The Effects of Hydrocarbons on NOx Reduction over Fe-based SCR Catalyst

Maruthi Devarakonda[1], Russell Tonkyn[1], Diana Tran[1], Darrell Herling[1], Jong Lee[1], Josh Pihl[2], Stuart Daw[2]

[1]Pacific Northwest National Laboratory
[2]Oakridge National Laboratory

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Motivation

- Selective Catalytic Reduction (SCR) effective over a wide range of temperatures.
- Higher NO_x reduction performance required to meet more stringent emission standards
- Cooler exhaust temperatures due to advanced combustion technologies.
- Factors that can affect NO_x conversion at low temperatures include:
  - ✓ Inhibition of NH_3 storage at low temperatures
  - ✓ Hydrocarbon slip from DOC/DPF during cold-start

Objectives

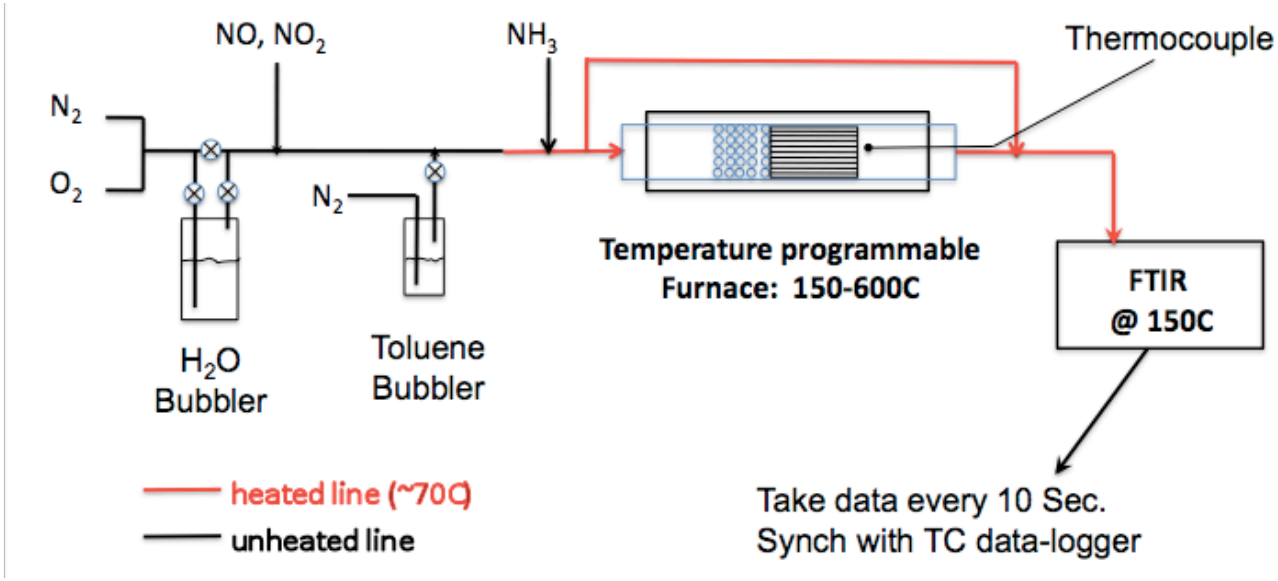
- Investigate the effects of hydrocarbons on various SCR reaction steps under controlled lab reactor conditions.

- Develop kinetic models to characterize competitive adsorption and inhibition, and to describe the impact on SCR performance quantitatively.

Outline

- Lab Reactor Experiments
- DRIFT Experiments
- Hydrocarbon Storage & Inhibition Modeling
- Conclusions & Future Work

Reactor Test Setup



Fe-zeolite catalyst

400/6.5

160g/L washcoat loading

Test Conditions

Component	Concentration
NO_x	350 ppm
NH_3	350 ppm
CO_2	0 or 5 %
O_2	14 %
Hydrocarbon ➢ C_2H_4 & C_3H_8 – combustion products ➢ Toluene – aromatic fuel component ➢ n-dodecane – long chain HC fuel component	350 ppm C1
Water	0 – 5%
N_2	balance
Space velocity	29k hr^{-1} for steady state tests 44k hr^{-1} for transient tests

NOx Reaction Pathways

In addition to NH_3 adsorption and desorption on SCR catalyst surface,

NH_3 oxidation: $2NH_3 + 3/2O_2 \rightarrow N_2 + 3H_2O$

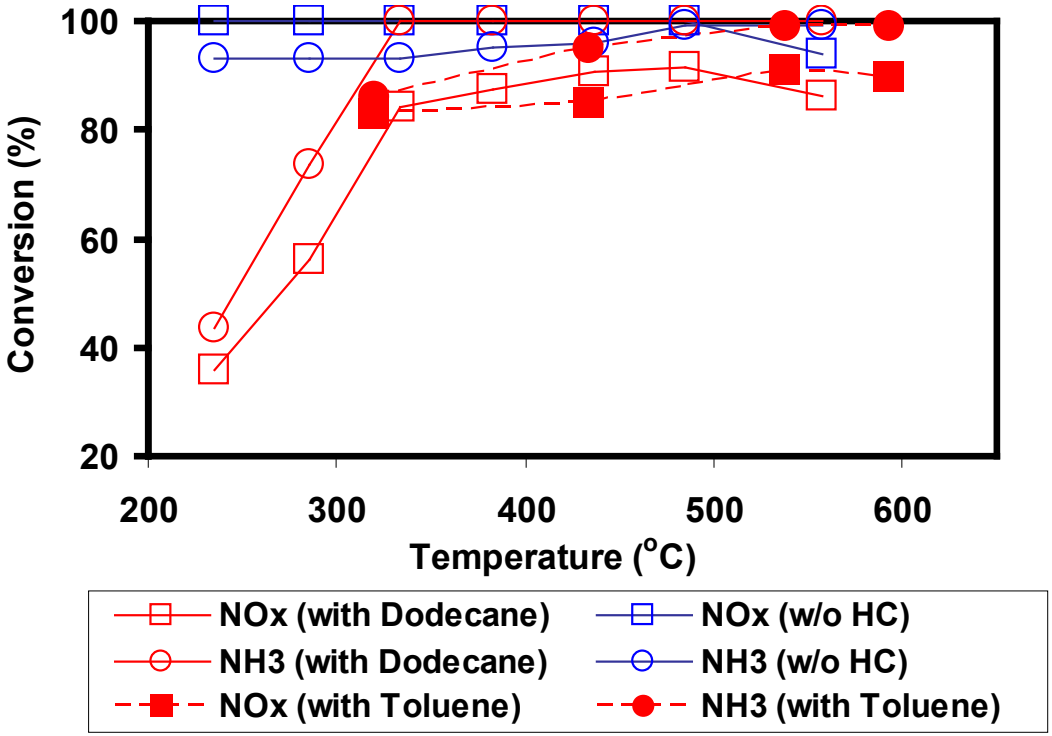
NO oxidation: $NO + 1/2O_2 \leftrightarrow NO_2$

