Development of Cu SCR Model using CLEERS Transient SCR Reactor Protocol

Maruthi Devarakonda[1], Jong Lee[1], Josh Pihl[2], Stuart Daw[2]

[1]Pacific Northwest National Laboratory
[2]Oak Ridge National Laboratory

DOE CLEERS Workshop
April 19th, 2011

Oak Ridge National Laboratory
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Pacific Northwest NATIONAL LABORATORY

Institute for INTERFACIAL CATALYSIS

Motivation

- NH_3/Urea Selective Catalytic Reduction (SCR) proven effective over wide range of conditions, but improvement necessary for:
    - increasingly stringent emission standards
    - higher engine-out NOx under high efficiency operating points
        - driven by fuel economy regulations
    - cooler exhaust temperatures from advanced combustion regimes
    - hotter exhaust temperatures from lean gasoline engines

- Model-based SCR system controls not sufficiently developed for adapting to catalyst aging/de-activation
    - better understanding of catalyst aging required

Objectives

- Characterize a commercially available 2010 Cu zeolite SCR catalyst through CLEERS transient reactor protocol.
- Develop a baseline SCR model and validate it against the transient reactor data for future catalyst aging studies.

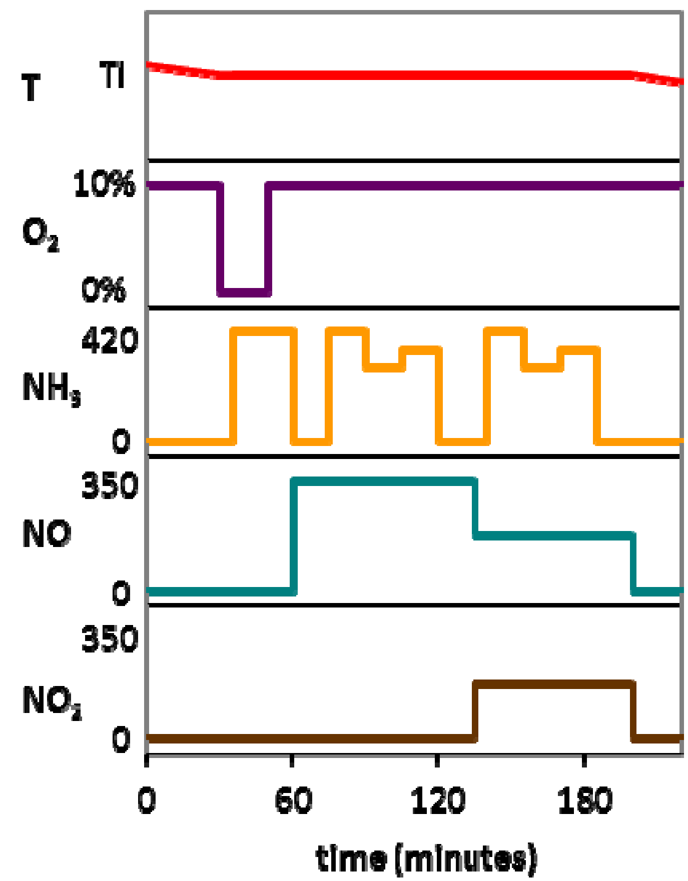
Outline

- CLEERS Transient Reactor Protocol
- Data Analysis
- Cu-SCR Model
- Model Validation
- Conclusions & Future Work

