Thermal Transient Effects on the Performance of Catalysts for the Selective Catalytic Reduction of NO_x

11th CLEERS Workshop
May 15, 2008
Dearborn, Michigan

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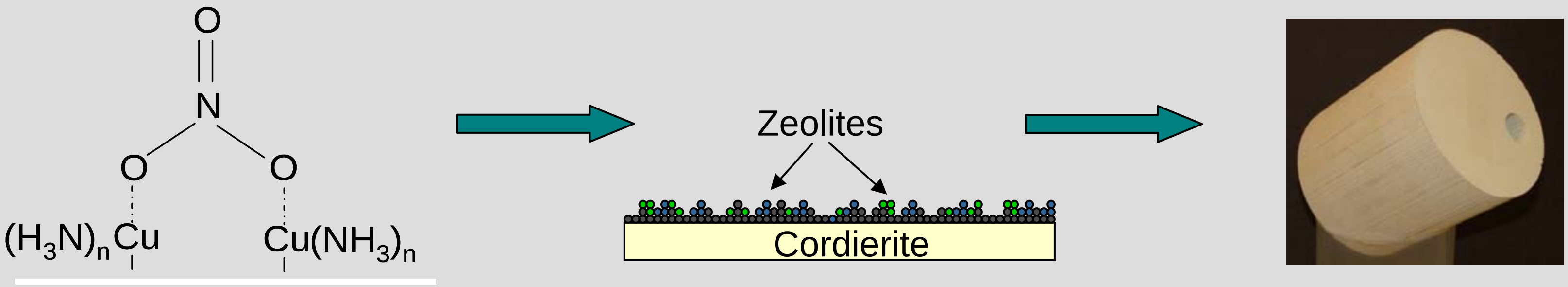
Outline

- Purpose of the work
- Approach
- Chemisorption of NH_3 on monoliths
- Thermal transient micro-reactor
  - Experimental controls
  - Effects of reactant concentrations
  - Thermal transient cycles
- Future Work
- Summary

Purpose of Work

- Accelerate the transition of the testing of powders under steady state conditions to transient test regimes
- Assess thermal transient capabilities of urea-SCR catalysts
- Mechanistic understanding of zeolitic urea-SCR catalysts for a pathway to optimize urea usage and enhance fuel efficiency
- Aid in mechanistic studies on steady and unsteady state of SCR catalysts in order to enable better models and improved transition to larger scale engine testing



T. Komatsu, M. Nunokawa, et al, *J. Catal.* 1994, *148*, 427.

Approach

- New and future regulations not only have average emission targets over entire test cycle but also “not-to-exceed” levels which need to be understood
- Upon integration of emission control technologies slippage from one component can impact a downstream process e.g. SCR-DPF [1]

- Probe thermal transient conditions within the standard SCR catalyst in order to yield optimal efficiency and aid in the pathway to integration with other components
- Examine the adsorption characteristics of NO_x and ammonia on an industrial standard zeolitic SCR catalyst
  - Examine thermal transients effects on NH_3, NO, N_2O, NO_2

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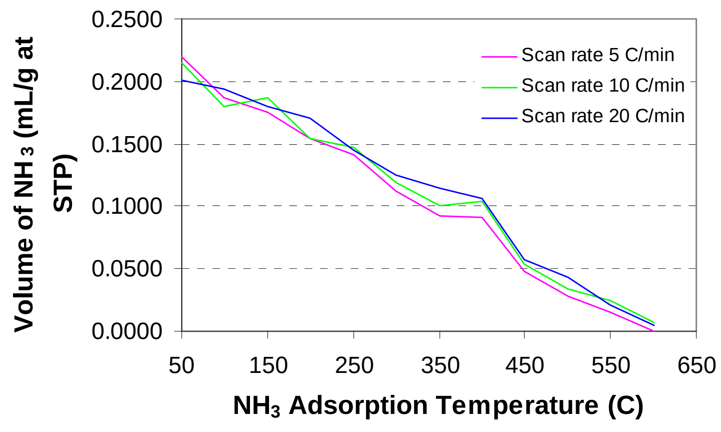
1 Girard, J.W. et al SAE 2007-01-1572.

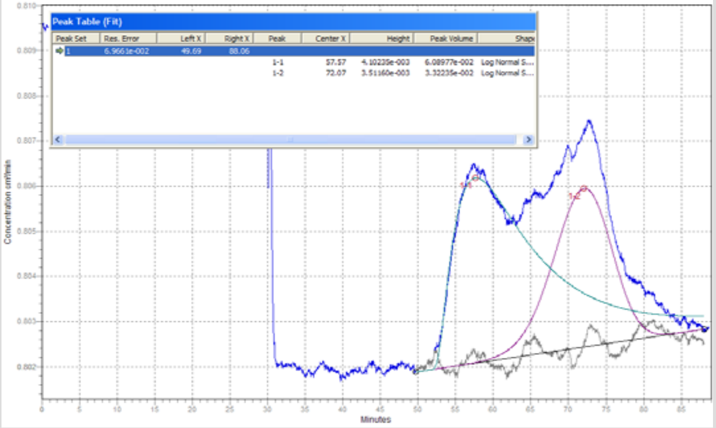
Chemisorption Studies on Monoliths

- Adsorption of NO, NO_2 or NH_3 on a monolith (zeolitic urea-SCR catalyst obtained from BASF, 400 cpsi, 183 μm wall thickness,1.8 g/in^3 coating) at probe temperatures and subsequent desorption ramping to 650 °C
- First NH_3 desorption peak, 284-351 °C, has first order kinetics and $E_{desorption} = 77 \pm 8$ kJ mol^{-1} [1]
- Second NH_3 desorption peak, 453-625 °C, may be second order kinetics, additional data is required

Monolith Capacity of chemisorbed NH_3



NH_3 TPD at Heating rate 20 °C/min



Peak Table (Fit)