Standard SCR: $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$

NO_2-SCR: $4NH_3 + 3NO_2 \rightarrow 7/2N_2 + 6H_2O$

Fast SCR: $2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$

Effect of Hydrocarbon on NOx Reduction



Feed Conditions

175 ppm NO

175 ppm NO_2

350 ppm NH_3

14% O_2

2% H_2O

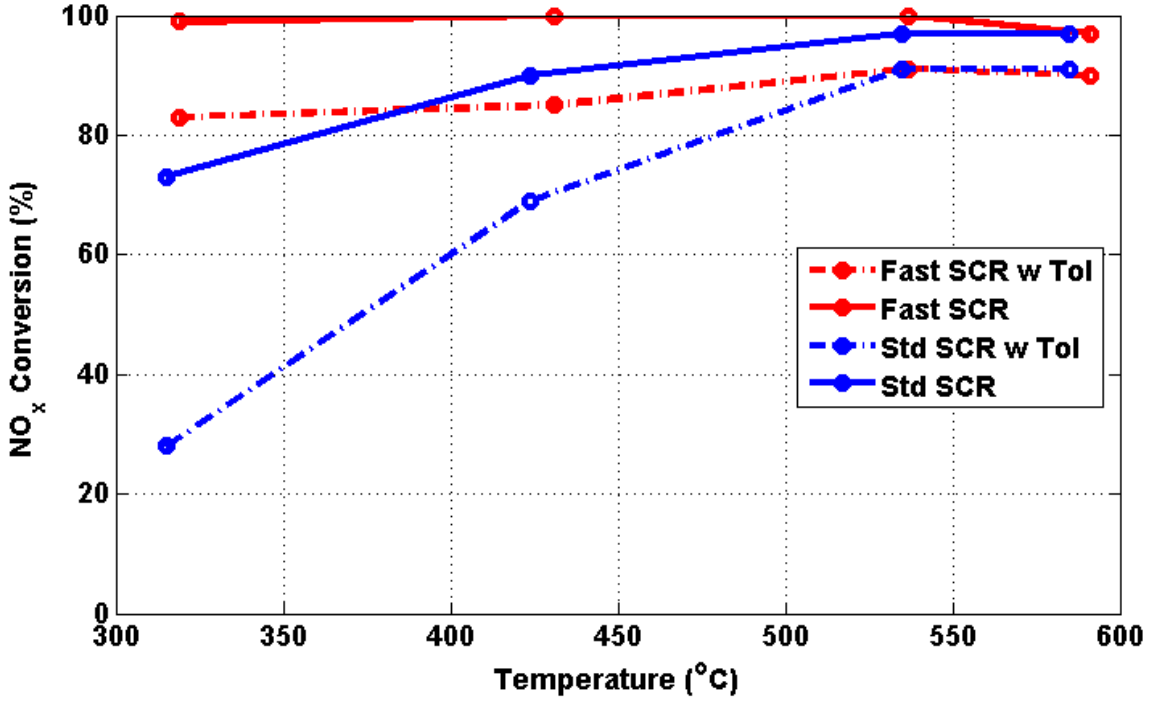
50 ppm toluene (350 C1)

29 ppm dodecane (350 C1)