Revised transient CLEERS SCR protocol; assessed with commercial Cu zeolite

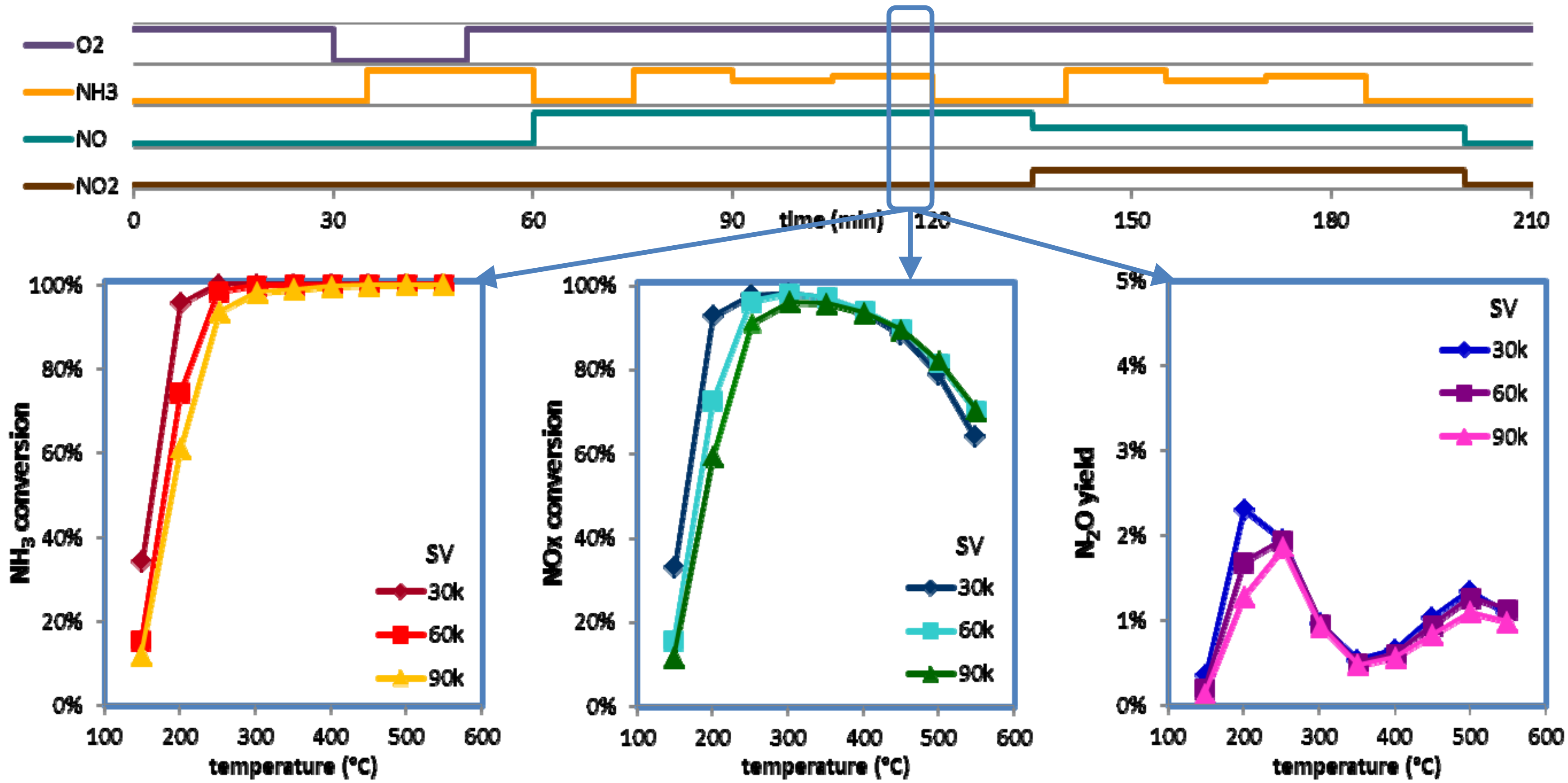
- Protocol designed to generate data needed for model calibration and performance evaluation
  - steady state points
    - SCR conditions:
      - NH_3/NOx = 0.8, 1.0, 1.2
      - NO_2/NOx = 0.0, 0.5
    - O_2 oxidation of NH_3 & NO
  - arranged to measure NH_3 storage capacities between points
  - goal: minimal operating time and expense

- Experiments conducted on Cu zeolite core sample cut from Ford F-series super duty SCR monolith
  - 150-550°C @ 50°C
  - 30k, 60k, 90k hr^{-1} (60k shown if not indicated)
  - 350 ppm NOx
- Data will serve as baseline for investigations of hydrothermal aging and HC fouling