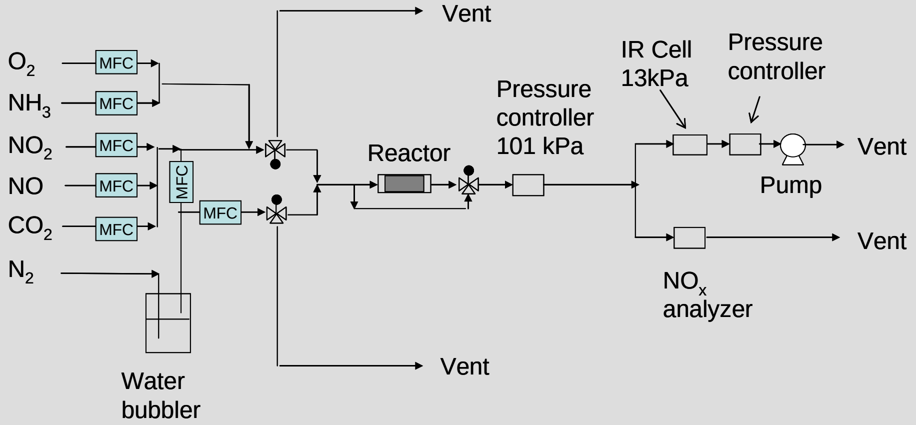
Peak Set	Res. Error	Left X	Right X	Peak	Center X	Height	Peak Volume	Shape
1	6.9661e-002	49.69	88.06					
				1-1	57.57	4.10235e-003	6.08977e-002	Log Normal S...
				1-2	72.07	3.51160e-003	3.32235e-002	Log Normal S...

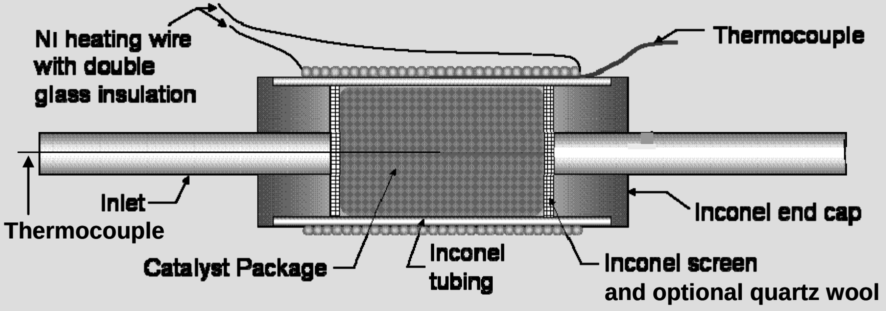
1 Webb, P.A.; Orr C. *Analytical Methods in Fine Particle Technology*, Micromeritics Instrument Corp., Norcross, GA 1997.

2 Chatterjee, D. et al SAE 2007-01-1136.

Thermal Transient Micro-Reactor

- Standard BASF monolith catalyst was crushed[1] for transient powder experiment (70-100 mesh) and tested under standard conditions: NO_x 350 ppm, 350 ppm NH_3, O_2 14%, CO_2 5%, H_2O 1- 4.5 %, balance dry N_2, total flow 210 mL/min (116,000 $scm^3\ hr^{-1}\ g^{-1}$)
- Inconel 600 reactor, with thermocouples in the reactor bed and between the resistive heater and the body
- Analyses performed with:
  Chemiluminescent detector - detection limits: $\leq$ 1 ppm NO_x, response: 3.5 s.
  FTIR - detection limits: 20 ppm NO, 10 ppm NO_2, 5 ppm N_2O, 10 ppm NH_3, 0.1 ppm $CO_{2,}$ response: < 6 s

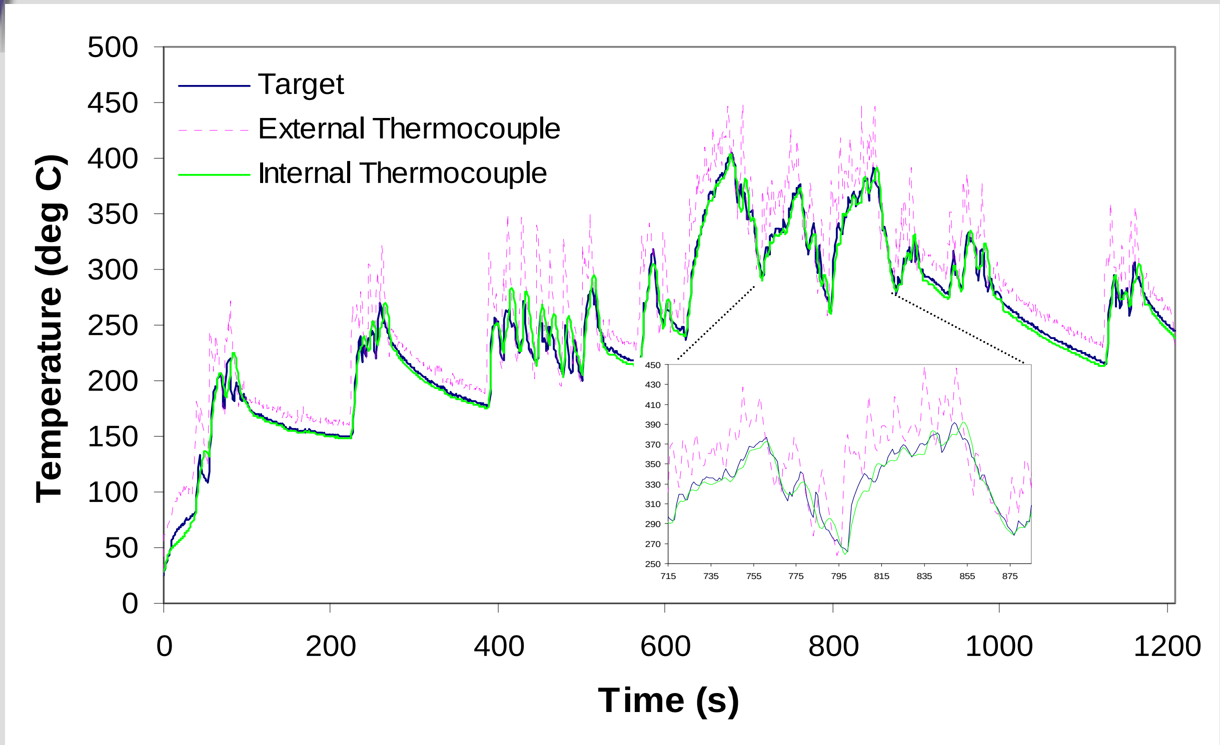




1 Chatterjee, D. et al SAE 2007-01-1136.

Thermal Transient Temperature Profile

- Internal and external thermocouples work with predictive component, a peak detection component and a feedback component to match heavy duty FTP target.
- Average difference between targeted temperature and catalyst temperature 0.46 ± 9.72 °C.