29k h^{-1}

- No effect of ethylene, propane
- Detrimental effects of toluene, dodecane

Effect of Toluene on NOx Reduction



Feed Conditions

350 ppm NO_x

350 ppm NH_3

14% O_2

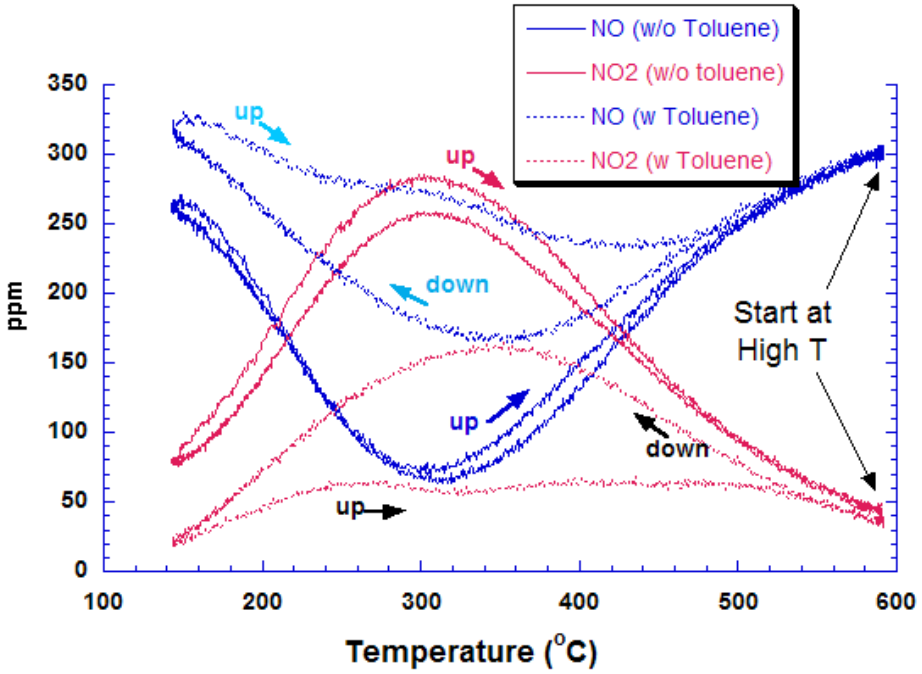
2% H_2O

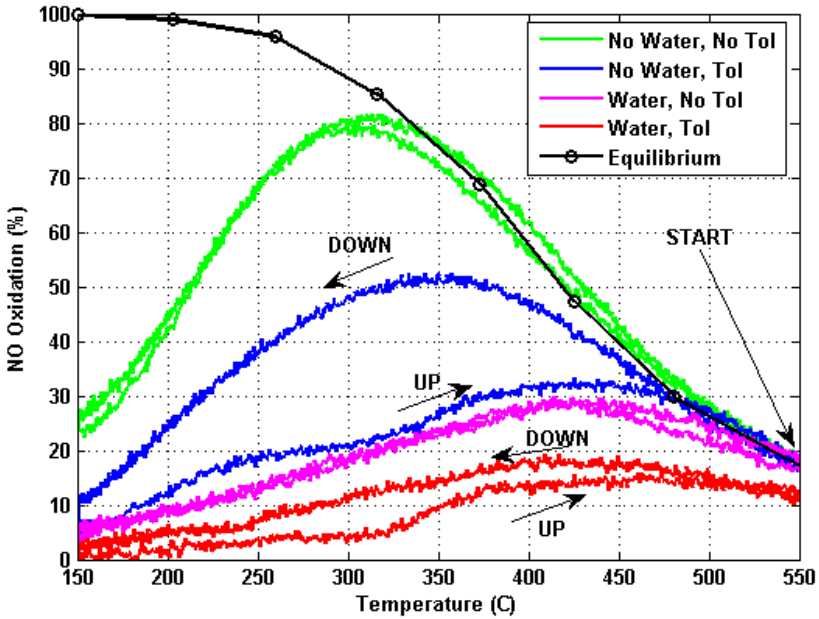
50 ppm toluene (350 C1)

29k h^{-1}

- More pronounced effect on Standard SCR
- No effect on NO_2-SCR

Effect of Toluene on NO Oxidation

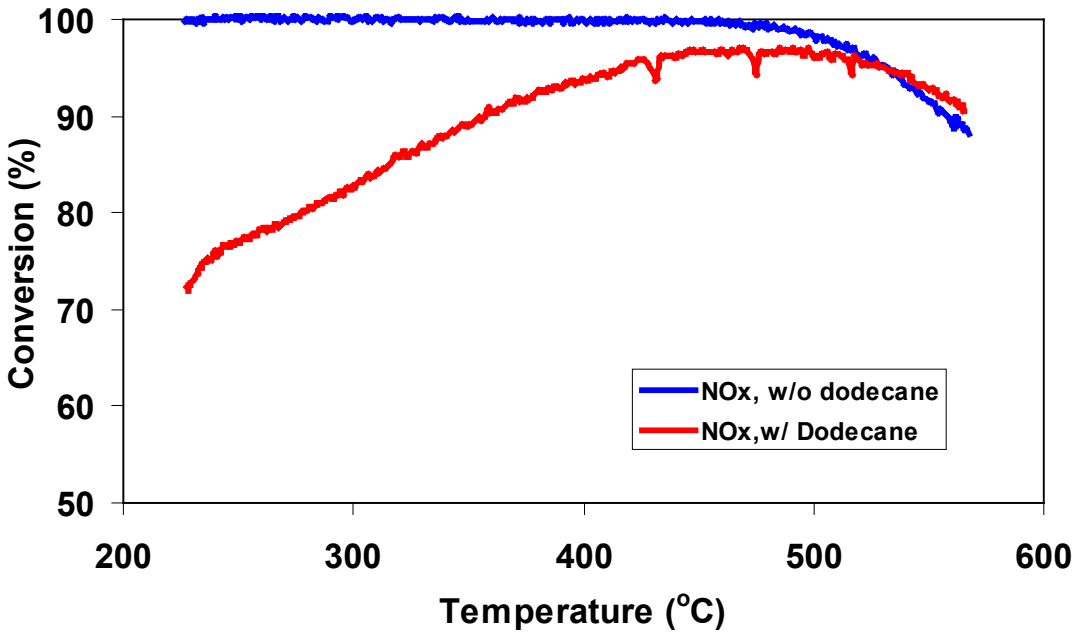




350 ppm NO, 14% O_2, 25 ppm toluene, 2% H_2O

- More pronounced inhibition effect during temp-up ramp
- Severe inhibition in the presence of H_2O

Effect of Dodecane on NOx Reduction



Feed Conditions

175 ppm NO

175 ppm NO_2

350 ppm NH_3

14% O_2

2% H_2O

29 ppm dodecane (350 C1)

- Decreased NOx reduction during temp-down ramp
- More pronounced effect on Standard SCR
- No effect on NO_2-SCR

