

Spatially Resolving SCR Reactions

Bill Epling, John Luo, Peter Hou,
Steve Schmieg and Wei Li



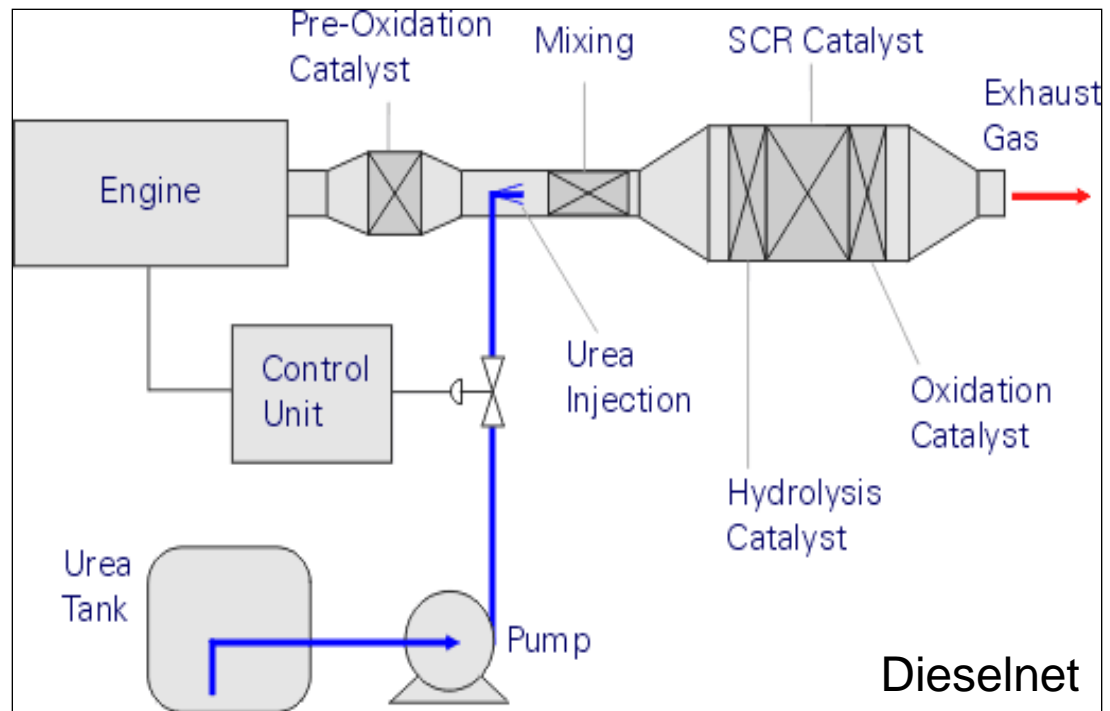
Introduction - NOX control options

- **Aftertreatment techniques**

- NO_x storage/reduction (lean NO_x trap)
- Selective catalytic reduction (SCR)
 - Selectivity between O₂ and NO_x
 - Reductants: NH₃ and/or HC
 - Standard SCR: $4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$
 - NO₂ leads to better low T performance (DOC)

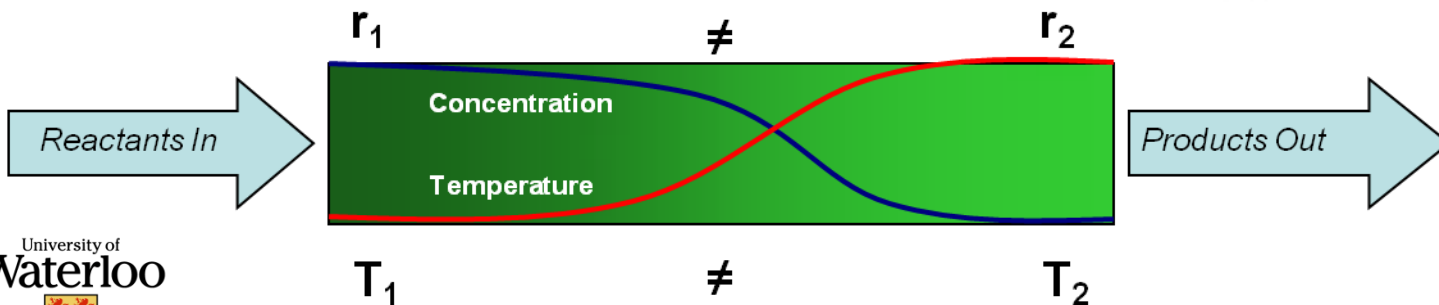
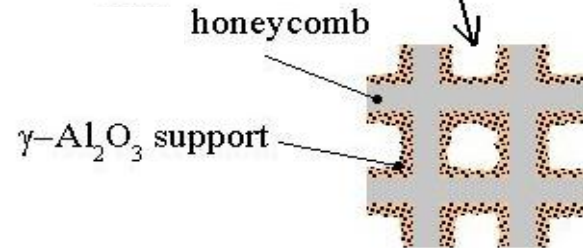
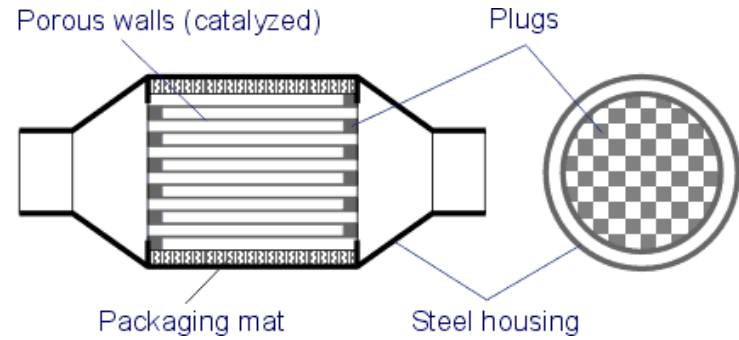
Introduction - application of SCR

- SCR has been used since ~2005 commercially
 - In Europe and NA
- And in combination with NSR (passive SCR)



Introduction - monoliths

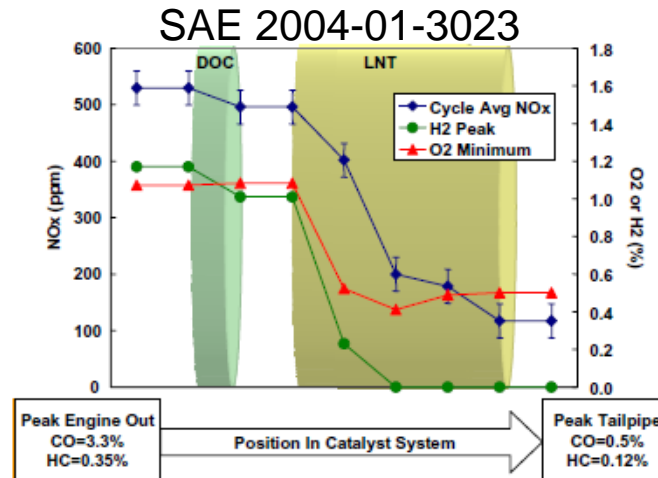
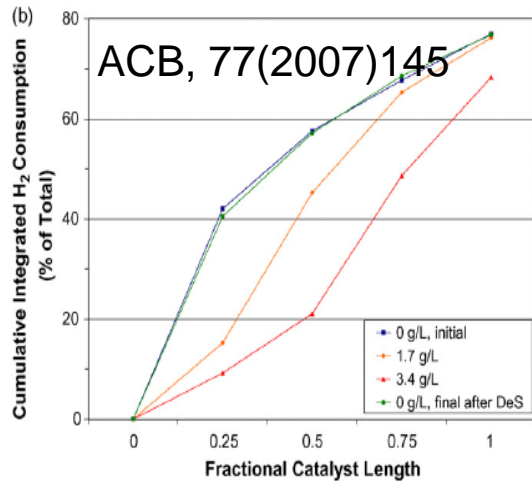
- Vehicle catalysts, all monolith supported
- Significant research in modeling the chemistry and reactions along a monolith channel (1 and 2D)



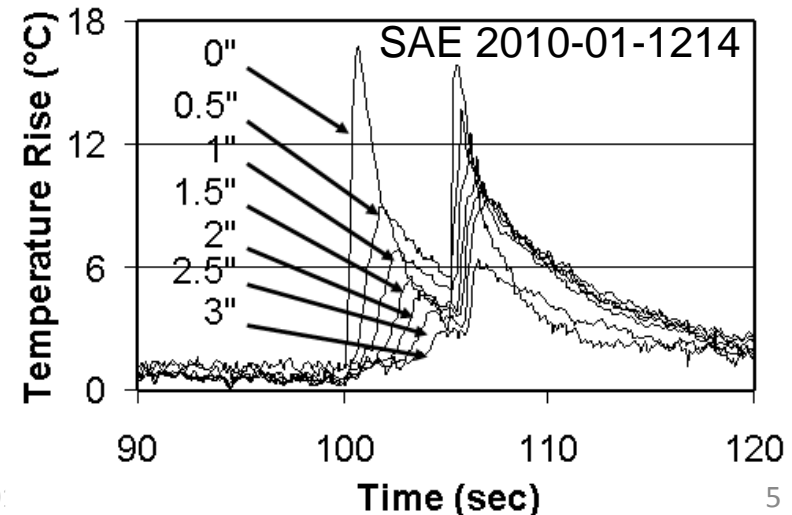
Introduction - spatial resolution (NSR)

Reactions over NSR catalysts characterized

- OSC, trapping, NH_3 and reductant evolution, S impact (Partridge, Choi et al)



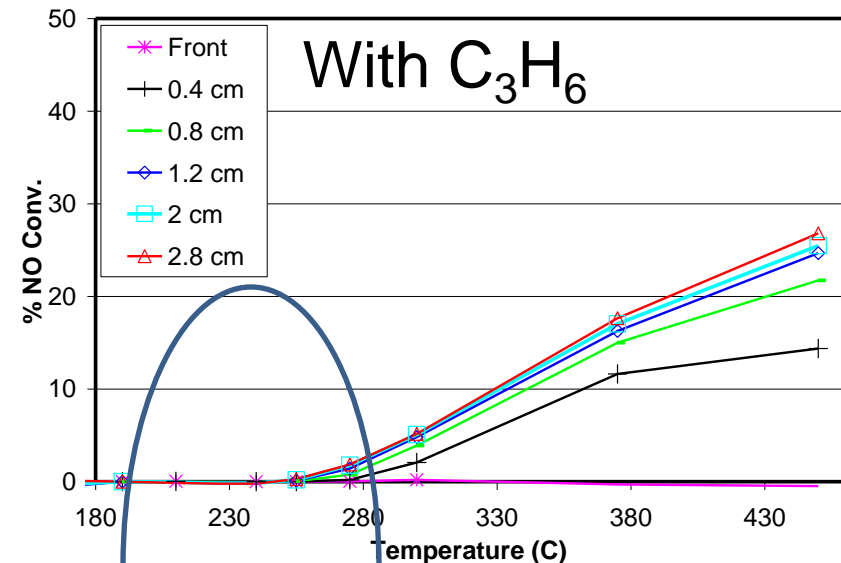
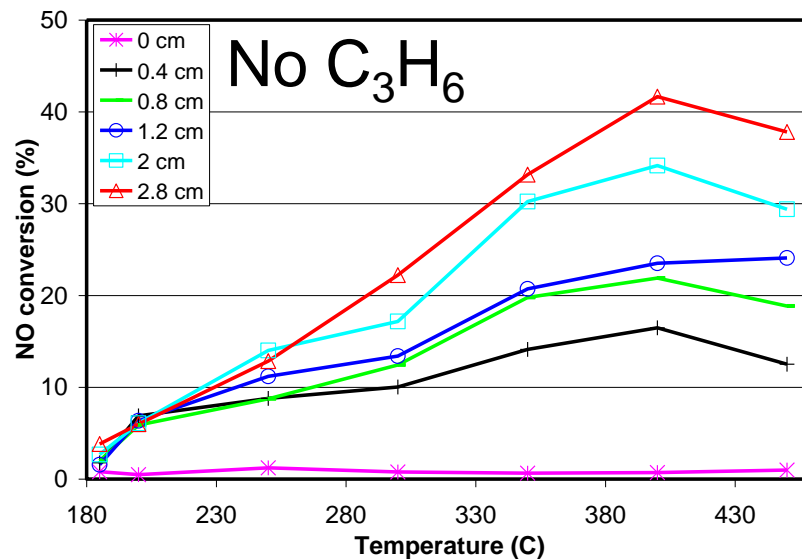
- Temperature waves through the catalyst (Russell, Partridge, Choi et al)



Introduction - spatial resolution (DOC)

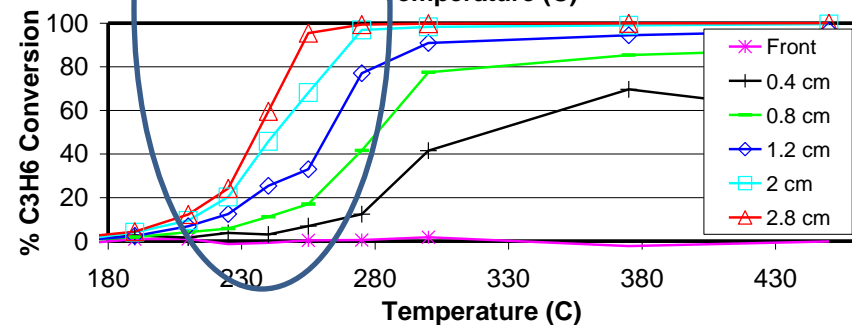
As well as over DOCs

- Competitive reactions between NO, CO, HCs (Irani)



- Impact of homogeneous and heterogeneous thermal degradation

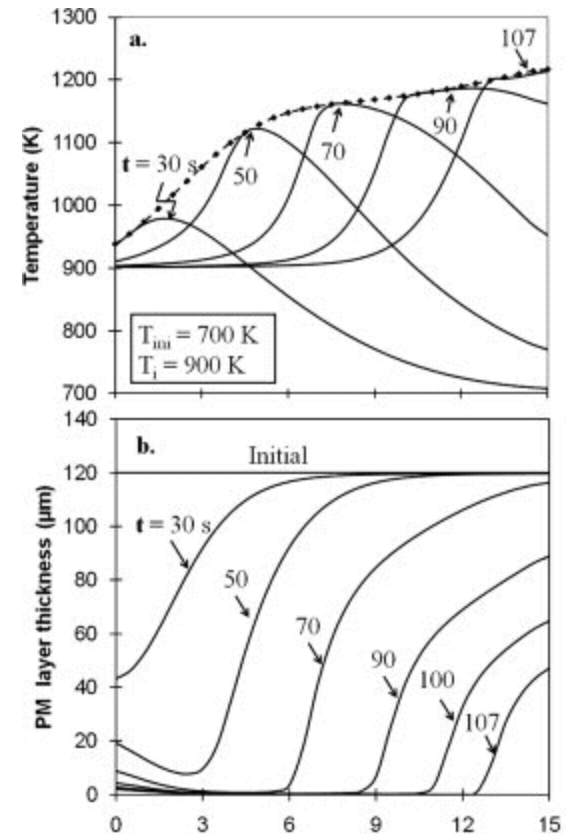
– Russell, Shakir et al



Introduction - spatial resolution (DPF)

Temperature profiles during soot burn

- Stationary conditions typically show back to front
- Luss et al have done substantial work recently in evaluating changes from high load (soot burning) to idle huge T changes observed

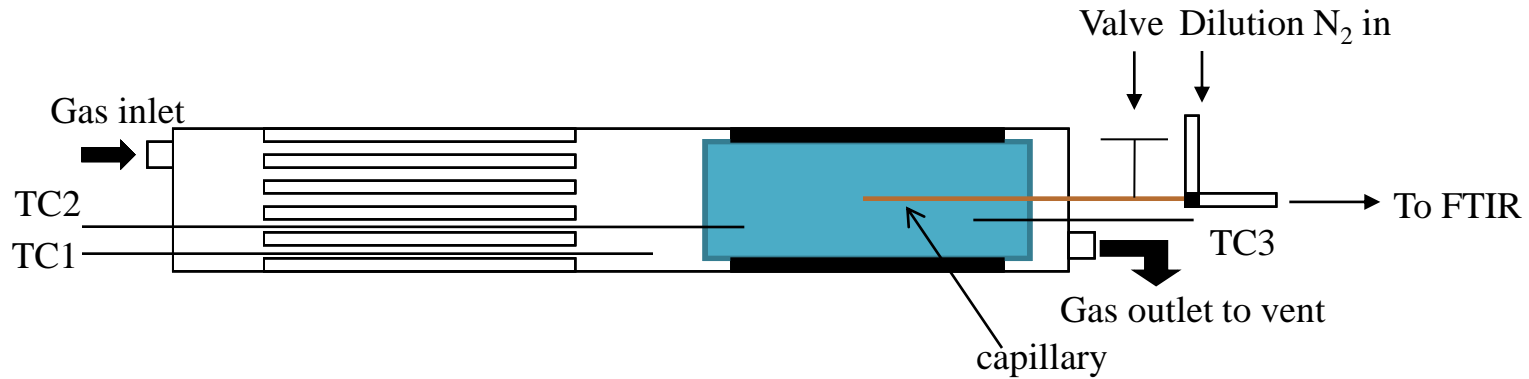


Ind. Eng. Chem. Res. 50(2011)832.

