Hydrocarbon Inhibition and HC Storage Modeling in Fe-Zeolite Catalysts for HD Diesel Engines

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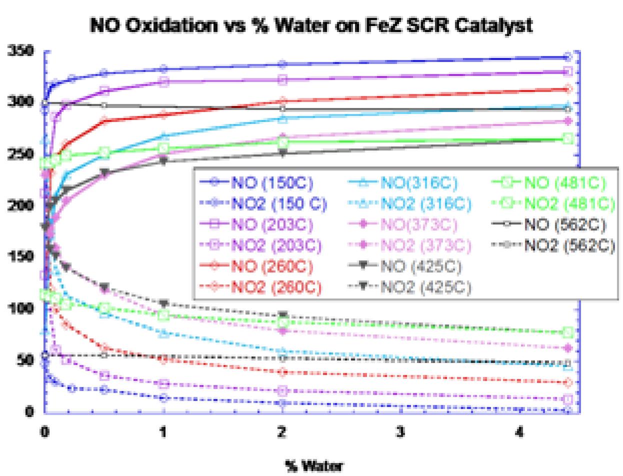
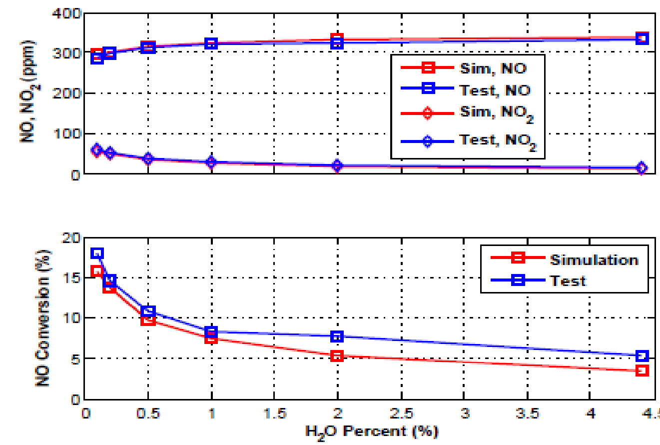
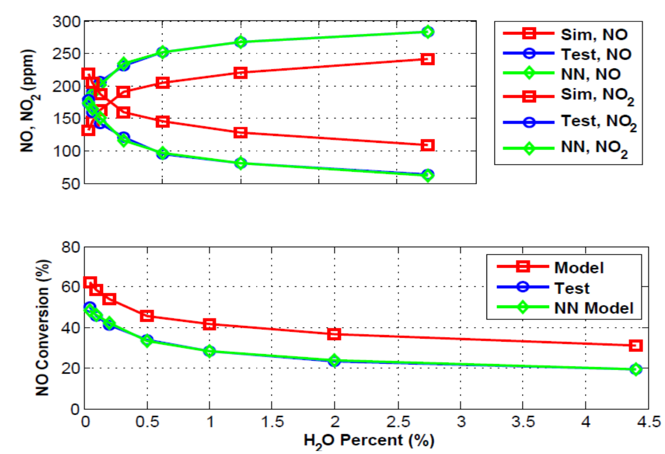
Dearborn, MI., August 5th 2009.

Background

- Research shifting slowly from individual catalytic converters to integrated systems.
- Need to investigate the dynamics between various aftertreatment devices for overall optimal performance to simultaneously reduce NO_x and PM. Ex: HC poisoning/inhibition on zeolites[1], catalyst aging, etc.
- Research activity is also seen in understanding detailed mechanistic pathways of various reactions. Ex: H_2O inhibition of NOx oxidation[2], NH_4NO_3 and N_2O formation, etc.







[1]Pihl et al., NAM Meeting, San Fransisco, CA., June 2009
[2]Devarakonda and Tonkyn, Catalysis Letters (Submitted)

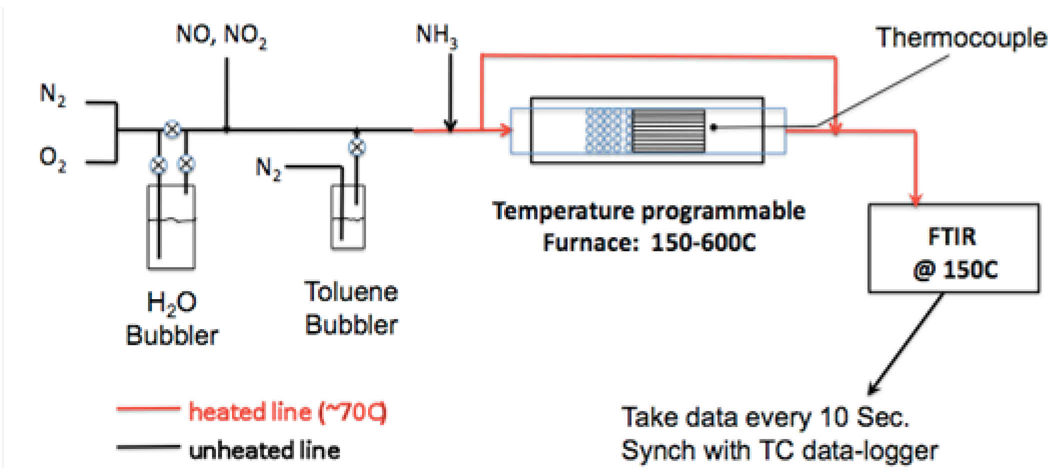
Presentation Outline

- Toluene Storage Model Development
- Toluene Inhibition of NO Oxidation
- Impact on NO_x & NH_3 Conversion (Steady State)
- Impact on NO_x & NH_3 Conversion (Transient Reactor)
- Conclusions & Future Work

Experimental Set-up

- 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)
- Tests conducted on a 9.31 cm^3 volume monolith core (1" L and 0.85" D) at a flow rate of 4.5 slm corresponding to a SV of 29 kh^{-1}.
- Surface isotherm tests similar to our recent work on NH_3 surface characterization[1] are done to investigate toluene adsorption.

Reactor Set-up

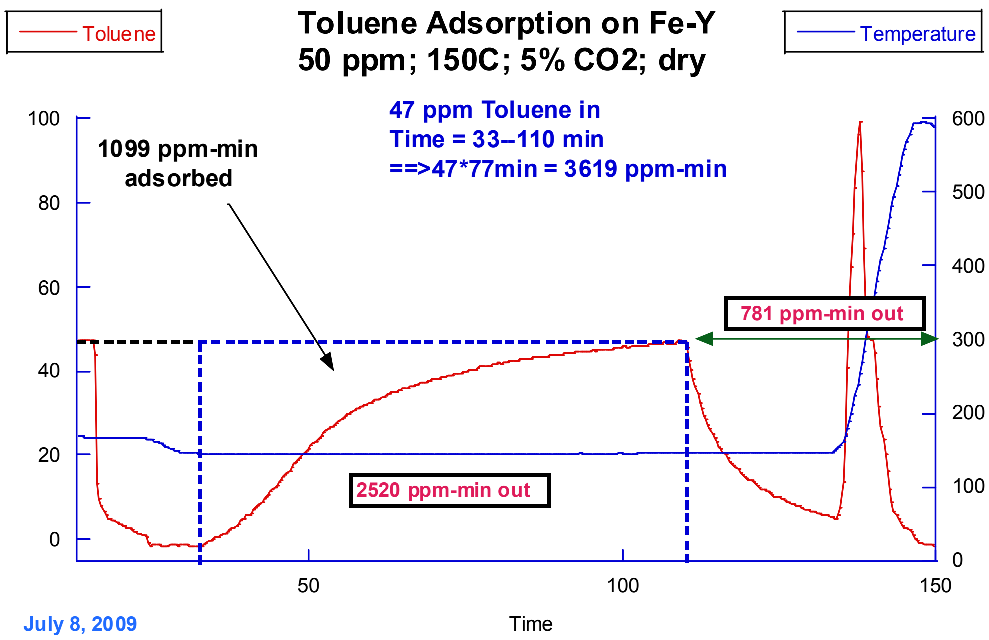


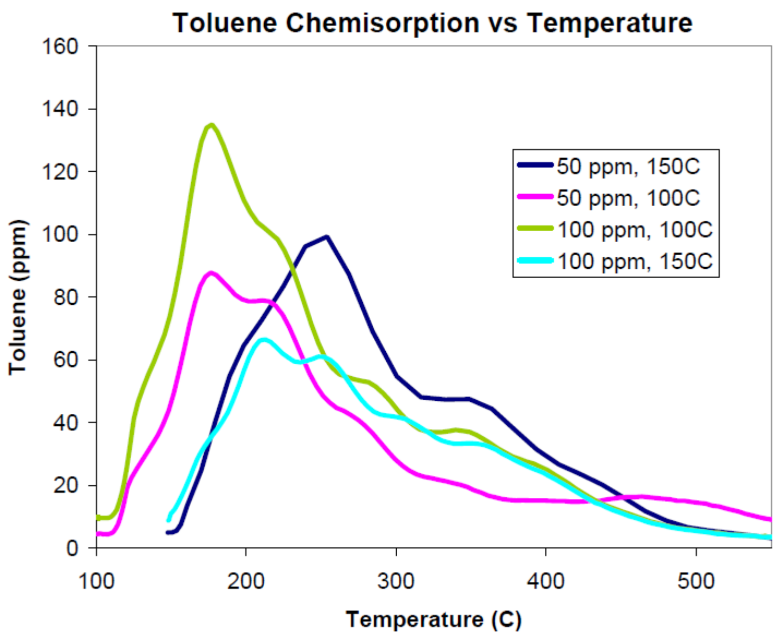
Isotherm Test Matrix

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

[1]Devarakonda, Tonkyn and Male, Chemical Engineering Journal (Submitted)

Multi-site Adsorption of Toluene on Fe-Zeolite





- Adsorption tests show multiple sites on the catalyst where toluene might be chemisorbed (observed during the temperature ramps).
- Need to investigate the number of adsorption sites through fundamental characterization.