The predictive algorithm drives the heater profile

$$Predicted(t) = A*d(t) + B*d'(t) + C*\sin(\pi*d'(t)/\max d'(t))*d'(t) + D$$

Feedback component applied during stable portions:

$$Sp' = Sp \pm 0.5*Sp(error^2/error\ band^2)$$

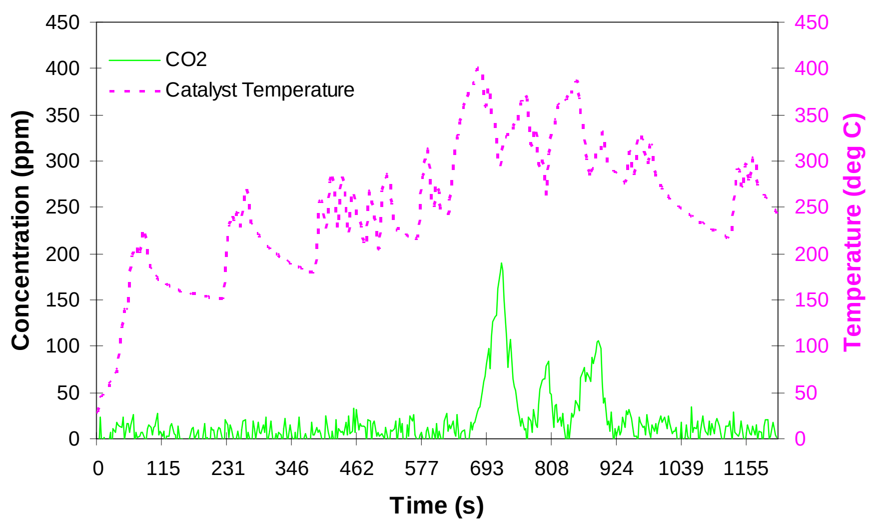
Sp' – modified external target

Sp – original external target

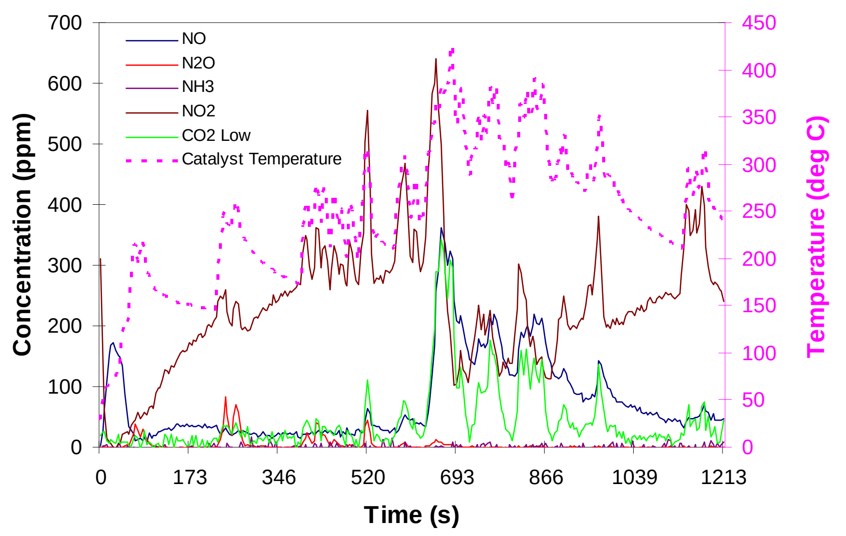
Khalek, I. A. Presentation at Ultrafine Particle Conference May 1-2, 2006.

Control Reactions for Thermal Transient Micro-Reactor

- The catalyst is supported on reticulated vitreous carbon foam 12.4 pores/cm^2 (2 x 3.8 mg/0.14 mL)
- Under O_2 and H_2O no CO was detected, minor CO_2 amounting to 47 μg of carbon/run
- Under NO_2, O_2 and H_2O, an average of 44 ppm CO_2 was observed amounting to 99 μg of carbon/run



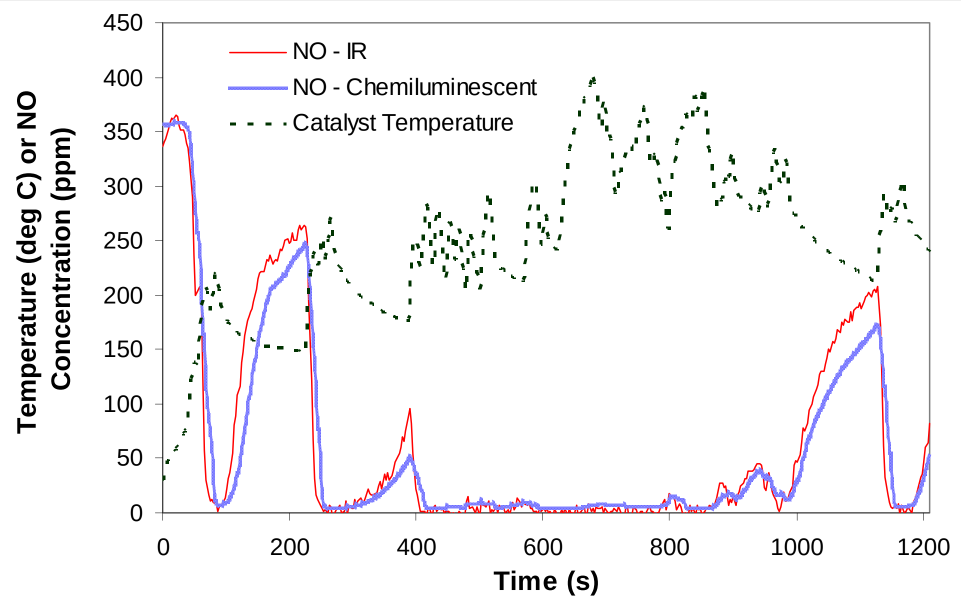
O_2 14 %, H_2O 2.6%, N_2 balance, total flow 210 mL/min.



