Bench Reactor Studies and Reactor Modeling for NOx Control in Diesel Engines using NH_3

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Presentation Outline

- Steady State Reactor: Tests and Model Development
- Steady State Tests: H_2O Effect on NO_x Oxidation
- HNCO Tests: Set-up and Status
- Future Work

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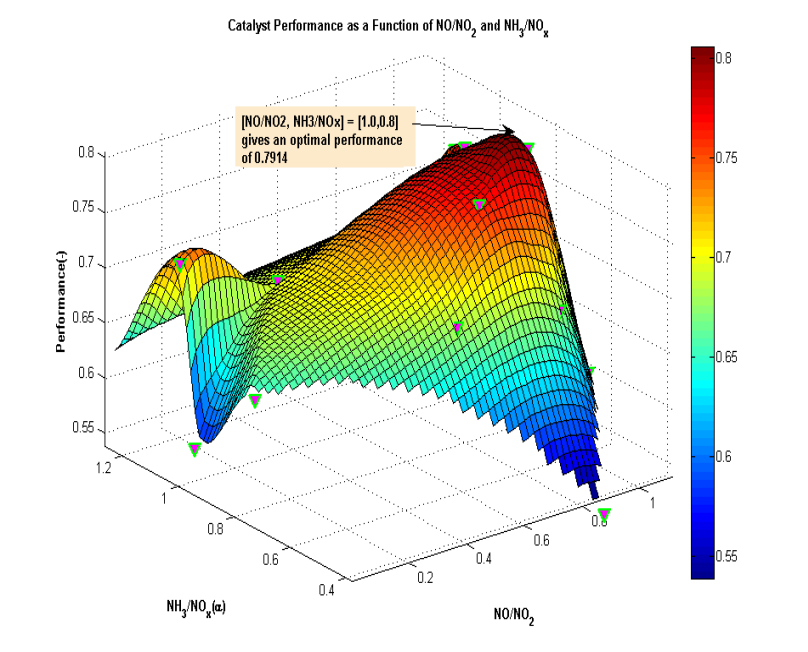
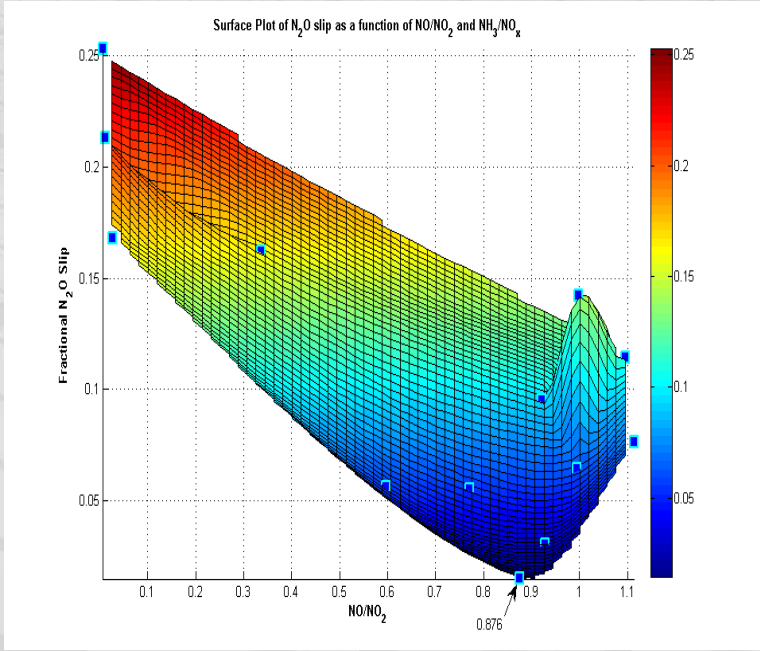
Review & Motivation

- Research focus in diesel emission control is slowly shifting from individual aftertreatment devices to integrated systems.
- There is a thorough 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, catalyst aging, etc.
- From recent literature, research activity is also seen in understanding detailed mechanistic pathways of various reactions. Ex: H_2O adsorption, NO_x adsorption on zeolites, NH_4NO_3 and N_2O formation, etc.
- Research in urea evaporation, decomposition and HNCO hydrolysis is gaining momentum to address the formation of cyanuric acid and other by-products.
- Based on the review, research is being done at PNNL on monolith cores/powders both from a steady state and transient standpoint to address issues related to SCR and integrated systems.
- Alternate reductants such as HNCO are also being explored for hydrolysis and NO_x control.

Transient Thermal Micro-reactor : Performance Analysis based on Transient Test Data





Performance: $J = \frac{1}{2}\left(f_{nox}^2 + (1 - f_{nh3})^2\right)$

$$f_{nox} = 1 - \frac{\left[\frac{\int_{t_0}^{t_f} NO_{out}\,dt + \int_{t_0}^{t_f} NO_{2,out}\,dt + \int_{t_0}^{t_f} N_2O_{out}\,dt}{N}\right]}{\frac{\int_{t_0}^{t_f} NO_{in}\,dt + \int_{t_o}^{t_f} NO_{2,in}\,dt}{N}}$$

$$f_{nh3} = \frac{\frac{\int_{t_0}^{t_f} NH_{3,out}\,dt}{N}}{\frac{\int_{t_0}^{t_f} NH_{3,in}\,dt}{N}}$$

Optimal operating point for catalyst performance: $[NO/NO_2, NH_3/NO_x] = [1.0, 0.8]$

Minimal N_2O Slip occurs at $NO/NO_2 = 0.9$

Devarakonda and Male, CTI International Forum for NOx Reduction, Dec 2008.

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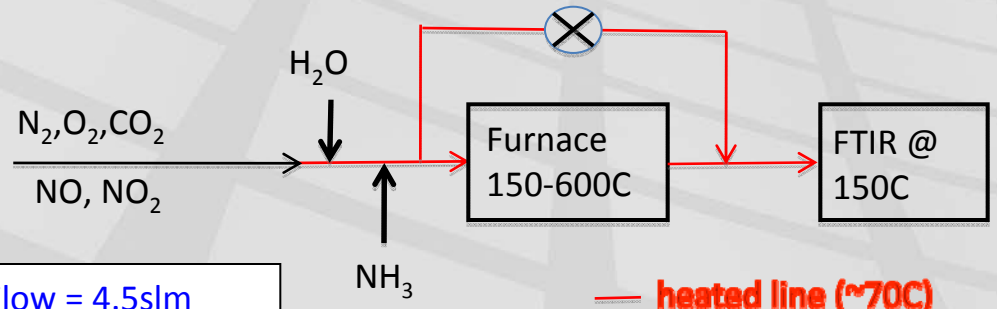
Steady State Tests on Fe-Zeolite

- 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 at a flow rate of 4.5 SLPM.
- Two different tests are conducted:
  - A. Steady state surface isotherm tests followed by TPD.
  - B. Controlled reactor tests for step-wise identification and validation.

Test Conditions

NO_x	350 ppm
NH_3	350 ppm
O_2	14%
CO_2	5%
H_2O	2%
N_2	Balance
SV	29 kh^{-1}

Reactor Set-up



Flow = 4.5slm
Cat Vol. = 9.3 cm3
Cat mass= 7.2 gm.

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NH_3 Adsorption-Desorption Model

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

$$r_{ads} = A_{ads} c_{s,NH_3} (1-\theta) N_{total}$$

$$r_{des} = A_{des} e^{-E_{des}/RT} \theta N_{total}$$

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

$$r_{ads} = A_{ads} c_{s,NH_3} (N_{total} - n_{st})$$

$$r_{des} = A_{des} e^{-E_{des}/RT} n_{st}$$

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

$$A_{ads} c_{s,NH_3} (N_{total} - n_{st,eq}) = A_{des} e^{-E_{des}/RT} n_{st,eq}$$

Where $n_{st,eq}$ is the NH_3 storage at equilibrium. NH_3 storage at equilibrium ($n_{st,eq}$) can be obtained by integrating the total NH_3 entering the catalyst minus the total NH_3 leaving the catalyst until equilibrium t_{eq}.

$$n_{st,eq} = \int_0^{t_{eq}} (\dot{n}_{NH_3,in} - \dot{n}_{NH_3,out}) dt$$

Dividing the above equation by $A_{ads} c_{s,NH_3} n_{st,eq} N_{total}$ throughout and rearranging the terms in the equation, we get

$$\frac{1}{n_{st,eq}} = \frac{1}{N_{total}} + \frac{1}{K(T) c_{s,NH_3} N_{total}}$$ Where

$$K(T) = \frac{A_{ads}}{A_{des} e^{-E_{des}/RT}}$$

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

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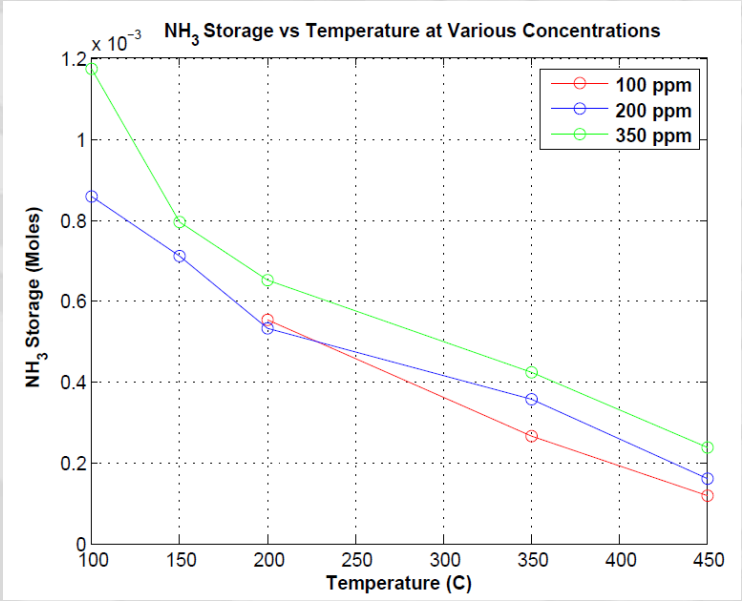
NH_3 Surface Isotherm Tests on Fe-zeolite : Data Analysis

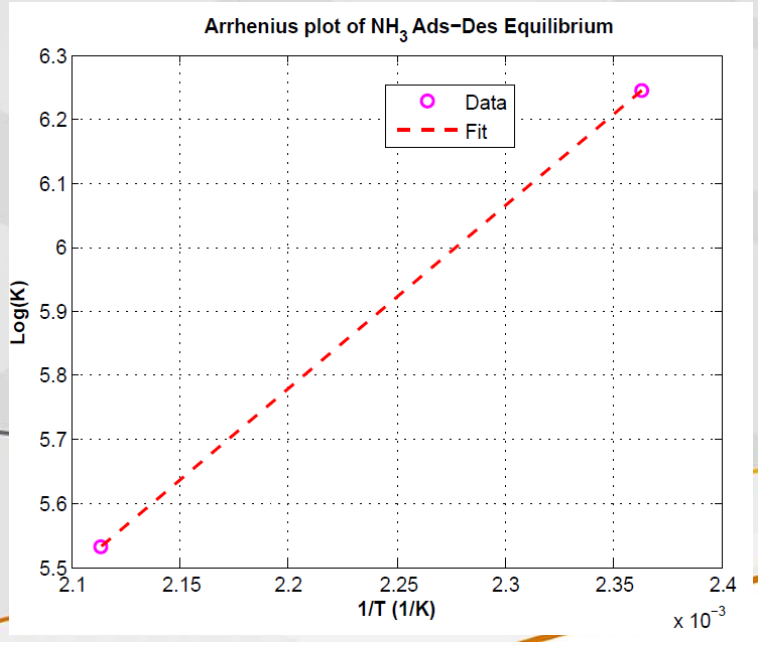
Storage vs Temperature Curve



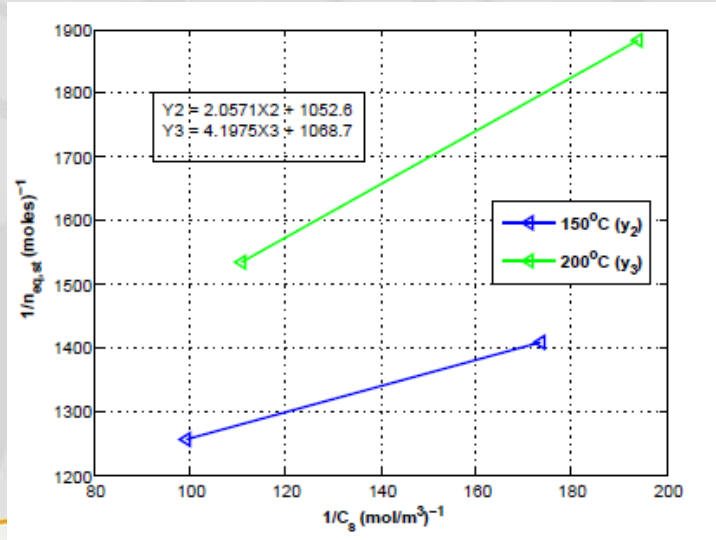
Test Matrix to study Langmuir Isotherms

No	$C_{NH3(ppm)}$	Temperature (C)
1	200	100
2	350	100
3	200	150
4	350	150
5	200	200
6	350	200

Adsorption-Desorption Equilibrium



Langmuir Isotherms



$$\frac{1}{n_{st,eq}} = \frac{1}{N_{total}} + \frac{1}{K(T)c_{s,NH_3}N_{total}}$$

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Micro-reactor Model: Equations

- The modeling equations are obtained by solving the gas phase and surface phase concentrations of the species and NH_3 storage states.