Introduction - SCR basics

- Three SCR reactions typically discussed
 - Standard SCR
 - $4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$
 - Fast SCR
 - $2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$
 - NO_2 SCR (slow)
 - $8\text{NH}_3 + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}$
- Other key reactions
 - $2\text{NO} + \text{O}_2 \leftrightarrow 2\text{NO}_2$
 - $4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}$

Experiment set-up



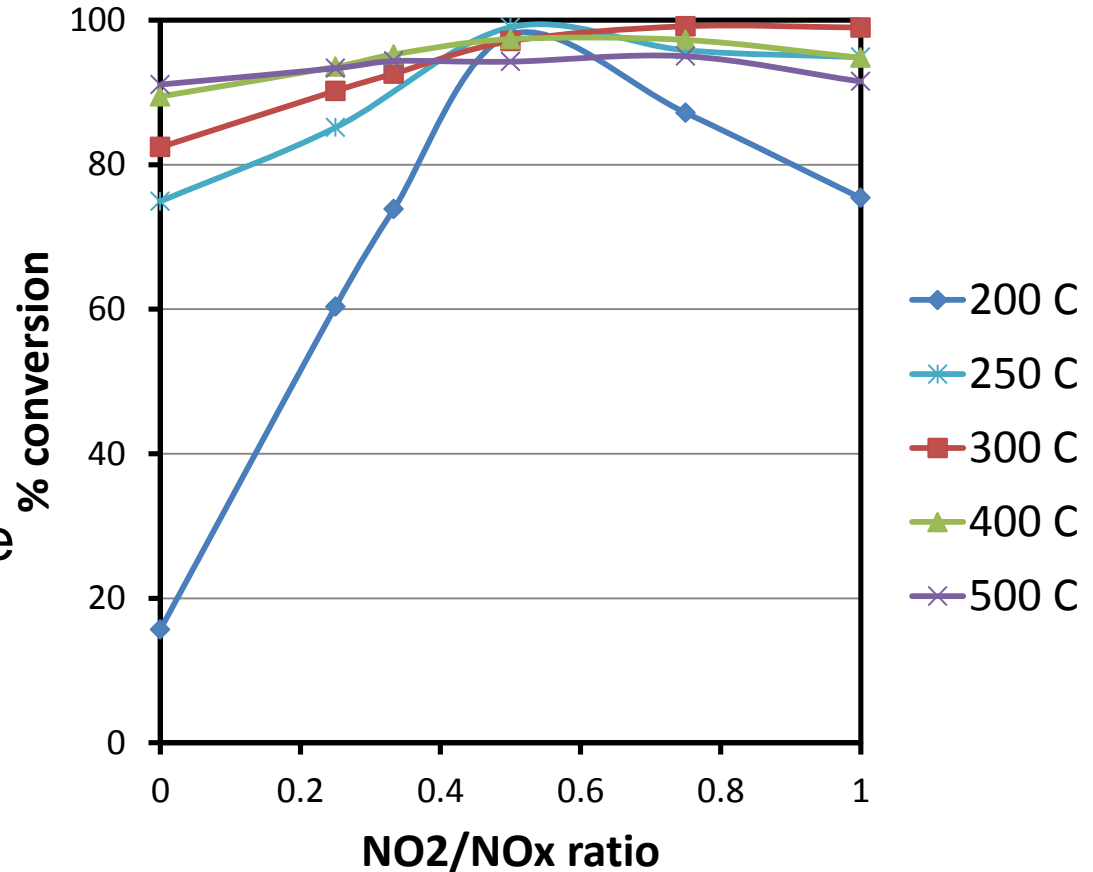
Spaci-FTIR

Typical gas composition: 600 ppm NO_x , 600 ppm NH_3 , 8% O_2 ,
2.5% H_2O , 5% CO_2 , balance N_2

Catalysts: Fe zeolite (provided by GM)
Cu zeolite (provided by GM)

Standard performance check

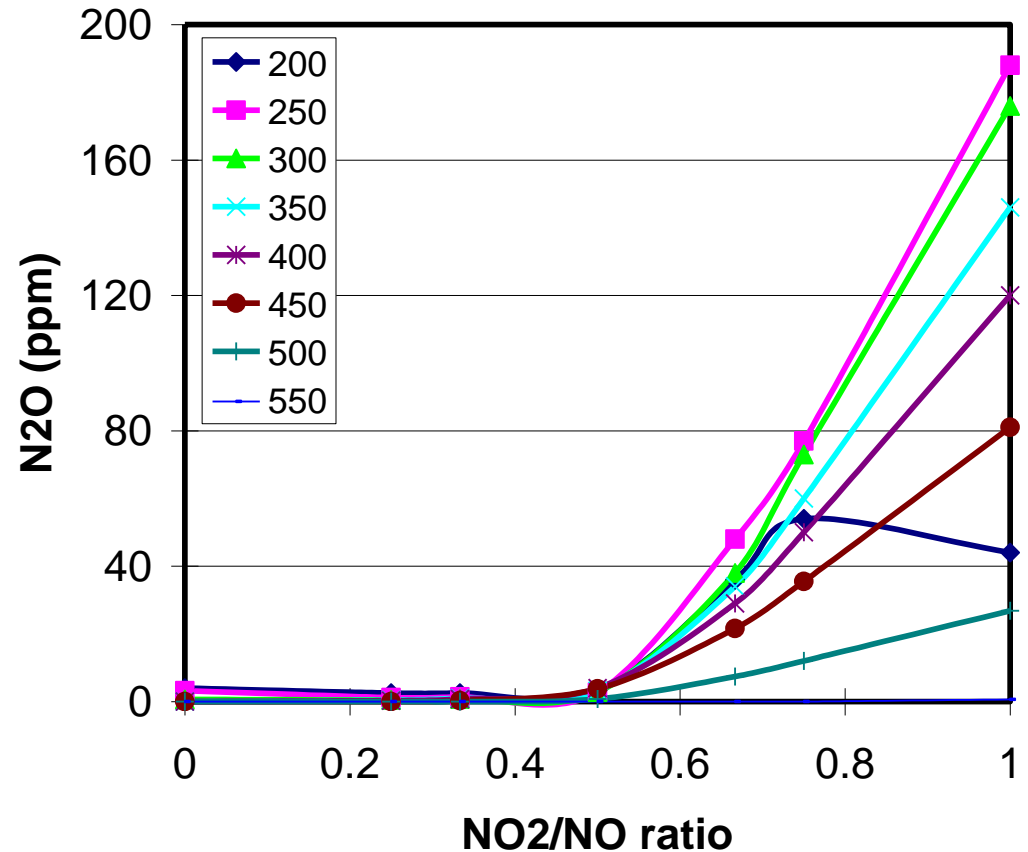
- NO_2 has noted impact at low T
 - Best is 1:1 NO_2 : NO at 200°C
- At $T > 200^\circ\text{C}$
 - Increasing NO_2 to 1:1 increases conversion
 - Past 1:1 small decrease in conv observed
- Best performance at 400°C
 - Little NH_3 loss, good SCR kinetics



Expt conditions: $\text{NO}_x = 600$ ppm,
 $\text{NH}_3 = 600$ ppm, 8% O_2 , 5% CO_2 , 2.5% H_2O ;
Catalyst: Fe-zeolite, space velocity= 28K hr^{-1}

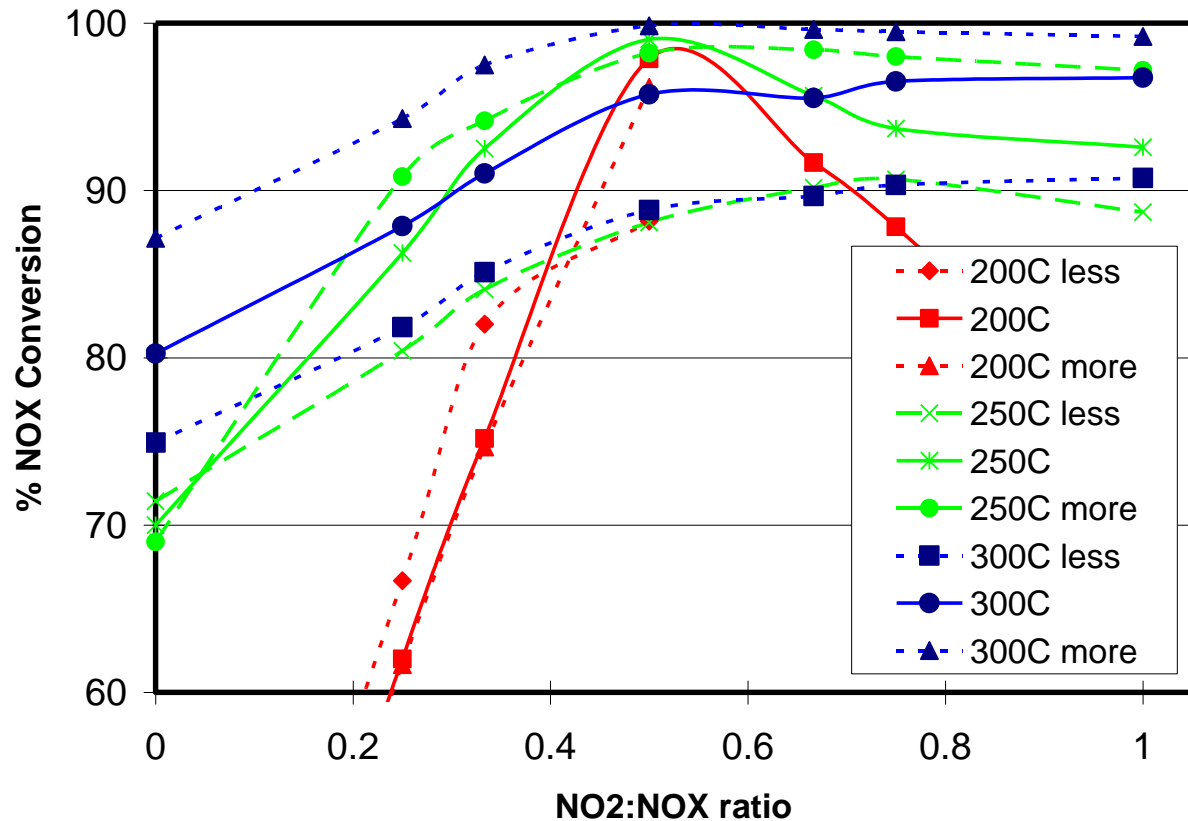
N₂O formation

- No N₂O observed until NO₂:NO ratio exceeds 1:1
- Maximum between 200 and 300°C
- Decrease with higher NO₂ at 200°C due to NH₄NO₃ formation



[NH₃] effect

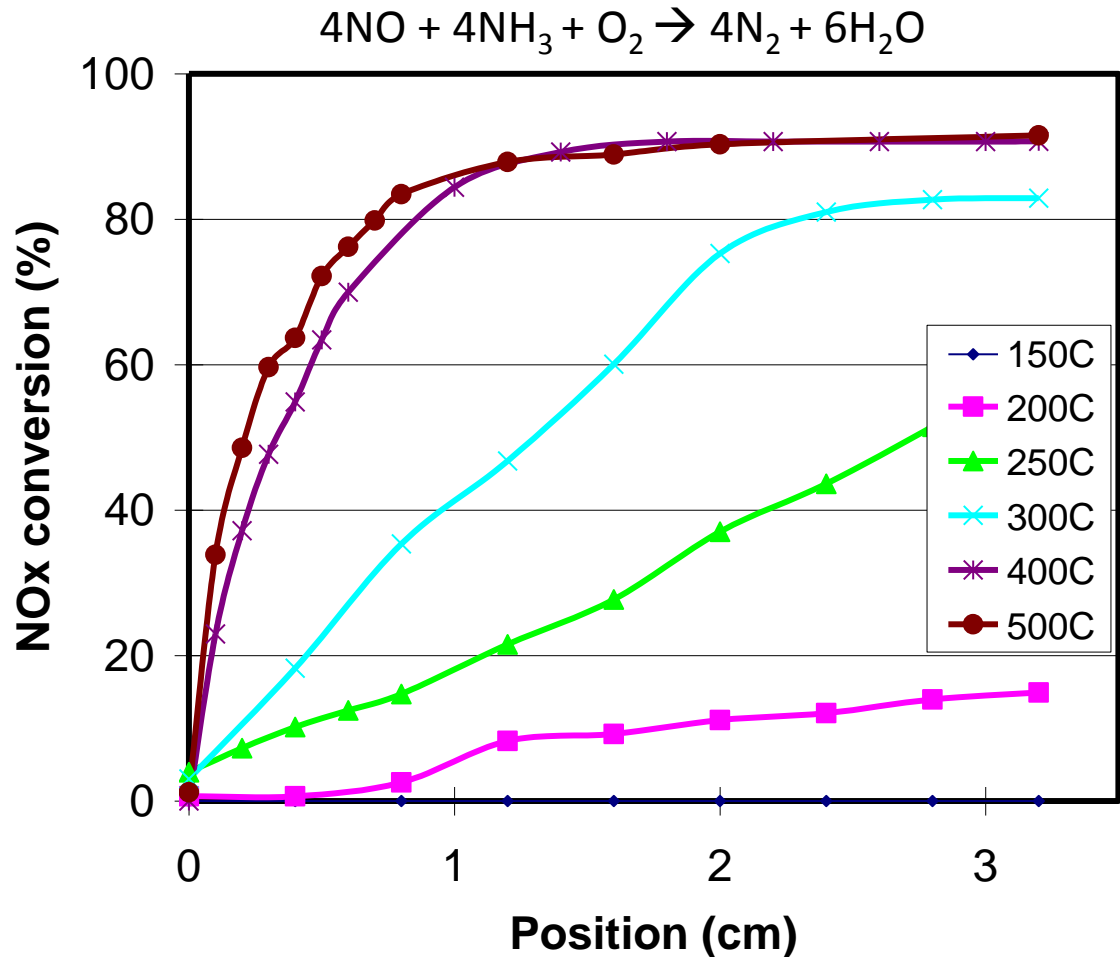
- NH₃ - slightly negative effect at 200° C and if NO₂/NO_x ratio is < 0.5, at 250° C also
- Positive effect at T > 300° C or NO₂/NO_x ratio > 0.5



NO_x = 600 ppm, NH₃ = 600 ppm or 540 ppm (less) or 660 ppm (more); 8% O₂, 5% CO₂ and 2.5% H₂O.