O_2 14 %, H_2O 2.2%, 342 ppm NO_2, N_2 balance, total flow 210 mL/min.

Analytical Techniques for Thermal Transient Micro-Reactor

- Added FT-IR to reactor to expand capability for more analytes (CO, CO_2, H_2O, NO, N_2O, NO_2)
- Analogous good correlation between FT-IR and NO_x chemiluminescent analyzer demonstrated for NO_x
- Good corroboration between the analytical techniques

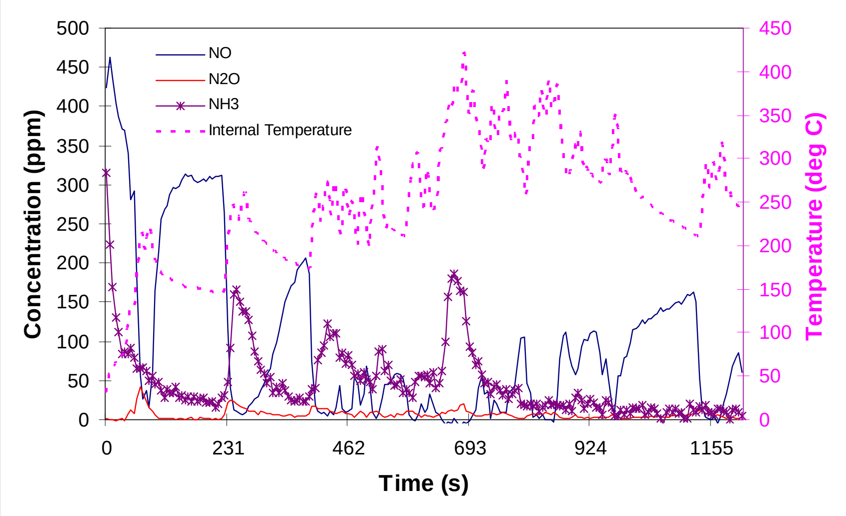


NO 343 ppm, NH_3 344 ppm, CO_2 4.5%, O_2 14 %, H_2O 2.6%, balance N_2, total flow 210 sccm.

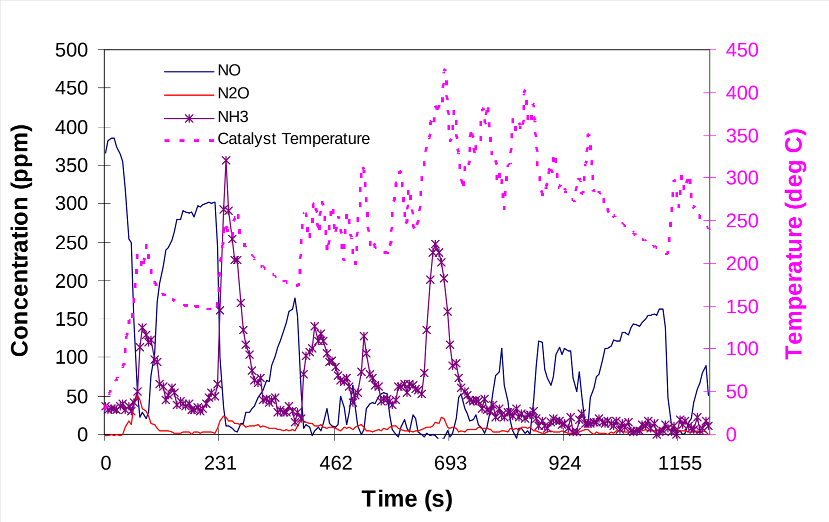
Sample's Gaseous History

- Time on stream impacts conversions: NO_x conversion : 71, 72, 74%, NH_3 slip: 14, 15, 16% for starting heating cycle 5, 65, 125 s after stream enters reactor
- Necessary to cool post reaction under N_2, 2% H_2O
- Protocol for studies was 5 s after stream starts and cooling under wet N_2

5 s on stream



125 s on stream

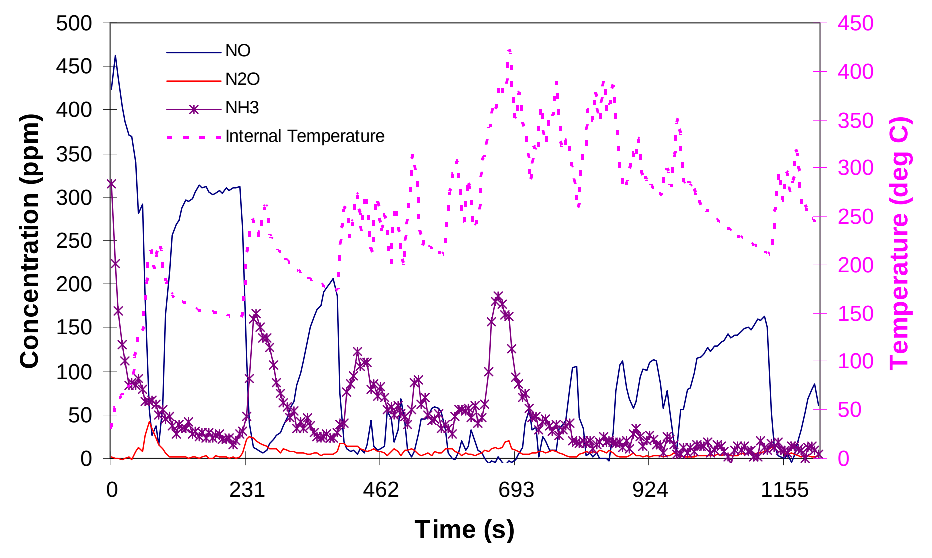


NO 362 ppm, NH_3 353 ppm, CO_2 4.9%, O_2 14 %, H_2O 2.0%, balance N_2, total flow 210 sccm.