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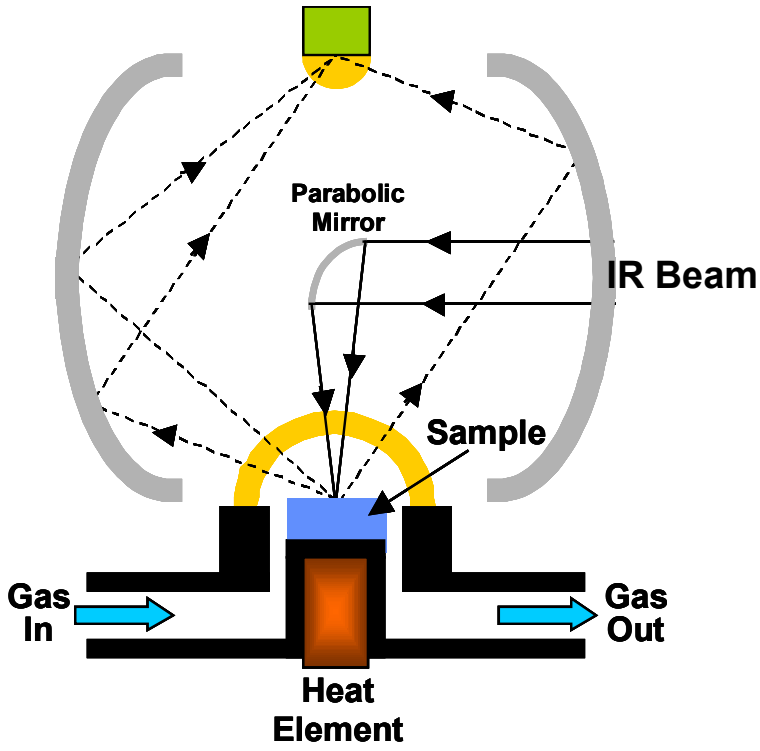
In Situ DRIFT Setup

- Diffuse reflectance IR FT spectroscopy (DRIFT)
  - ✓ Adsorbates on the particle surfaces under SCR reaction conditions
- Typical experiment:
  - ✓ Under 14% O_2, 5% CO_2, 4.5% H_2O:
    - Heat to 500 C to clean surface
    - Cool to experiment temperature
    - Take background spectrum
  - ✓ Turn on 350 ppm NOx
  - ✓ Turn on 350 ppm NH_3
  - ✓ Turn on 350 ppm [C1] HC
  - ✓ Continue scanning after turning off HC