Standard SCR

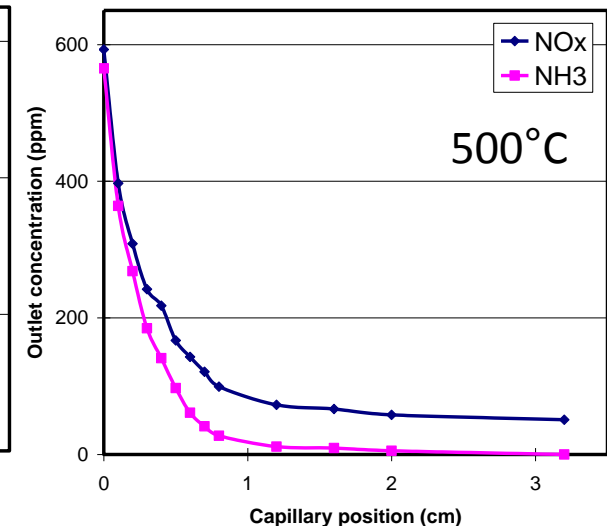
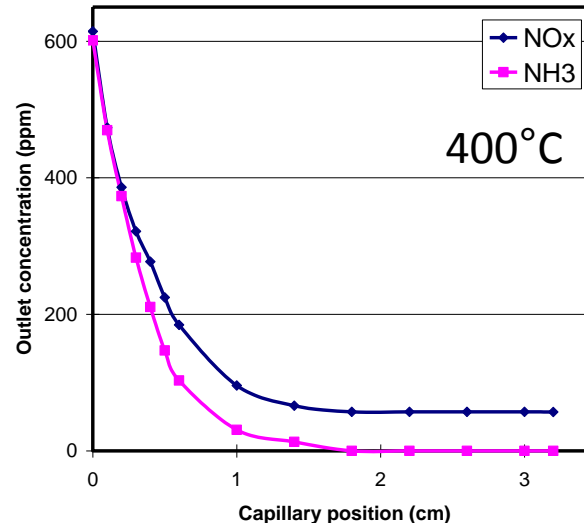
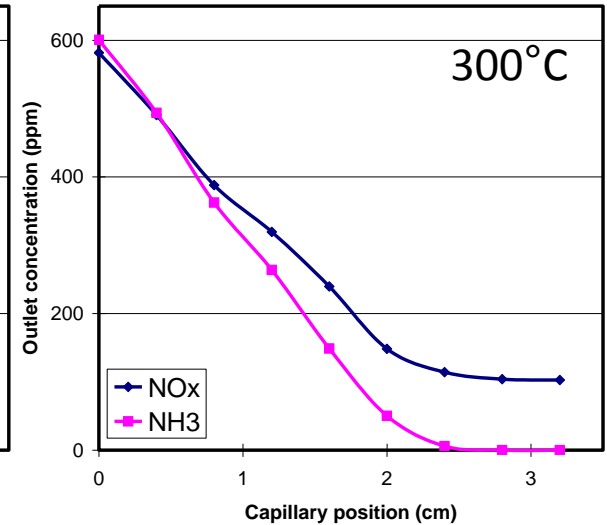
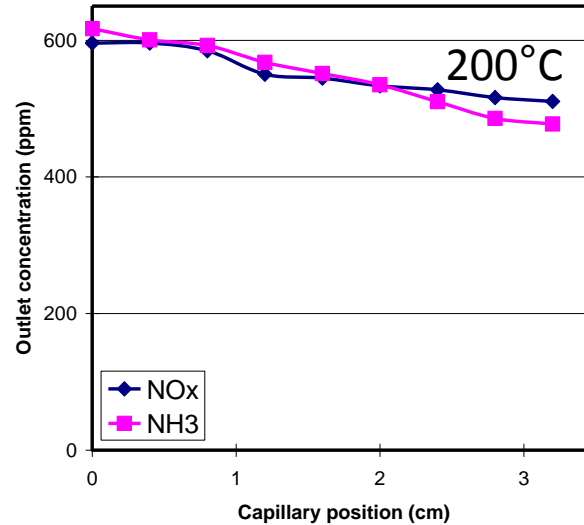
- Increasing T, increasing conversion
- Increasing T, reaction zone moves closer to inlet
- At $T \geq 300^\circ\text{C}$, not all the catalyst is being used



NO = 600 ppm, NH₃ = 600 ppm,
8% O₂, 5% CO₂, 2.5% H₂O

Standard SCR

- At 200°C, some conversion – overall slow SCR kinetics
- NH₃ over-consumption limits total conversion at higher temperatures



NH₃ oxidation

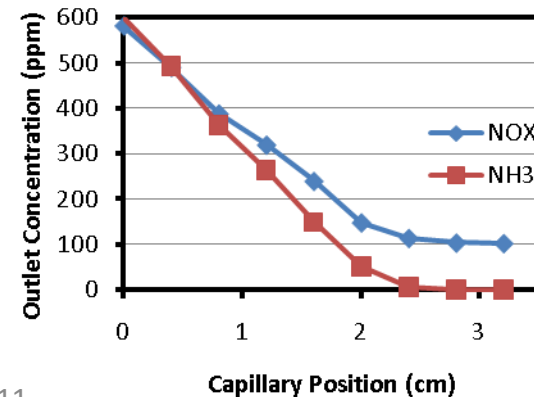
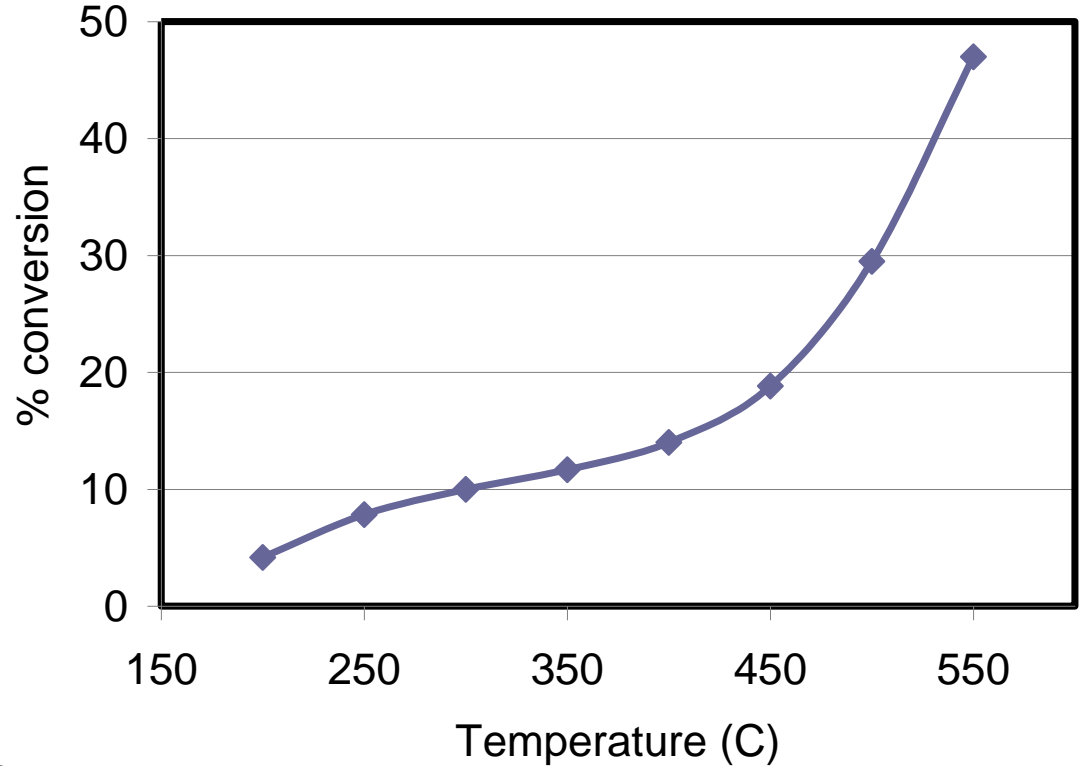
Where does NH₃ over-consumption come from?

“light-off” ~ 400°C

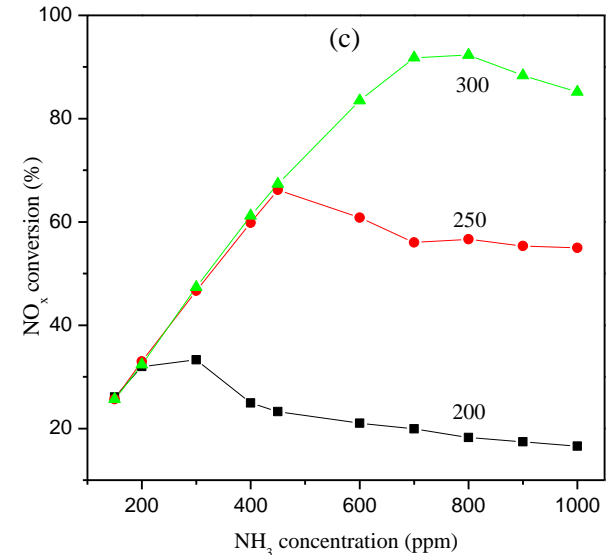
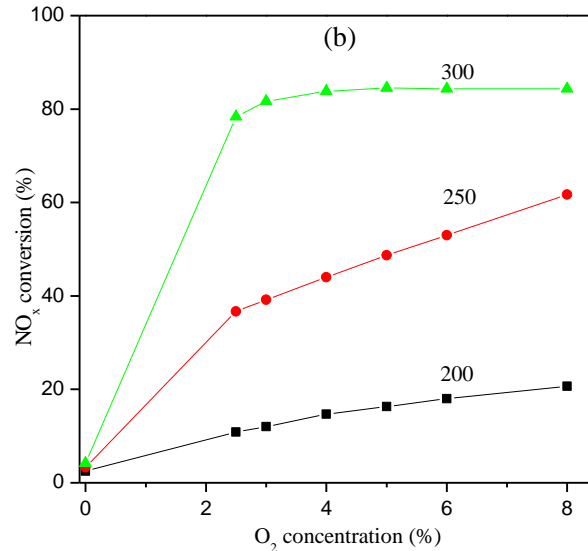
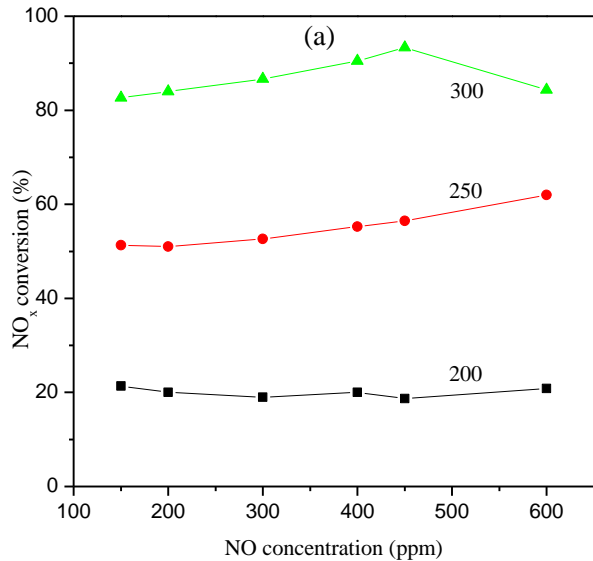
NH₃ limitation due to oxidation in standard SCR at 400, 500°C

NH₃ limited at 300°C

- slow reaction, therefore more NH₃ oxidation residence time

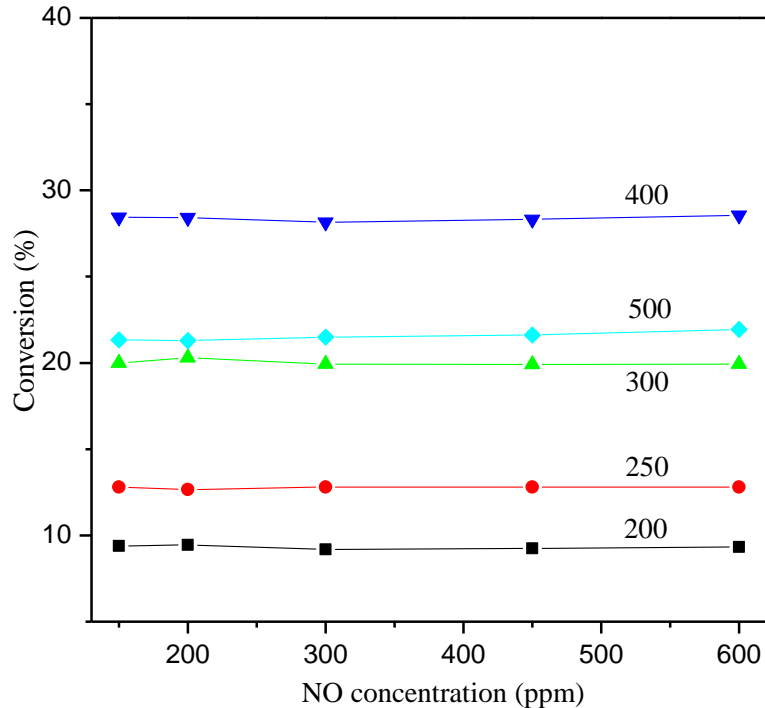


Kinetic analysis



- NO dependency \rightarrow 1st order in NO (0.97)
 - Obvious at 200°C, \uparrow conv at 250 and 300°C is due to \downarrow NH₃ inhibition
- O₂ dependency \rightarrow 1/2 order (0.56)
- NH₃ dependency \rightarrow - order (-0.43)
 - Low NH₃ \rightarrow total consumption, theoretical NO_x conv attained (low NH₃ coverage, good reactivity)
 - Increasing NH₃, increasing surface coverage \rightarrow theoretical NO_x conversion not met

Kinetic analysis (NO oxidation)