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

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

$$\frac{d\theta}{dt} = \frac{1}{\Omega} (r_{ads} - r_{des} - \sum_j r_{NH_3,j} n_{NH_3,j})$$

Here i corresponds to NO, NO_2 and NH_3 species and j is the number of reactions that species i is involved.

- Simulated using a variable step solve 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.

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Reactor Model: Reaction Scheme, Kinetics

No	Reaction Name	Reaction	Reaction Rate
1	NH_3 Adsorption	$NH_3 + S \rightarrow NH_3^*$	$R_1 = k_1 C_{NH3}(1-\theta)\Omega$
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	$NO+1/2O_2 \Leftrightarrow NO_2$	$R_7 = k_{7,f} C_{NO} C_{O2}^{1/2} - k_{7,b} C_{NO2}$

$$k_2 = A_2 e^{\frac{-E_2(1-\gamma\theta)}{RT}}$$

- Rate parameters for the above reactions are taken from these references

Ref: Chaitanya Sampara (Ph.D. Dissertation, University of Michigan, 2008)

L. Olsson et al, Applied Catalysis B: Environmental, 2008

L. Olsson et al, Applied Catalysis B: Environmental, 2009

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Parameter Identification as an Optimization Problem

- Matlab's simplex based optimization function 'fminsearch' is used.

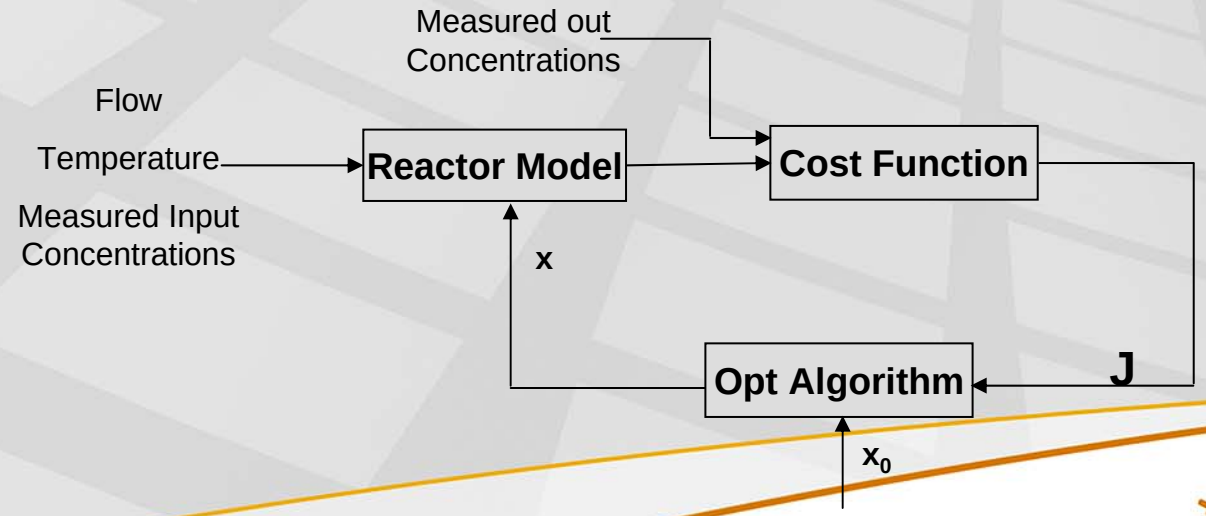
  Find the model parameters (x_i) where x_i are the pre-exponentials and activation energies of the reactions while minimizing the cost function

$$J = \frac{1}{N}\sum_{i=1}^{N}\left|c_{i,NH_3,s} - c_{i,NH_3,m}\right|$$

Where N is the number of test data points.

Subscripts 's' and 'm' in the cost function refer to the simulated and measured concentrations respectively.

Optimization Schematic



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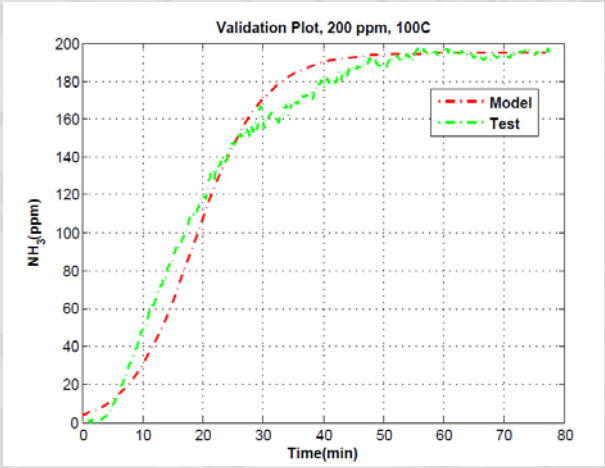
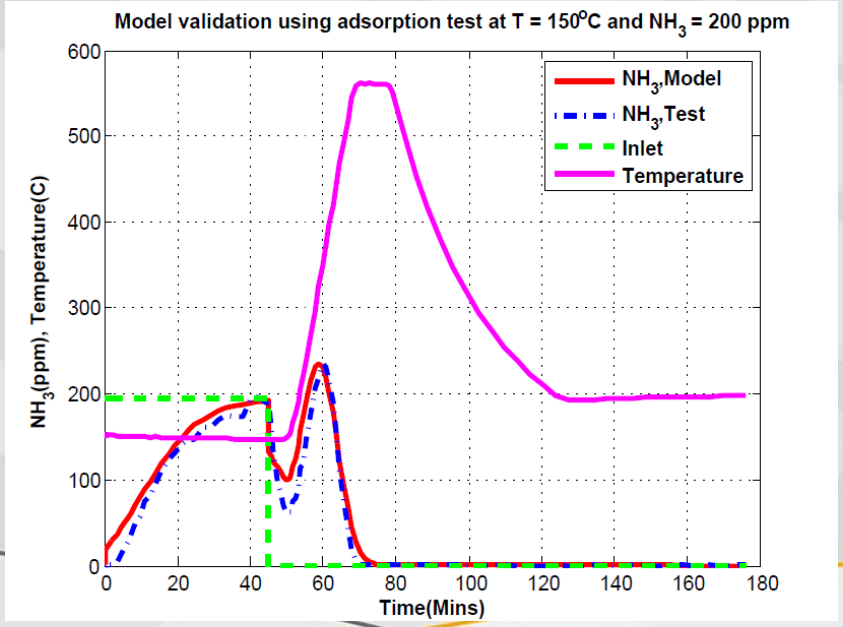
NH_3 Adsorption-Desorption Model Validation

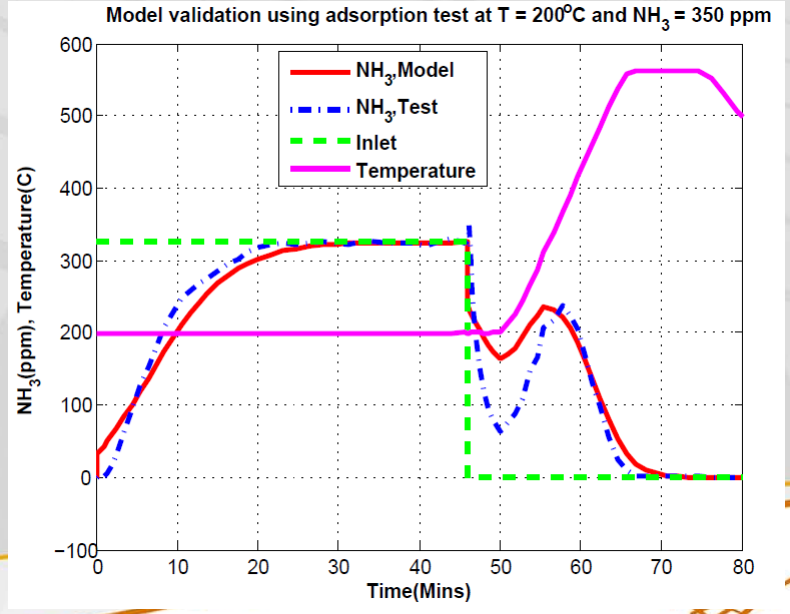
Adsorption Validation



- Data during adsorption phase is used to identify A_{ads}.
- Other test cases are used to validate the overall ads/des model.
- Discrepancy during the physisorption phase just after the NH_3 injection is shut off. Need to incorporate multi-site kinetics.
- Multi-site kinetic model will be explored in the future.

Overall Model Validation





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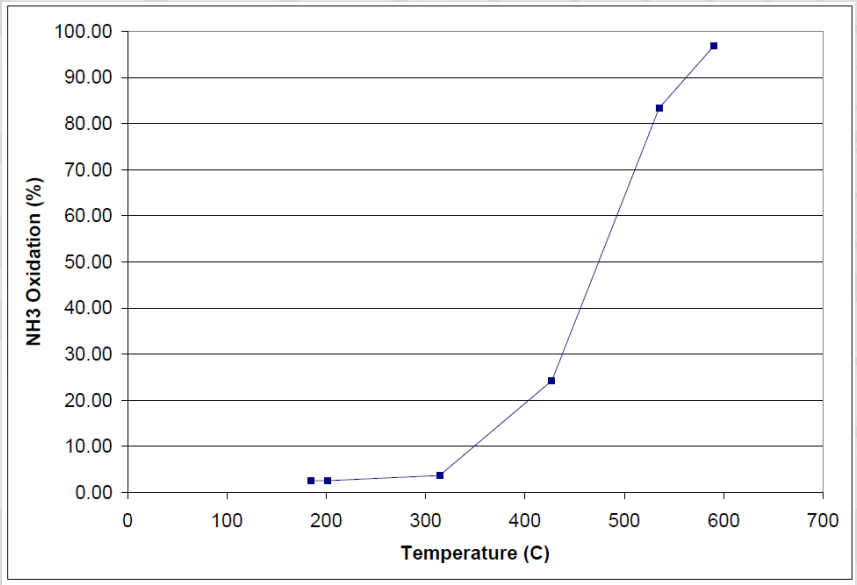
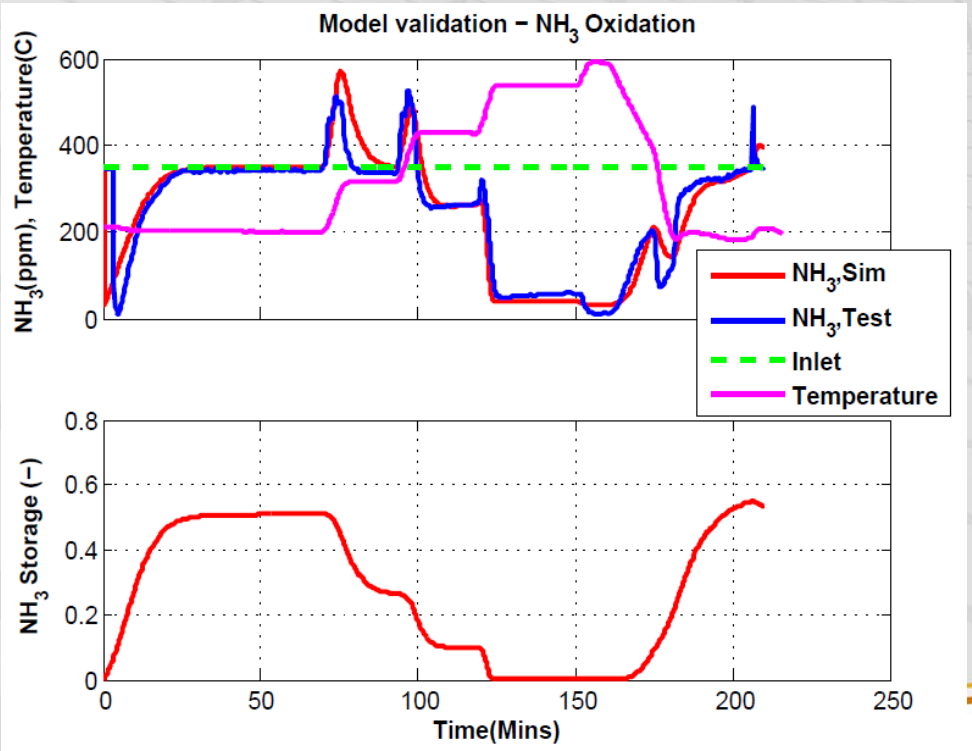
NH_3 Oxidation – Model Validation



NH_3 Oxidation as a function of Gas Temperature

- The oxidation activity is observed at temperatures greater than 300°C, reaching the maximum conversion at T = 600° C.
- Input data is not recorded, so inputs are given as step inputs in the simulation.