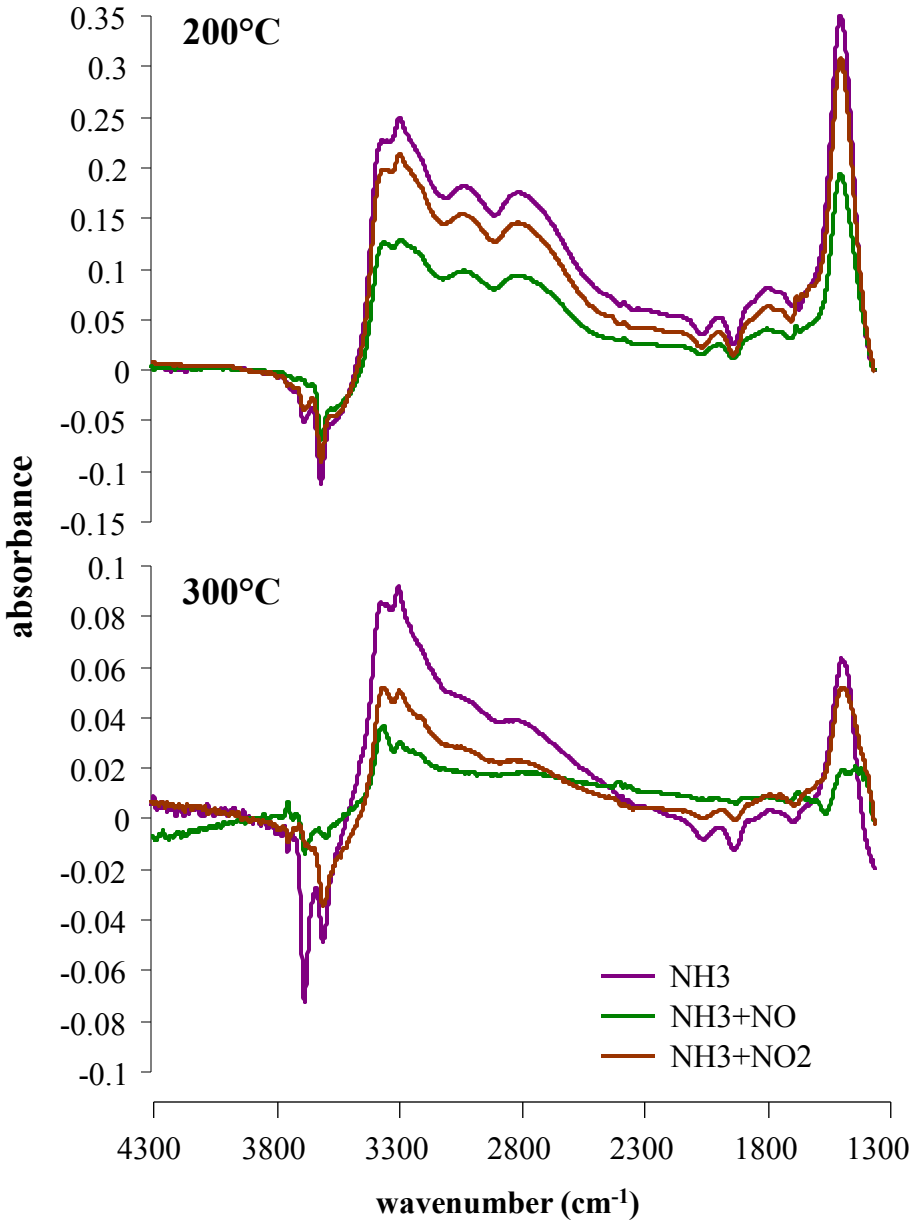
***in situ* DRIFTS reactor**



NH_3 Consumption by NOx

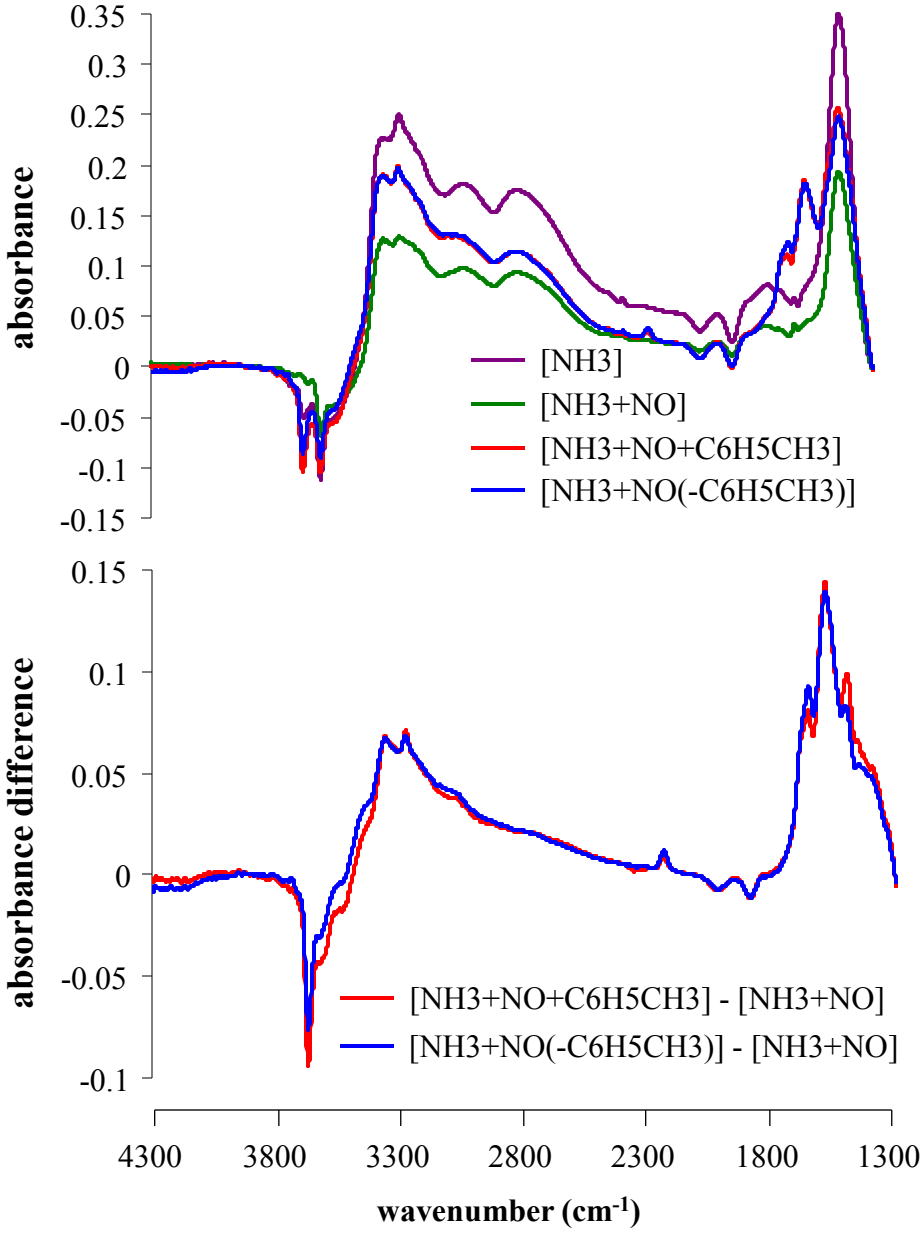
Exposure conditions: 350 ppm NO or NO_2, 350 ppm NH_3, 14% O_2, 5% CO_2, 4.5% H_2O

- Surface NH_3 continually consumed by SCR reactions
- NO more effective than NO_2 at decreasing adsorbed NH_3