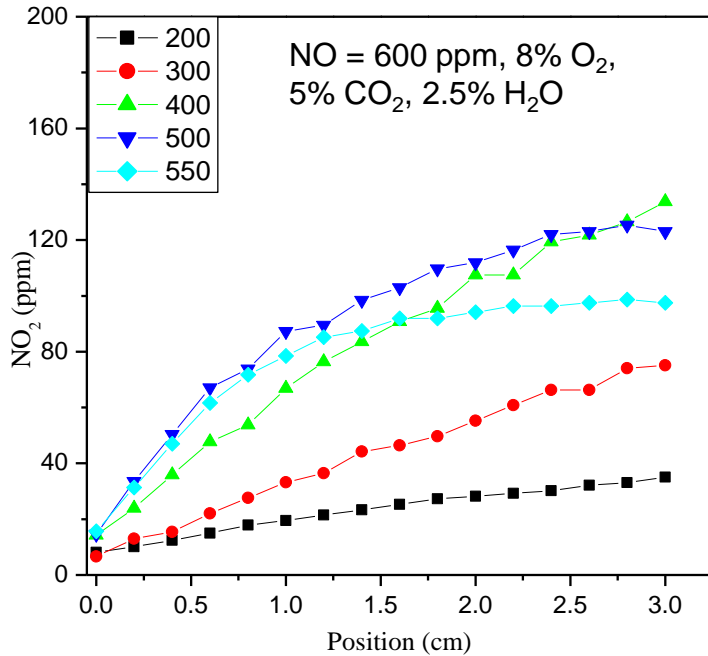


NO dependency \rightarrow 1st order in NO (1.0)
 O₂ dependency \rightarrow ½ order (0.57)

Reaction	NO	O ₂	NH ₃
NO oxidation	1.00 (0.99)	0.57 (0.99)	n/a
standard SCR	0.97 (0.99)	0.56 (0.99)	-0.43 (0.99)

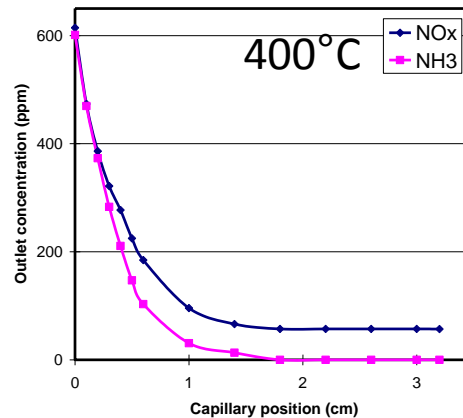
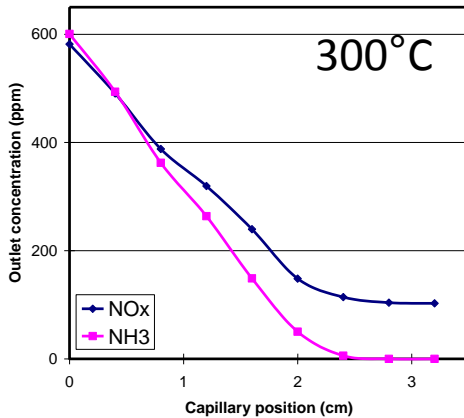
Similarity in reaction orders suggests NO oxidation is rate limiting, key for low T performance

NO oxidation



200→300→400°C, increased oxidation

500→550°C less oxidation, thermo limited



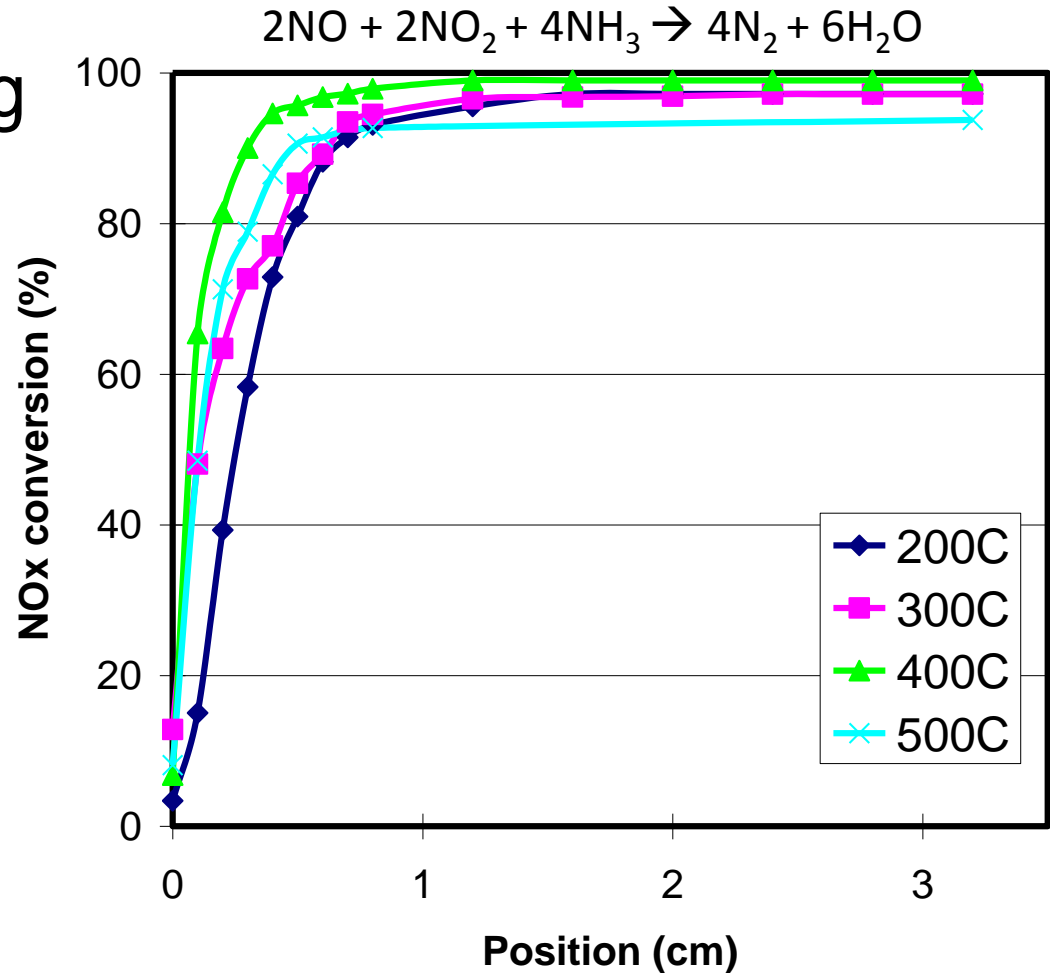
Standard SCR

- Increased conversion at 400°C
- Due to better selectivity for NH₃ use
- Due to improved NO oxidation (and SCR) and
- NH₃ oxid just at light off

Fast SCR

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

Better conversion at 400°C than 500°C

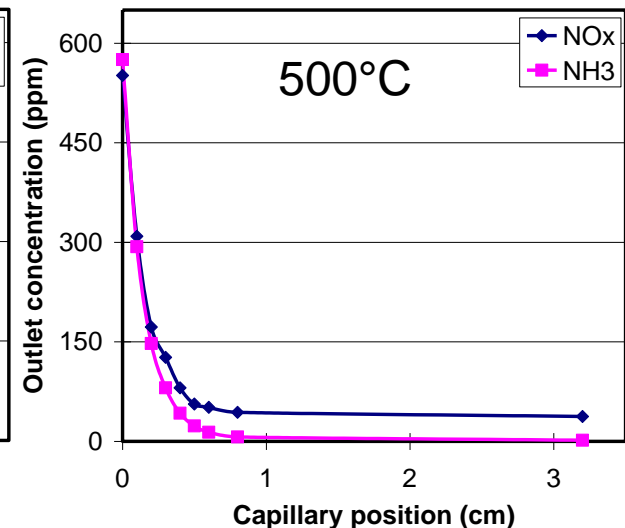
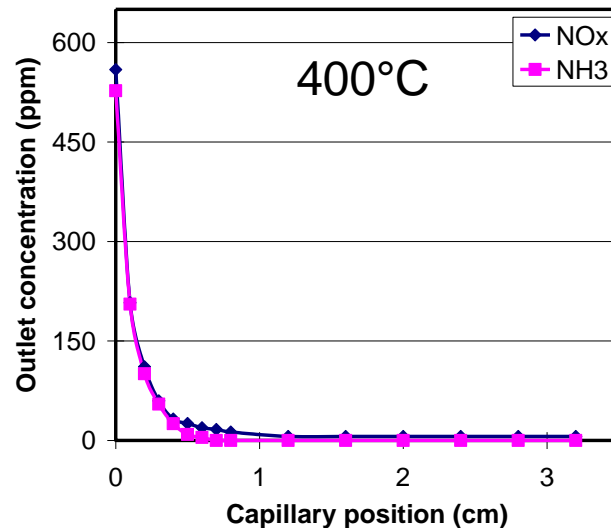
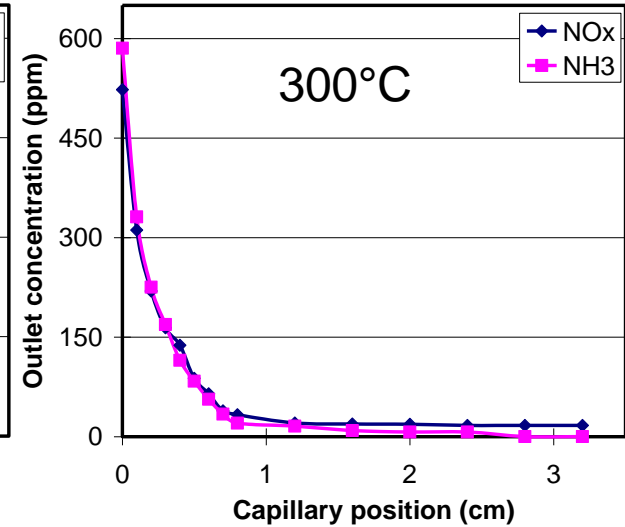
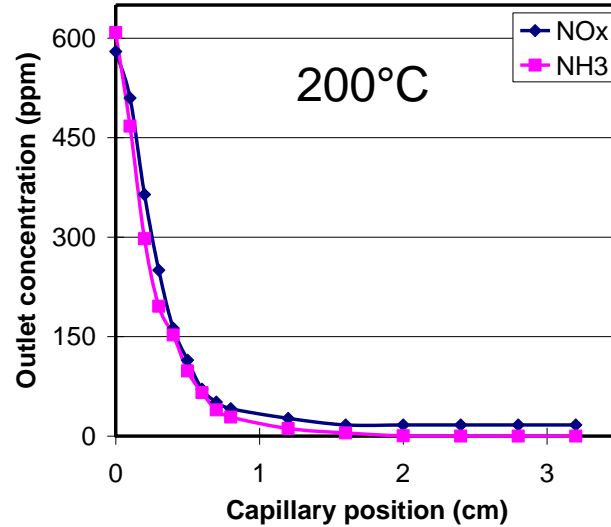


NO = NO₂ = 300 ppm, NH₃ = 600 ppm, 8% O₂, 5% CO₂, 2.5% H₂O

Fast SCR

High selectivity between NO_x and NH_3 below 400°C

At 500°C , more NH_3 consumed via oxidation, but small zone



NO₂ decomposition

Why is performance better at 400 than 500?

NO ₂ Decomposition		
Temperature (°C)	NO outlet (ppm)	NO ₂ outlet (ppm)
200	298	310
300	283	330
400	295	315
500	449	146

300 ppm NO, 300 ppm NO₂, 8% O₂, 5% CO₂, 2.5% H₂O

With ~1:1 NO₂:NO in, NO₂ decomposition begins between 400 and 500°C (500°C conversion similar to standard SCR)

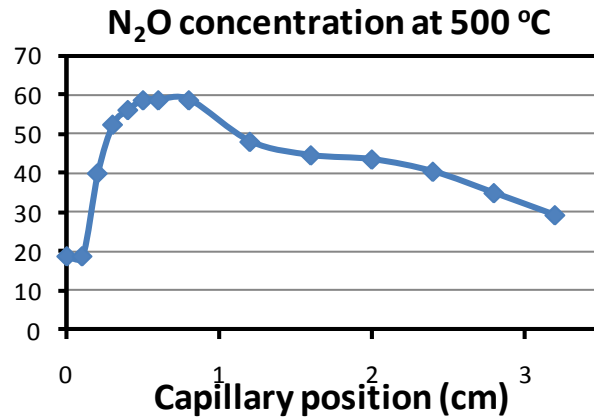
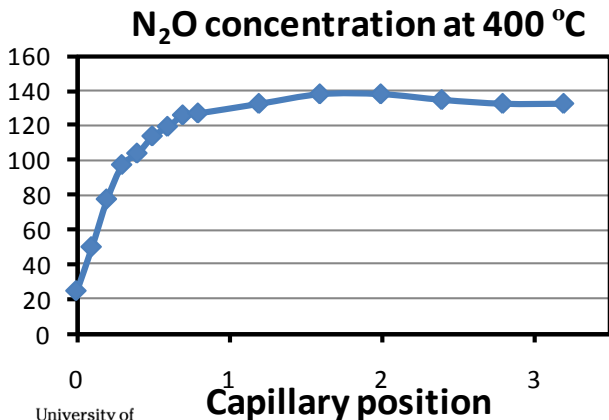
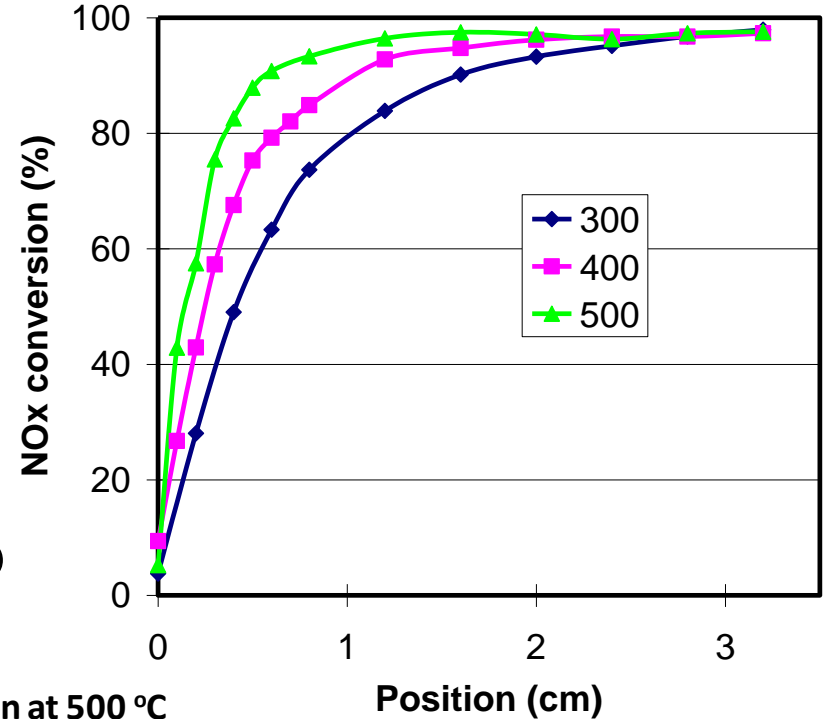
Therefore, above 400°C, fast SCR can be limited by NO₂ decomposing, but admittedly NH₃ oxidation light-off as well