350 ppm of NH_3, 5% CO_2, 2% H_2O and 14% O_2 at a SV of 29 k/hr



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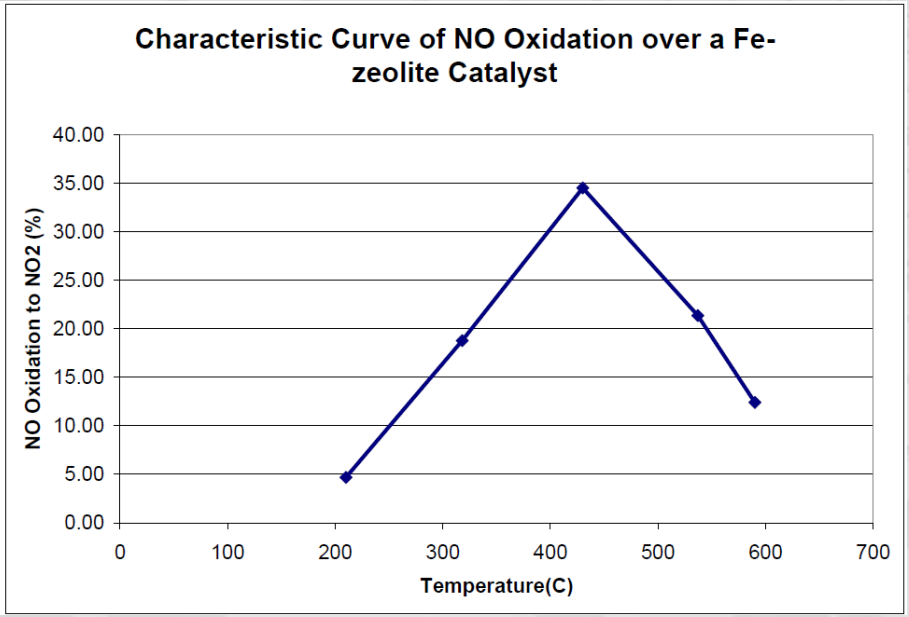
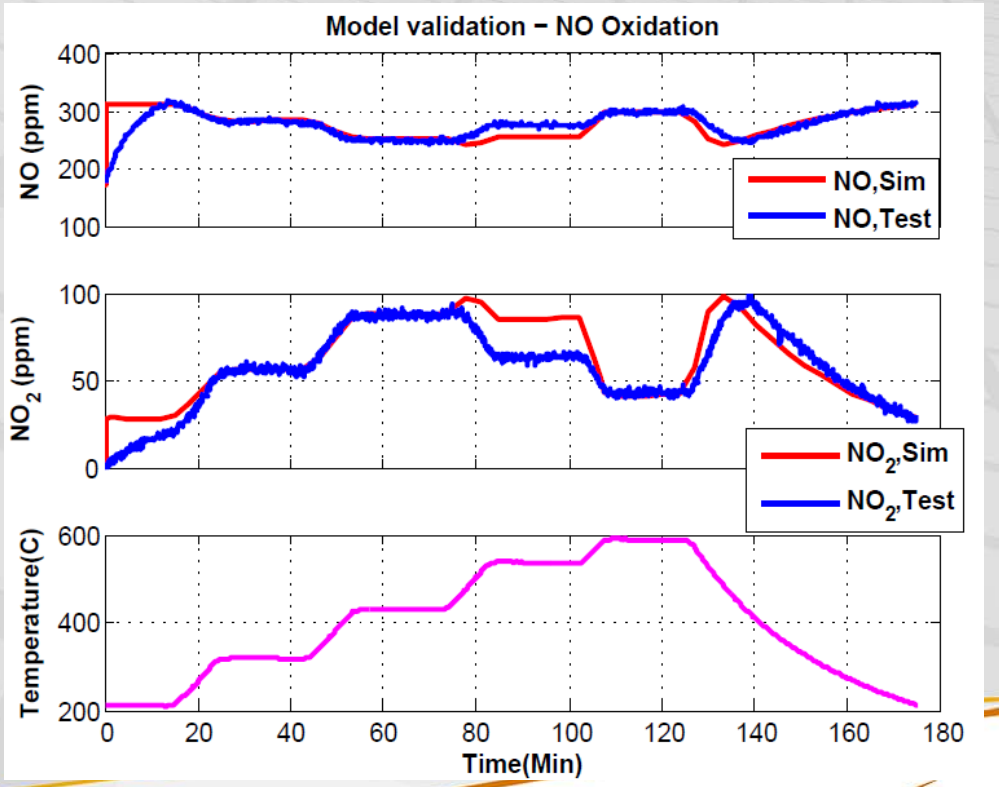
NO Oxidation - Model Validation



350 ppm of NO, 5% CO_2, 2% H_2O and 14% O_2 at a SV of 29 k/hr



- Maximum NO to NO_2 conversion obtained at 434°C on Fe-zeolites which is close to 450°C, the temperature at which maximum NO_2 conversion was observed by L.Olsson's group on a Cu-ZSM-5 catalyst.
- Input data is not recorded, so inputs are given as step inputs in the simulation.

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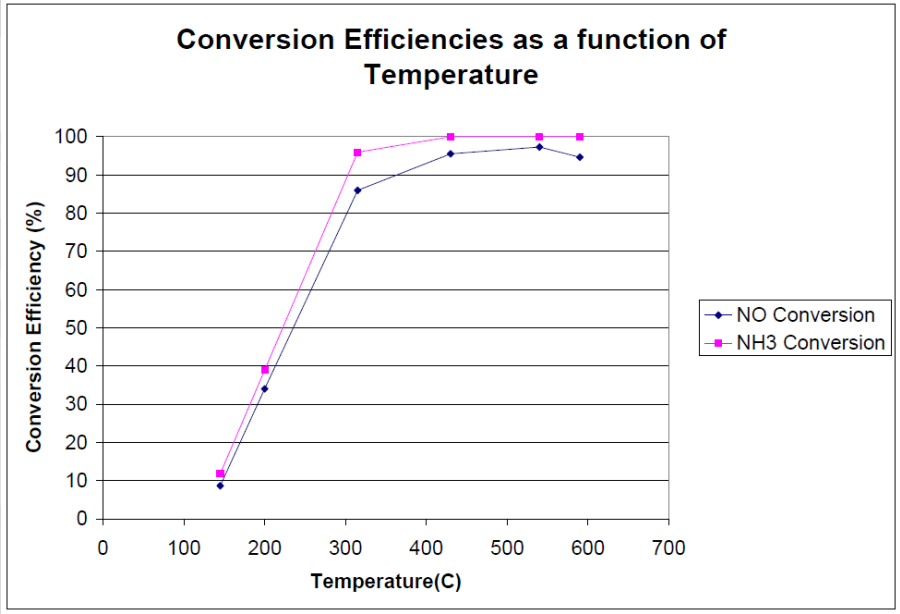
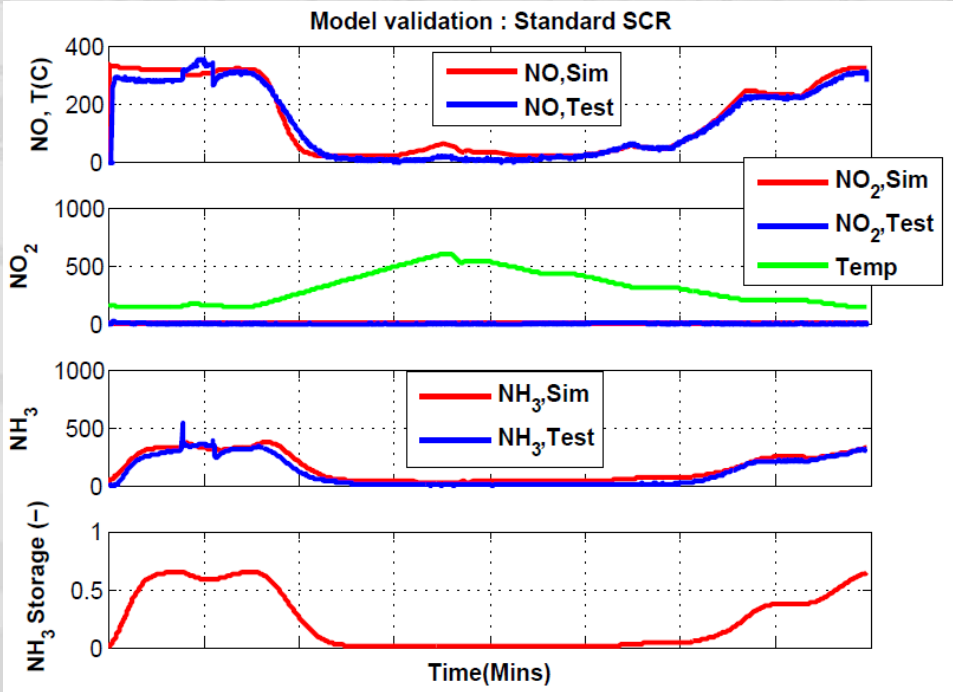
Standard SCR - Model Validation



350 ppm of NO, 350 ppm of NH_3, 5% CO_2, 2% H_2O and 14% O_2 at a SV of 29 k/hr



- Poor NO_x conversion at low (200°C) temperatures in the absence of NO_2.
- Disparity in NO_x and NH_3 conversion efficiencies at high temperatures due to NH_3 oxidation to N_2.
- Simulated NH_3 storage values consistent during the start and end of the test (at T = 200°C).