Toluene Storage Model (Single Site Kinetics)

Assuming non-activated adsorption rate constant, the adsorption and desorption rate expressions are given by

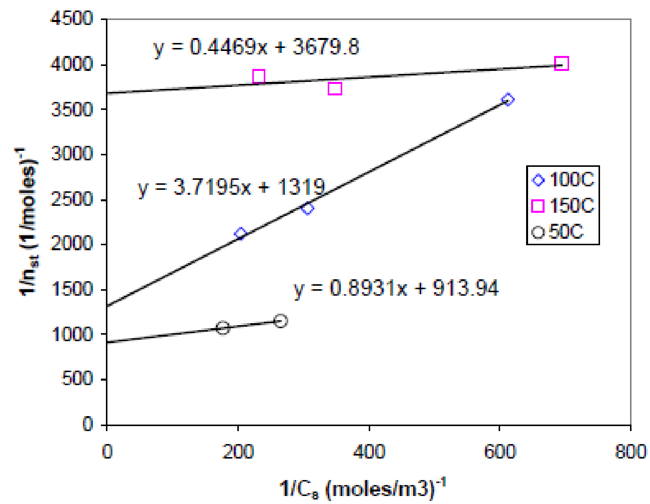
Define $\theta = \frac{n_{st}}{N_{total}}$ then

$$r_{ads} = A_{ads} c_{s,C_7H_8} (1-\theta) N_{total}$$
$$r_{des} = A_{des} e^{-E_{des}/RT} \theta N_{total}$$

$$r_{ads} = A_{ads} c_{s,C_7H_8} (N_{total} - n_{st})$$
$$r_{des} = A_{des} e^{-E_{des}/RT} n_{st}$$

At equilibrium, $R_{ads} = R_{des}$

$$A_{ads} c_{s,C_7H_8} (N_{total} - n_{st,eq}) = A_{des} e^{-E_{des}/RT} n_{st,eq}$$



Where $n_{st,eq}$ is the toluene storage at equilibrium. Toluene storage at equilibrium ($n_{st,eq}$) can be obtained by integrating the total C_7H_8 entering the catalyst minus the total C_7H_8 leaving the catalyst until equilibrium t_{eq}.

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

Ω	97.65 mol/m^3
E_{des}	28606 J/mol
A_{ads}/A_{des}	0.029273

Dividing the above equation by $A_{ads} c_{s,C_7H_8} n_{st,eq} N_{total}$ throughout and rearranging the terms in the equation, we get

$$\frac{1}{n_{st,eq}} = \frac{1}{N_{total}} + \frac{1}{K(T) c_{s,C_7H_8} N_{total}}$$ Where $$K(T) = \frac{A_{ads}}{A_{des} e^{-E_{des}/RT}}$$

Approach followed from ref:
C. Sampara (U.Michigan., Ph.D. Dissertation, 2008)

Reactor Model (Single Site Kinetics)

The modeling equations are obtained by solving the gas phase and surface phase concentrations of the species and toluene storage states.

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

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

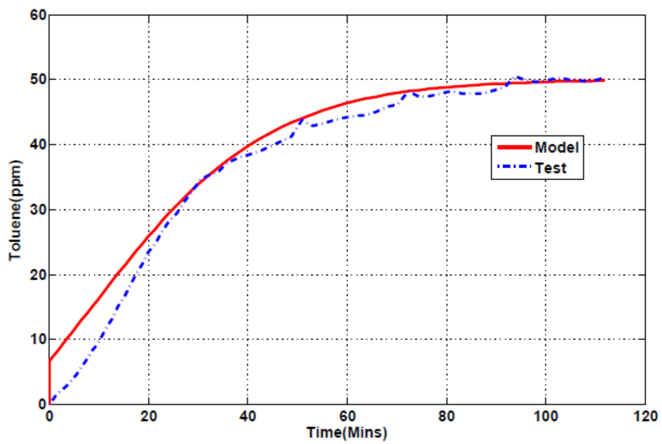
$$\frac{d\theta}{dt} = \frac{1}{\Omega}\left(r_{ads} - r_{des}\right)$$

j corresponds to the adsorption and desorption reactions.

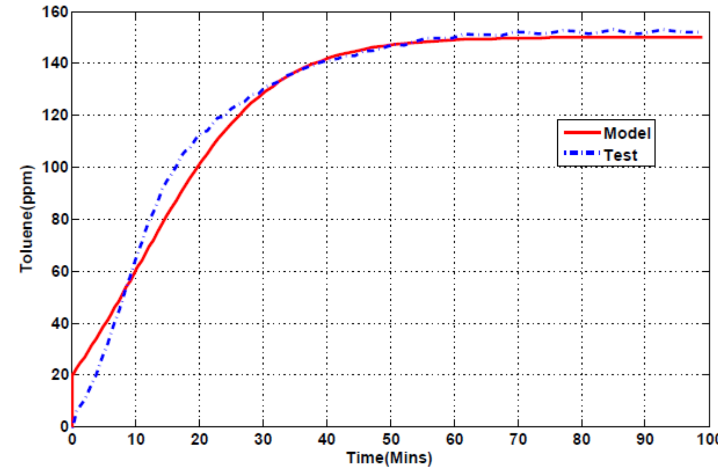
- Simulated using a variable step solver ode23tb, a TR-BDF2 algorithm.
- Spatial derivative term approximated by a first order Euler integration scheme.
- A total of 10 tanks (cells or axial increments) are considered in series, each represented by a 'C' s-function and implemented in Matlab/Simulink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

Model Validation

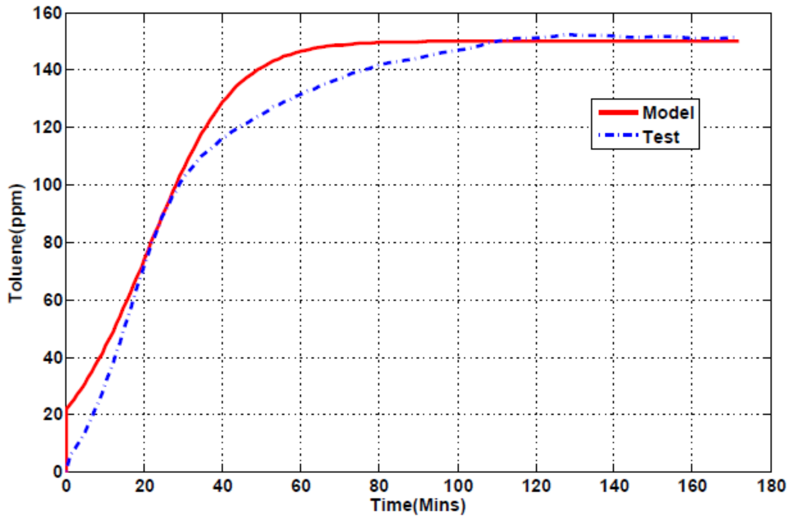
- Adsorption parameter (A_{ads}/A_{des}) identified on 100 ppm, 100C test case using the information obtained from Langmuir isotherms.
- The adsorption model is then validated on three other test data sets.



50 ppm, 100C

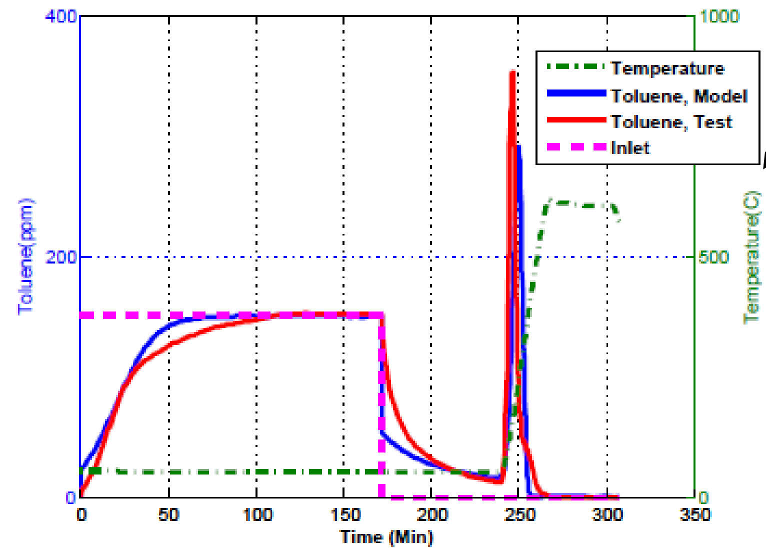


150 ppm, 100C



150 ppm, 50C

Overall Model Validation at 150 ppm, 50C



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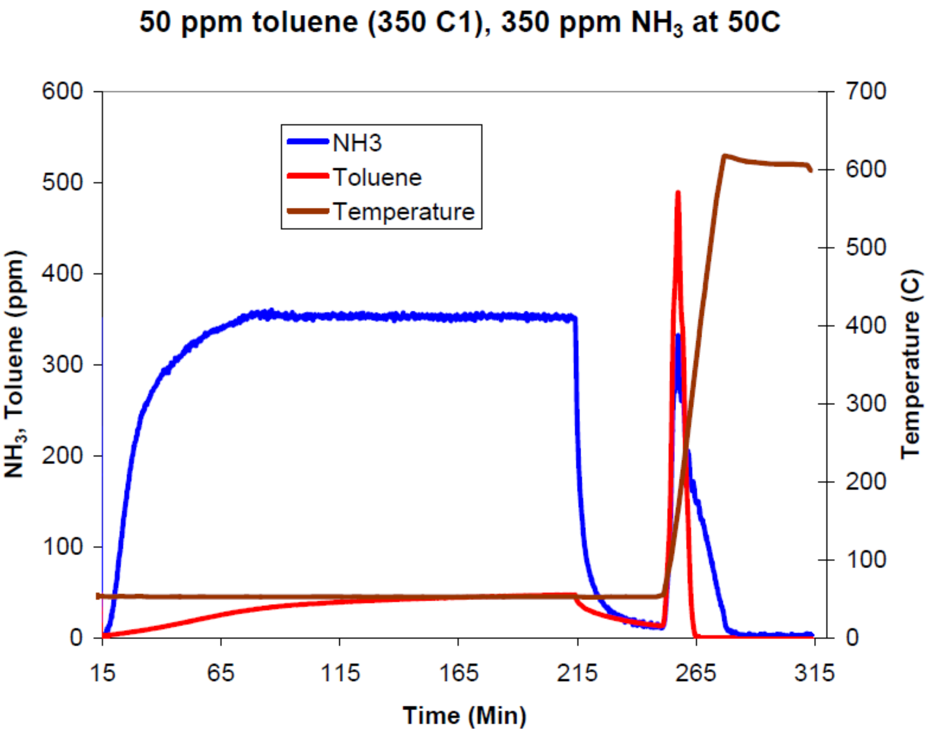
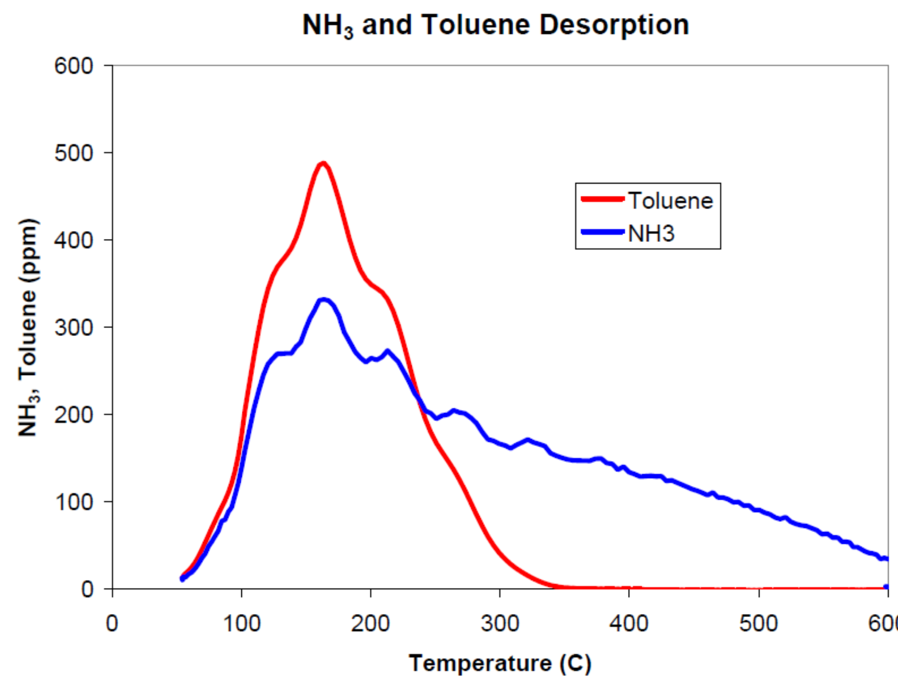
Competitive Adsorption between NH_3 and Toluene (Dry)