NO₂ SCR

Increasing T, increasing conversion

N₂O

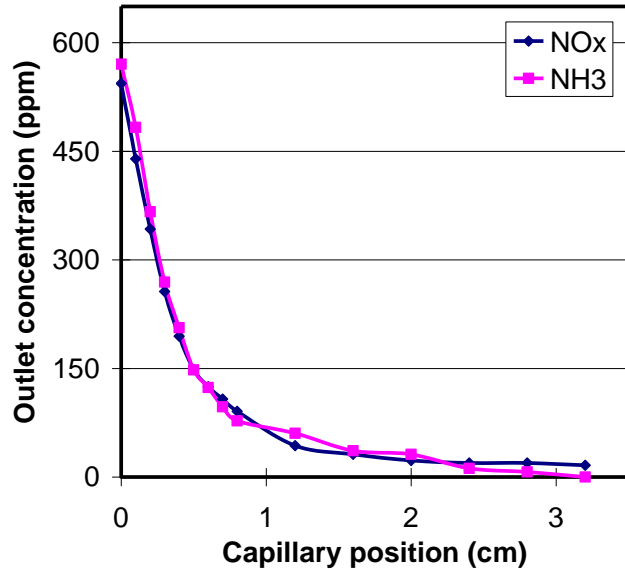
- At 400°C, follows conversion
- At 500°C, a max occurs near cat in - N₂O decomp after



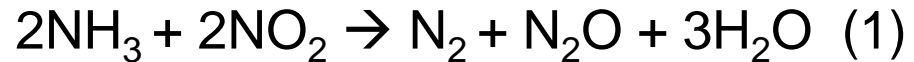
NO₂ = 600 ppm, NH₃ = 600 ppm, 8% O₂, 5% CO₂, 2.5% H₂O

NO₂ SCR analysis

Highly selective: NO₂ and NH₃ are consumed in a 1:1 ratio



Proposed NO₂ SCR:



NO₂/NH₃ data indicate NO₂ SCR occurs via reaction (1) not (2)

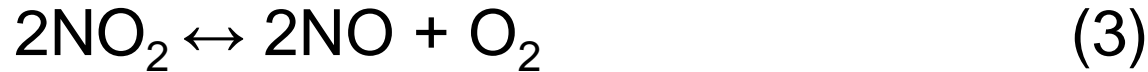
But the outlet N₂O concentration is lower than would be predicted

- Example, 600 ppm NH₃, 600 ppm NO₂ → theoretically 300 ppm N₂O
- N₂O = 170 (300°C) and 130-140 ppm (400°C)
- N₂O does not decompose at these temperatures

NO₂ SCR analysis

How to justify the “imbalance”?

Some reaction must occur through NO₂ decomposition into NO, allowing fast SCR

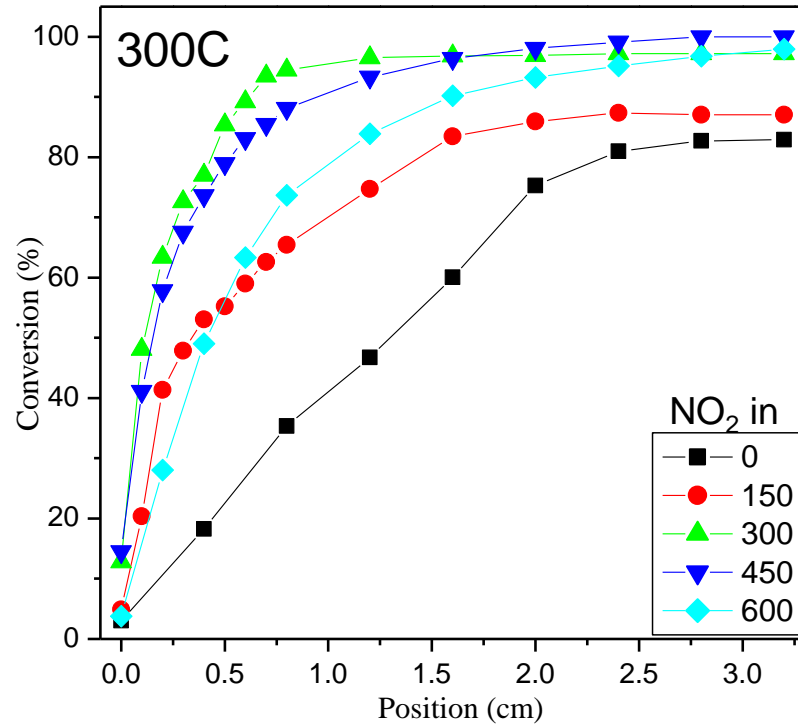
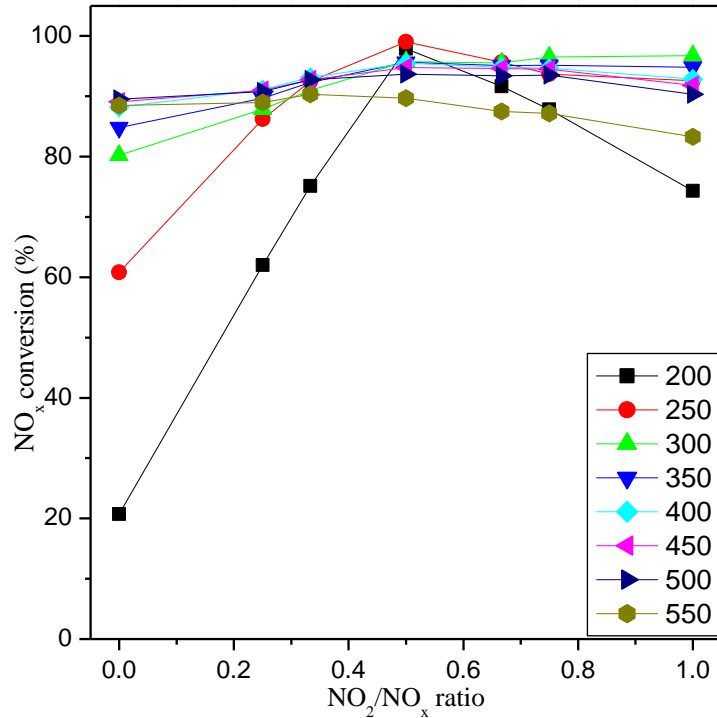


NO₂ Decomposition		
Comp.	600 ppm NO ₂ , 8% O ₂ , 5% CO ₂ , 2.5% H ₂ O	
Temp (C)	NO₂ outlet (ppm)	NO outlet (ppm)
300	597	13
400	446	134
500	395	140

No NO in

NO:NO₂ ratio

NO_x = 600 ppm, NH₃ = 600 ppm, 8% O₂, 5% CO₂, 2.5% H₂O

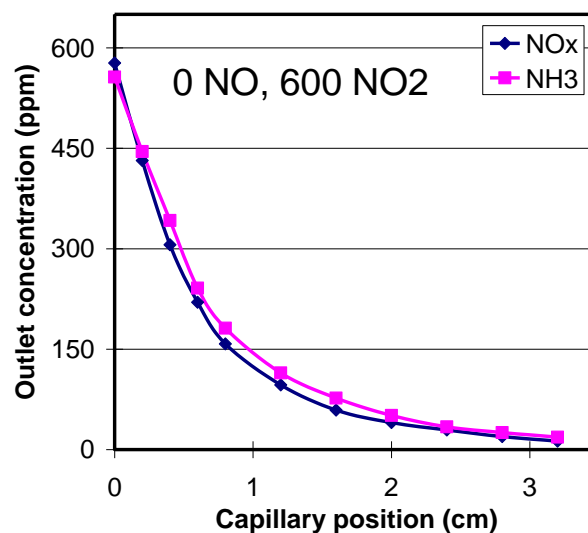
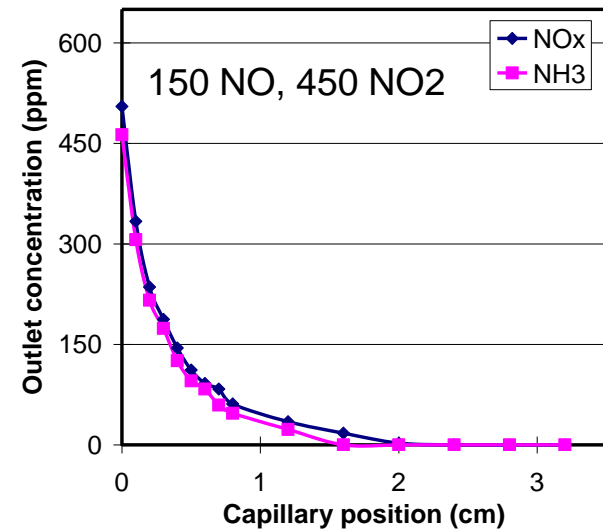
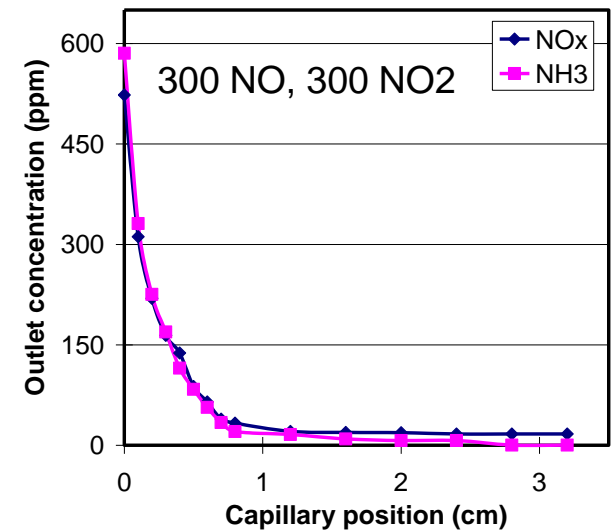
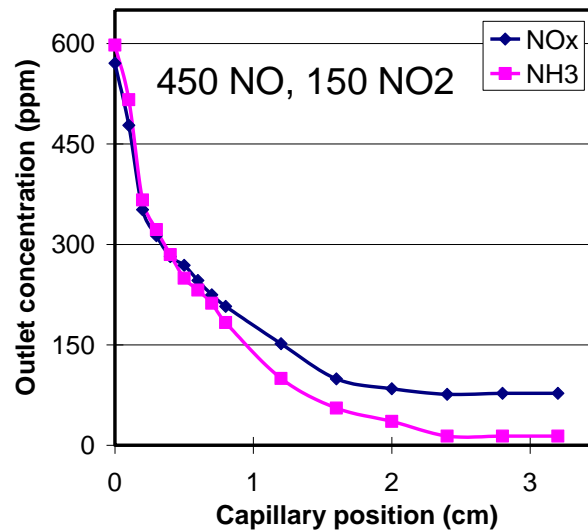
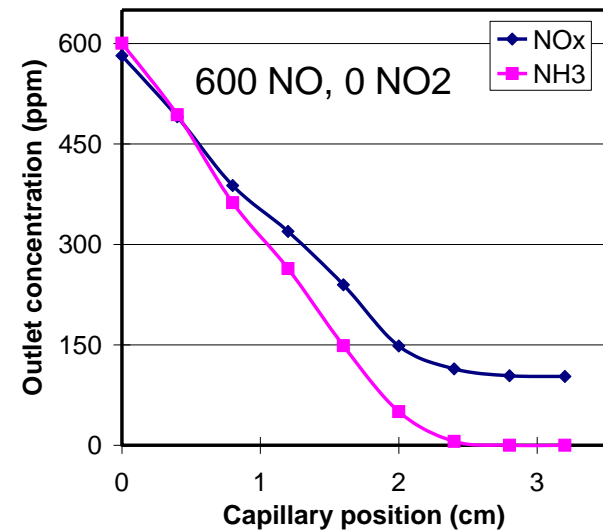


1:1 leads to best performance and least amount of catalyst required, followed by NO₂ SCR then standard

Question – reactions in parallel, series?

NO:NO _x ratio	L for 80% conversion
1	2.4
0	1.2
0.5	< 0.5

SCR at 300°C

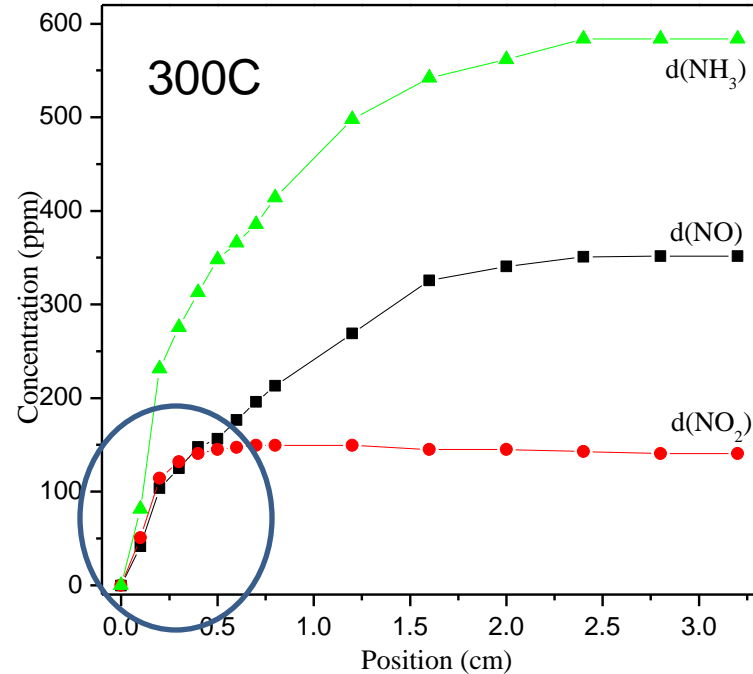
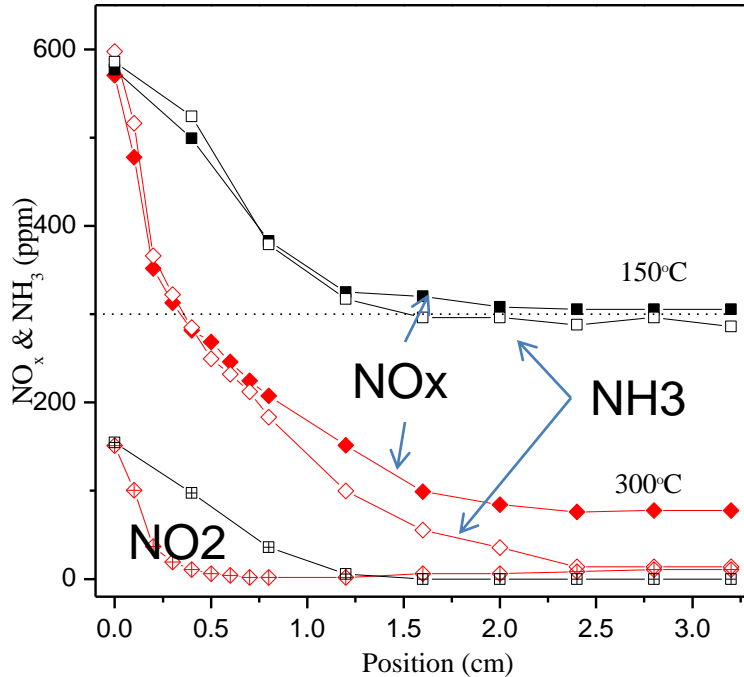