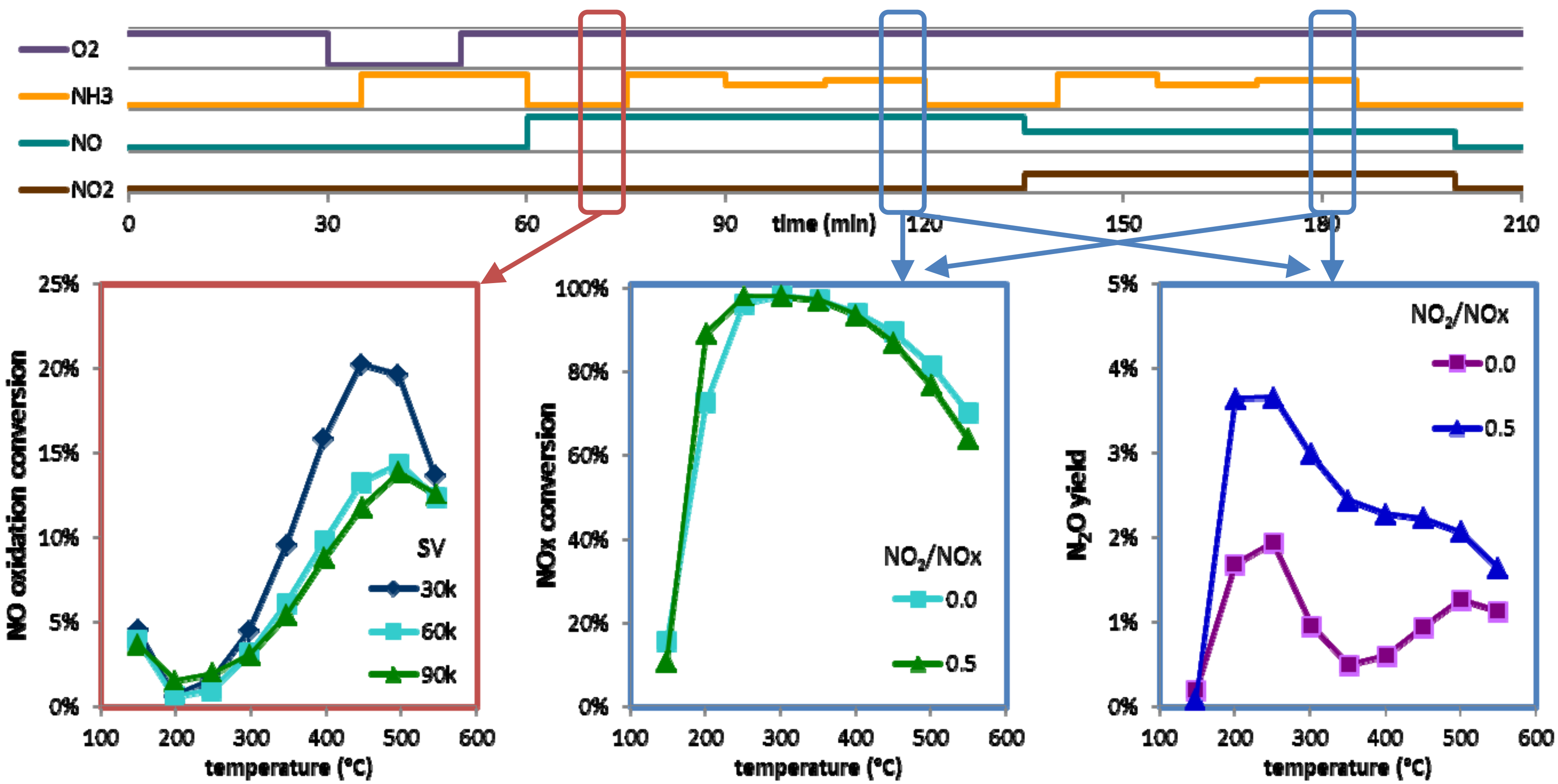
note: 5% H_2O & 5% CO_2 in all steps

Steady state points illustrate wide operating window of fresh Cu zeolite SCR catalyst



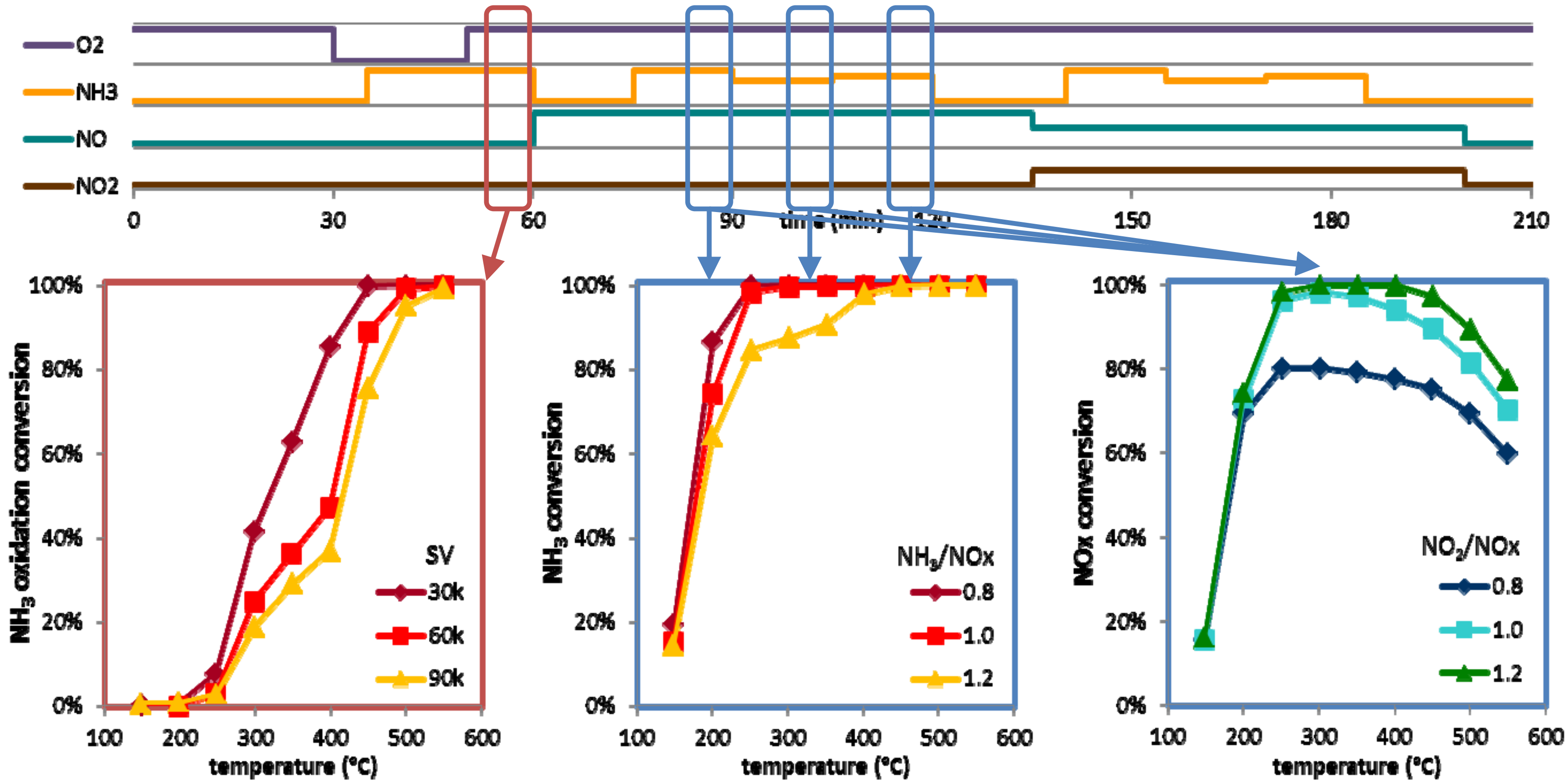
- Fresh commercial Cu SCR shows:
  - minimal NH_3 slip
  - good NOx conversion for 250°C ≤ T ≤ 450°C, but drop off at high T
  - high selectivity to N_2