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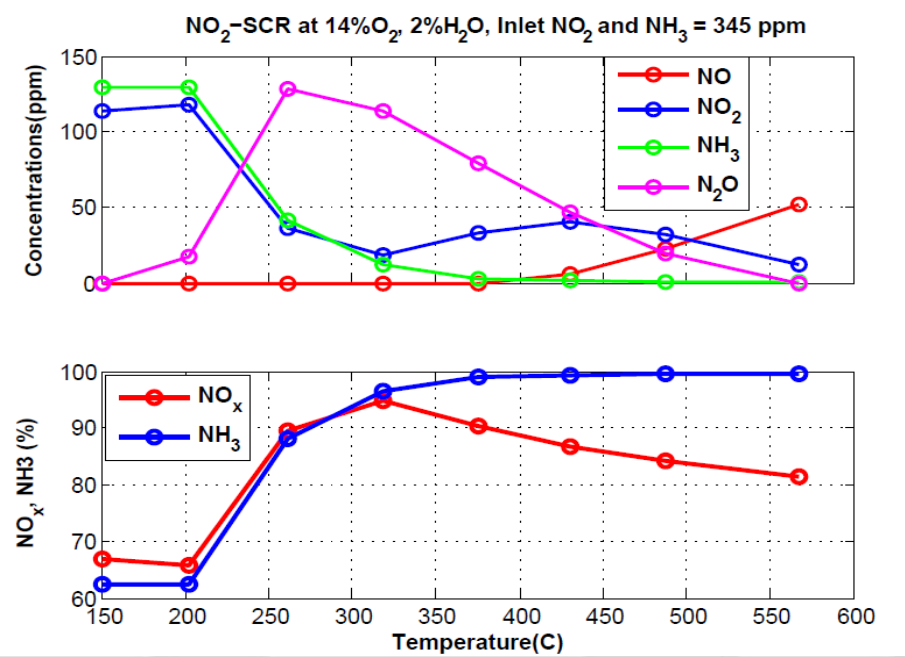
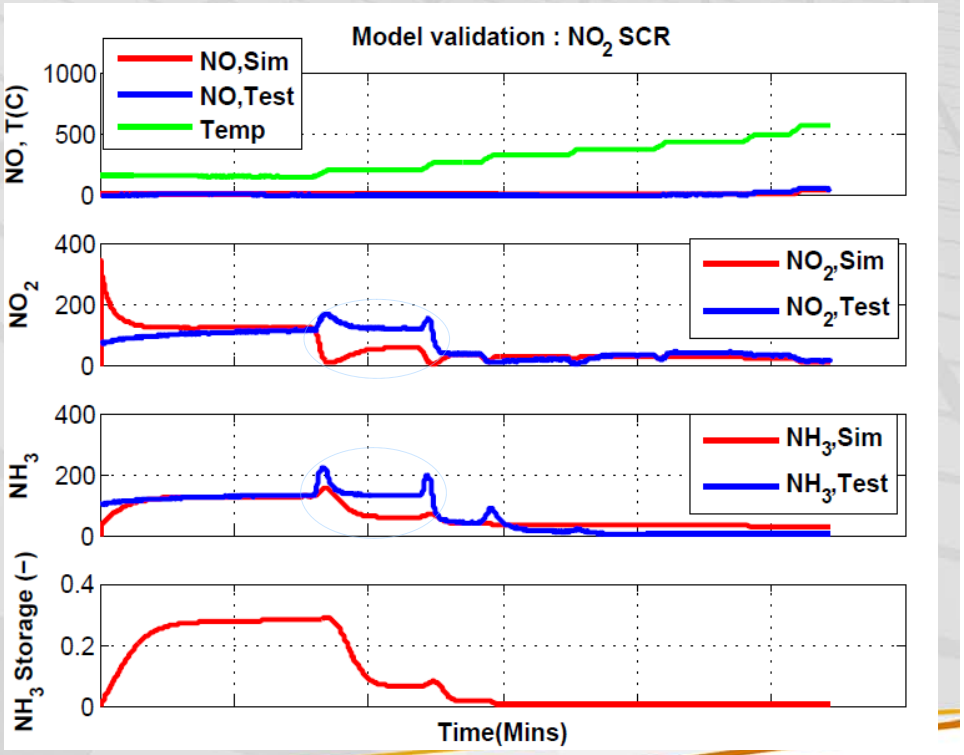
NO_2 SCR - Model Validation



350 ppm of NO_2, 350 ppm of NH_3, 5% CO_2, 2% H_2O and 14% O_2 at a SV of 29 k/hr



- Surge of N_2O at 250°C due to the formation of NH_4NO_3 at low temperatures and its subsequent decomposition to N_2O (Grossale, 2008).
- Equal outlet concentrations of NO_2 and NH_3 until 250°C further illustrate the formation of NH_4NO_3 due to 1:1 NO_2:NH_3 reaction, rather than 4:3 which takes place at high temperatures.

$$2NH_3 + 2NO_2 \rightarrow N_2 + NH_4NO_3 + H_2O$$

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

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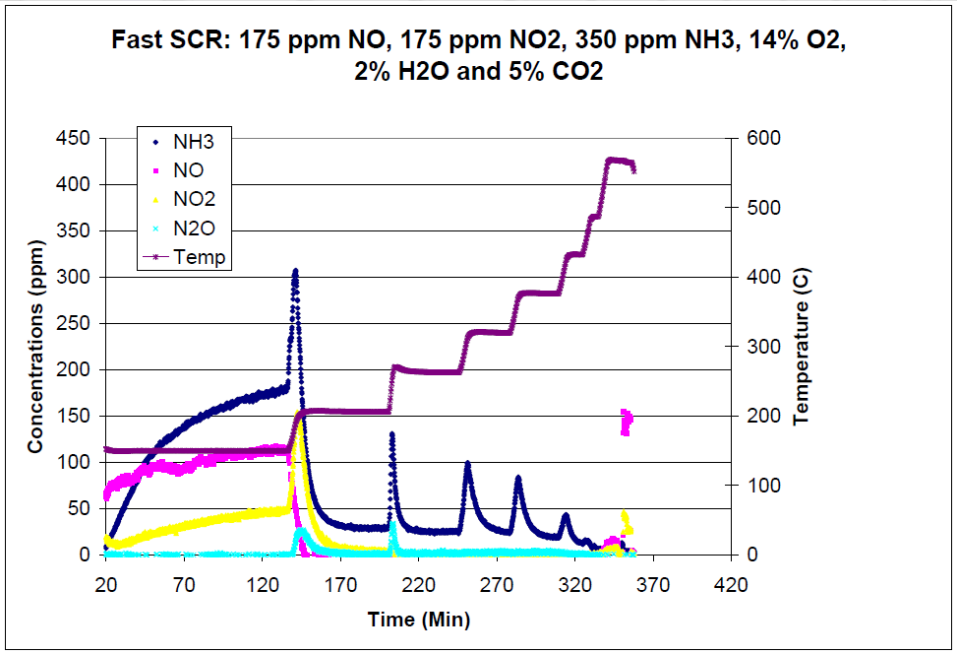
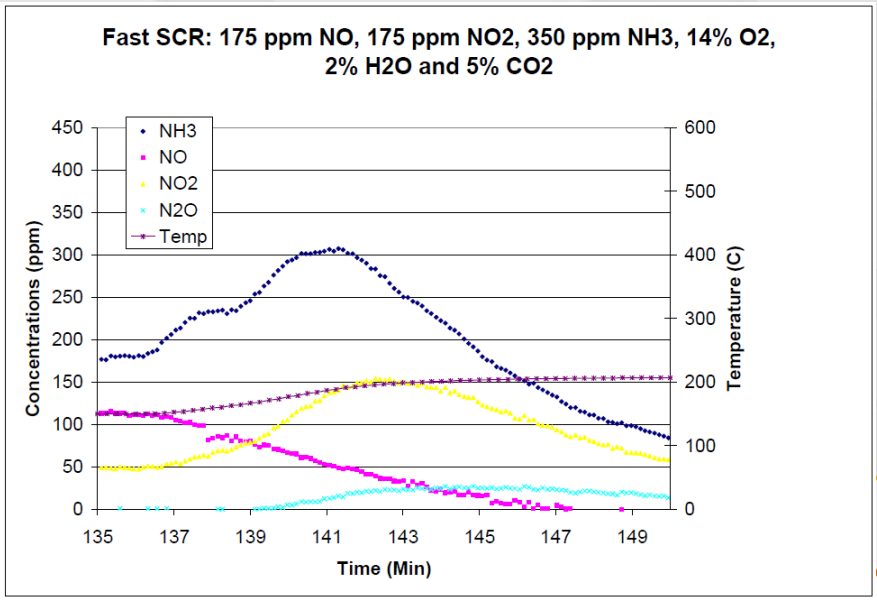
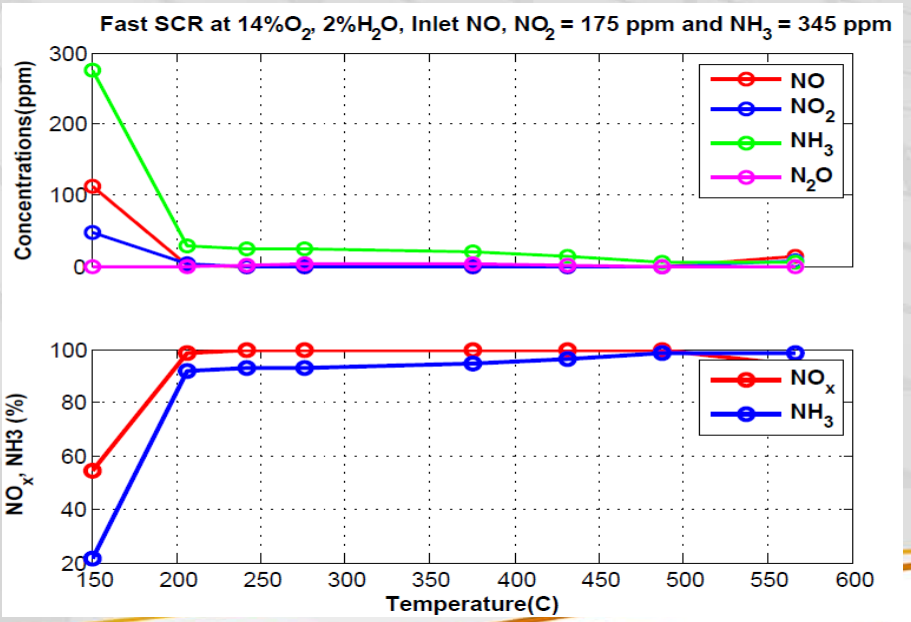
Fast SCR – Tests





- Sudden surge in NO_2 and NH_3 due to NH_4NO_3 formation and its subsequent decomposition to NH_3 and HNO_3.
- HNO_3 reacts with NO to form NO_2 and H_2O.
- At 200°C, 29 ppm of NH_3 is measured when no NO and NO_2 are observed at the outlet, because of extra NH_3 formed from NH_4NO_3 decomposition.



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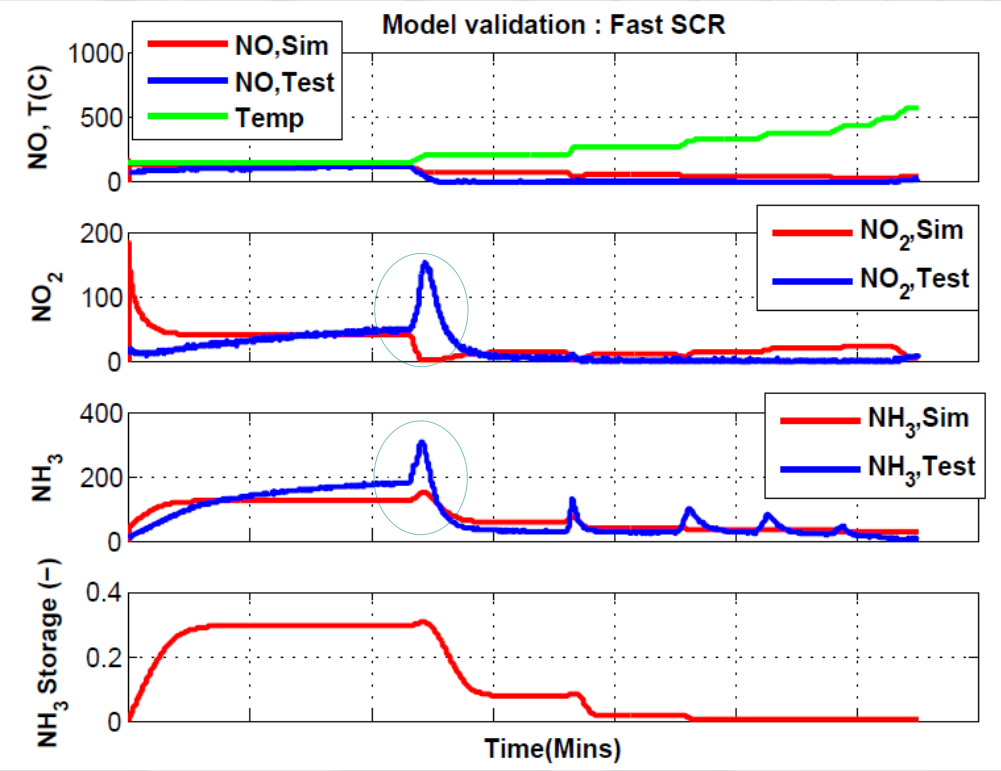
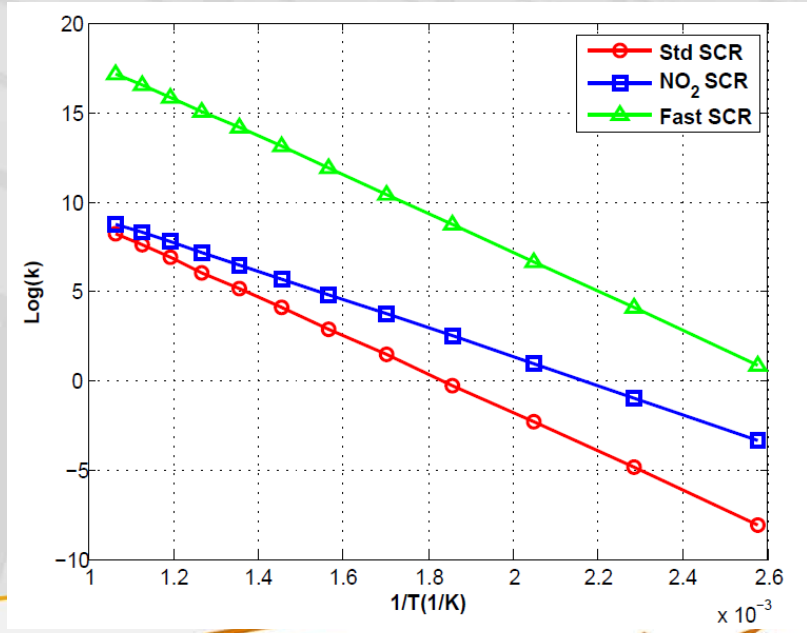
Fast SCR – Model Validation