Increasing NO₂ from 0 to 0.5 NO₂/NO_x, leads to better conversion, selectivity

NH₃ oxidation effect lessens as more reaction occurs nearer front

NO:NO₂ ≠ 1:1

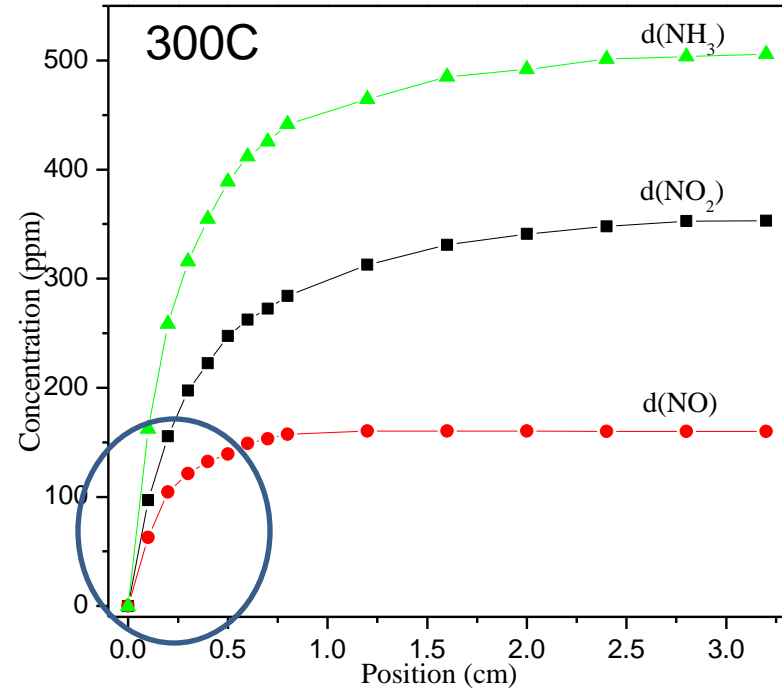
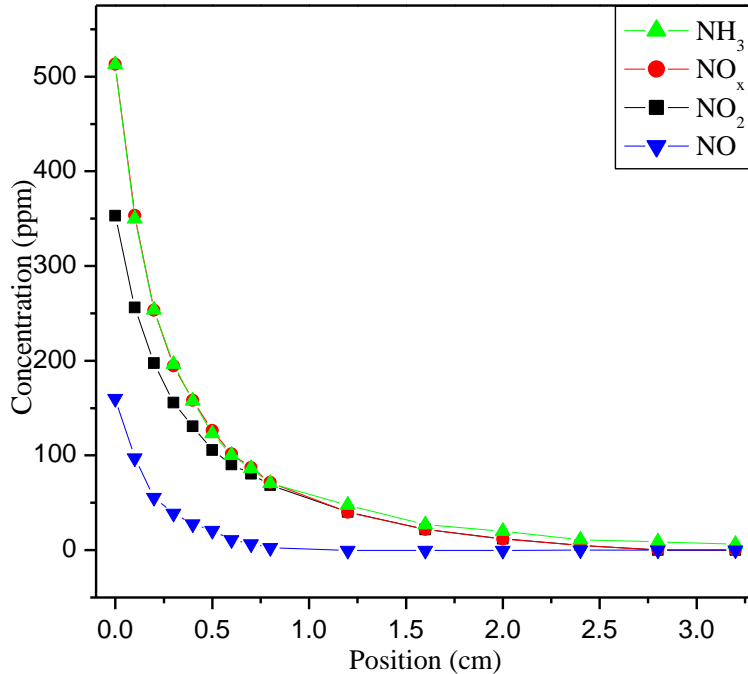
450 ppm NO, 150 ppm NO₂, 600 ppm NH₃, 8% O₂, 2.4% H₂O, 5% CO₂, balance N₂



With NO > NO₂, fast SCR reaction is followed by standard SCR
→ reactions in series

$\text{NO}:\text{NO}_2 \neq 1:1$

450 ppm NO_2 , 150 ppm NO , 600 ppm NH_3 , 8% O_2 , 2.4% H_2O , 5% CO_2 , balance N_2 , 300C



With $\text{NO} < \text{NO}_2$, fast SCR reaction and NO_2 SCR occur at the same time \rightarrow reactions in parallel

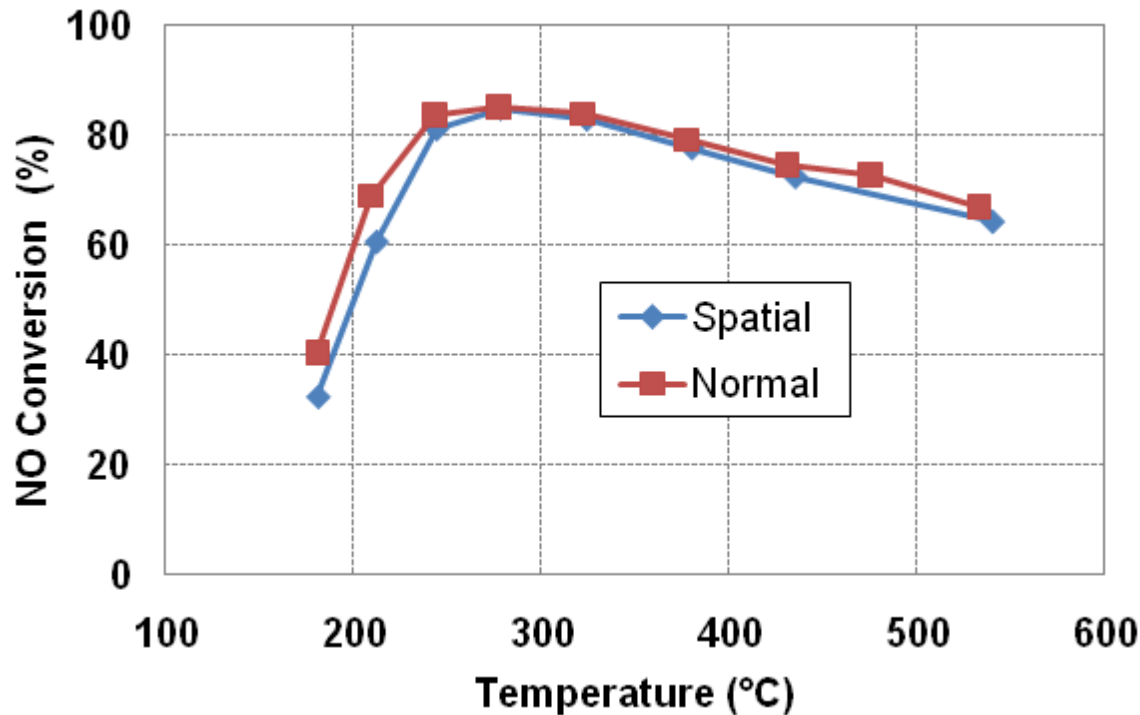
Conclusions

- Method proven for spatially resolving steady state SCR reactions
- With $\text{NO} > \text{NO}_2$, reactions in series, with $\text{NO} < \text{NO}_2$, reactions in parallel
- NO_2 -SCR is complicated by simultaneous fast SCR
→ some NO_2 decomposes to NO
- Competition between NH_3 oxidation, SCR and NO oxidation critical for NH_3/NOX vs NH_3/O_2 selectivity

Effects of aging

- Catalyst – Cu zeolite
- Hydrothermal (10% H₂O in air) aging at 500, 700 and 800°C
- Same FTIR sampling method in principle

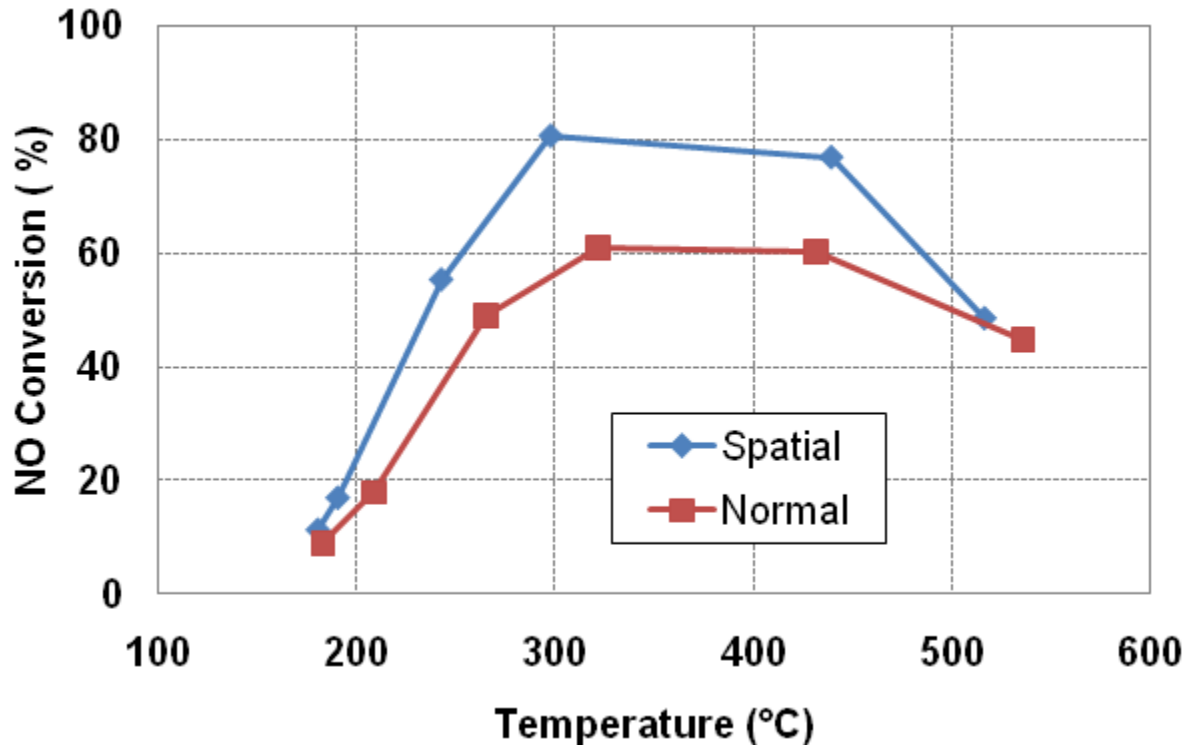
Comparing spatially resolved data to “normal”



700°C-aged sample, GHSV = 48,000 h⁻¹, NO = NH₃ = 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%

For the lightly and medium aged samples (500 and 700°C), the results are a good match

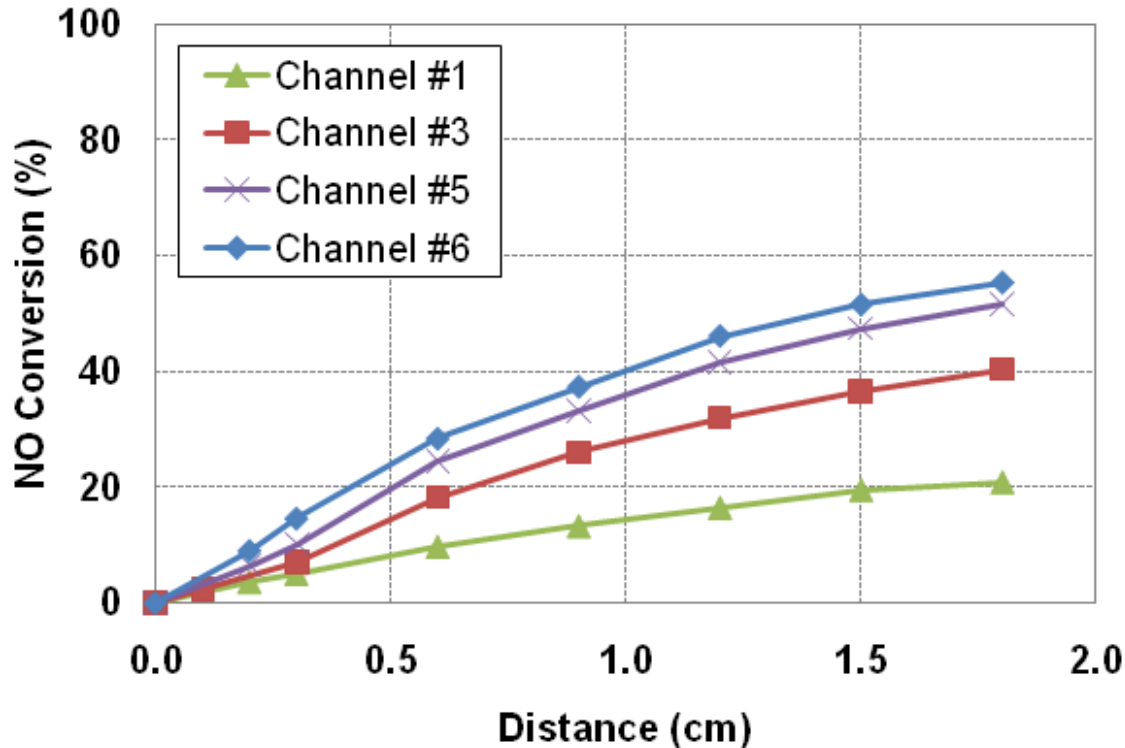
Comparing spatially resolved data to “normal”



Highly aged catalyst, GHSV = 48,000 h⁻¹, NO = NH₃ = 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%

For the highly aged sample (800°C), the results show a mis-match

Radial distribution check

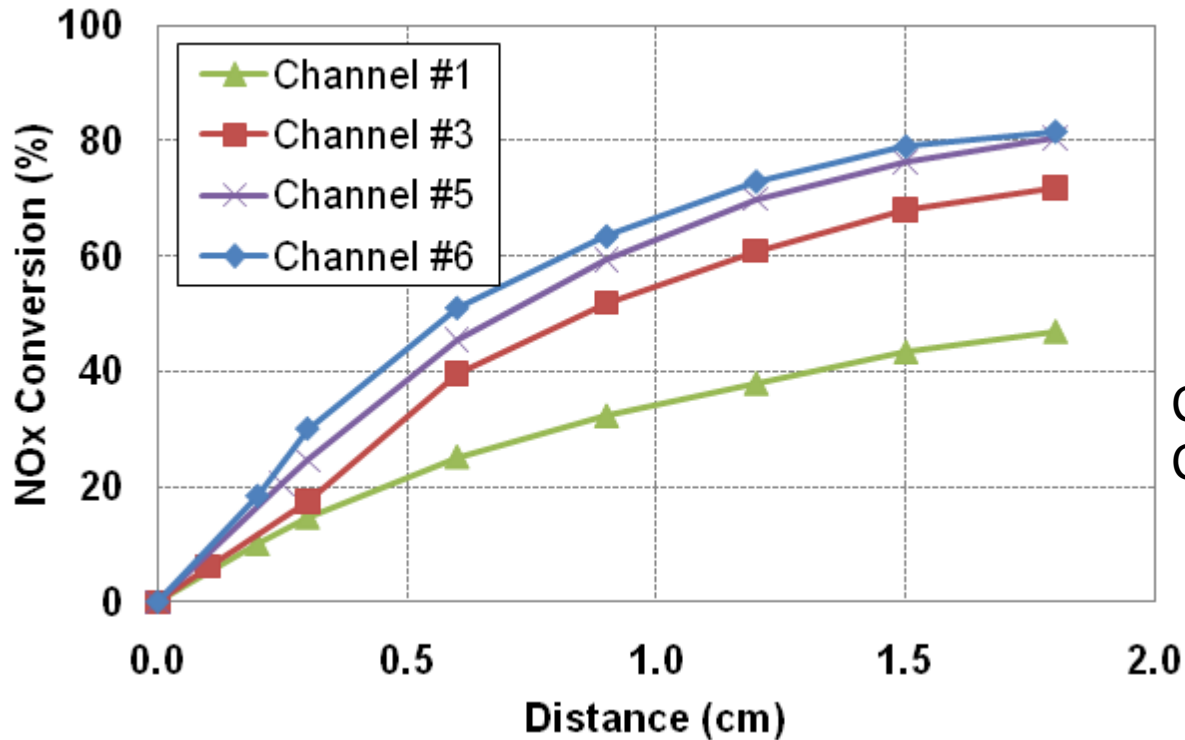


Highly aged catalyst, GHSV = 48,000 h⁻¹, NO = NH₃ = 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%