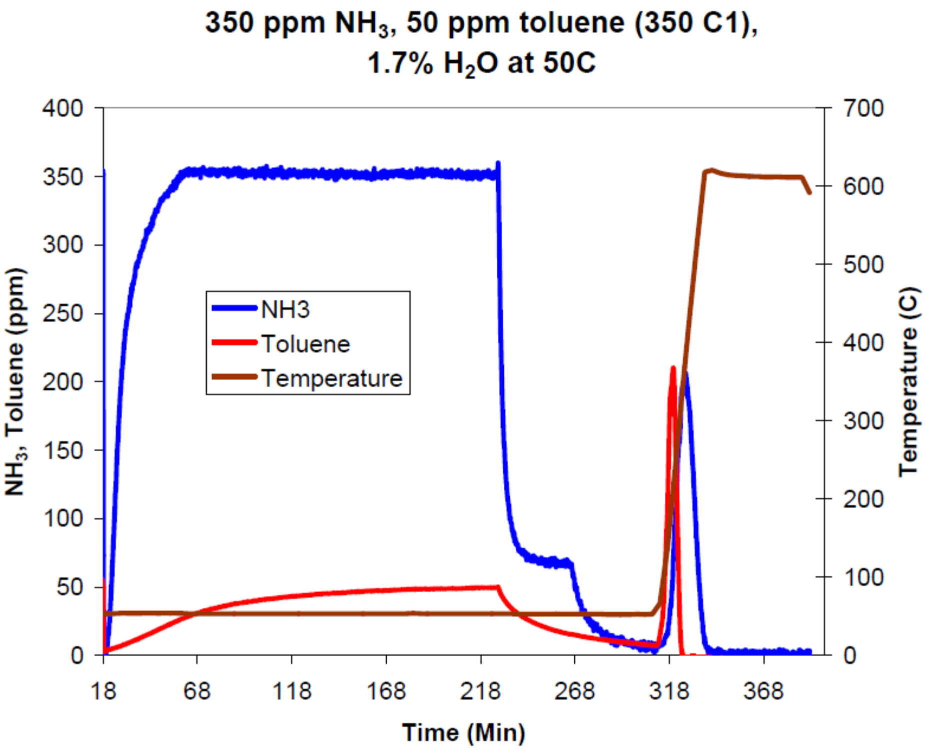


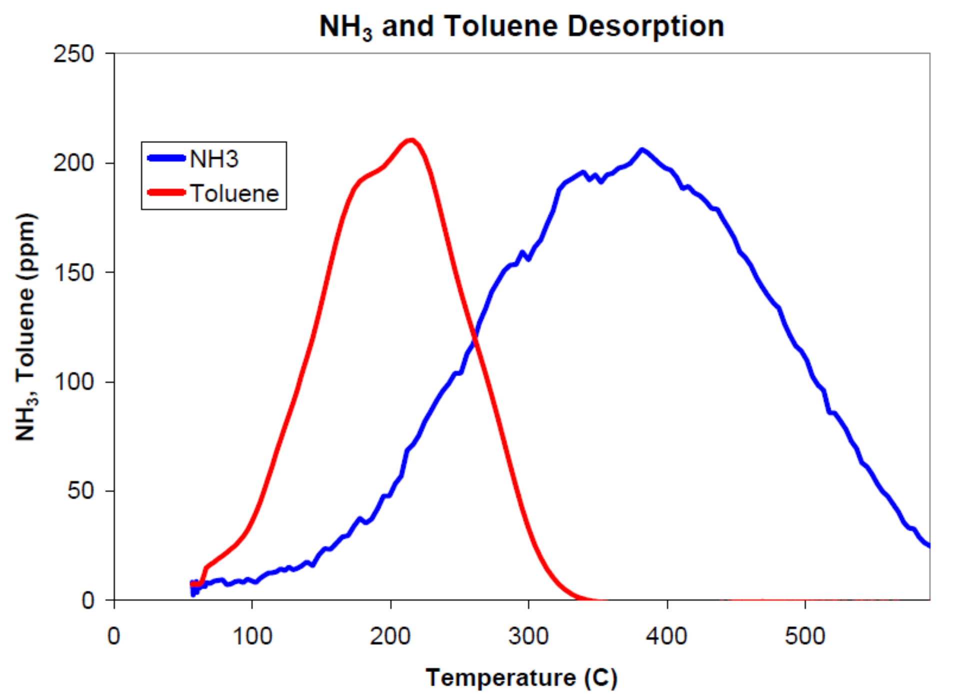


Ammonia and toluene exhibit similar desorption peaks in the absence of H_2O in the stream.

	Injected (ppm-min)	Out (ppm-min)	Absolute Error (%)	Stored (μ-moles)
NH_3	70000	70099	0.1	1058
Toluene	10000	10259	2.6	666

Competitive Adsorption between NH_3 and Toluene (Wet)



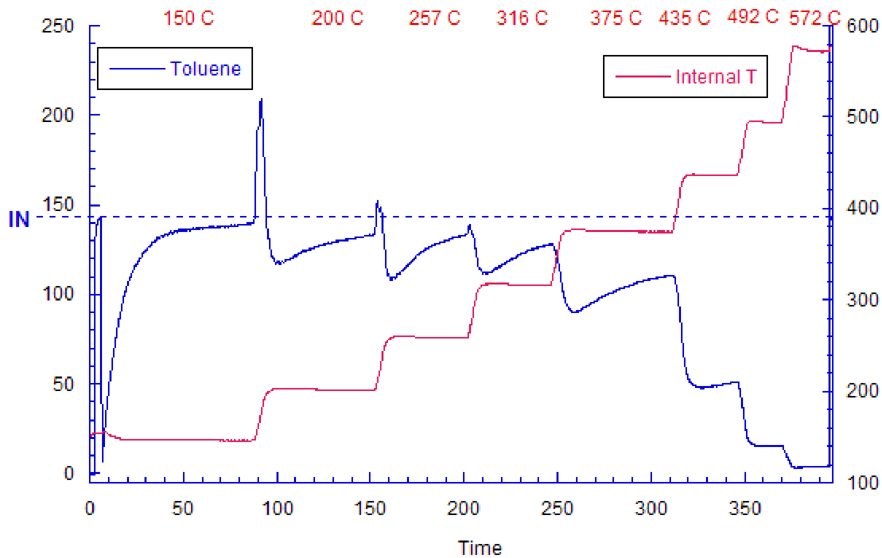


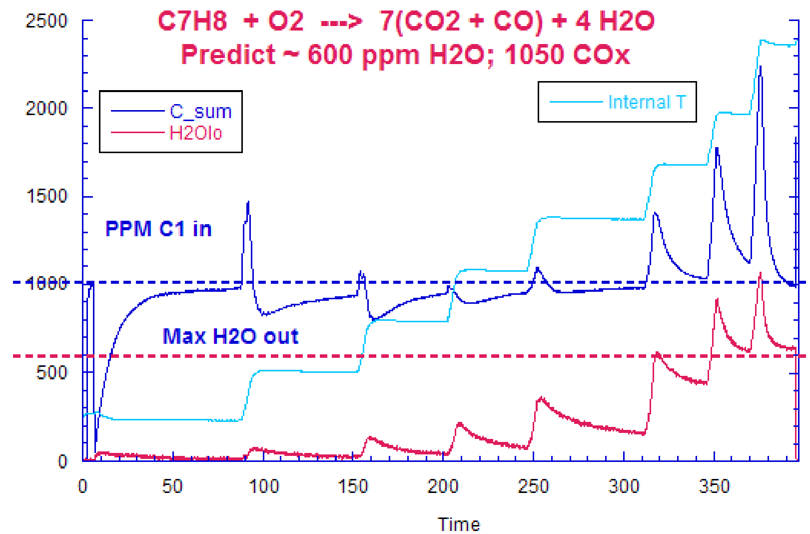
- Competition for sites between NH_3, toluene and H_2O (NH_3 and toluene storage decreases).
- Ammonia sticks to the catalyst in the presence of H_2O and requires high temperatures to desorb completely.

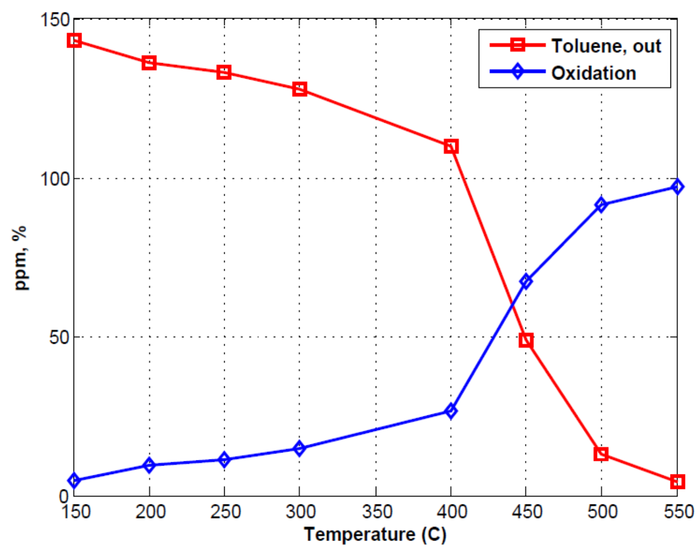
	Injected (ppm-min)	Out (ppm-min)	Absolute Error (%)	Stored (μ-moles)
NH_3	73150	76208	4.2	697
Toluene	10450	10606	1.5	507

Toluene Oxidation

- 150 ppm of toluene and 14% O_2, balance N_2 introduced to reactor at 4.5 slm.