Thermal Transient Test of Standard SCR Reaction

- Standard SCR reaction - significant amounts of NO during cold or cooling sections, release of stored reservoir of NH_3 at rapid temperature increases leading to NH_3 slip

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



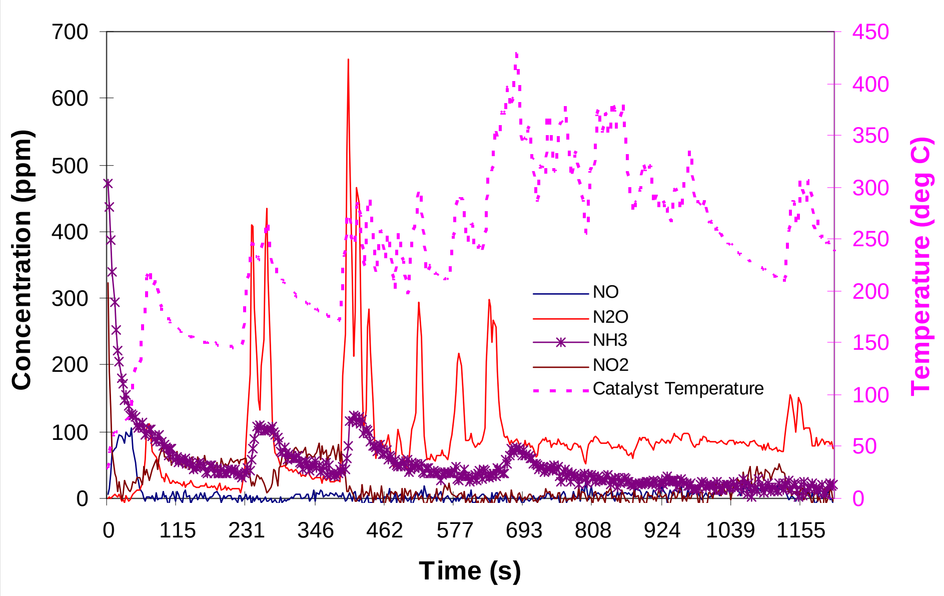
Fractional average NO_x conversion 0.71, fractional average ammonia slip 0.14

NO 362 ppm, NH_3 353 ppm, CO_2 4.9%, O_2 14 %, H_2O 2.0%, balance N_2, total flow 210 sccm.

Thermal Transient Test of NO_2 SCR Reaction

- NO_2 SCR reaction – large amounts of N_2O during rapid heating presumed via NH_4NO_3 decomposition 150-275 °C.[1]
- First and last quadrant not symmetrical

$$8NH_3 + 6NO2 \longrightarrow 7N_2 + 12H_2O$$



Fractional average NO_x conversion 0.79, fractional average ammonia slip 0.14

NO_2 351 ppm, NH_3 467 ppm, CO_2 5.0%, O_2 14 %, H_2O 1.8%, balance N_2, total flow 210 sccm.

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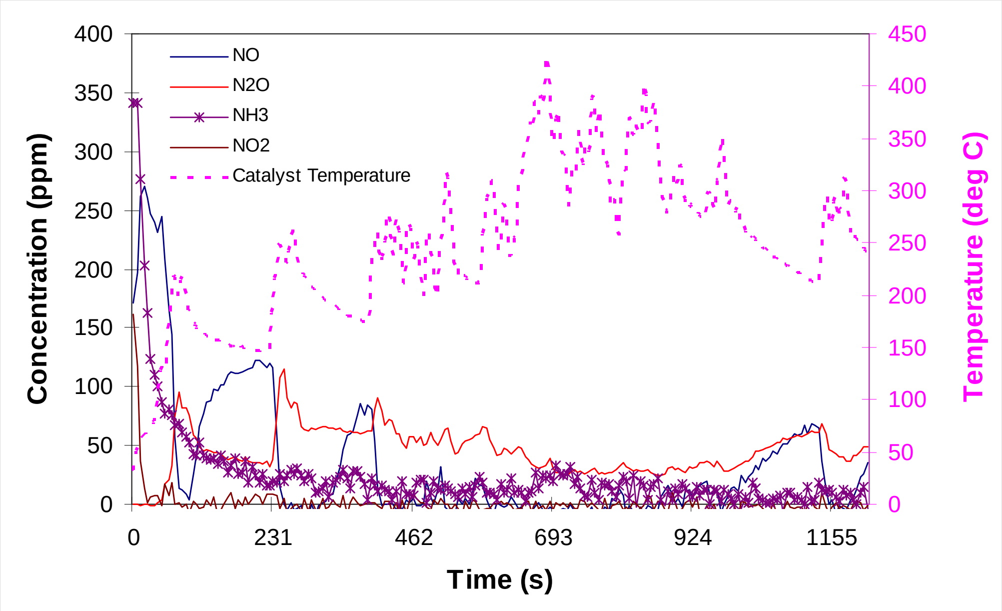
1 Ciardelli, C. et al *Appl. Catal. B; Environmental* **2007**, *70*, 80-90.

2 Schuler A. et al *SAE* 2008-01-1323.

Thermal Transient Test of Fast SCR Reaction

- Fast SCR – NO and N_2O looks like a linear combination of prior 100% NO or 100% NO_2 runs (350 ppm of each individually))
- NH_3 is markedly different (modest amounts detected only at highest temperatures)