Channel 1 = outer edge
Channel 6 = middle

- The mis-match between “normal” and the centered capillary is due to radial distribution in performance → the outer edge is more heavily damaged
- An estimate is ~ 20-25°C variation in T at 800°C
- XRD results at PNNL show loss of structure at 800°C

Radial distribution check

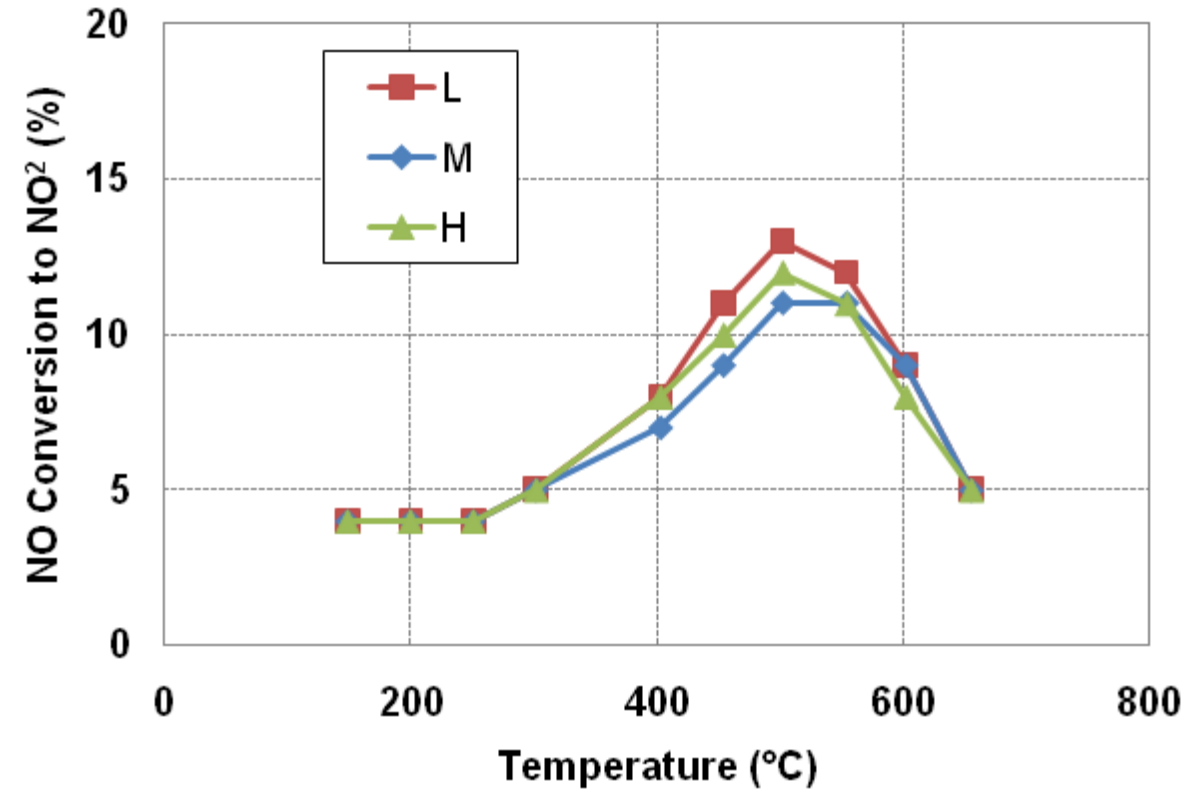


Highly aged catalyst, GHSV = 48,000 h⁻¹, NH₃ = 400 ppm, NO = 200 ppm, NO₂ = 200 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%

Channel 1 = outer edge
Channel 6 = middle

- The mis-match is also apparent under fast SCR conditions

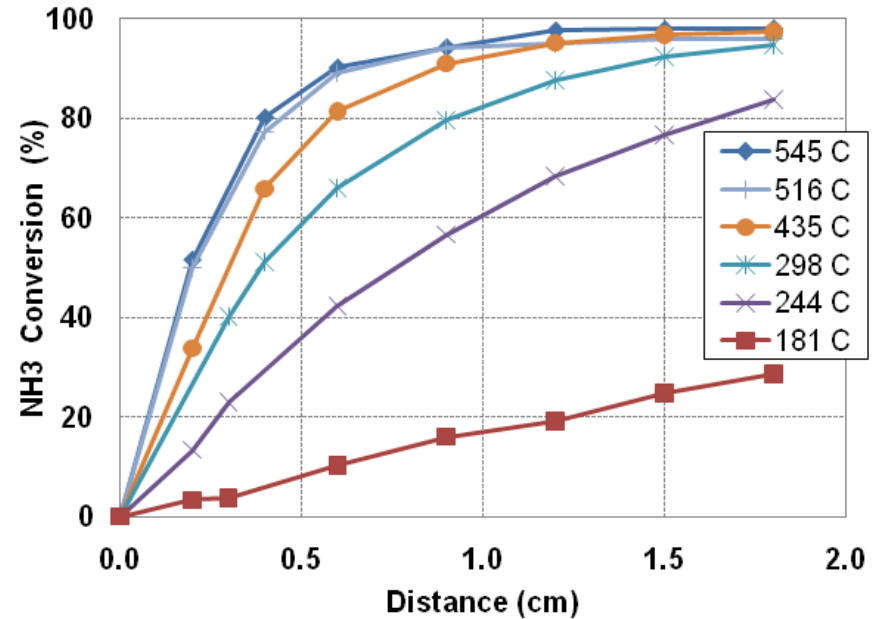
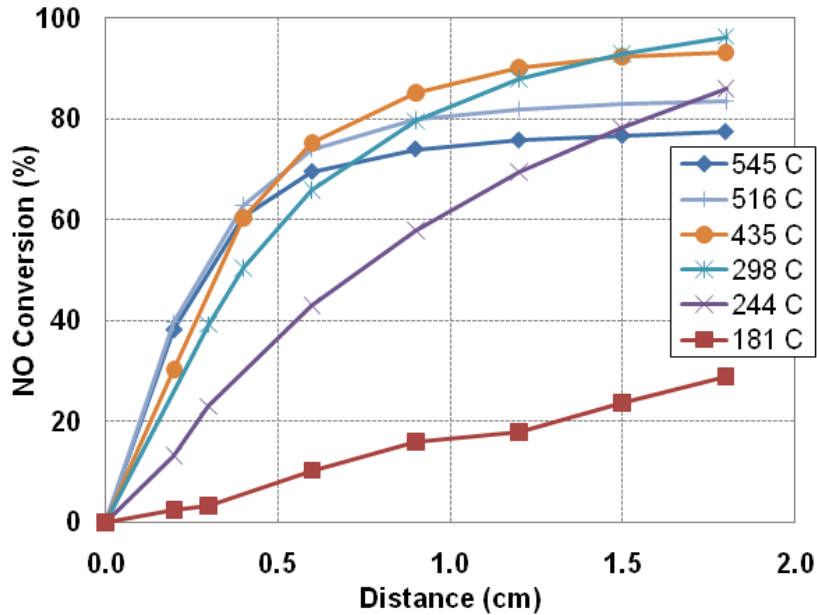
NO oxidation



GHSV = 30,000 h⁻¹, NO = 200 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%

- Little effect of aging on NO oxidation
- NO₂ TPD results do indicate that there are less sites available for NO_x adsorption

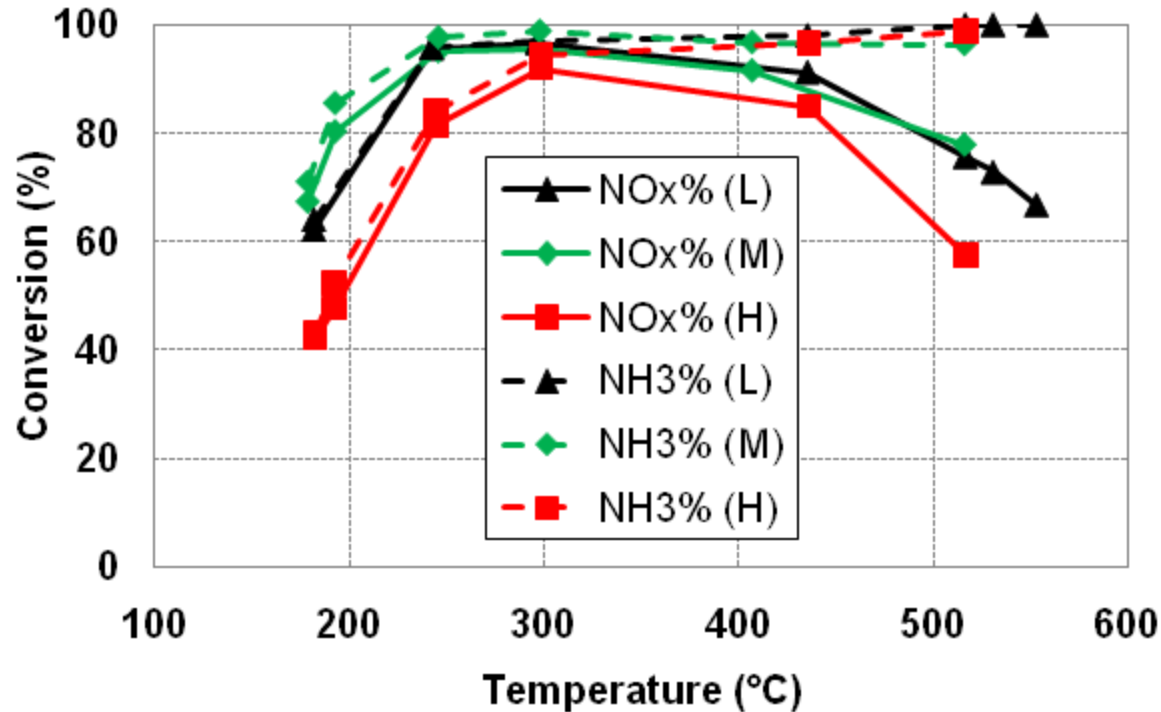
Standard SCR - performance



Lightly aged catalyst, NO = NH₃ = 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%

- Increasing T → more NO_x conversion at front of catalyst, and more NH₃ conversion throughout
- Above 298°C, the outlet conversion decreases with increasing temperature → NH₃ loss via oxidation
- At the inlet section, the extent of NH₃ oxidation is still small enough that NO conversion does increase with T

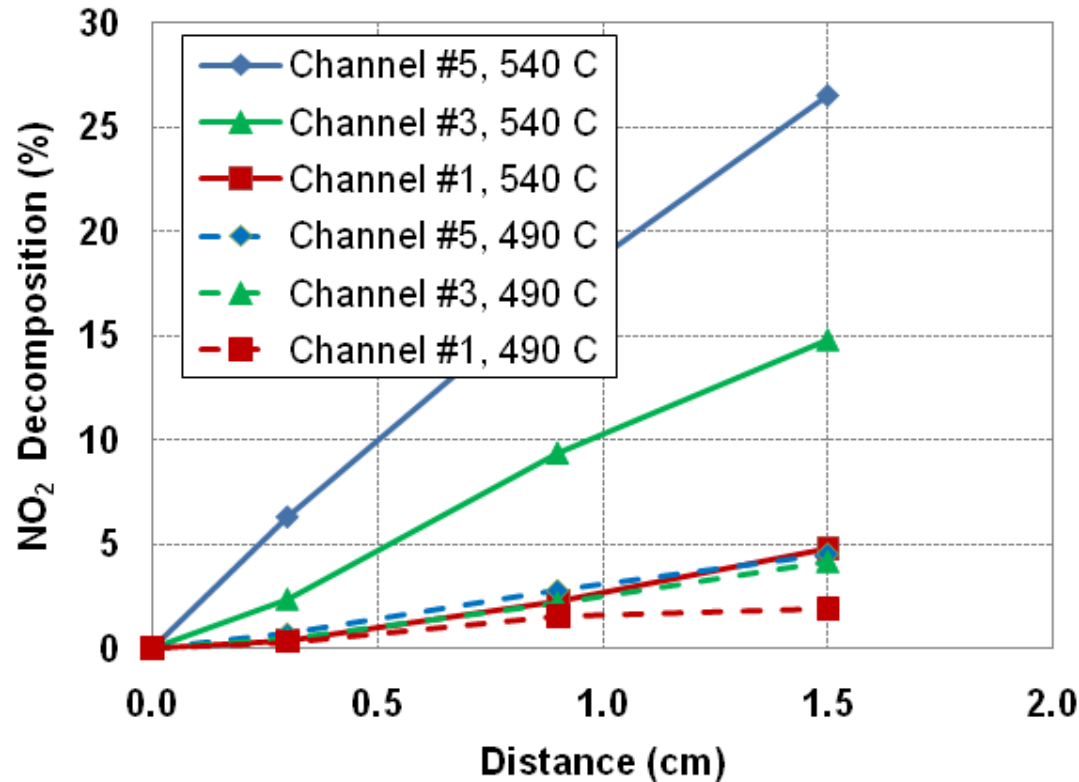
Fast SCR – aging effects



GHSV = 48,000 h⁻¹, NH₃ = 400 ppm, NO = 200 ppm, NO₂ = 200 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%

- Although at the T extremes decreased conversion is observed – in the mid-T range, only a small decrease is observed
- NH₃ loss via oxidation is smaller – better competition between fast SCR and NH₃ oxidation