- Toluene adsorbs at low temperature and oxidizes to CO and CO_2 at high temperatures.
- A good material balance for total carbon and H_2O was observed at high temperatures.

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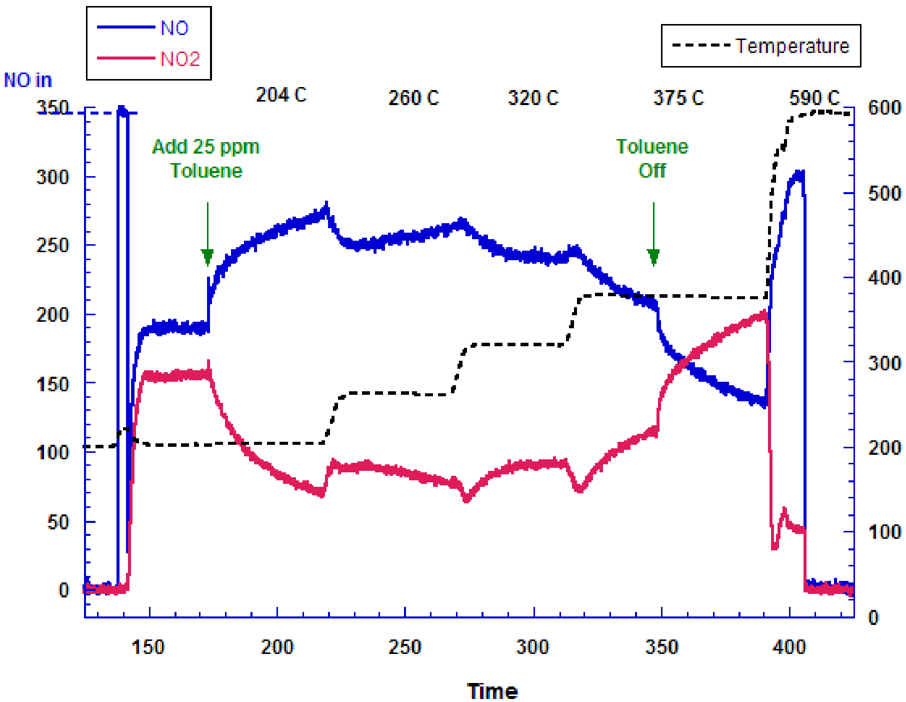
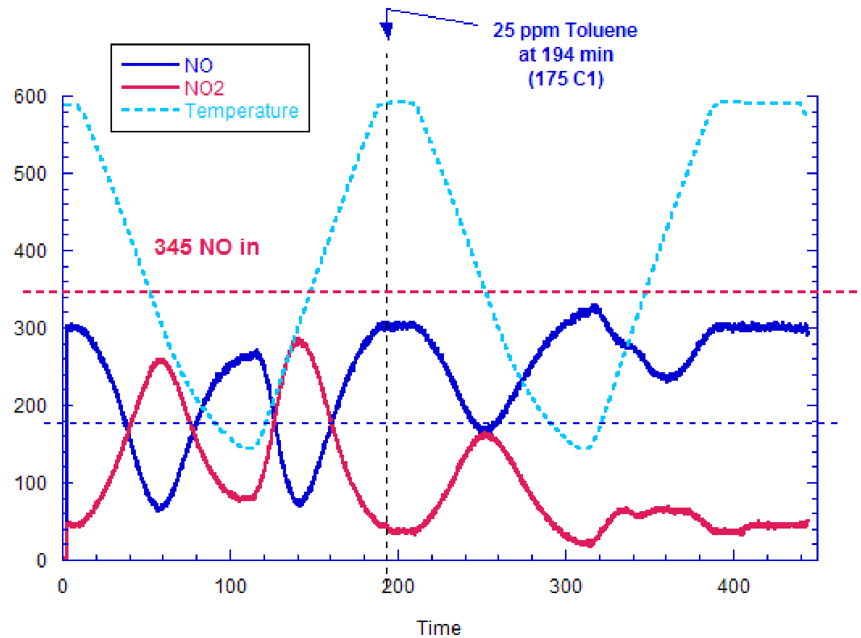
Toluene Inhibition of NO Oxidation (Dry)

Step Temperature Test

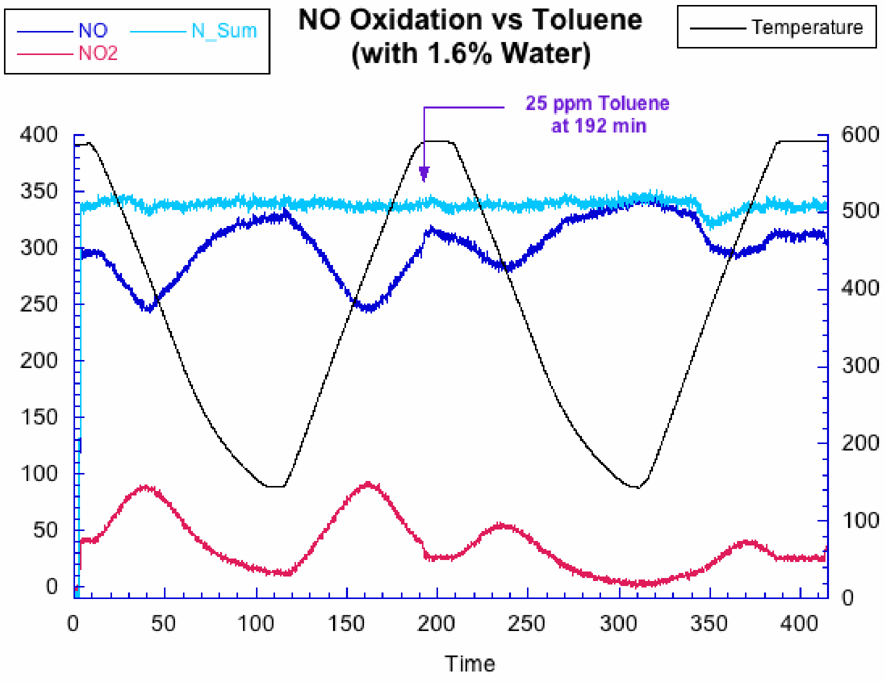


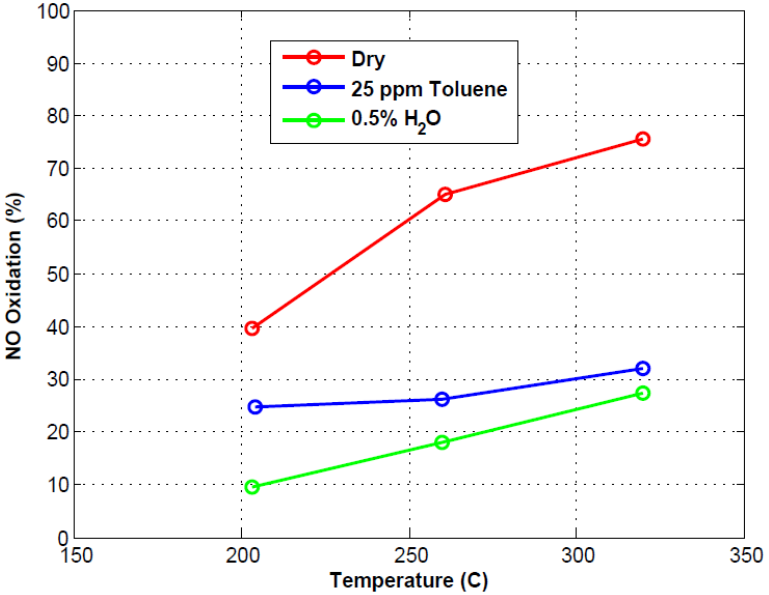
Periodic Temperature Ramp Test



- NO oxidation as a function of temperature without and with toluene shows noticeable inhibition effects of toluene.
- Toluene inhibits oxidation of NO without prior storage on the down ramp and shows a greater inhibition on the up ramp due to storage.

Toluene Inhibition of NO Oxidation (Wet)





A comparison of NO oxidation for the dry, 25 ppm of toluene and 0.5% H_2O as a function of temperature indicates that 0.5% H_2O inhibits NO oxidation more than 25 ppm toluene at low temperatures but the effects are comparable at higher temperatures.

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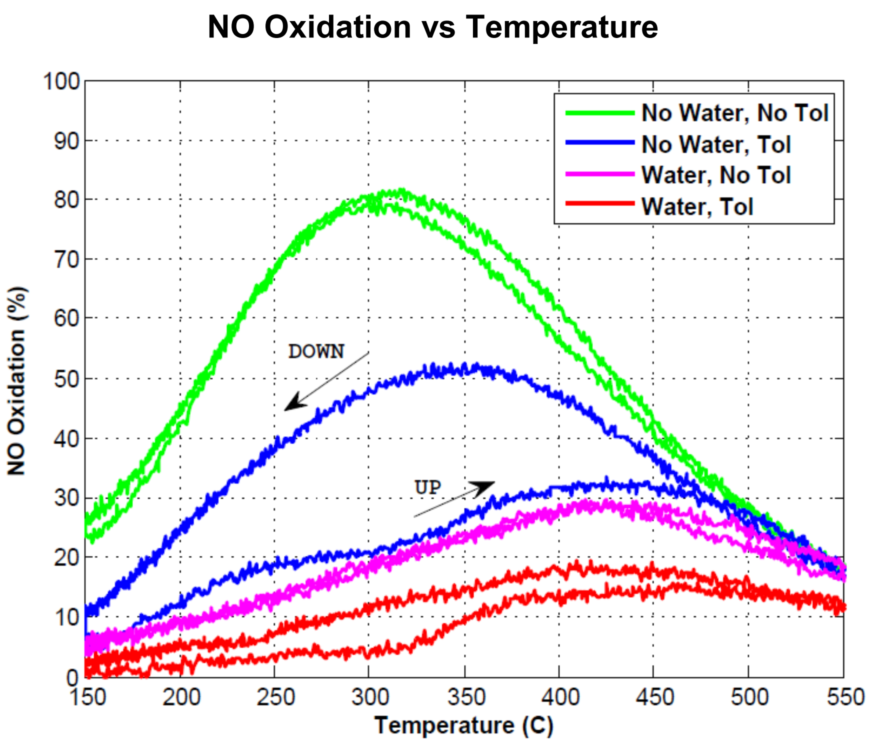
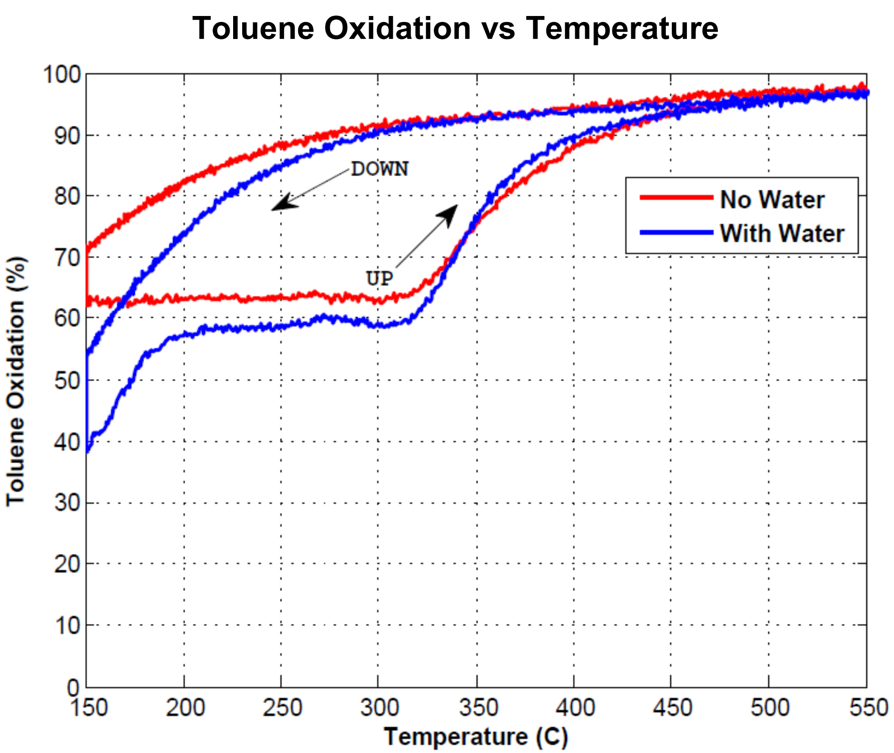
Toluene Inhibition increases in the presence of H_2O!!