Catalyst has relatively low sensitivity to NO_2/NOx



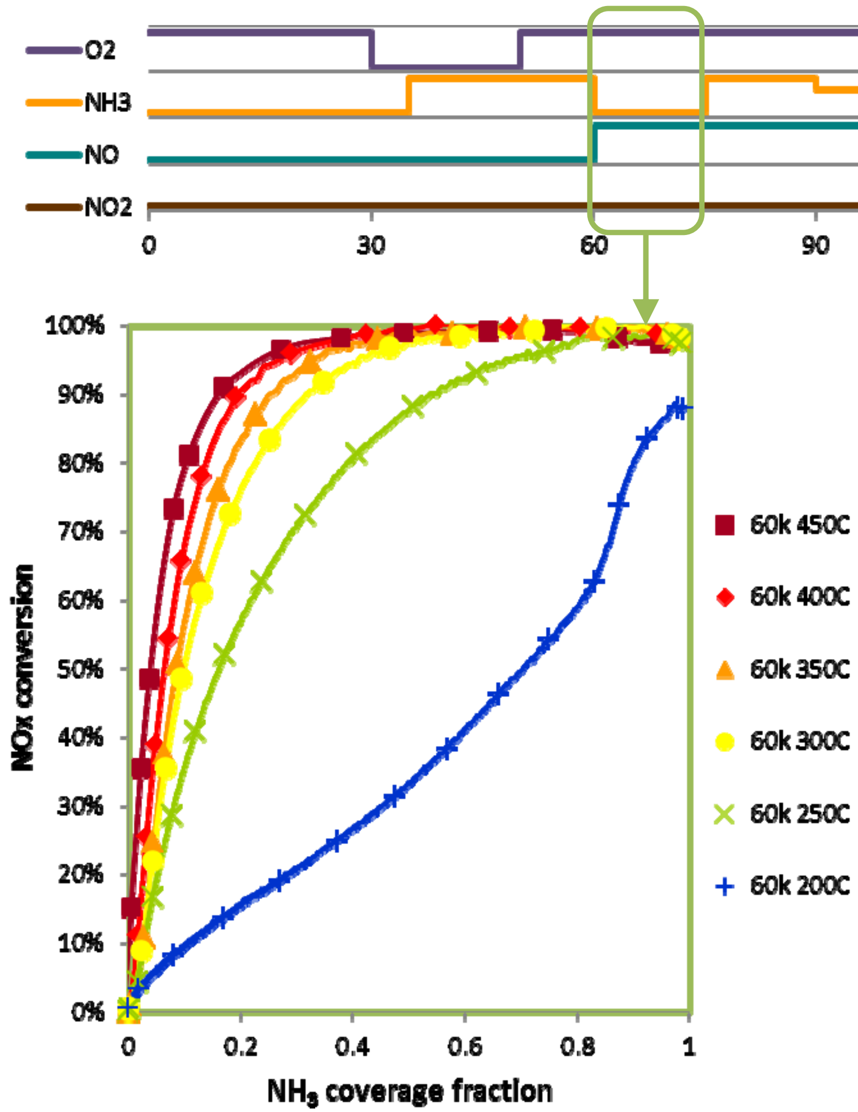
- Inclusion of NO_2 increases NOx conversion near light-off
- NO_2 increases N_2O formation, but high N_2 selectivity maintained
- High NO oxidation could reduce need for NO_2 in feed

High T NOx conversion limited by NH_3 oxidation



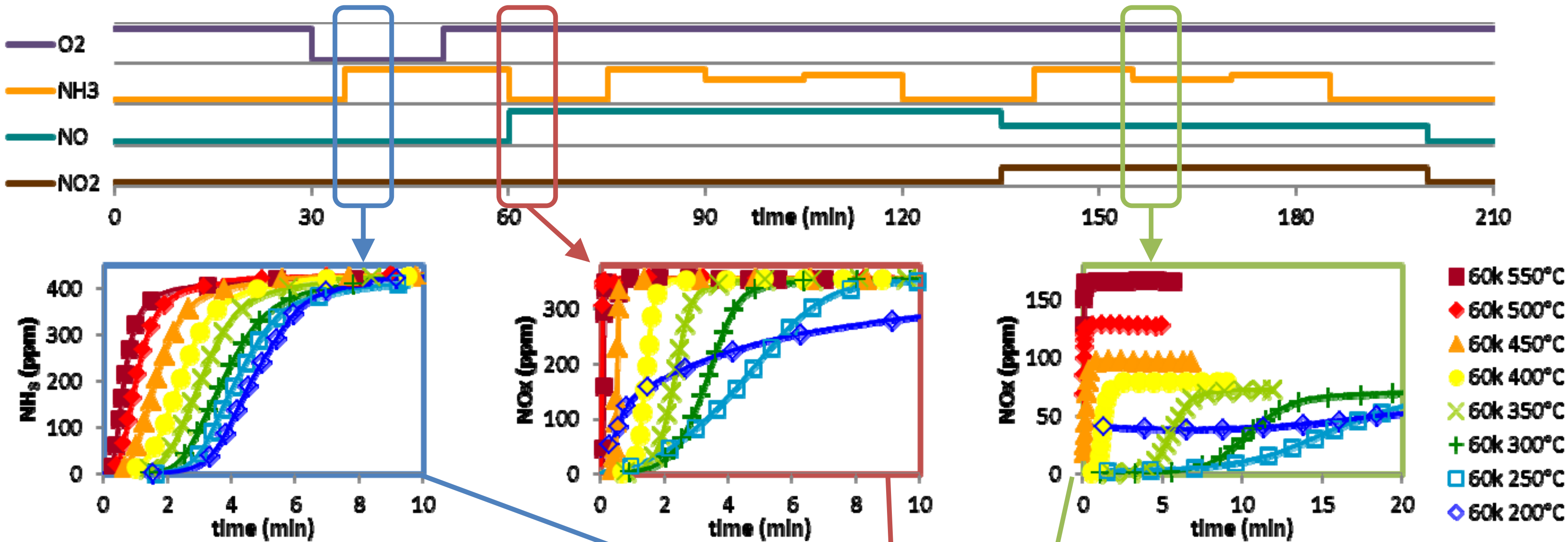
- All NH_3 consumed at high T
- NOx conversion improves with increasing NH_3 dose
- High NH_3 oxidation activity: competes with SCR at high T

