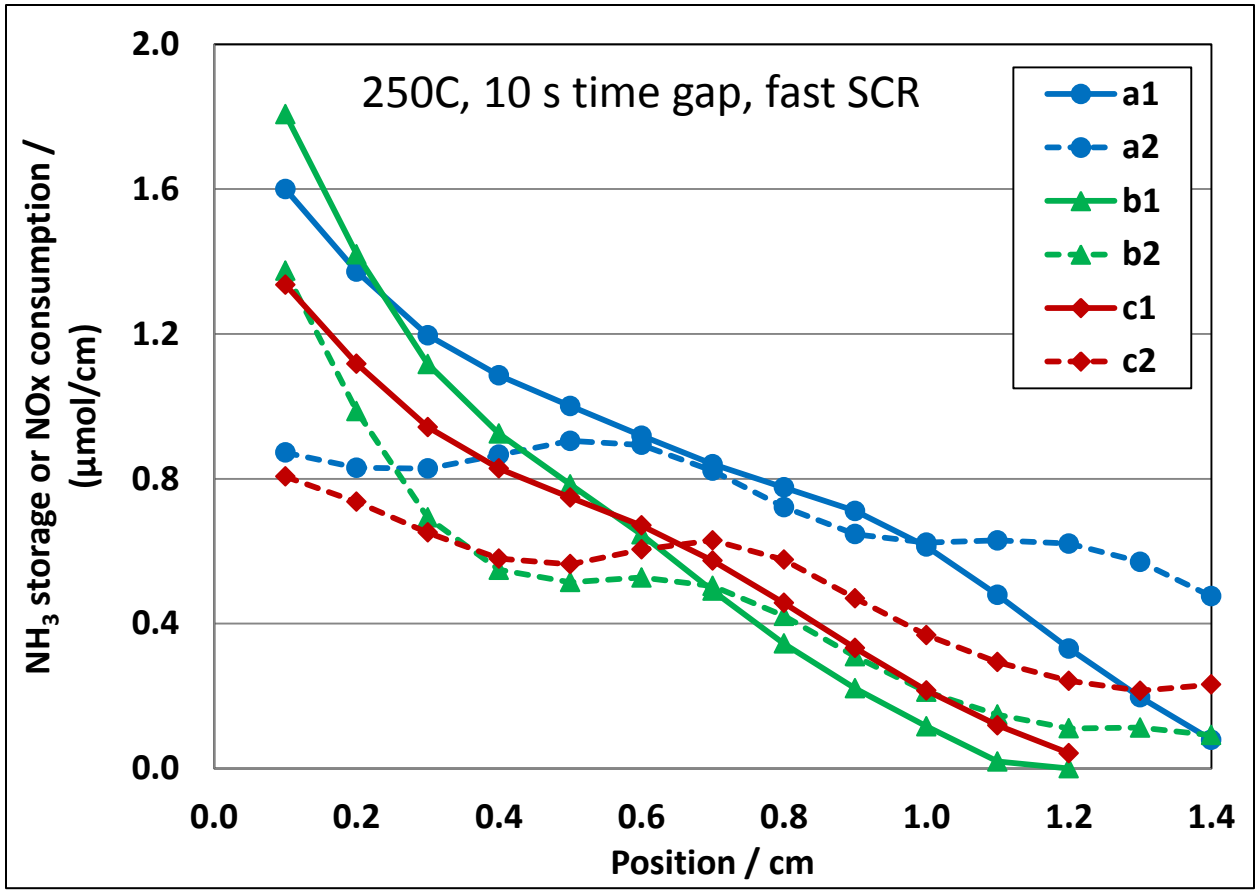
Effect on SCR



a1: 90 s 419 ppm NH_3 storage;
a2: 90 s 419 ppm NH_3 storage followed by a 90 s, 416 ppm NOx pulse;
b1: 20 s 1150 ppm NH_3 storage;
b2: 20 s 1150 ppm NH_3 storage followed by a 60 s, 416 ppm NOx pulse;
c1: 60 s 419 ppm NH_3 storage;
c2: 60 s 419 ppm NH_3 storage followed by a 60 s, 416 ppm NOx pulse