• Water displaces toluene from the active sites and hence less toluene oxidation in the presence of water at lower temperatures (T < 300C).

• Water also inhibits NO oxidation and therefore the cumulative inhibition of NO oxidation by toluene and water is extreme.

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Tonkyn, Devarakonda and Tran, Manuscript in Preparation.

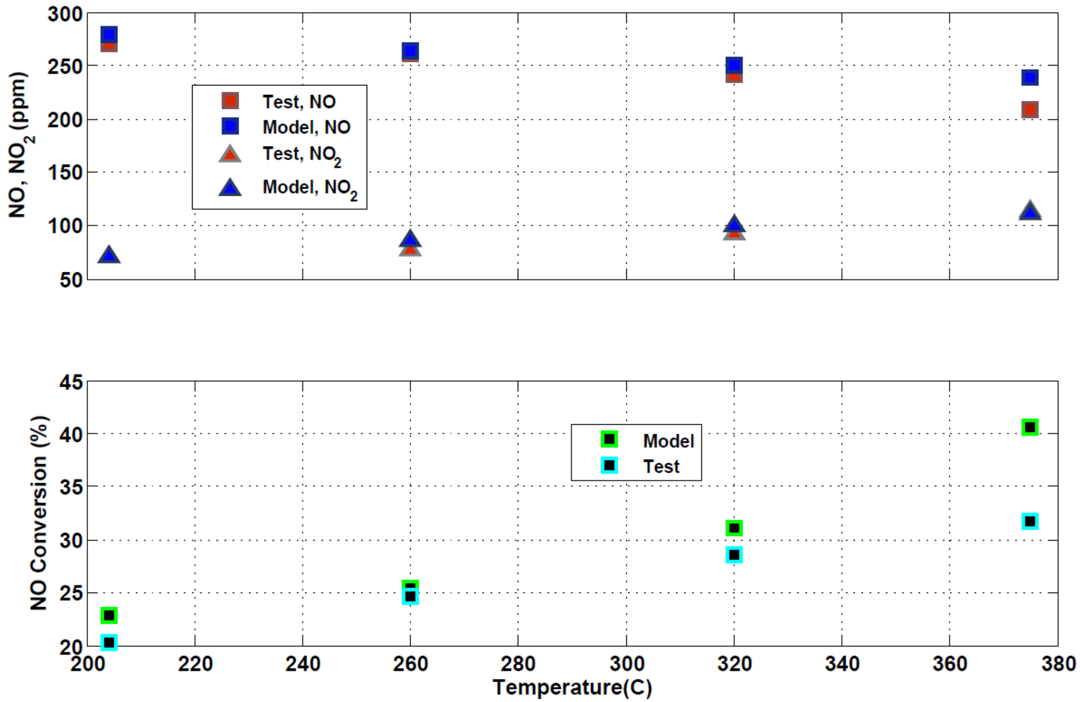
A Model for Toluene Inhibition of NO Oxidation

- Following the recently developed water inhibition model for NO oxidation[1], a model to predict toluene inhibition of NO oxidation under dry conditions is developed.
- Rate parameters for NO oxidation and NO_2 dissociation are taken from Olsson et al[2].

The kinetic rates of NO oxidation and NO_2 reduction are defined as a function of net toluene storage and an equilibrium constant as shown.

$$r_{f,oxi} = \frac{A_{f,oxi} e^{\frac{-E_{f,oxi}}{RT}} c_{NO} \sqrt{c_{o_2}}}{\left(1 + K \frac{\theta_{Tol}}{1-\theta_{Tol}}\right)}$$

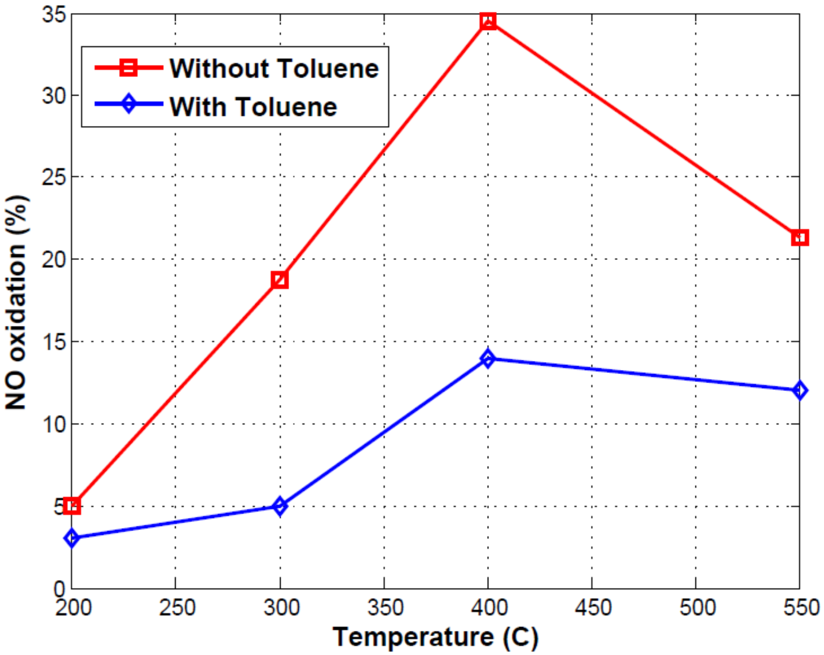
$$r_{b,oxi} = \frac{A_{b,oxi} e^{\frac{-E_{b,oxi}}{RT}} c_{NO_2}}{\left(1 + K \frac{\theta_{Tol}}{1-\theta_{Tol}}\right)}$$



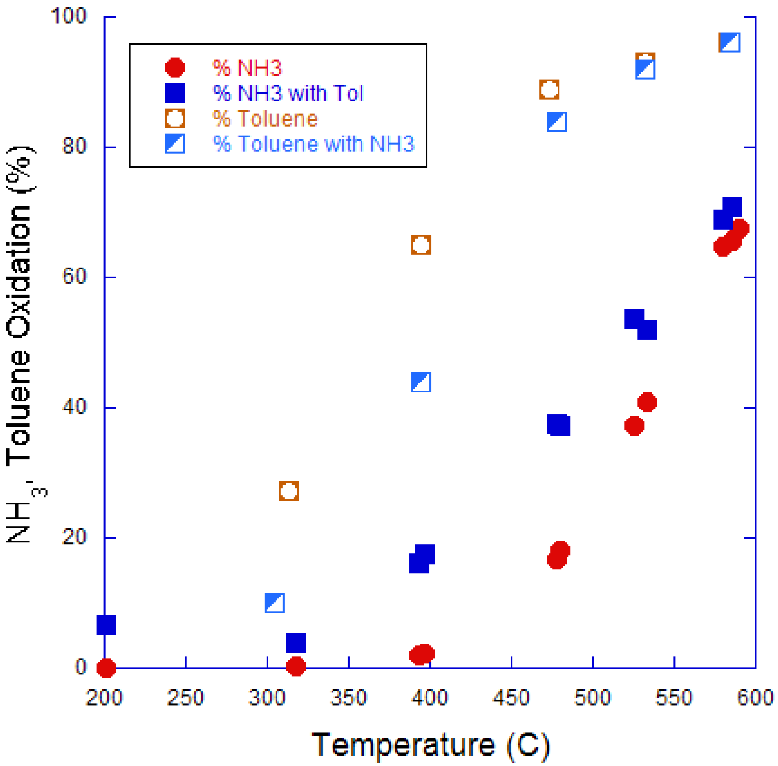
[1]Devarakonda and Tonkyn, Catalysis Letters (Submitted).
[2]L. Olsson, H. Sjovall and R. Blint, App Cat B: Environmental, 87, 2009, 200-210.