Transients reveal critical NH_3 coverage

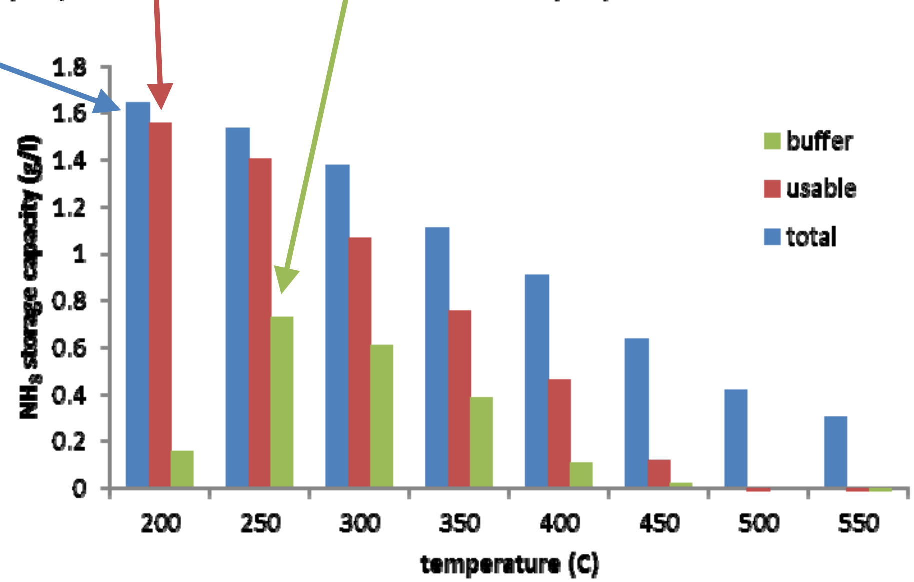


- NOx conversion vs. NH_3 coverage:
  1. saturate with NH_3
  2. turn NH_3 off, NOx on
  3. observe NOx conversion as stored NH_3 is consumed
- NH_3 coverage to achieve high NOx conversion:
  - decreases with T
  - < saturation for all but lowest T
- No evidence of NH_3 inhibition of SCR reactions

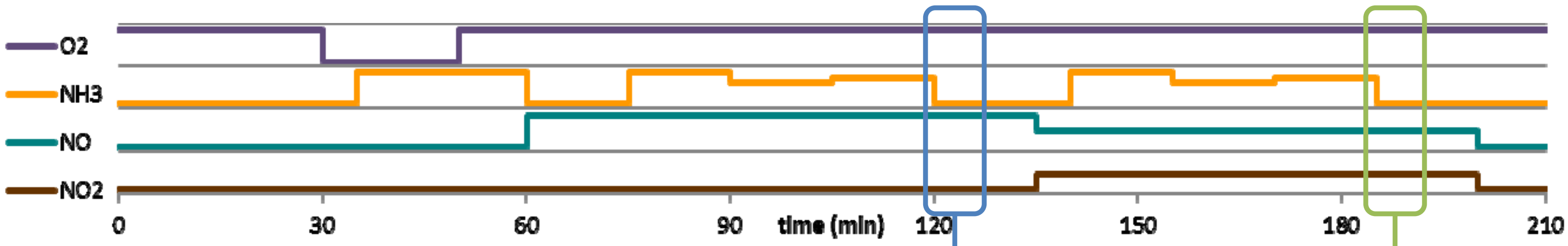
Transients quantify details of NH_3 storage capacity