- Discrepancy in model and test data is attributed to NH_4NO_3 formation and its decomposition which are not incorporated in the model.
- NH_4NO_3 formed at 150C, decomposes to NH_3 and HNO_3 at T > 200C

  $NH_4NO3 \Leftrightarrow NH_3 + HNO_3$
- HNO_3 in turn reacts with NO to form NO_2 and H_2O at higher temperatures

  $2HNO_3 + NO \rightarrow 3NO_2 + H_2O$
- Observations consistent with Grossale, 2008.
- Fast SCR rate parameters used in the model are directly taken from Olsson, 2008.



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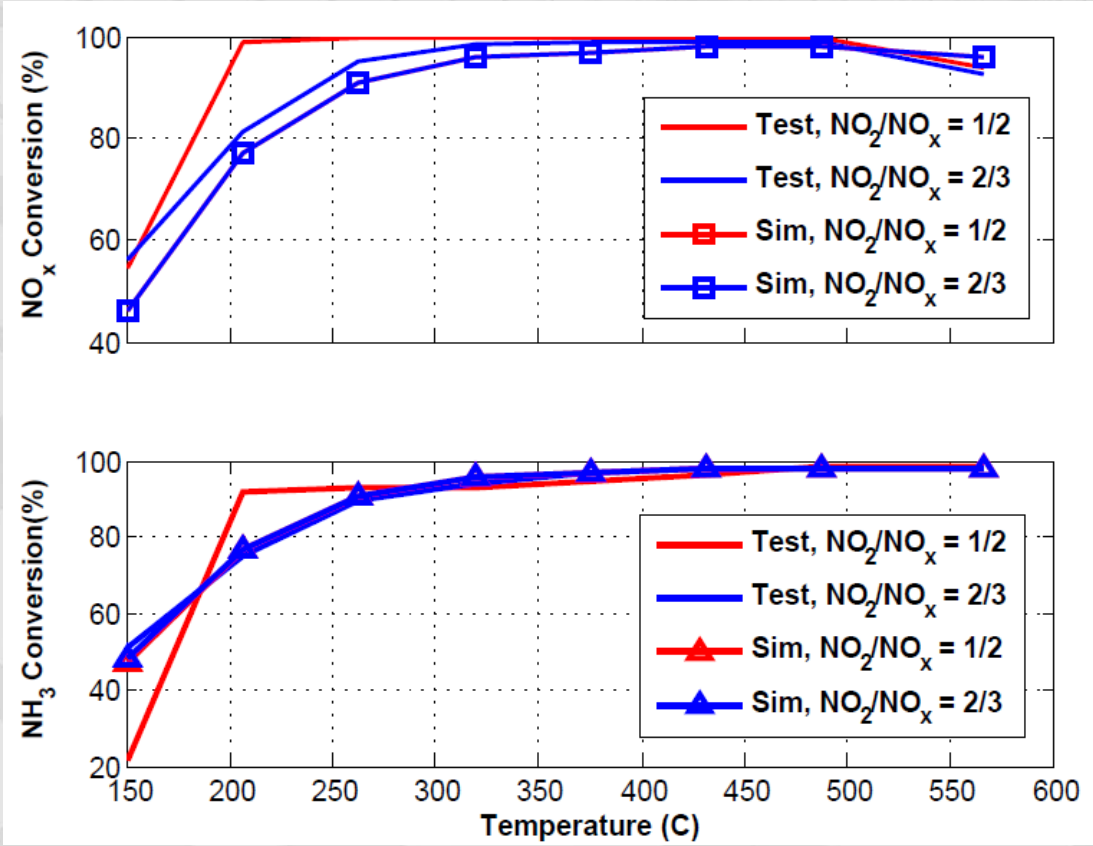
Overall Model Validation



- Two different tests were conducted at various temperatures ranging from 150°C to 600°C by varying the ratios of NO/NO_2 = ½ and NO/NO_2 = 2/1 in the exhaust.
- The reactor model is then validated to compare the NO_x and NH_3 conversion efficiencies for a couple of cases.
- A good match is observed in both the cases, except at T < 200°C.

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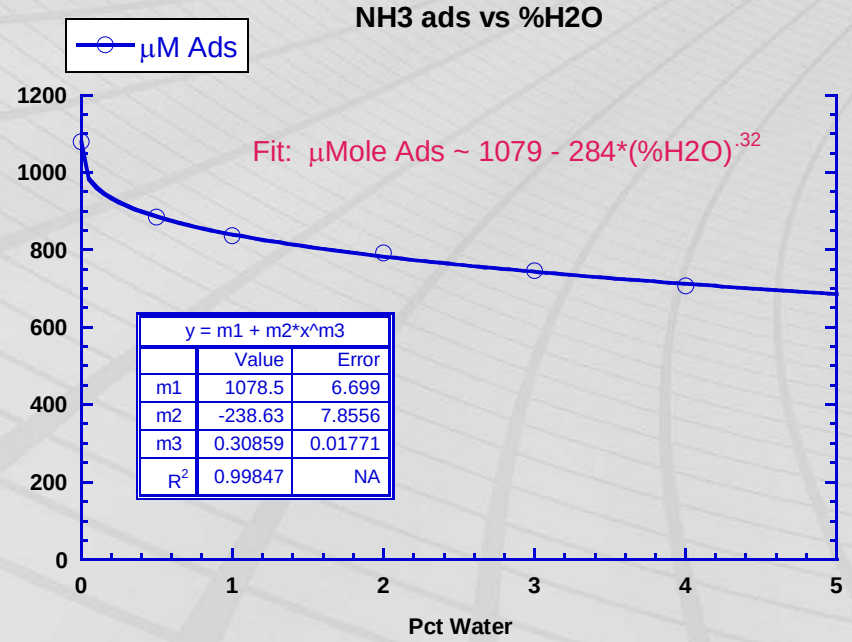
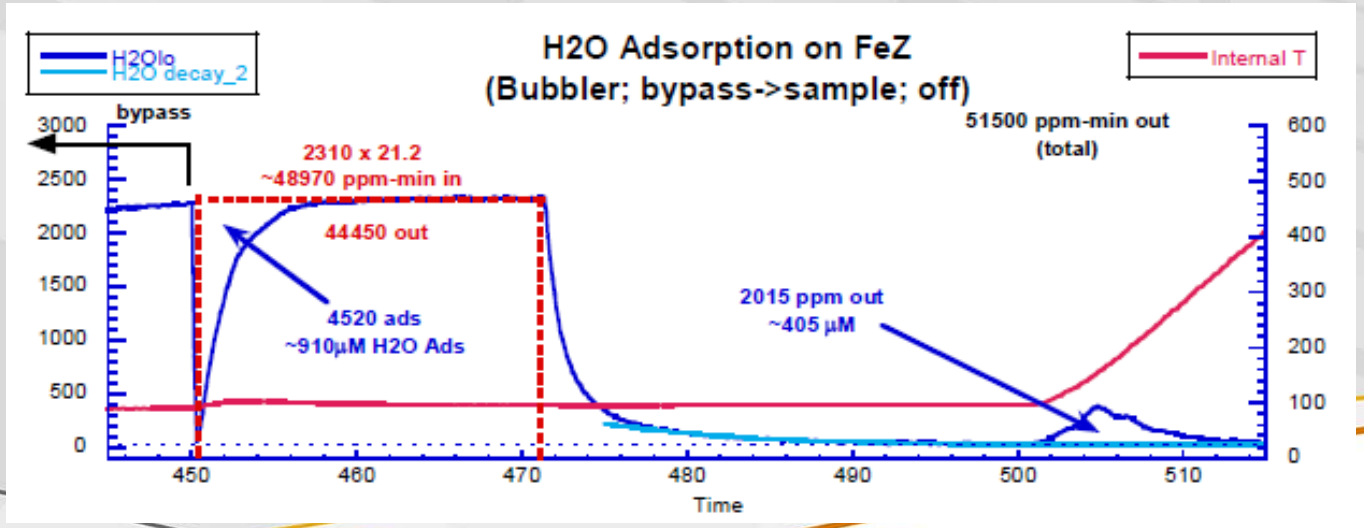
H_2O Adsorption Studies

- NH_3 adsorption decreases as percent H_2O increases in the stream. Effect of H_2O on NH_3 can be represented by a power law.
- Multiple peaks observed in H_2O adsorption suggests more than one H_2O adsorption site on the zeolite catalyst.
- Consistent results obtained when a syringe and a bubbler are used for H_2O injection individually.