Combining NH_3 storage and SCR data (storage after migration) shows reaction and migration pattern

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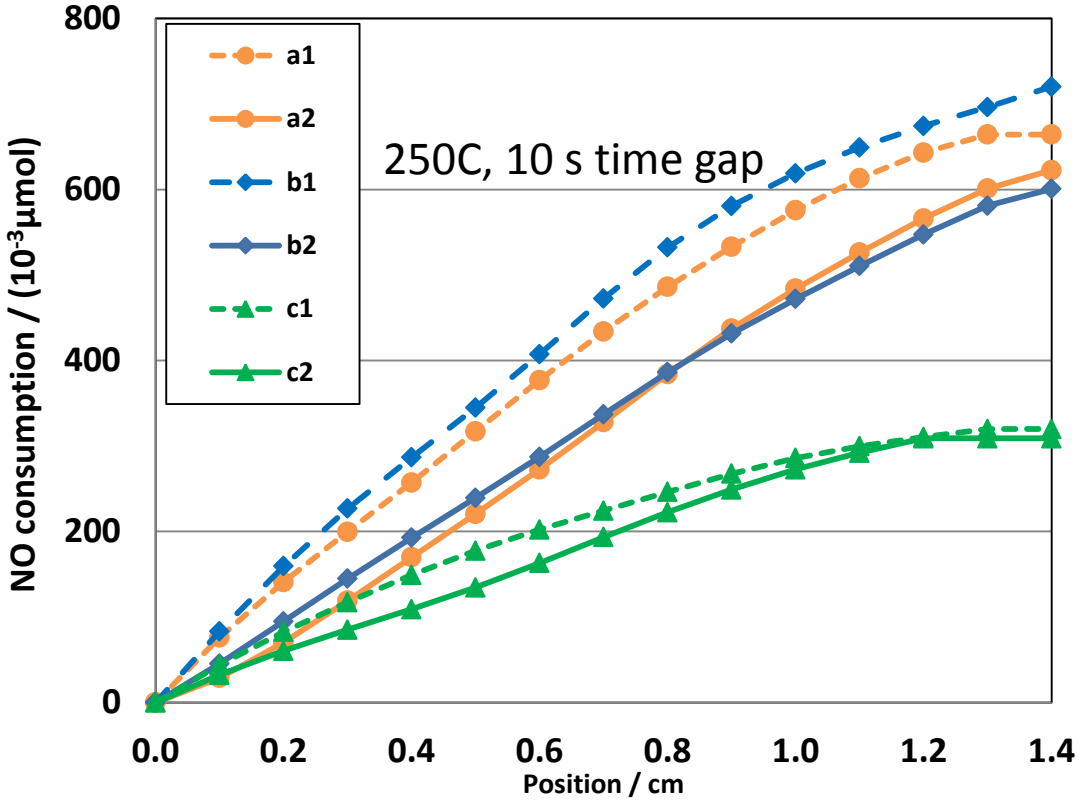
NOX consumption on predosed surface



a1: 60 s NH_3 → 60 s NO; lightly aged catalyst
a2: 60 s NH_3 → 60 s NO; highly aged catalyst;
b1: 60 s NH_3 → 60 s NOx (1:1 $NO:NO_2$); lightly aged catalyst;
b2: 60 s NH_3 → 60 s NOx (1:1 $NO:NO_2$); highly aged catalyst;
c1: 60 s NH_3 → 30 s NO; lightly aged catalyst;
c2: 60 s NH_3 → 30 s NO; highly aged catalyst

With aging → less NH_3 adsorbed

- Obvious difference in performance when there is not "enough" NH_3
- High adsorbed NH_3:NO ratios → less difference in performance

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Conclusions

- NH_3 adsorption profiles were measured using SpaciFTIR
- Migration of adsorbed NH_3 was observed
  - at short time gaps,
  - increased temperature, and
  - with aging, the more weakly adsorbed NH_3 migrated

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