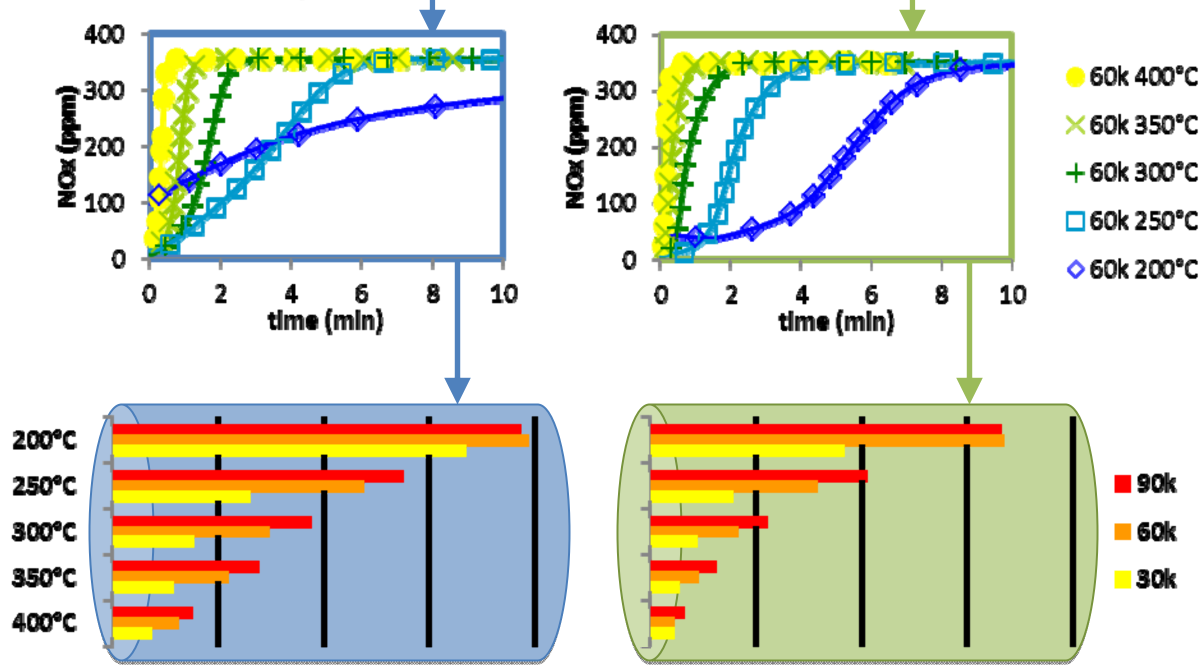
- Example capacities:
  - Total: NH_3 uptake without O_2
  - Usable: NH_3 stored under O_2
  - Buffer: capacity for temporary NH_3 overdose/underdose
- Available NH_3 storage capacity changes with current conditions & operating history



SCR surface NH_3 inventory shows catalyst utilization



- Estimation of fractional catalyst utilization:
  1. Turn NH_3 off at end of SCR steps
  2. Integrate NOx reduced by stored NH_3
  3. Divide by Usable NH_3 capacity at same T
- Utilization decreases with
  - higher T
  - lower SV
  - NO_2 in feed



NH_3 coverage (catalyst utilization)
NO_2/NOx = 0.0
NH_3/NOx = 1.0
'standard' SCR

NH_3 coverage (catalyst utilization)
NO_2/NOx = 0.5
NH_3/NOx = 1.0
'fast' SCR

Single Site NH_3 Storage Model

- All SCR models developed in Matlab/Simulink
- First order Euler integration in space – 100 elements (cells) along the axis
- Simulated using a variable step solver (ode 23tb) in Simulink
- Nonlinear constrained minimization (fmincon) used to identify rate parameters using Matlab's Optimization toolbox

$$\frac{\partial c_{g,NH_3}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NH_3}}{\partial x} + \frac{\Omega}{\varepsilon}(r_{des} - r_{ads})$$

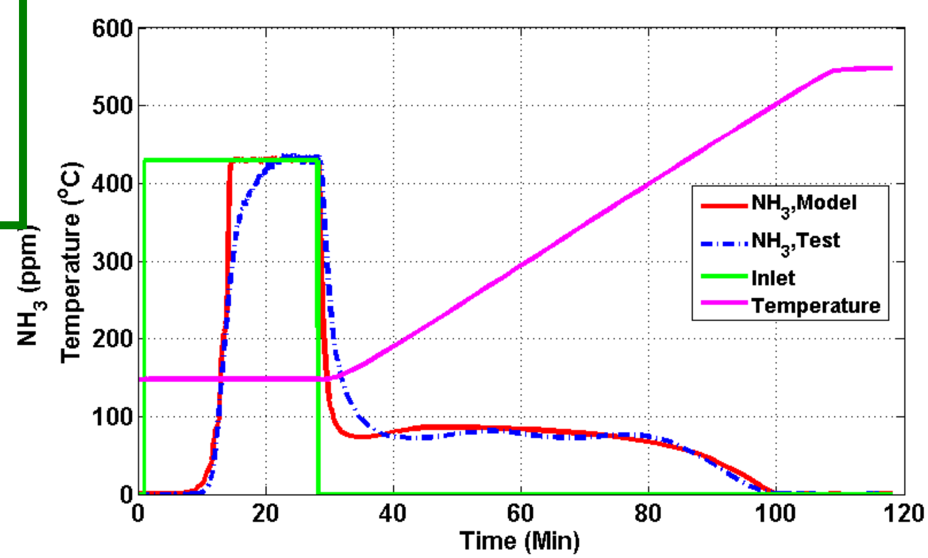
$$\frac{d\theta_{NH_3}}{dt} = r_{ads} - r_{des}$$