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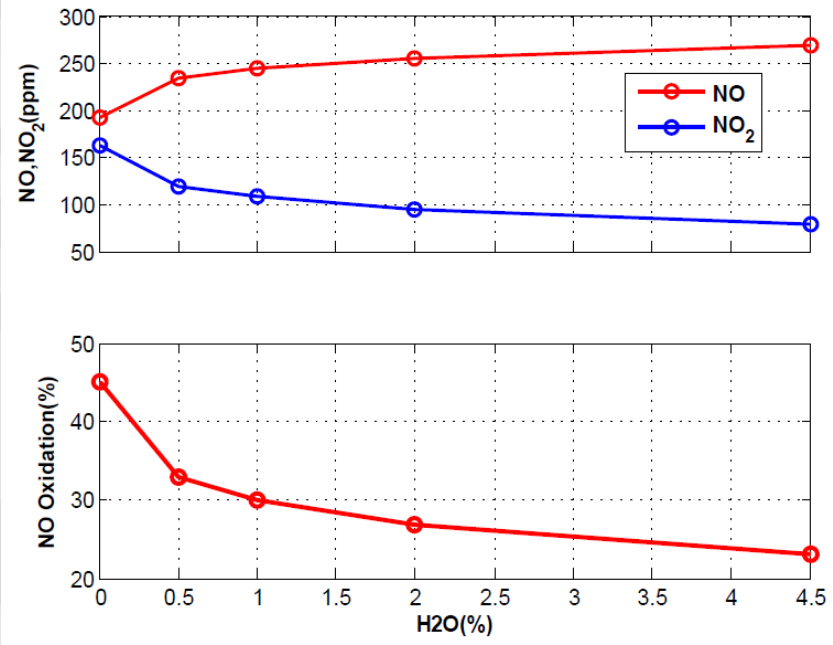
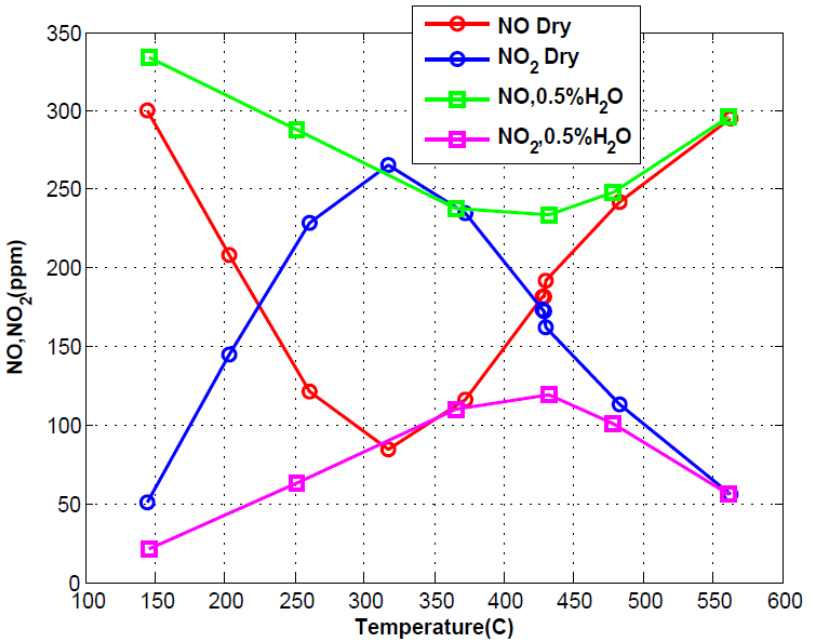
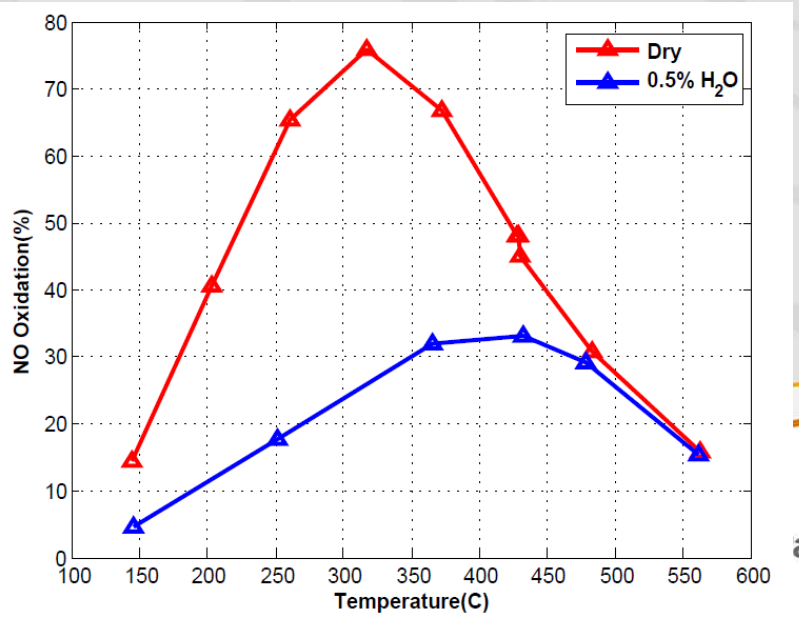
Effect of H_2O on NO + ½ O_2 → NO_2



NO oxidation vs H_2O at T = 430°C



- NO oxidation decreases as H_2O percent increases in the feed.
- Steep downward slope of NO oxidation from dry to 0.5% feed indicates that it is affected by smaller fractions of H_2O at all temperatures.
- H_2O delays the temperature at which maximum NO oxidation occurs.



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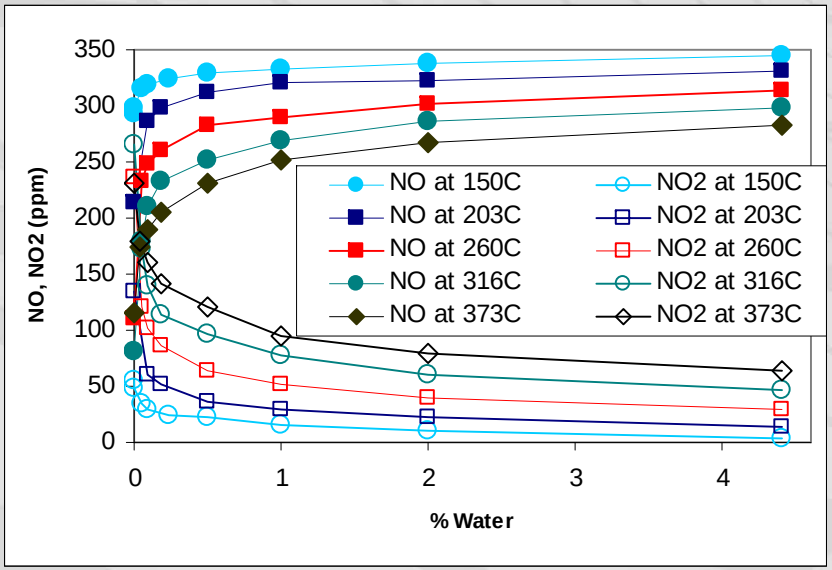
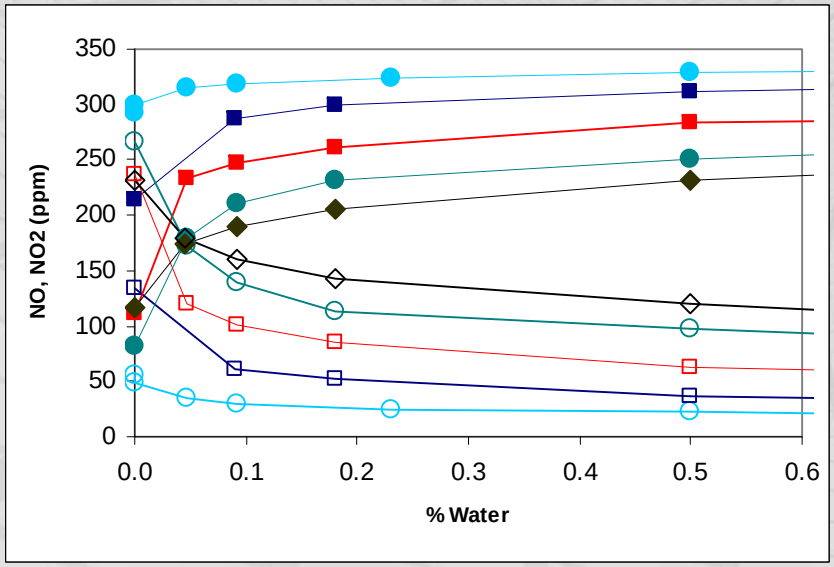
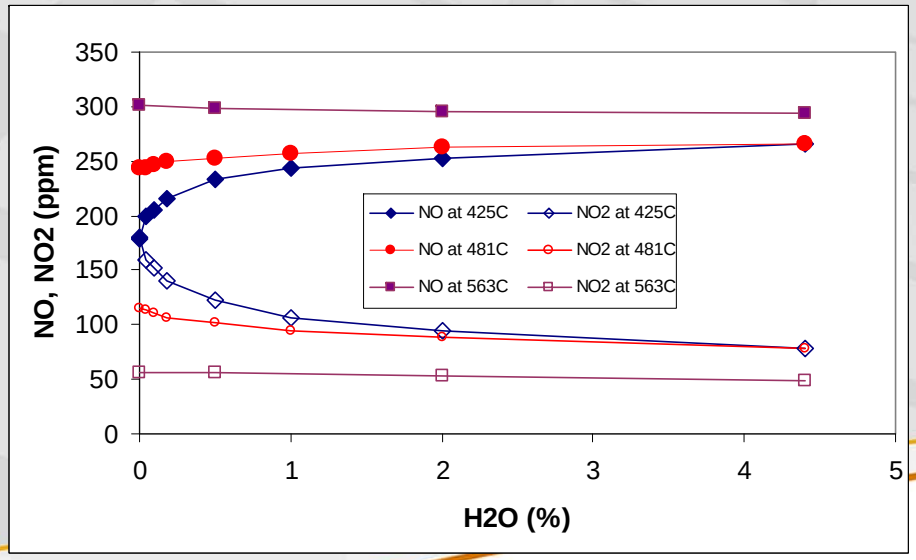
Effect of H_2O on NO + ½ O_2 → NO_2





- H_2O inhibition worsens at high temperatures.
- At T =150°C, H_2O inhibition is not prominent, but as temperature increases, it becomes significant for 0.1% to 0.5% H_2O feeds.
- At very high temperatures (T > 485°C), H_2O effect on NO oxidation drops off. One reason might be due to very little H_2O adsorption at those temperatures.



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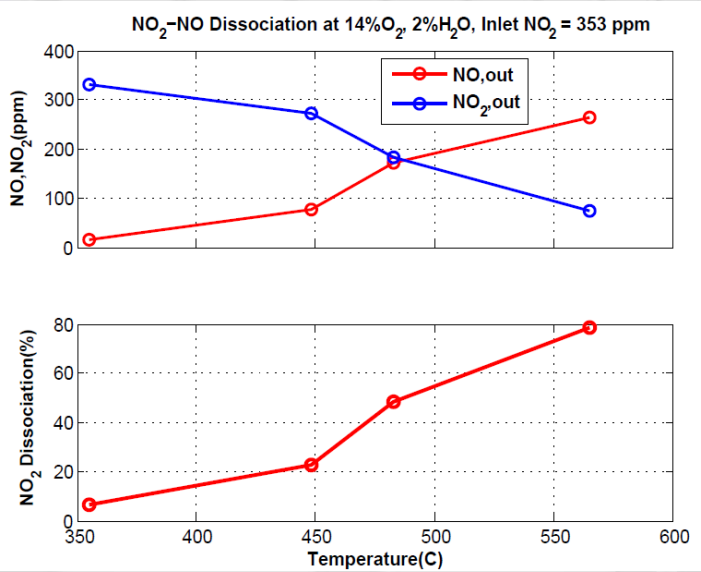
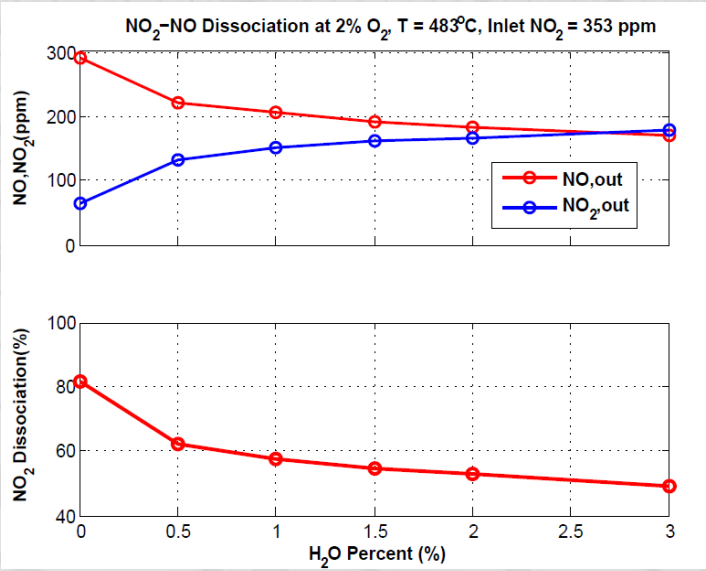
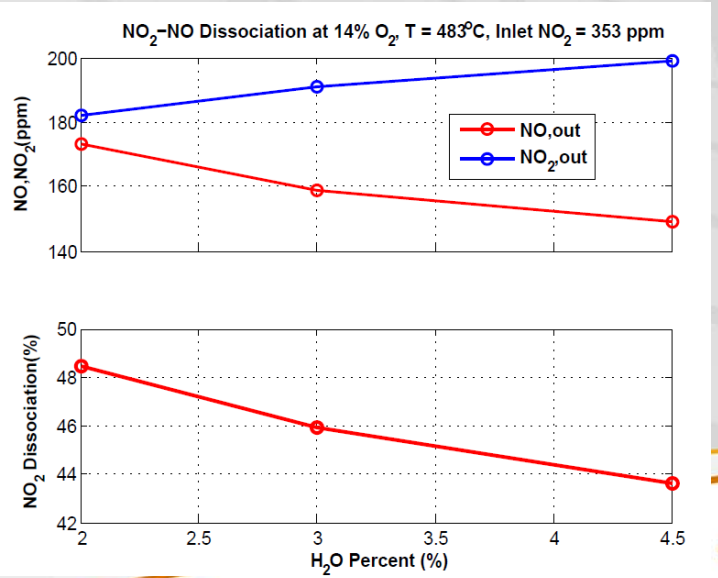
Effect of H_2O and O_2 on $NO_2 \rightarrow NO + ½ O_2$





- H_2O inhibits NO_2 dissociation and the inhibition increases as the temperature increases.
- Similar trend of H_2O inhibition is observed at 2% O_2 and 14% O_2 at T = 483°C.
- At T = 483°C and H_2O = 3%, NO_2 dissociation slightly decreases as O_2 percent increases.