Toluene Effect – NO oxidation & NH_3 Oxidation

NO Oxidation: 350 ppm NO, 14% O_2, 2% H_2O at 29000 hr^{-1} SV

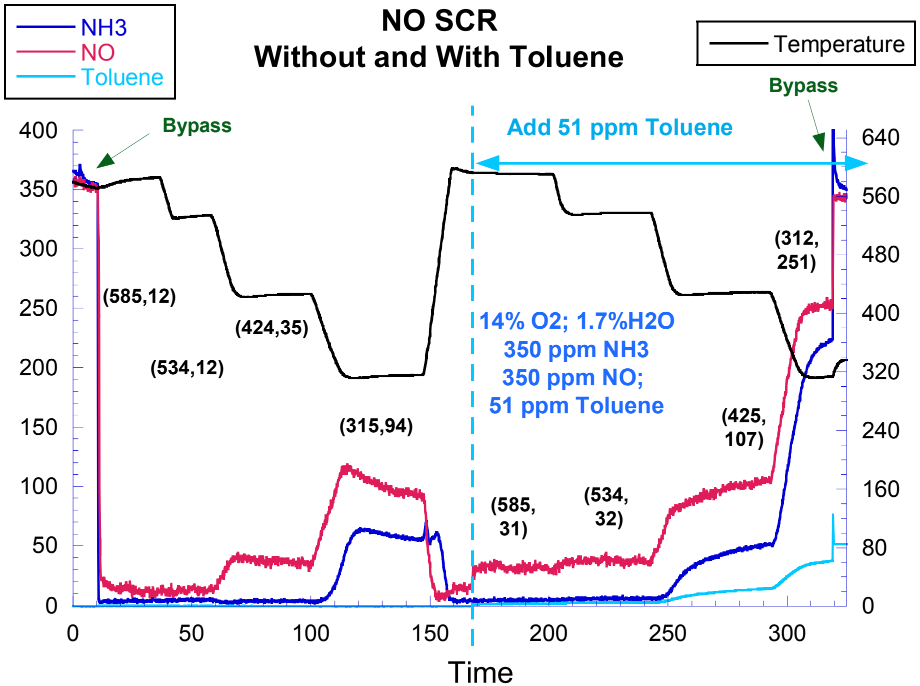


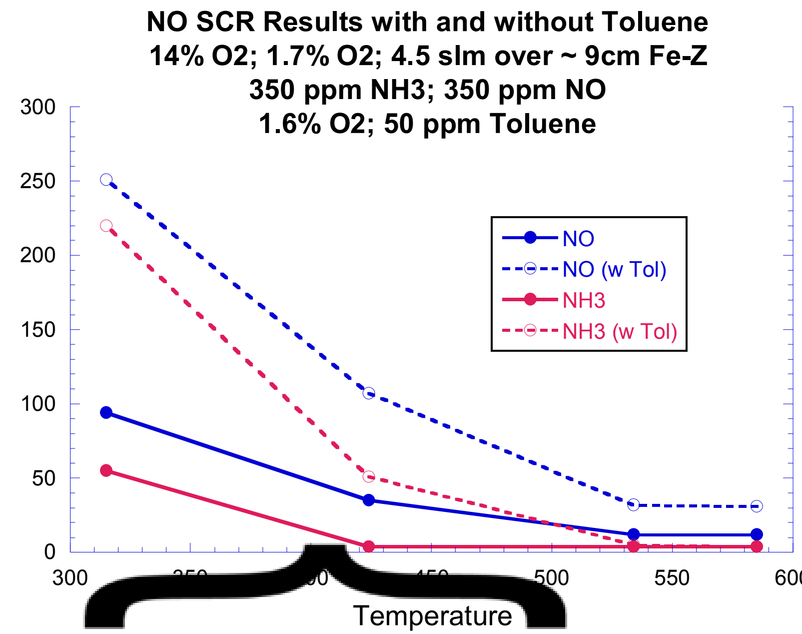
NH_3, Toluene Oxidation: 350 ppm NH_3, 50 ppm toluene, 14% O_2, 2% H_2O at 29000 hr^{-1} SV



- NH_3 oxidation is higher in the presence of toluene at all temperatures.
- Toluene helps NH_3 oxidation and NH_3 hurts toluene oxidation.

Toluene Effect: Standard SCR

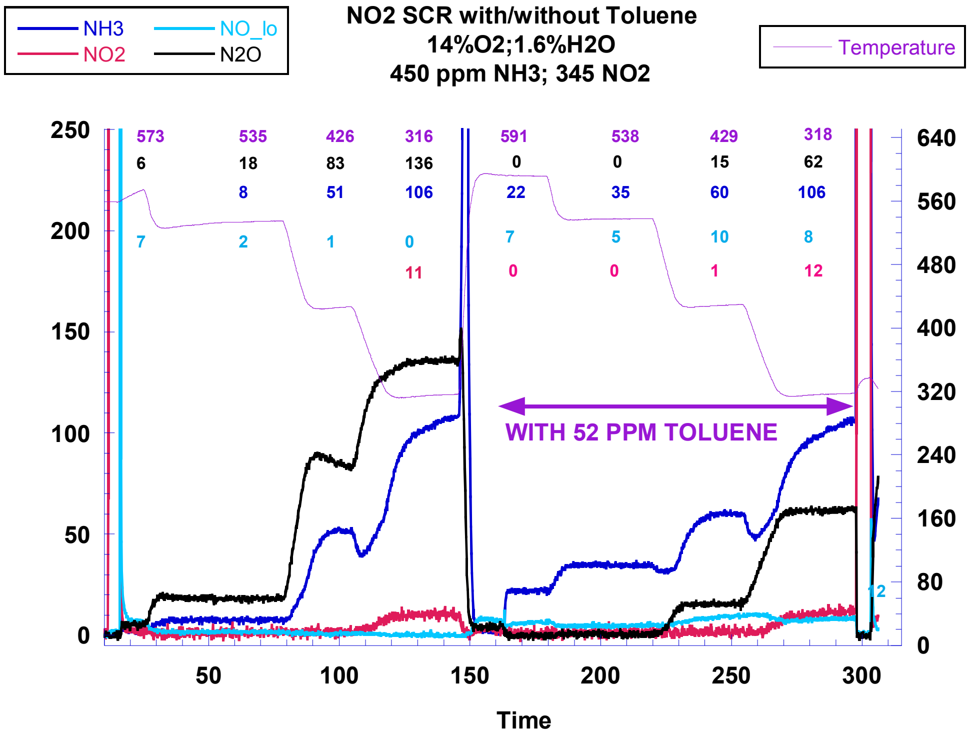


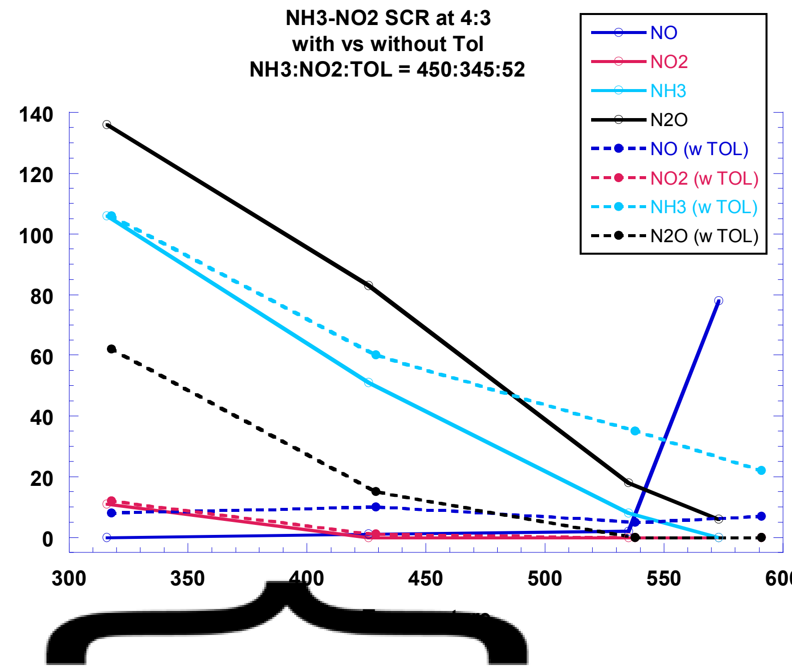


With Toluene

Temperature (C)	NOx Conv (%)	NH3 Conv (%)	NOx Conv (%)	NH3 Conv (%)
315	73	84	28	37
424	90	99	69	85
535	97	99	91	99
585	97	99	91	99

Toluene Effect: NO_2- SCR (4:3 NH_3: NO_2)

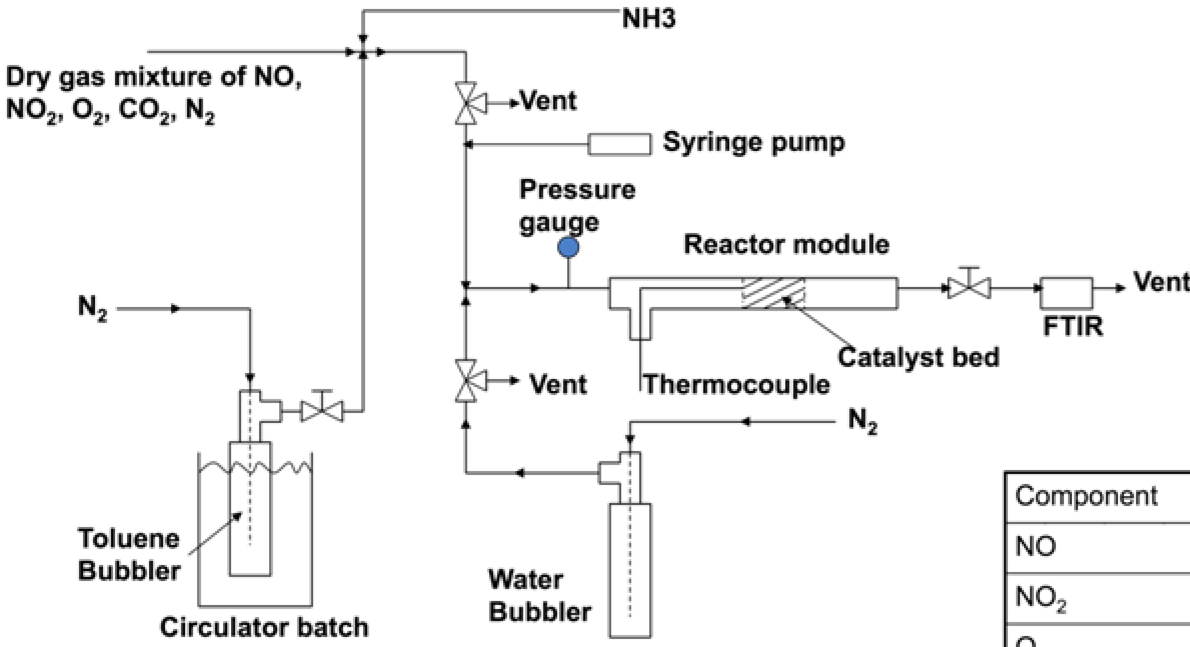




With Toluene

Temperature (C)	NOx Conv (%)	NH3 Conv (%)	NOx Conv (%)	NH3 Conv (%)
318	97	76	93	76
429	96	89	95	87
538	99	98	97	92
591	97	100	97	95

Tests on Thermal Transient Micro-Reactor



Transient Catalyst Test Bench

Reactor tube: Inconel 600, 4.78 mm O.D., 3.81 mm I.D.