$$2NH_3 + NO + NO_2 \longrightarrow 2N_2 + 3H_2O$$

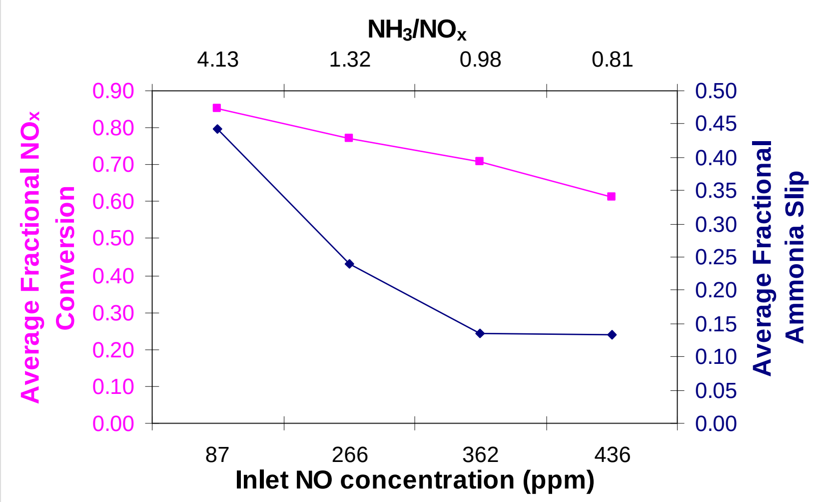


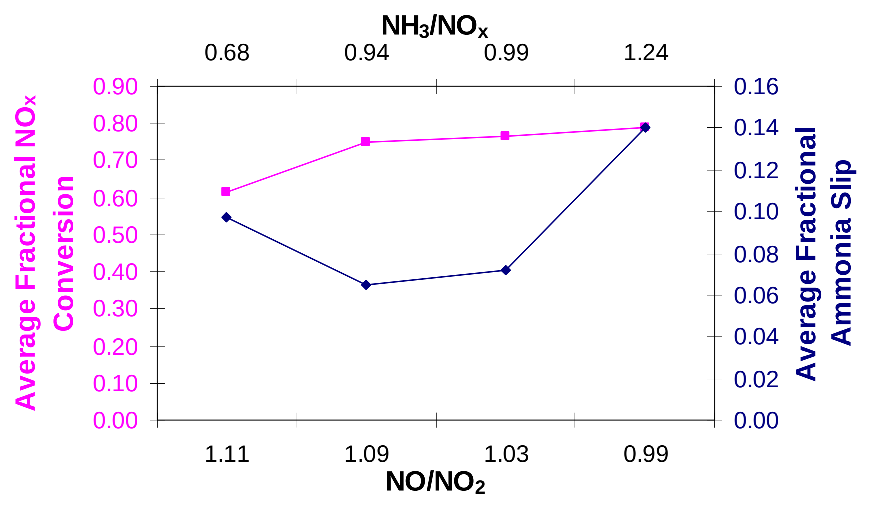
Fractional average NO_x conversion 0.77, fractional average ammonia slip 0.07

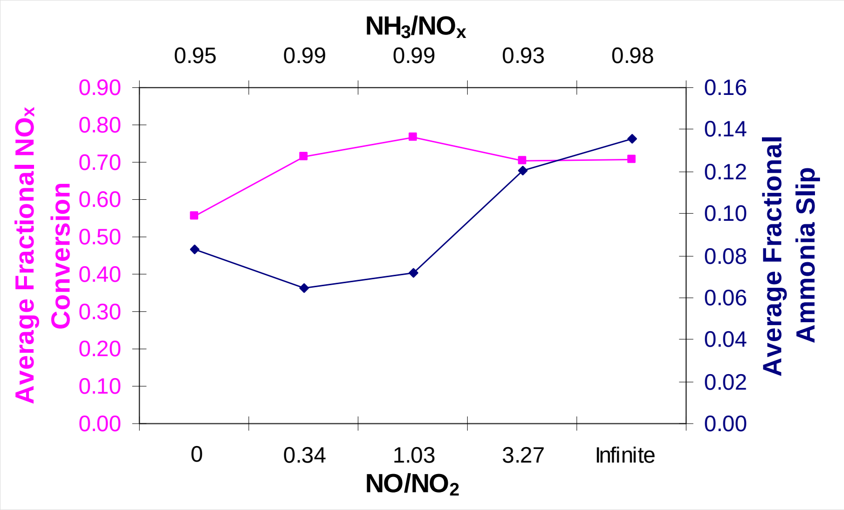
NO 177 ppm, NO_2 172 ppm, NH_3 343 ppm, CO_2 4.9%, O_2 14 %, H_2O 1.9%, balance N_2, total flow 210 sccm.

Sensitivities of Transient Thermal Cycle to Concentration Changes

- Fast SCR conditions are desirable particularly for impact on NH_3 slip
- NO/NO_2 ratio is quite robust 0.3-1.0 with NH_3:NO_x 1:1



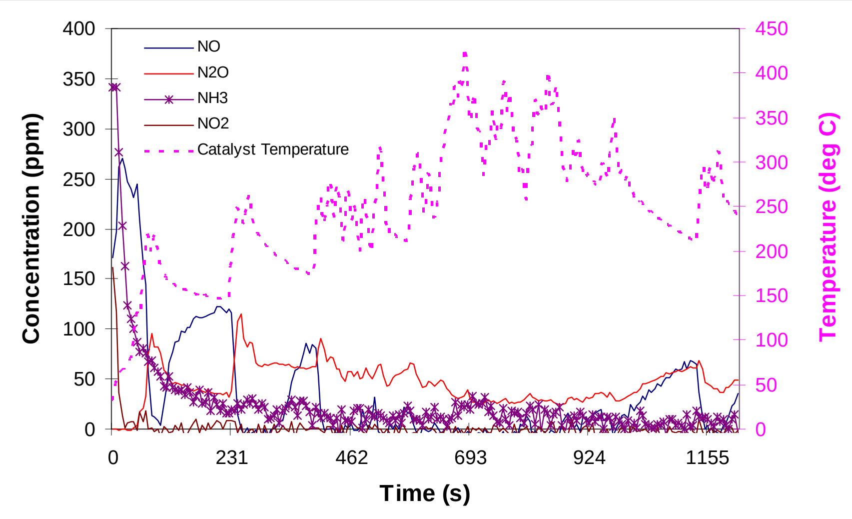




Thermal Transient Cycles

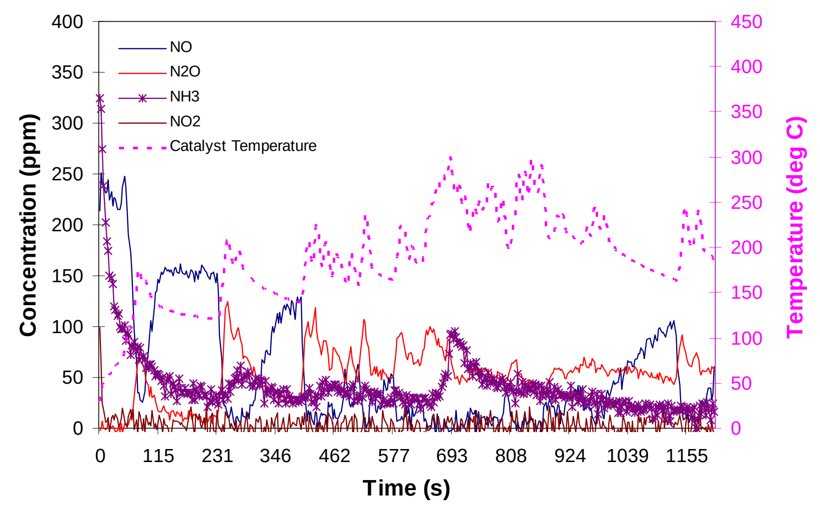
- Assuming HCCI idle is reduced to 125 °C and heavy load is reduced to 325 °C and applying the change across the HDD FTP
- HDD FTP % NO_x conversion 77% NH_3 slip 7%, Estimated HCCI NO_x conversion 69% and 12% NH_3 slip as expected due to the lower temperatures

HDD FTP



NO 177 ppm, NO_2 172 ppm, NH_3 343 ppm, CO_2 4.9%, O_2 14 %, H_2O 1.9%, balance N_2, total flow 210 sccm.