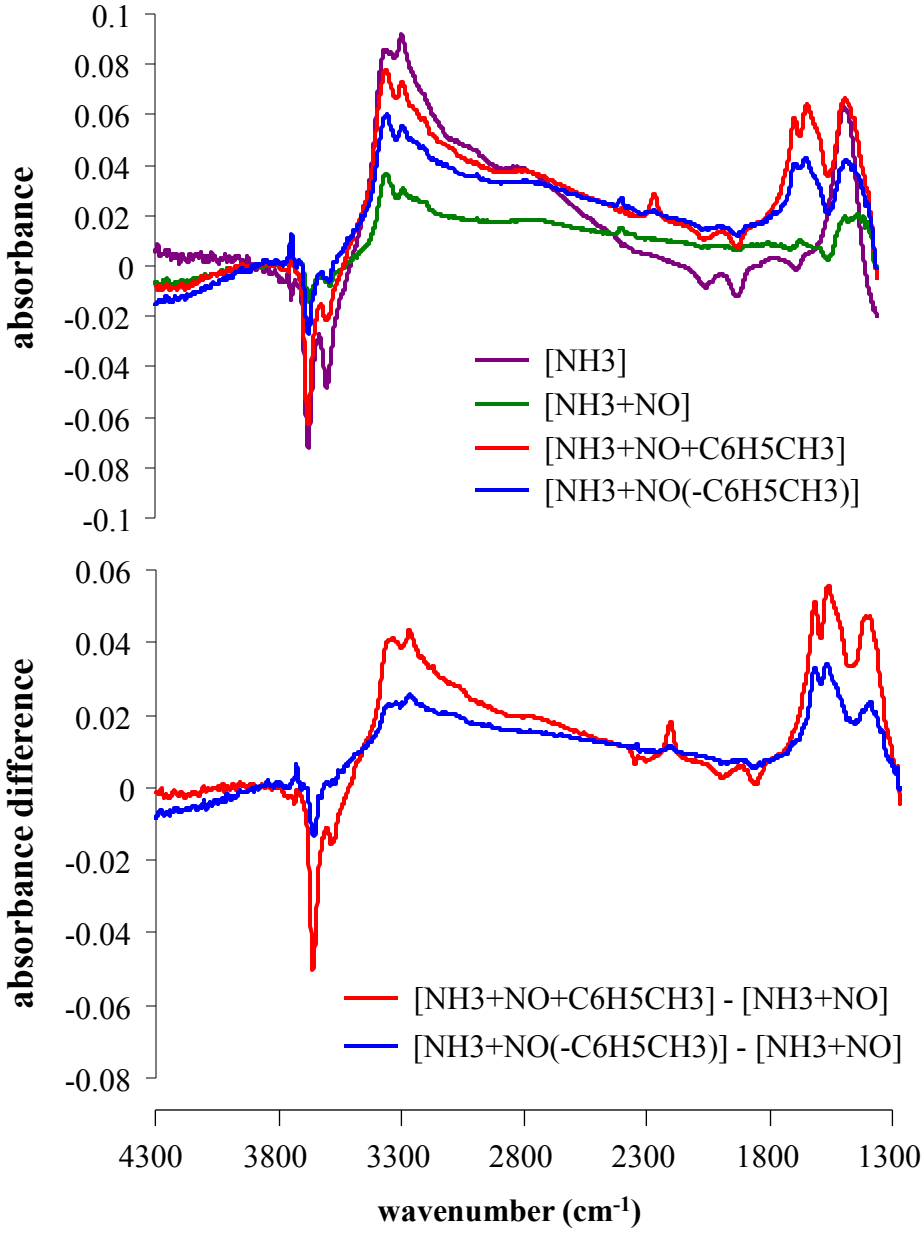
Toluene Inhibition at 200°C

- Introduction of toluene generates new adsorbates
  - 1300-1800 cm^{-1}: most likely toluene and derivatives
- Increased NH_3 on surface due to poisoned $NO+NH_3$ reaction
- No changes upon removal of toluene
  - Poisoning irreversible at 200 C
- Little effect on NO_2-SCR



Reduced Inhibition at 300°C

- Toluene addition shifts spectrum considerably
  - Increased NH_3 on the surface
  - Increased toluene-derived species
- Some recovery upon removal of toluene
  - Increased NH_3 consumption
  - Reduced toluene-derived species



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Overview of PNNL 1-D SCR Model

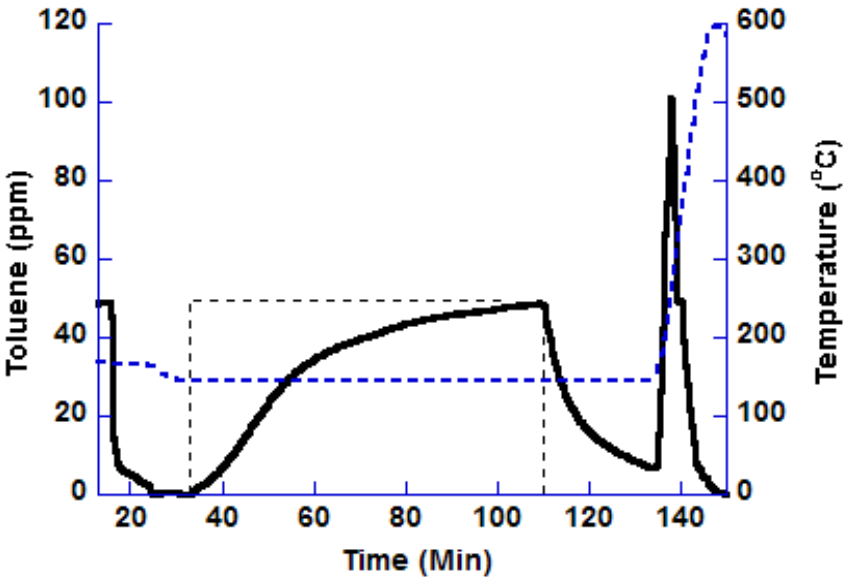
- Gas phase, surface phase concentrations and NH_3 storage as states
- Coded as 'C' S-functions and developed in Matlab/Simulink
- Optimized and validated using steady state and thermal transient reactor data

No	Reaction Name	Reaction	Reaction Rate
1	NH_3 Adsorption	$NH_3 + S \rightarrow NH_3^*$	$R_1 = k_1 C_{s,NH3}(1-\theta)\,\Omega$
2	NH_3 Desorption	$NH_3^* \rightarrow NH_3 + S$	$R_2 = k_2\,\theta\,\Omega$
3	Fast SCR	$2NH_3+NO+NO_2 \rightarrow 2N_2+3H_2O$	$R_3 = k_3 C_{NO} C_{NO2}\,\theta\,\Omega$
4	Standard SCR	$4NH_3+4NO+O_2 \rightarrow 4N_2+6H_2O$	$R_4 = k_4 C_{NO}\,\theta\,\Omega$
5	NO_2-SCR	$4NH_3+3NO_2 \rightarrow 3.5N_2+6H_2O$	$R_5 = k_5 C_{NO2}\,\theta\,\Omega$
6	NH_3 Oxidation	$2NH_3+3/2O_2 \rightarrow N_2+3H_2O$	$R_6 = k_6 C_{O2}\,\theta\,\Omega$
7	NO-NO_2 Oxidation	$NO+1/2O_2 \Leftrightarrow NO_2$	$R_7 = k_{7,f} C_{NO} C_{O2}^{1/2} - k_{7,b} C_{NO2}$