Adsorption and Desorption Rates

$$r_{ads} = A_{ads} c_{g,NH_3} (1 - \theta_{NH_3})$$

$$r_{des} = A_{des} e^{\frac{-E_{des}(1-\gamma\theta_{NH_3})}{RT}} \theta_{NH_3}$$

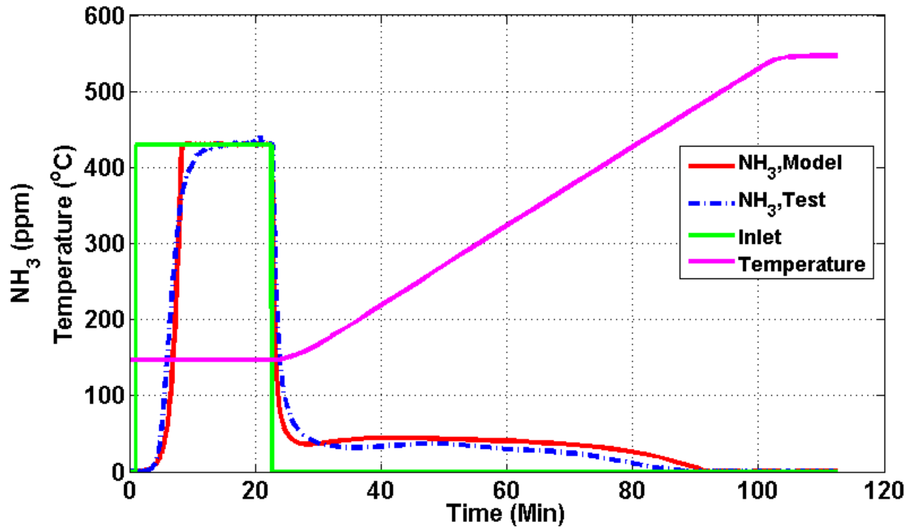
430 ppm of NH_3, 5% H_2O, 5% CO_2 at T = 150°C

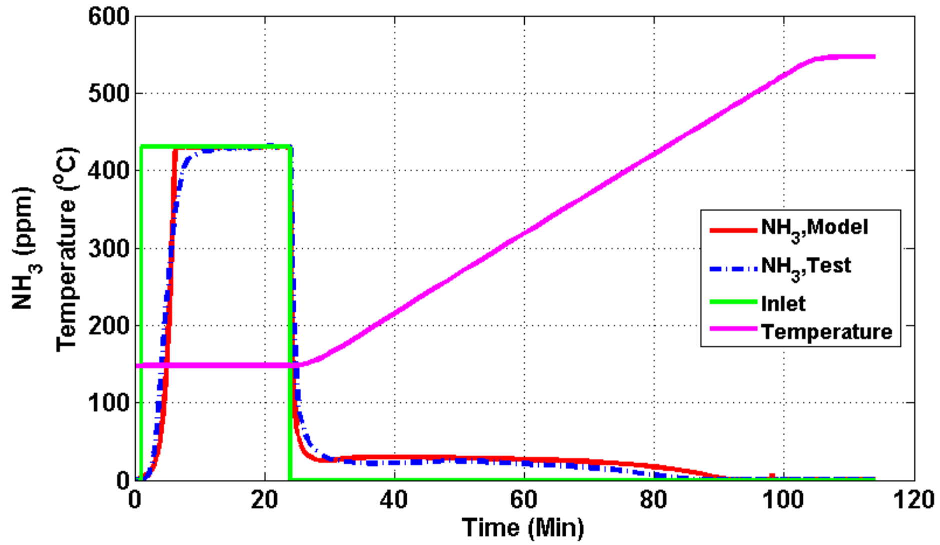


Rate parameters identified on TPD data at 30000/hr SV

L. Olsson's single site rate parameters on Cu-ZSM-5 (ACatB, 2008) considered as initial conditions

Single Site Storage Model Validation on TPD Tests





A_{ads}	$m^3/mol/s$	0.99
A_{des}	1/s	1.01E11
E_{des}	kJ/mol	180.2
γ	-	0.81
Ω	mol/m^3	225

Validation at 60000/hr and 90000/hr SV data

NO_x Reaction Pathways

In addition to NH_3 adsorption and desorption on SCR catalyst surface, the following reactions have been incorporated in this version of Cu-Z SCR model

NH_3 oxidation	$2NH_3 + 3/2O_2 \rightarrow N_2 + 3H_2O$
NO oxidation	$NO + 1/2O_2 \leftrightarrow NO_2$
Standard SCR	$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$
Fast SCR	$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O$
NO_2 SCR	$4NH_3 + 3NO_2 \rightarrow 7/2\ N_2 + 6H_2O$

NH_3 Oxidation Model

$$\frac{\partial c_{g,NH_3}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NH_3}}{\partial x} + \frac{\Omega}{\varepsilon}(r_{des} - r_{ads})$$

$$\frac{d\theta_{NH_3}}{dt} = r_{ads} - r_{des} - r_{NH_3,oxi}$$

$$\frac{\partial c_{g,O_2}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,O_2}}{\partial x} - \frac{\Omega}{\varepsilon}(\frac{3}{4} r_{NH_3,oxi})$$

$$4\mathrm{NH_3}.S + 3\mathrm{O_2} \rightarrow 2\mathrm{N_2} + 6\mathrm{H_2O} + 4\mathrm{S}$$