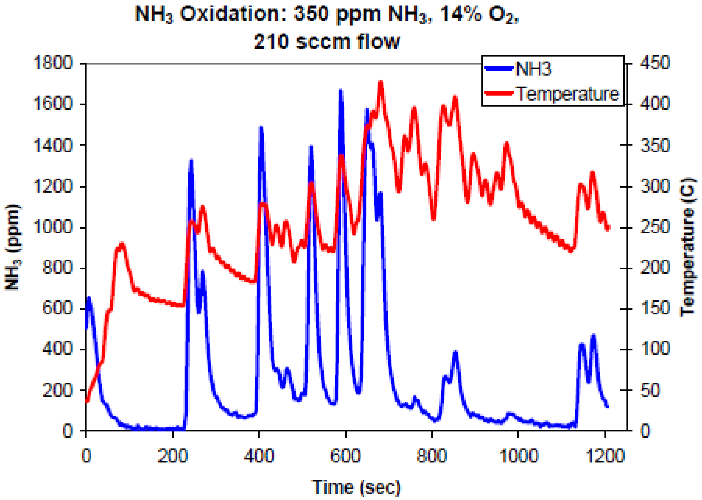
Catalyst information: 141 mg, 100 - 150 mesh

Component	Concentration	Unit
NO	0 to 350	ppm
NO_2	0 to 350	ppm
O_2	14	%
CO_2	5	%
NH_3	350	ppm
Toluene	50	ppm
Water	5	%
N_2	balance	
Total Flow Rate	210 sccm	

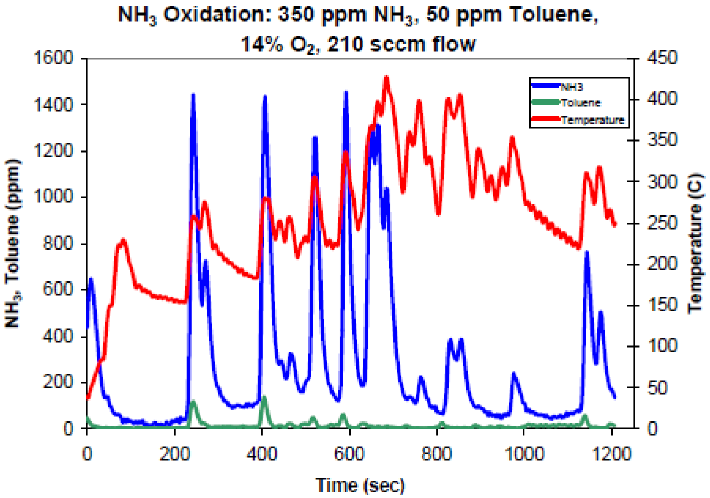
To illustrate the effect of toluene on various reactions on the urea-SCR catalyst, average NO_x and NH_3 conversion efficiencies were calculated for each data set.

Toluene Effect – NH_3 Oxidation (Transient)

NH_3 Oxidation (dry) – Without Toluene

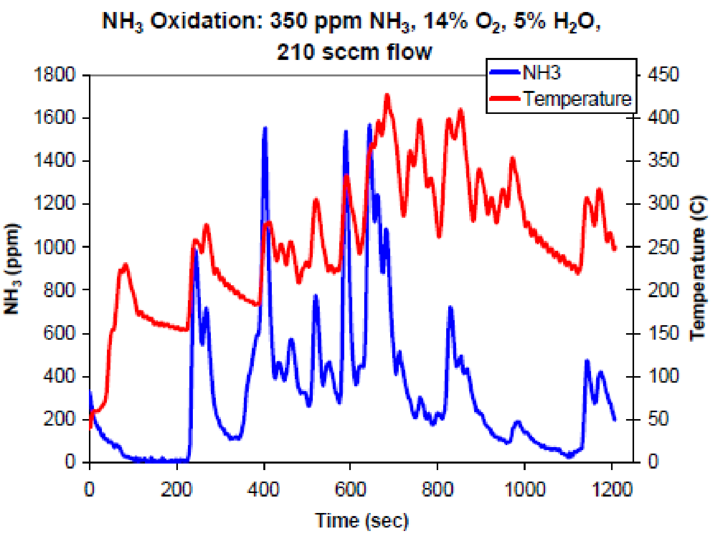


NH_3 Oxidation (dry) – With Toluene

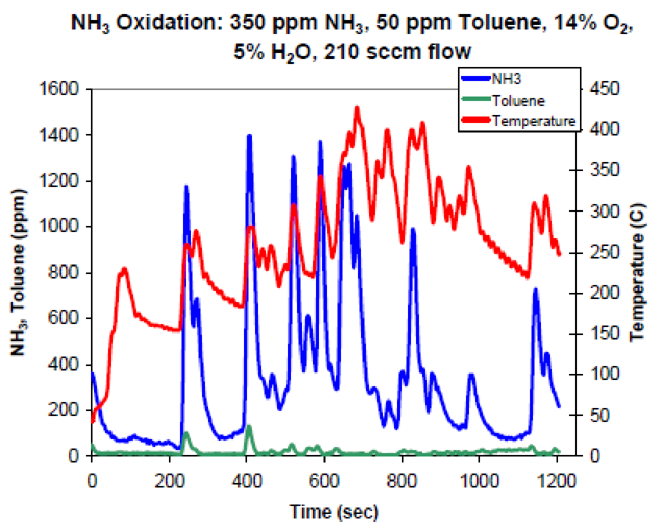


Case	% Oxidized
Without Toluene	25
With Toluene	23

NH_3 Oxidation (wet) – Without Toluene



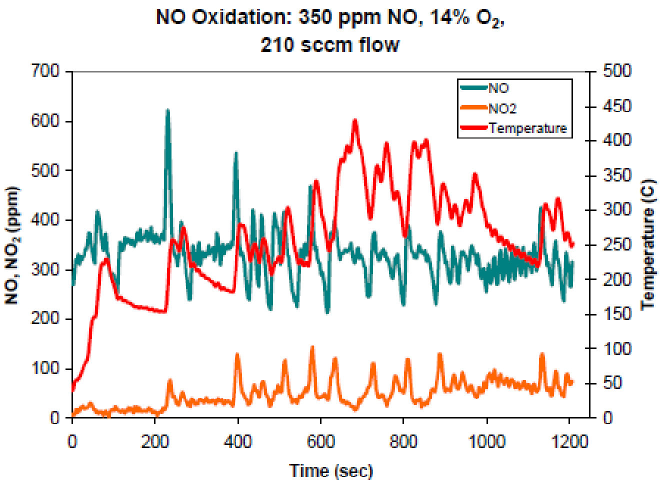
NH_3 Oxidation (wet) – With Toluene



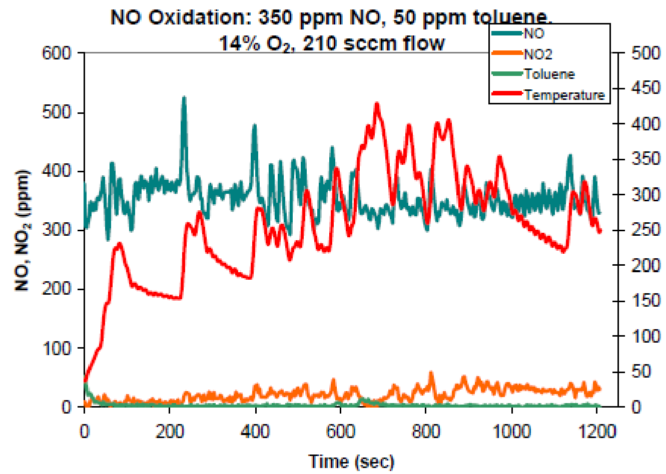
Case	% Oxidized
Without Toluene	11
With Toluene	7

Toluene Effect – NO Oxidation (Transient)