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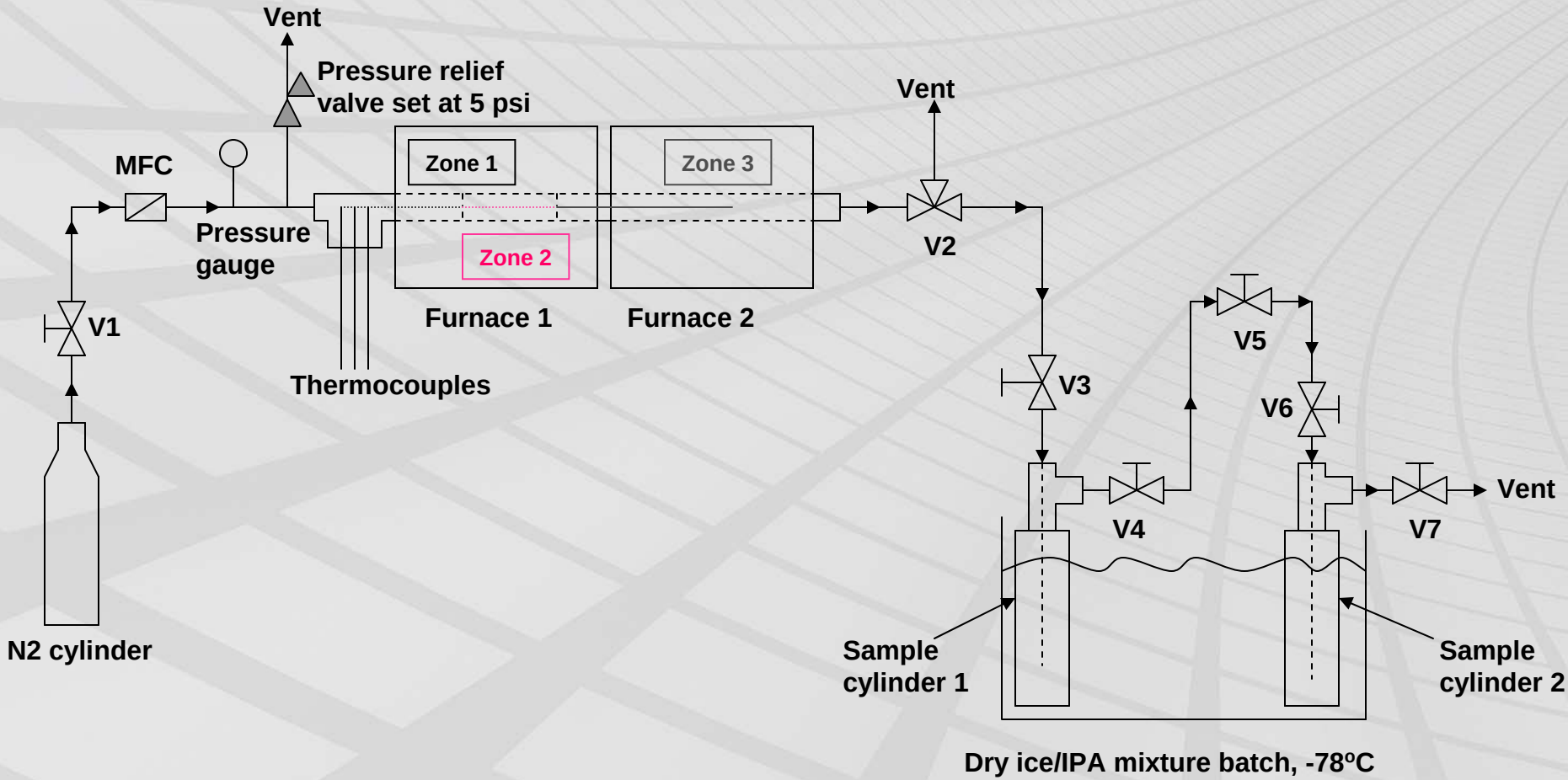

Zone 1: Preheating carrier gas N2, packed with quartz beads, ~300°C
Zone 2: Sublimation of cyanuric acid, ~ 320°C to 330°C
Zone 3: Catalytic de-polymerization of cyanuric acid vapor over gamma alumina, ~370°C
V1, V3, V4, V5, V6, V7: 2-way ON/OFF valves
V2: 3-way ON/OFF valve

HNCO Synthesis Bench

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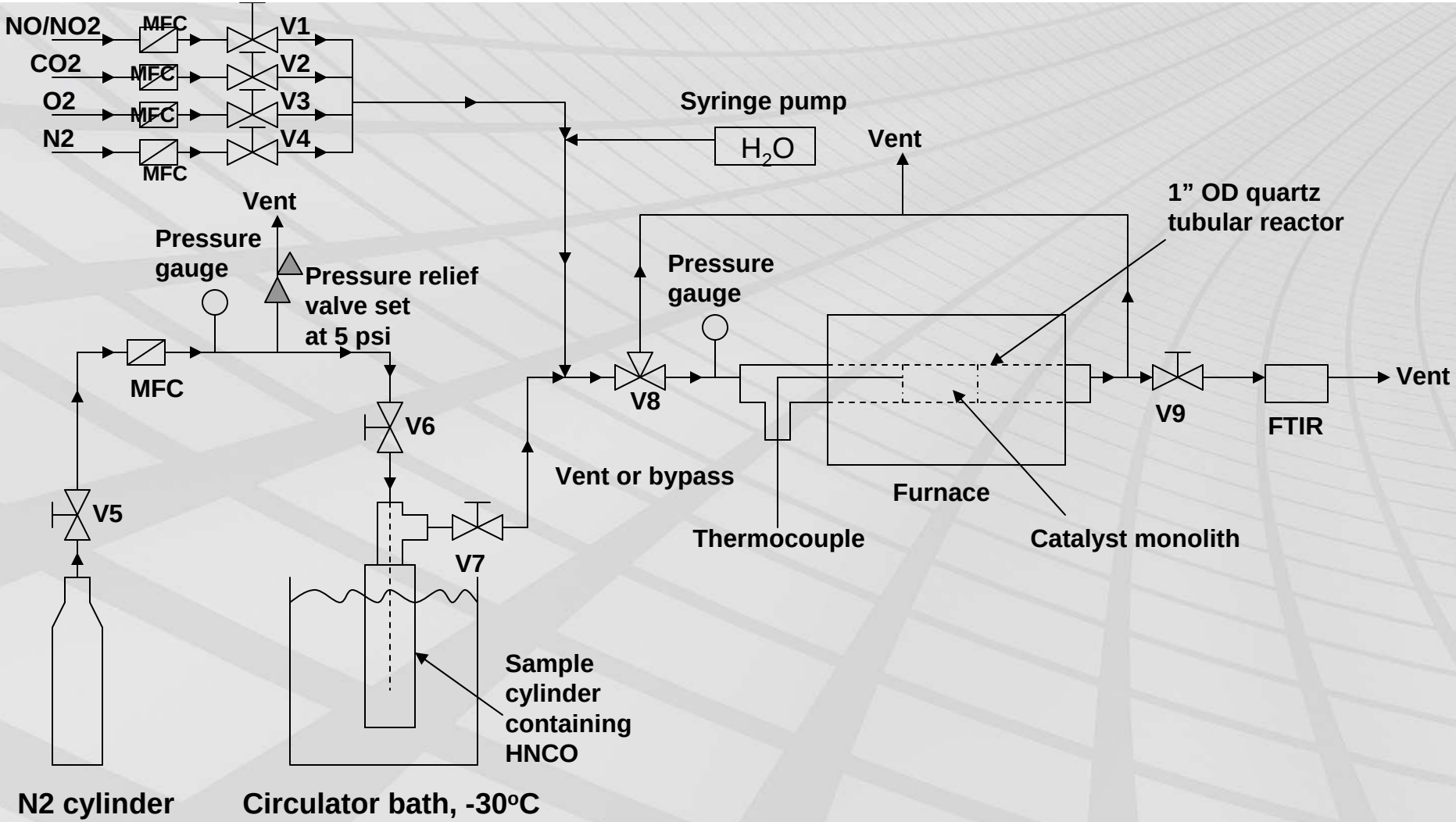

Steady State Catalyst Test Bench

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Conclusions

- H_2O inhibits both NO oxidation and NO_2 dissociation reactions.
- NH_3 adsorption decreases as percent H_2O increases in the stream.
- Steep downward slope of NO oxidation from dry to 0.5% H_2O feed indicates that it is affected by smaller fractions of H_2O at all temperatures.
- N_2O formation is significant when $NO_2/NH_3 = 1.0$ at low temperatures with no NO in the stream.
- NH_4NO_3 is a critical intermediate in the fast SCR reaction at low temperatures and needs to be tracked for better model predictability and effective NO_x control.
- Micro-reactor model predicts the outlet concentrations reasonably well in the test cases considered. Overall model validation in steady state NO_x and NH_3 conversions show good predictability.
- Further model improvement is needed by incorporating H_2O, NH_4NO_3 and HC based reactions to understand the various mechanistic pathways on Fe-zeolites.
- HNCO generation set-up is complete and preliminary tests are being done to evaluate HNCO purity.

Future Work

- Detailed model based analysis of H_2O effect on NO oxidation, NO_2 dissociation, NH_4NO_3 and N_2O formation.
- Investigation of competitive adsorption between HC and NH_3 storage in active catalytic sites.
- Transient testing of Fe-zeolite micro-reactor using NH_3.
- Steady state and transient testing of the reactor using HNCO.
- Steady state kinetic modeling of HNCO hydrolysis and adsorption.