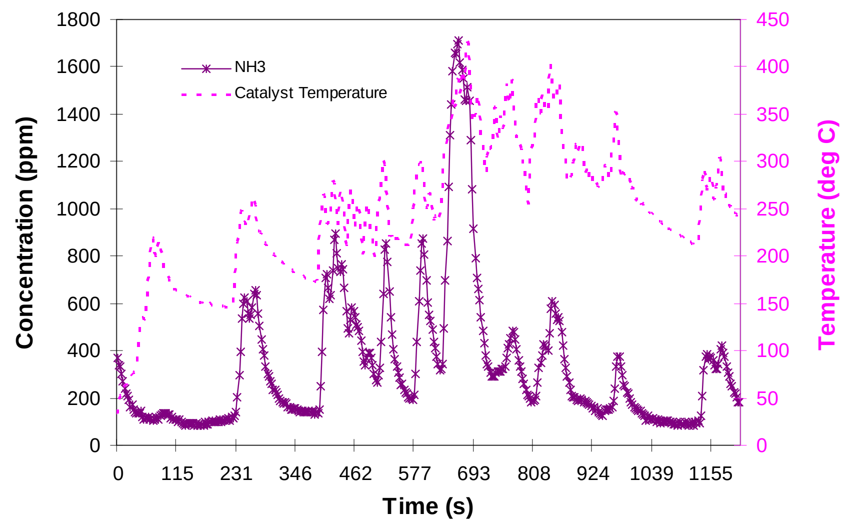
Estimated HCCI



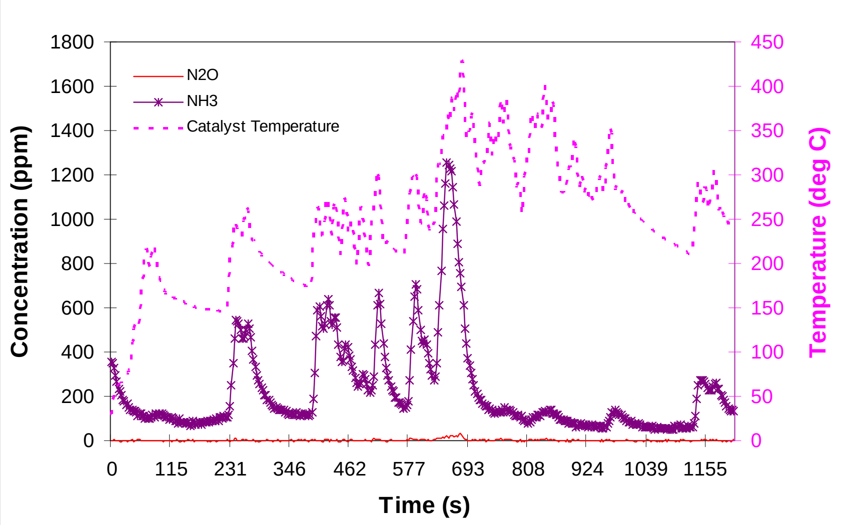
NO 183 ppm, NO_2 184 ppm, NH_3 344 ppm, CO_2 5.0%, O_2 14 %, H_2O 1.8%, balance N_2, total flow 210 sccm.

Ammonia Interaction During Thermal Transient Cycle

- In the absence of O_2 an average of 351 ppm NH_3 was observed over the cycle, 4% conversion and 96% NH_3 released
- The largest release corresponding to the 284-351 °C adsorption peak
- Upon addition of 14% O_2 an average 225 ppm NH_3 was observed over the cycle, 36% conversion and 64% NH_3 released [1]



NH_3 353 ppm, CO_2 5.0%, H_2O 2.4%, balance N_2, total flow 210 sccm.

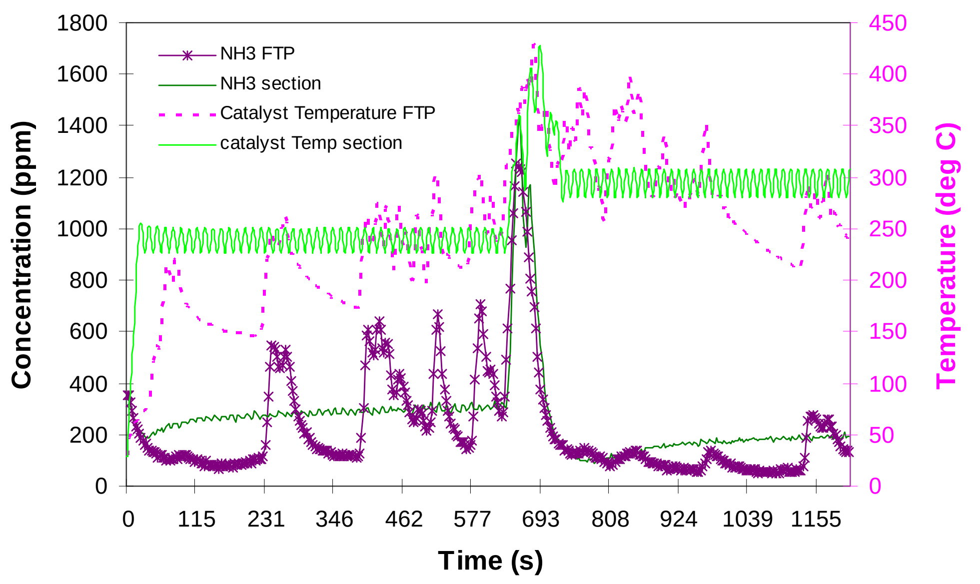


NH_3 353 ppm, CO_2 5.0%, O_2 14 %, H_2O 2.0%, balance N_2, total flow 210 sccm.