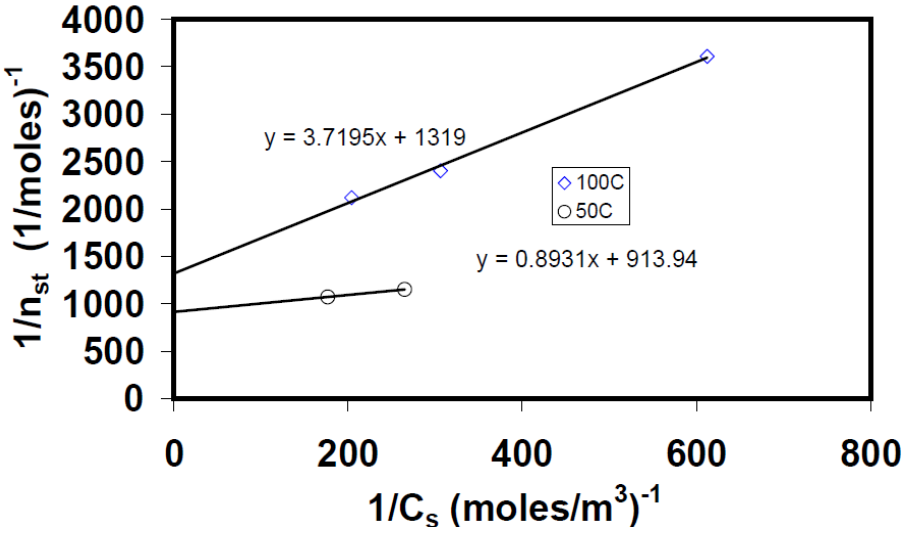
Hydrocarbon Storage Model: Toluene

T(°C) / C(ppm)	50	100	150
50		X	X
100	X	X	X
150	X	X	X

Test Matrix



Typical Adsorption Test



Langmuir Isotherms

$$n_{st,eq} = \int_0^{t_{eq}} (\dot{n}_{C_7H_8,in} - \dot{n}_{C_7H_8,out})dt$$

$$\frac{1}{n_{st,eq}} = \frac{1}{N_{total}} + \frac{1}{K(T)c_{s,C_7H_8}N_{total}}$$

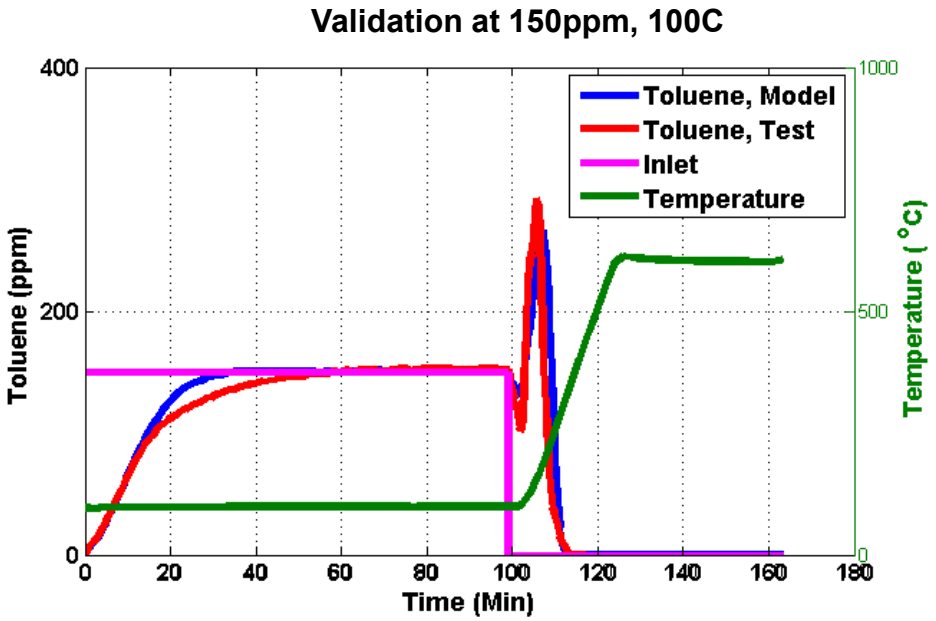
Storage rate parameters are obtained through approximation of Langmuir isotherms.

Single Site Kinetics Model for HC Storage

$$\varepsilon \frac{\partial c_{g,i}}{\partial t} = -\varepsilon u \frac{\partial c_{g,i}}{\partial x} - \beta_i A_g \left(c_{g,i} - c_{s,i} \right)$$