Acknowledgements

- Umicore
- Ken Howden and Gurpreet Singh – US DOE, OVT
- CLEERS

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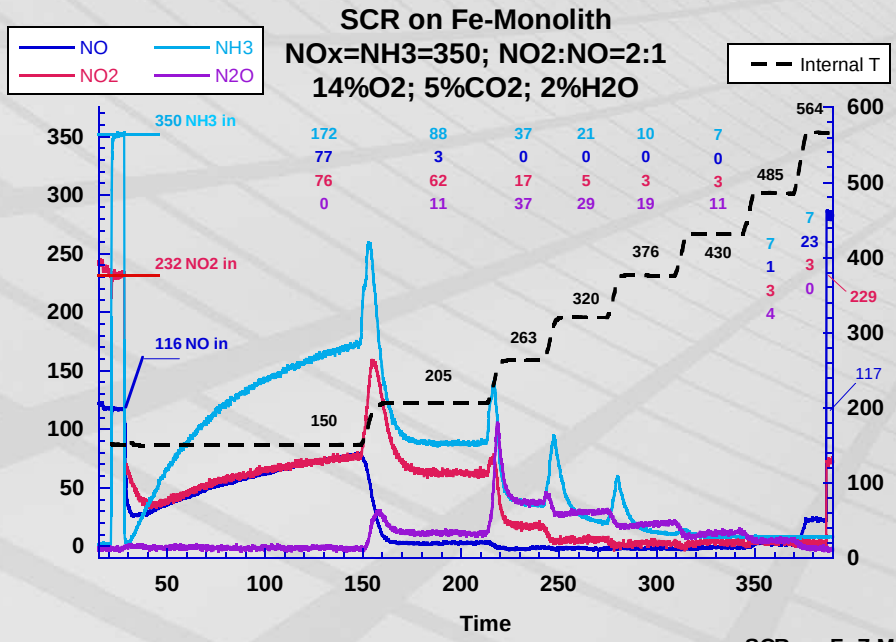
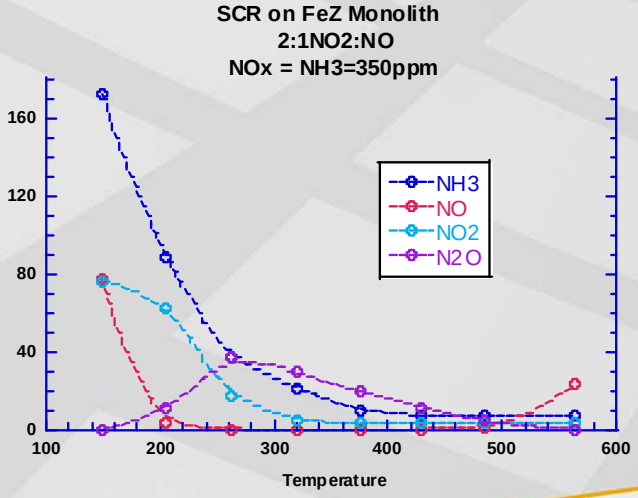
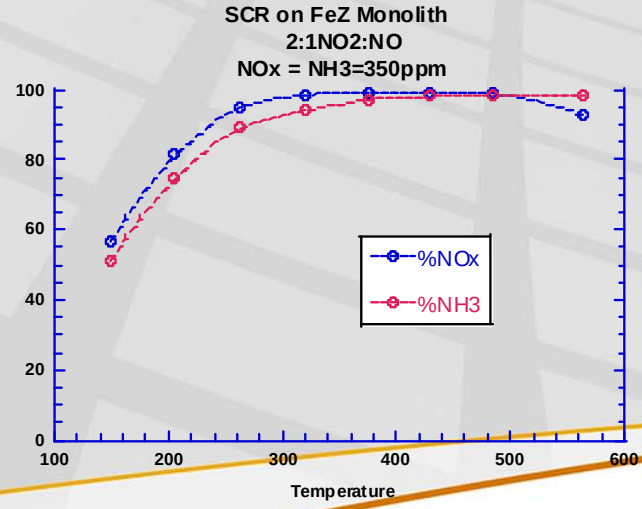
Back-up Slides: SCR, NO/NO_2 = ½ ; NO_x/NH_3 = 1:1







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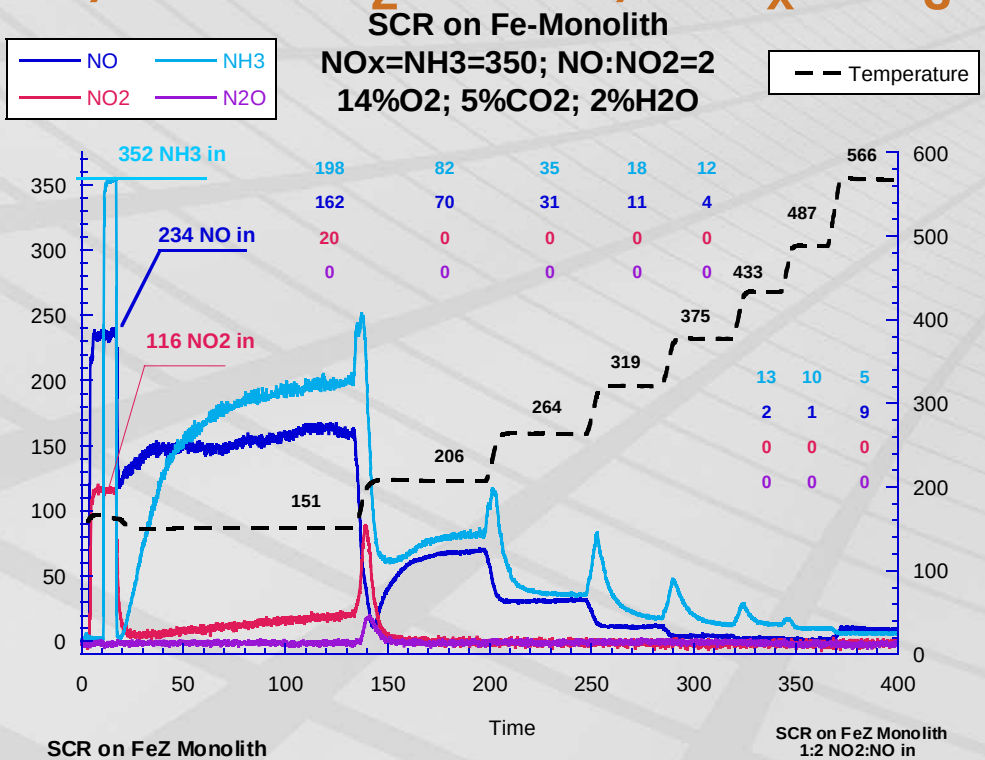
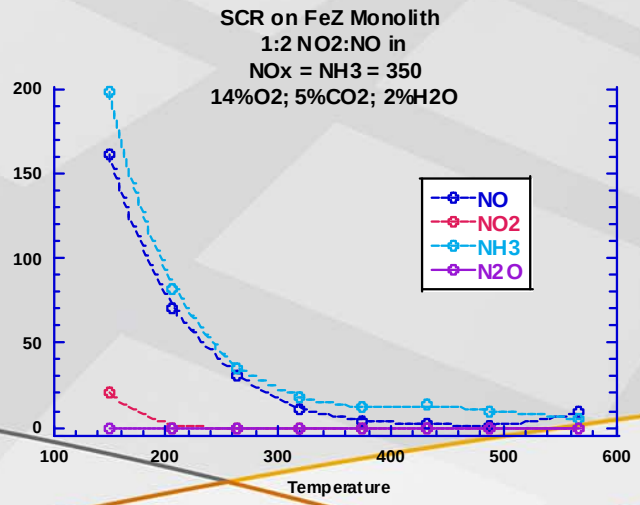
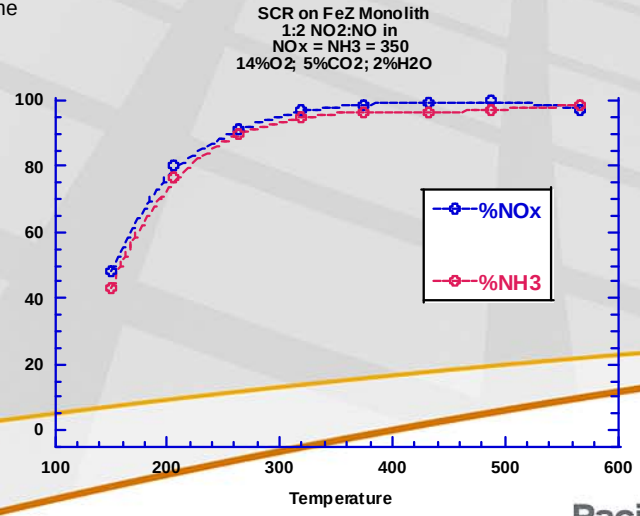
SCR, NO/NO_2 = 2/1 ; NO_x/NH_3 = 1:1







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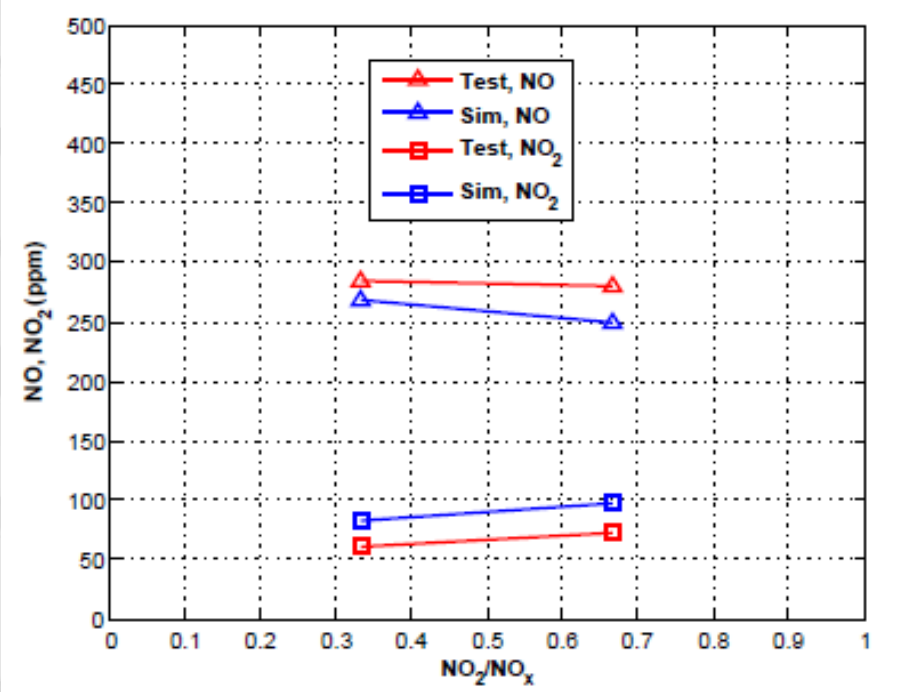
Overall Model Validation – NO/NO_2



- At the end of each run of the tests shown in the previous slide, NH_3 is shut off and NO ⇔ NO_2 is investigated at T = 563°C by switching NO off and then switching NO_2 off.
- Simulated NO and NO_2 concentrations match with the test data within 10-15 ppm error margin.

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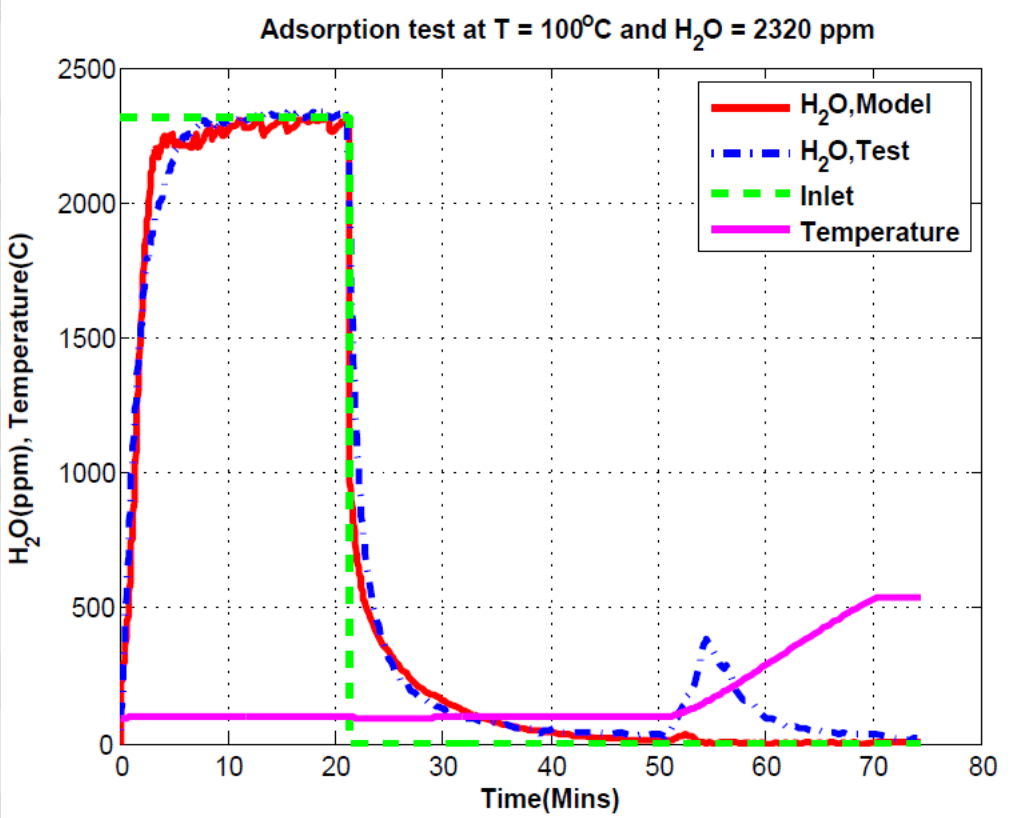
H_2O Adsorption Model



- Model matches well with the data except at the second peak illustrating that there may be more than one site where H_2O is adsorbed.

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