[1] Gang L. et al *Catal. Today* **2000**, *61*, 179-185.

Ammonia Usage During Thermal Transient Test

- Small section of thermal transient FTP cycle isolated (635-727 s) and ammonia release compared for whole cycle versus section
- Good agreement between the whole cycle and section at the maximum temperature
- Differences ascribed to the non-steady state conditions during the cycle



NH_3 356 ppm, CO_2 5.0%, O_2 14 %, H_2O 2.0%, balance N_2, total flow 210 sccm.

Future Work

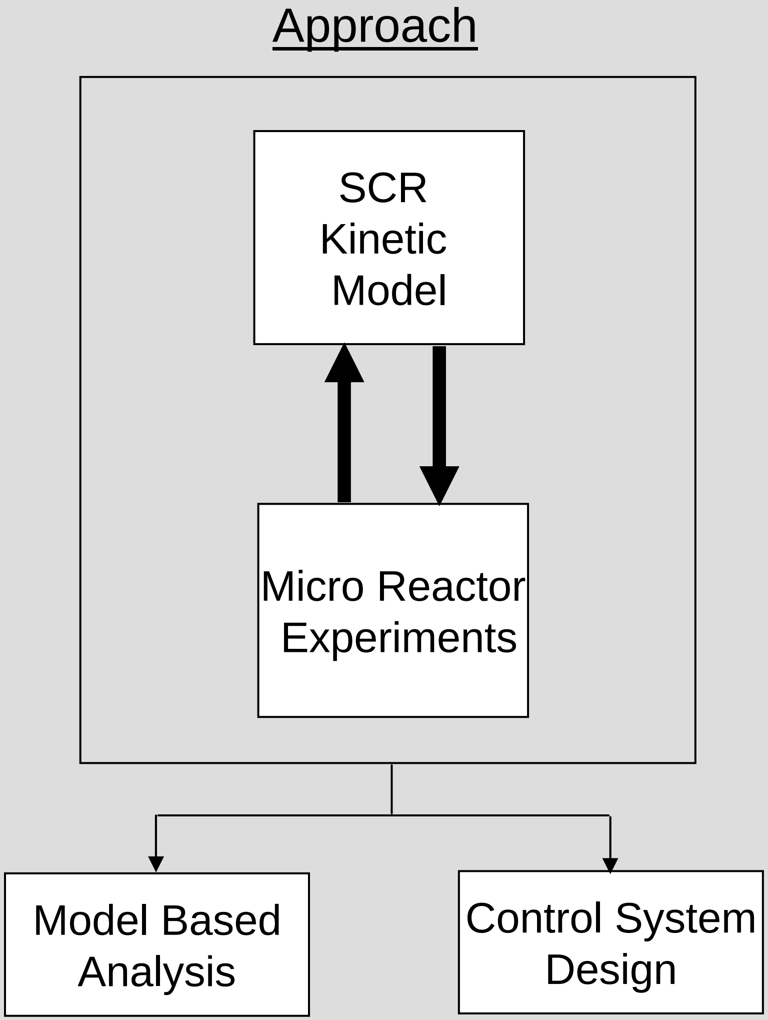
- Continue the characterization of storage and release mechanisms for NO, NO_2, N_2O and NH_3 on zeolitic urea-SCR catalyst:
  - Activation energy of adsorption and desorption of gaseous species
  - probe competitive adsorption rates (CO_2, H_2O, C_3H_6) in pathway to integration of SCR with other emission control technologies
- Thermal transient reactor study to:
  - Continue to probe reactant interactions (H_2O, CO_2, C_3H_8) to seek optimal performance
  - Install rapid reaction stream switching capability to enable controlled variability in concentrations of species and more closely mimic engine testing
  - Install de-polymerization of cyanuric acid system to enable probing both isocyanic acid and NH_3 as reductant

Future Work - Modeling

- Development of kinetic models to investigate the dynamics of the catalyst under transient thermal operation
- Comprehensive analysis of the impact of the SCR catalyst dynamics from a systems perspective

Current Status

- A kinetic model in combination with micro reactor experiments is being developed and is being studied for various test cases
- Models are developed in ‘C’ and are incorporated into Matlab/Simulink for model based analysis



Approach

SCR Kinetic Model

Micro Reactor Experiments

Model Based Analysis

Control System Design

New CLEERS Standard Urea-SCR Catalyst

- Obtained a new commercial urea-SCR catalyst to act as a standard
- Catalyst is based on iron zeolite technology (400 cpsi, 0.0065" substrate wall thickness, washcoat loading 160 g/L, SA 77 m^2/g, 0.5 % atomic concentration Fe in washcoat)
- Monolith bricks at both PNNL and ORNL for testing
- Collaboration with Josh Pihl and Todd Toops at ORNL to use DRIFTS to examine catalyst bound species and competing species
- Installing in-situ Raman at PNNL to capture complimentary data at PNNL

Summary

- Initiated experimental plan characterizing adsorption/desorption phenomena within a zeolitic urea-SCR catalyst
    - Effective interaction of reactants with active sites is important for efficient urea usage
- Demonstrated a diesel transient temperature cycle on a zeolitic SCR catalyst powder sample
    - Enables increased fundamental understanding of transient effects / unsteady state conditions on catalysts
    - Demonstrated the same trend of relative performance of standard-, 100% NO_2-- and fast-SCR reactions over thermal transient cycle – the fast SCR has optimal usage of ammonia
    - Begun to look at sections of the transient cycle in more detail
    - The ability to test small powder samples for transient performance enables faster technology transfer to engine testing of viable catalysts and a means to probe "not-to-exceed" limits in the laboratory

Acknowledgements

- Maruthi N. Devarakonda, Darrell R. Herling, George G. Muntean, Kenneth G. Rappé, Russell G. Tonkyn, Diana N. Tran
- BASF and Umicore
- Ken Howden and Gurpreet Singh – Department of Energy, OVT
- CLEERS

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