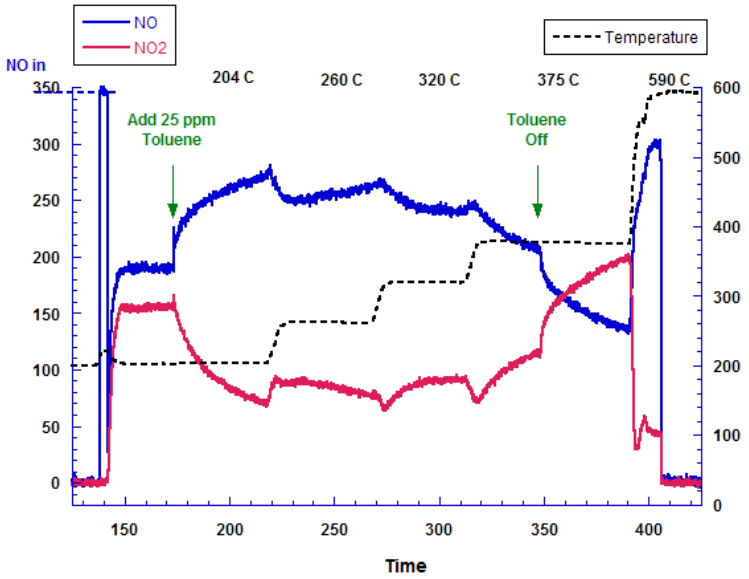
$$(1-\varepsilon) \frac{\partial c_{s,i}}{\partial t} = \beta_i A_g \left(c_{g,i} - c_{s,i} \right) + \sum_j r_{i,j}$$

$$\frac{d\theta_{tol}}{dt} = \frac{1}{\Omega} (r_{ads} - r_{des})$$



- Simulated using a variable step solver ode23tb, a TR-BDF2 algorithm
- Spatial derivative term approximated by a first order Euler integration scheme
- A total of 10 tanks (cells or axial increments) considered in series, each represented by a ‘C’ s-function and implemented in Matlab/Simulink

Modeling HC Inhibition of NO Oxidation

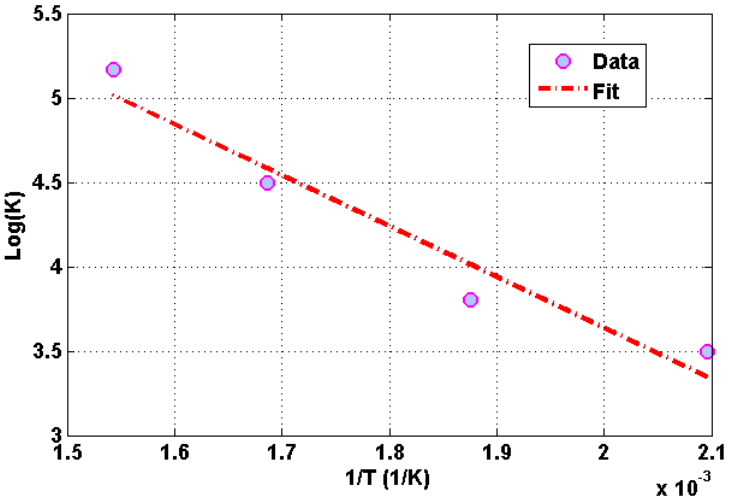


Step Temperature Test

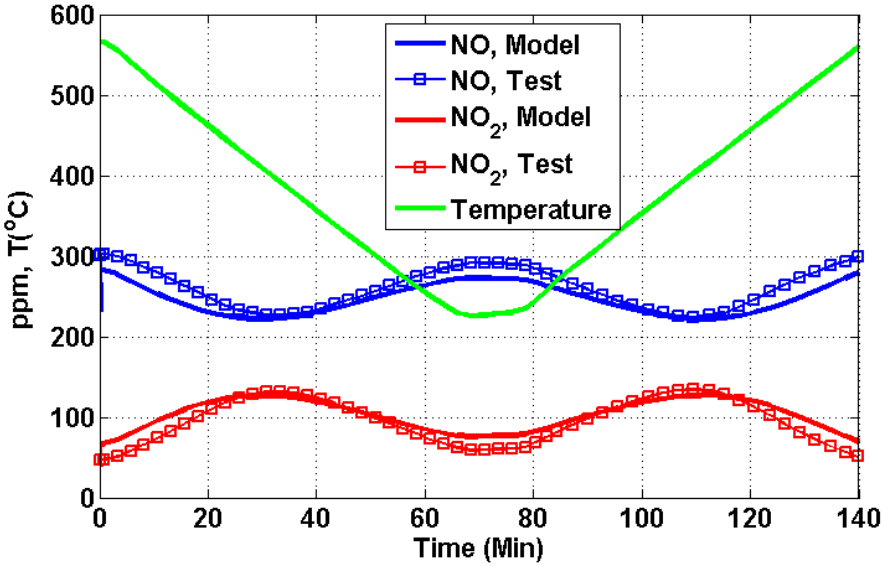
Feed: 350 ppm NO, 14% O_2, 25 ppm toluene (175 C1)

Rate parameter (K_{tol}) for the inhibition model, follows Arrhenius dependency. It is calculated from steady state data and validated on temperature ramp tests.

$$r = \frac{k_{f,oxi}\left(c_{NO}c_{o_2}^{0.5} - \frac{c_{NO_2}}{K_{eq}}\right)}{1 + K_{tol}\frac{\theta_{tol}}{1-\theta_{tol}}}$$



Arrhenius Plot for rate parameter (K_{tol})



Model Validation on Temperature Ramps

Conclusions

- Effects of hydrocarbons on NO_x reduction pathways over Fe-zeolite catalyst has been investigated.
  - ✓ No effect of ethylene and propane on NO_x reduction
  - ✓ Detrimental effects of toluene and n-dodecane on Standard SCR through suppressed NO oxidation
  - ✓ Increased surface NH_3 due to suppressed SCR
  - ✓ HC poisoning irreversible at low temps
- 1-D model has been developed to describe the effects of hydrocarbons on SCR reaction kinetics.
  - ✓ HC storage model developed using Langmuir isotherms
  - ✓ A single site kinetic model developed and validated to predict the effects of toluene & dodecane on NO oxidation and SCR reaction

Next Steps

- Investigate the competitive adsorption kinetics (NH_3, H_2O, HC) on Cu-zeolite SCR catalysts through experiments and modeling.

- Investigate the effects of catalyst aging on kinetic parameters and physicochemical properties of Cu-zeolite catalysts, and develop a catalyst aging model.

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