NO Oxidation (dry) – Without Toluene

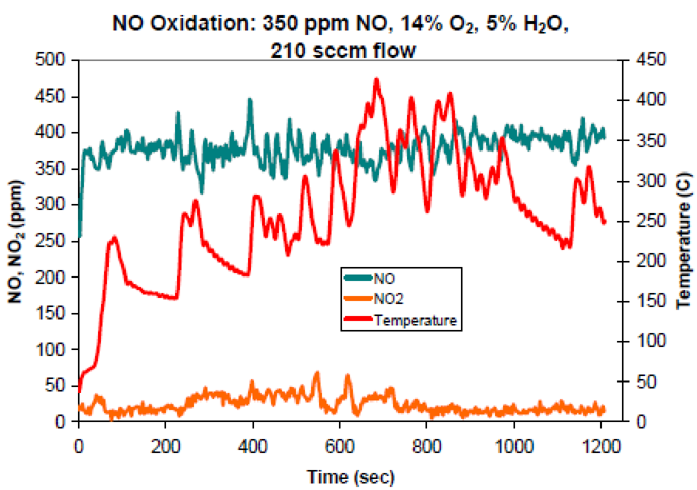


NO Oxidation (dry) – With Toluene

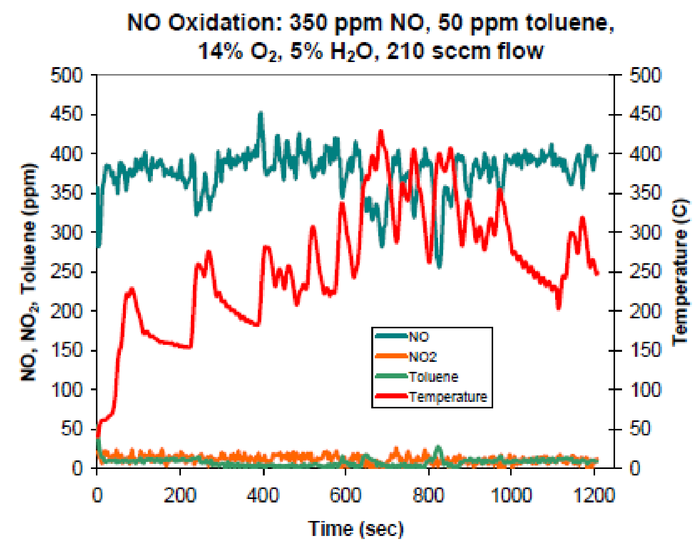


Case	% Oxidized
Without Toluene	14
With Toluene	10

NO Oxidation (wet) – Without Toluene



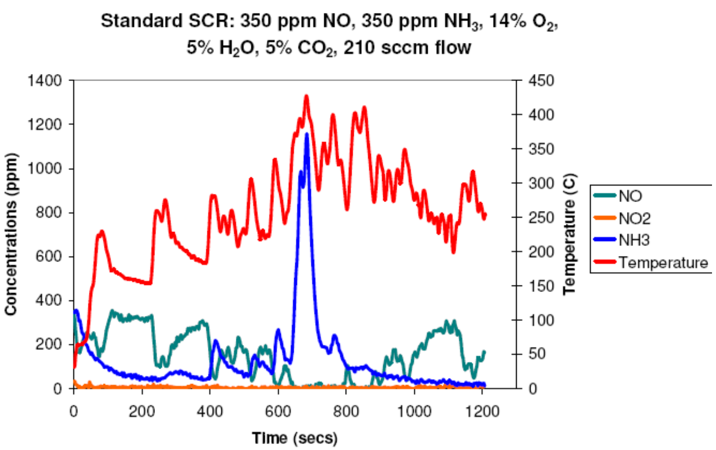
NO Oxidation (wet) – With Toluene



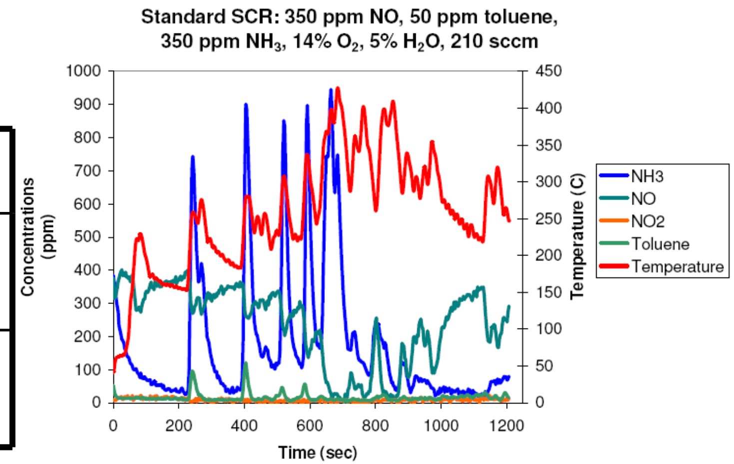
Case	% Oxidized
Without Toluene	3
With Toluene	1

Toluene Effect: SCR Reactions (Transient)

Standard SCR (Without Toluene)



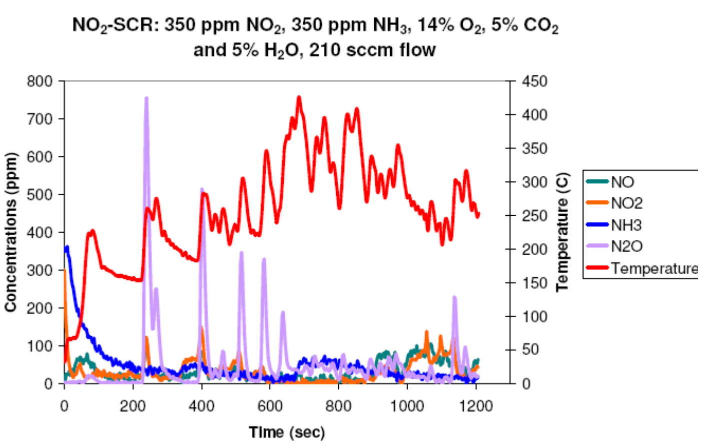
Standard SCR (With Toluene)



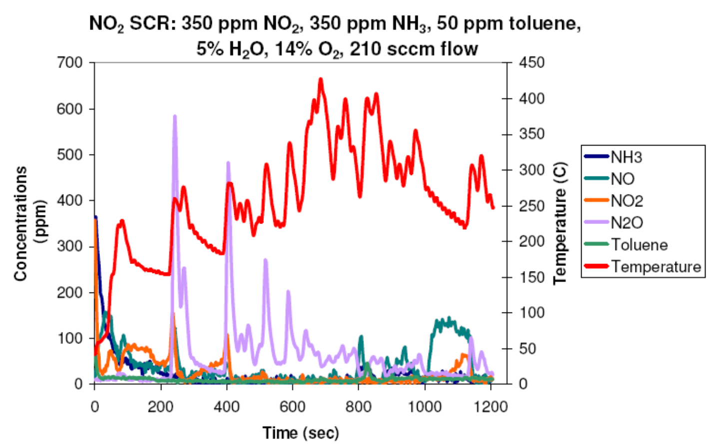
Standard SCR

Case	NH_3 (%)	NO_x (%)
Without Toluen e	63	54
With Toluen e	52	37

NO_2-SCR (Without Toluene)



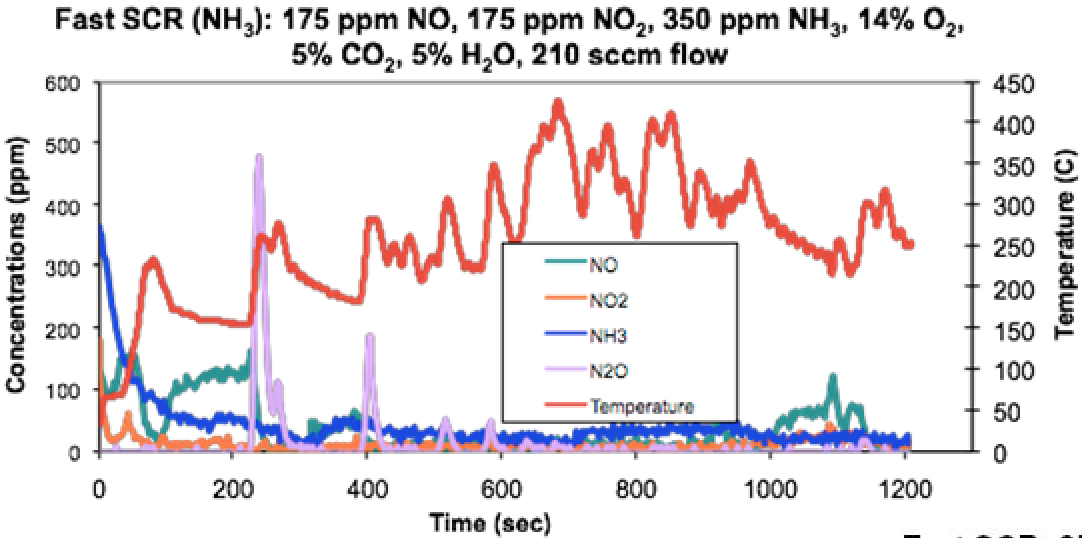
NO_2-SCR (With Toluene)

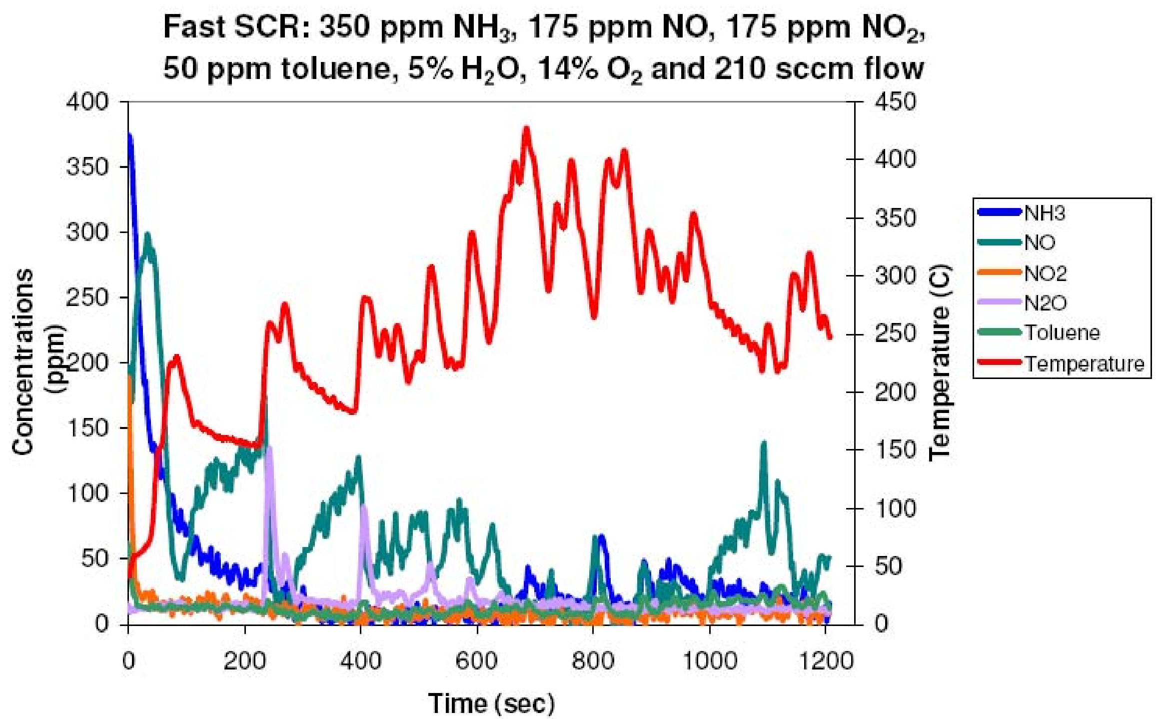


NO_2- SCR

Case	NH_3 (%)	NO_x (%)
Without Toluen e	86	81
With Toluen e	93	82

Toluene Effect: Fast SCR (Transient)





Case	NH_3 (%)	NO_x (%)
Without Toluene	88	86
With Toluene	91	81

Conclusions

- ✓ Adsorption tests reveal that toluene is adsorbed on multiple sites on the catalyst.
- ✓ Designing Langmuir isotherms is a promising approach to characterize the toluene adsorption-desorption characteristics.
- ✓ A single site model shows a reasonably good match with the test data. Multi-site kinetic model is being developed and will be updated in future reports.
- ✓ Competitive adsorption tests indicate that NH_3 sticks to the catalyst in the presence of H_2O.
- ✓ Step temperature and periodic temperature ramp tests in the absence of H_2O indicate heavy toluene inhibition of NO oxidation at low temperatures.
- ✓ A simple model developed to predict toluene inhibition of NO oxidation, showed good agreement with the test data.
- ✓ NH_3 oxidation is higher in the presence of toluene.
- ✓ Toluene has a strong, negative effect on NOx conversion during NH_3-SCR. NO_x conversion decreases at all temperatures during standard-SCR, with significant toluene effect at low temperatures. Lesser N_2O formation during NO_2-SCR.
- ✓ Transient tests on Fe-Z micro-reactor reveal toluene impact on NO_x conversion.

Future Work

- Model toluene inhibition effect on various SCR reactions, both from a steady state and transient cycle perspective.
- Model competitive adsorption between various species (H_2O, toluene and NH_3) on the catalyst.
- Investigate catalyst deactivation mechanisms due to hydrocarbon poisoning.
- Develop a mathematical tool to compare NO_x/NH_3 conversion efficiencies from transient cycle as a function of temperature to its steady state performance.

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