NO₂ decomposition

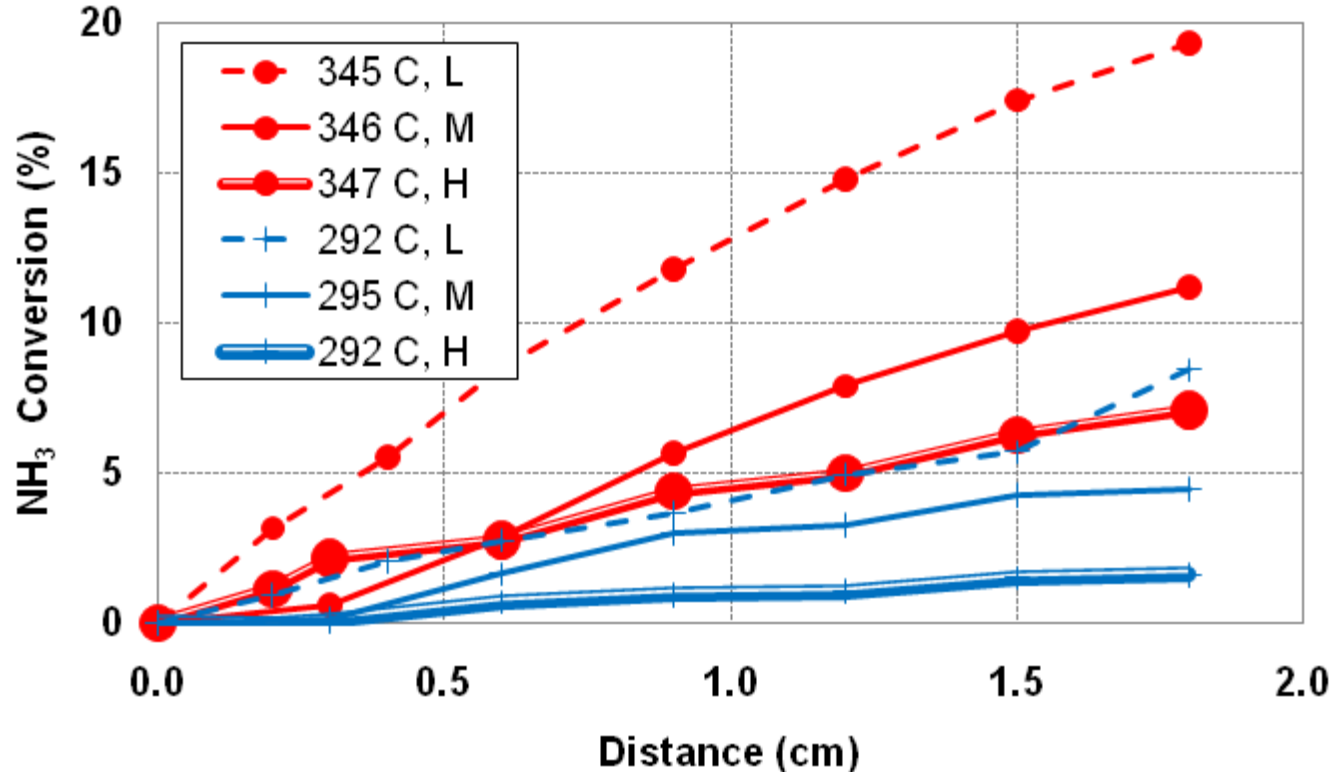


Highly aged Cu-zeolite catalyst,
GHSV = 48,000 h⁻¹, NO = 200
ppm, NO₂ = 200 ppm, O₂ = 10%,
H₂O = 5%, CO₂ = 7%

Channel 1 = outer edge
Channel 6 = middle

- NO₂ decomposition extent decreases with aging
 - this helps maintain fast SCR conditions (supporting the initial evidence of less loss in fast SCR activity with aging)

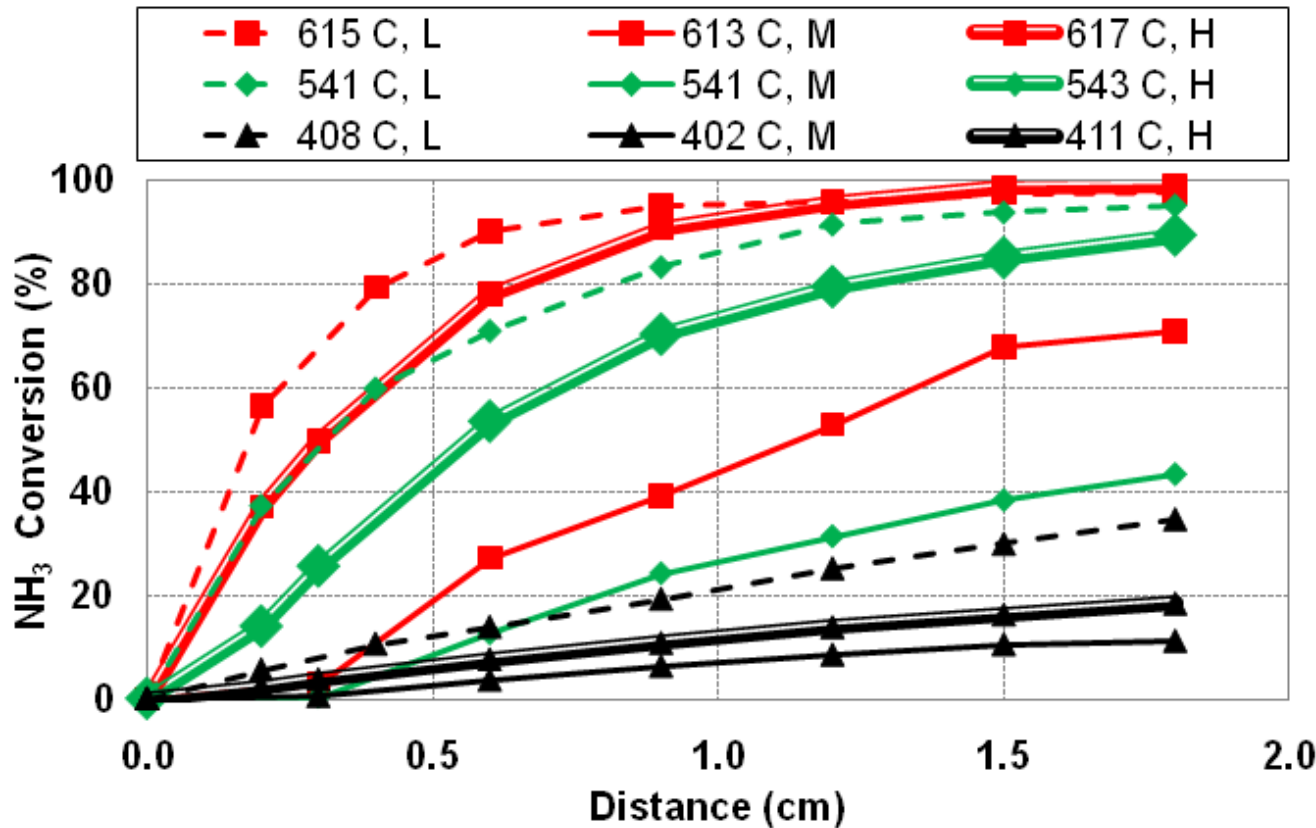
Low T NH₃ oxidation



GHSV = 48,000 h⁻¹,
NH₃ = 360 ppm, O₂ =
10%, H₂O = 5%, CO₂
= 7%

- With catalyst aging, in this temperature range, NH₃ oxidation extent decreased
- Monotonic increase through catalyst length

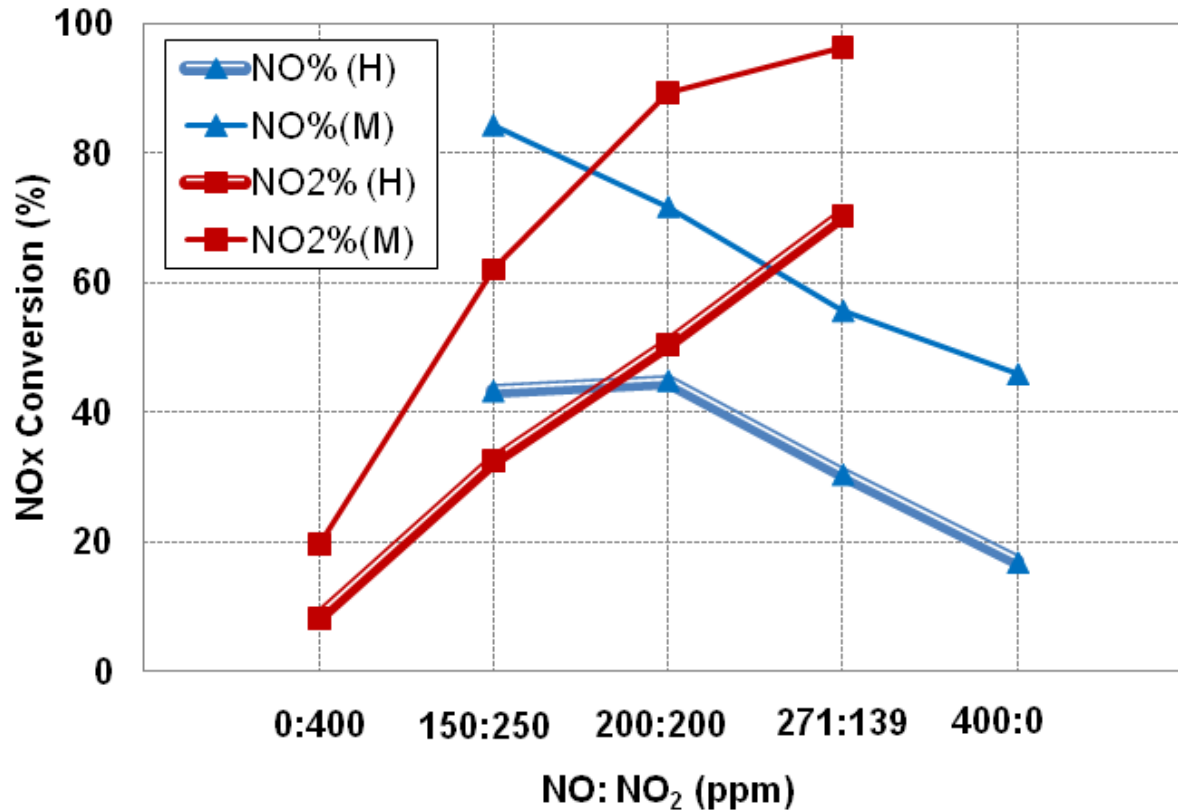
High T NH₃ oxidation



GHSV = 48,000 h⁻¹,
 NH₃ = 360 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%

- At higher T, there is a different trend
 - lightly aged catalyst still has the highest NH₃ oxidation extent
 - but the 700°C aged catalyst results in less NH₃ oxidation relative to the highly aged sample
- With higher conversions, inflection in conversion noted – mass transfer

Varied NO:NO₂ ratio



200°C, GHSV = 48,000 h⁻¹,
NO_x = NH₃ = 400 ppm, O₂
= 10%, H₂O = 5%, CO₂ =
7%.

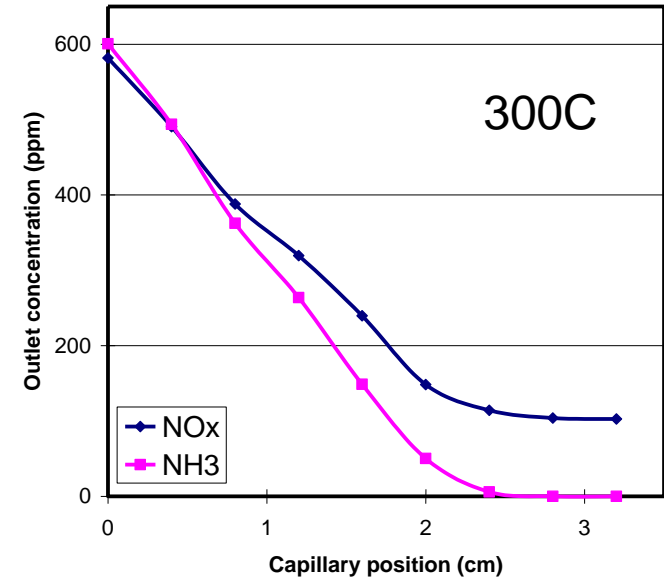
- NO and NO₂ conversions are affected similarly with aging
- Results also show reaction pathways
 - at 1:1, more NO₂ is converted → parallel pathways occurring; NO₂ and fast SCR (as was the case for the Fe zeolite data presented previously)
 - Data also validate that with NO > NO₂, fast SCR occurs, then standard (reactions in series)

Conclusions (aging)

- Little effect on NO oxidation
- Similar effects on both standard and fast SCR
- NH_3 oxidation, at higher T, decreased with mild aging
- NO_2 decomposition decreased with aging

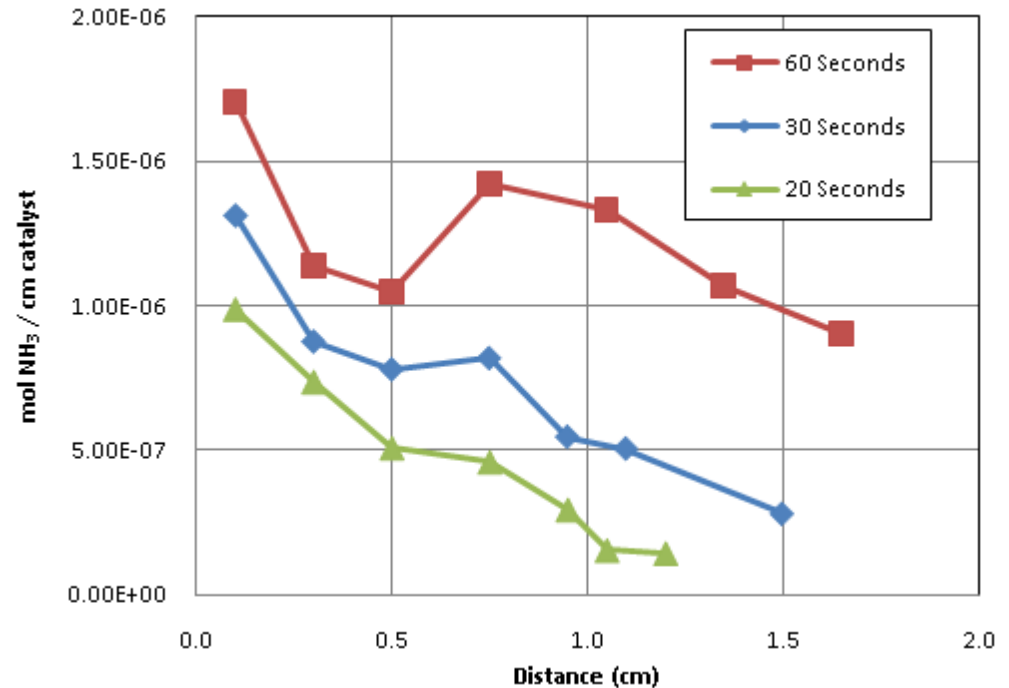
NH₃ adsorption

- Typically, above 200°C, NH₃ is not available at downstream sites
 - SCR and NH₃ oxidation
- Literature suggests surface is covered by NH₃ - dominant surface species (little to no NO_x is adsorbed)
- Passive SCR
 - Using an upstream TWC or NSR catalyst



NH₃ adsorption

- Increasing exposure time increases amount adsorbed
- Overall, a relatively gradual adsorption pattern
- Data actually provide some info regarding catalyst washcoat properties as well



300°C, Cu zeolite, 1000 ppm NH₃, 7% CO₂, 5% H₂O

Acknowledgements

People who did the work

John Luo

Keith Christensen

Peter Hou

Prasanna Wijayakoon

People who paid for the work

National Sciences and Engineering Research Council of Canada
(NSERC)

Ontario Centres of Excellence (OCE)

General Motors

BASF

Thank you