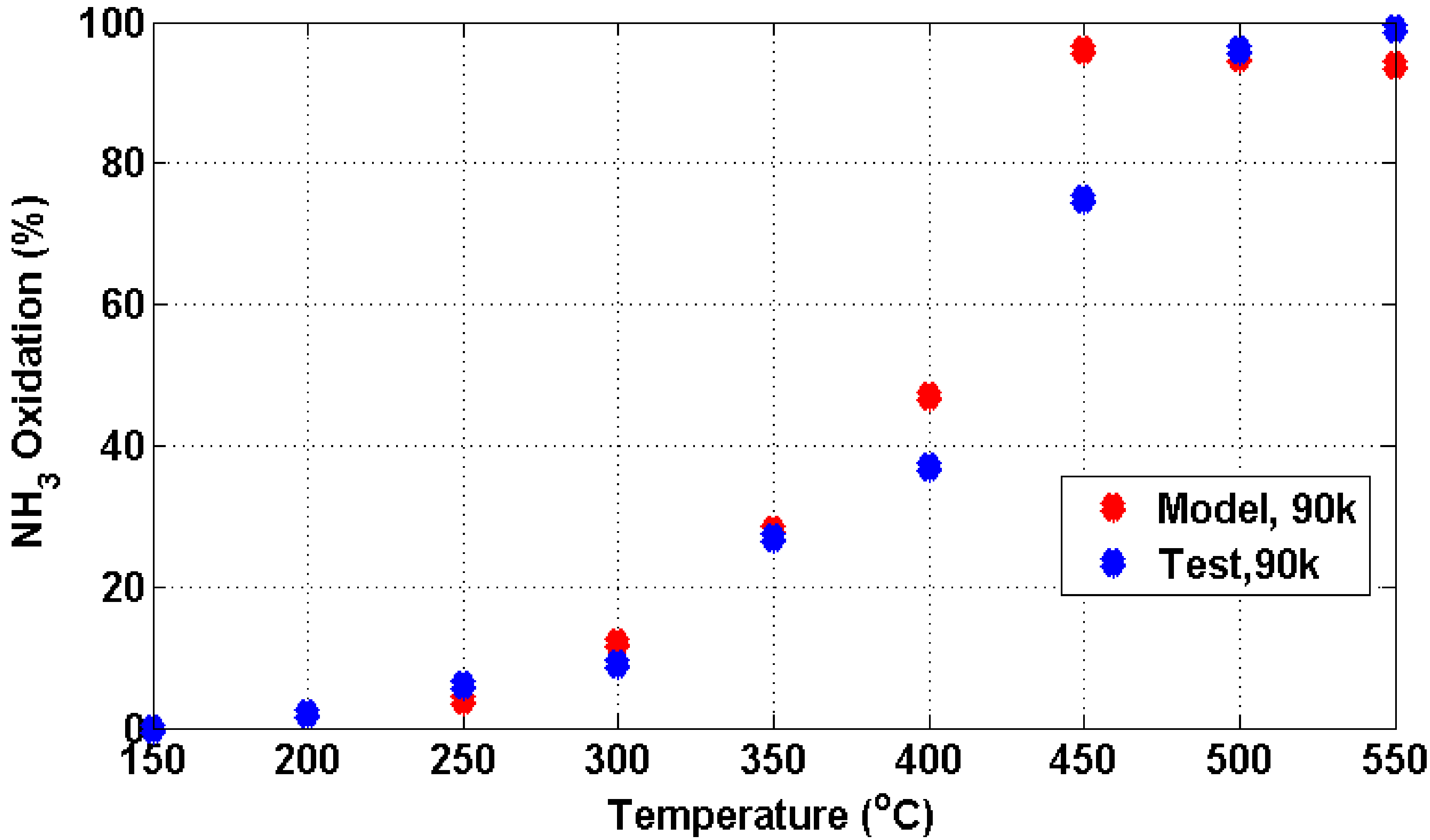
$$r_{NH_3,oxi} = k_{NH_3,oxi} c_{g,O_2} \theta_{NH_3}$$

A = 2.22E3 m^3/mol/s

E = 74 kJ/mol

- **Parameters identified at 60k/hr data using unconstrained nonlinear minimization function in Matlab (*fminsearch*).**
- **Cost function to be minimized is defined as the average sum of absolute error between the test and simulated NH_3 concentrations.**

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


100
80
60
40
20
0
150
200
250
300
350
400
450
500
550
NH3 Oxidation (%)
Temperature (°C)
Model, 90k
Test,90k

NO Oxidation Model

$$\frac{\partial c_{g,NO}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NO}}{\partial x} - \frac{1}{\varepsilon}(r_{NO,oxi})$$

$$\frac{\partial c_{g,NO_2}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NO_2}}{\partial x} + \frac{1}{\varepsilon}(r_{NO,oxi})$$

$$r_{NO,oxi} = k_{NO,oxi}(c_{g,NO}c_{g,O_2}^{\frac{1}{2}} - \frac{c_{g,NO_2}}{k_{eq}})$$

$$k_{eq} = A_{eq}\sqrt{T}e^{\frac{E_{eq}}{RT}}$$

$$\mathrm{NO} + \frac{1}{2}\mathrm{O}_2 \Leftrightarrow \mathrm{NO}_2$$

A = 9.4E3 m^3/mol/s

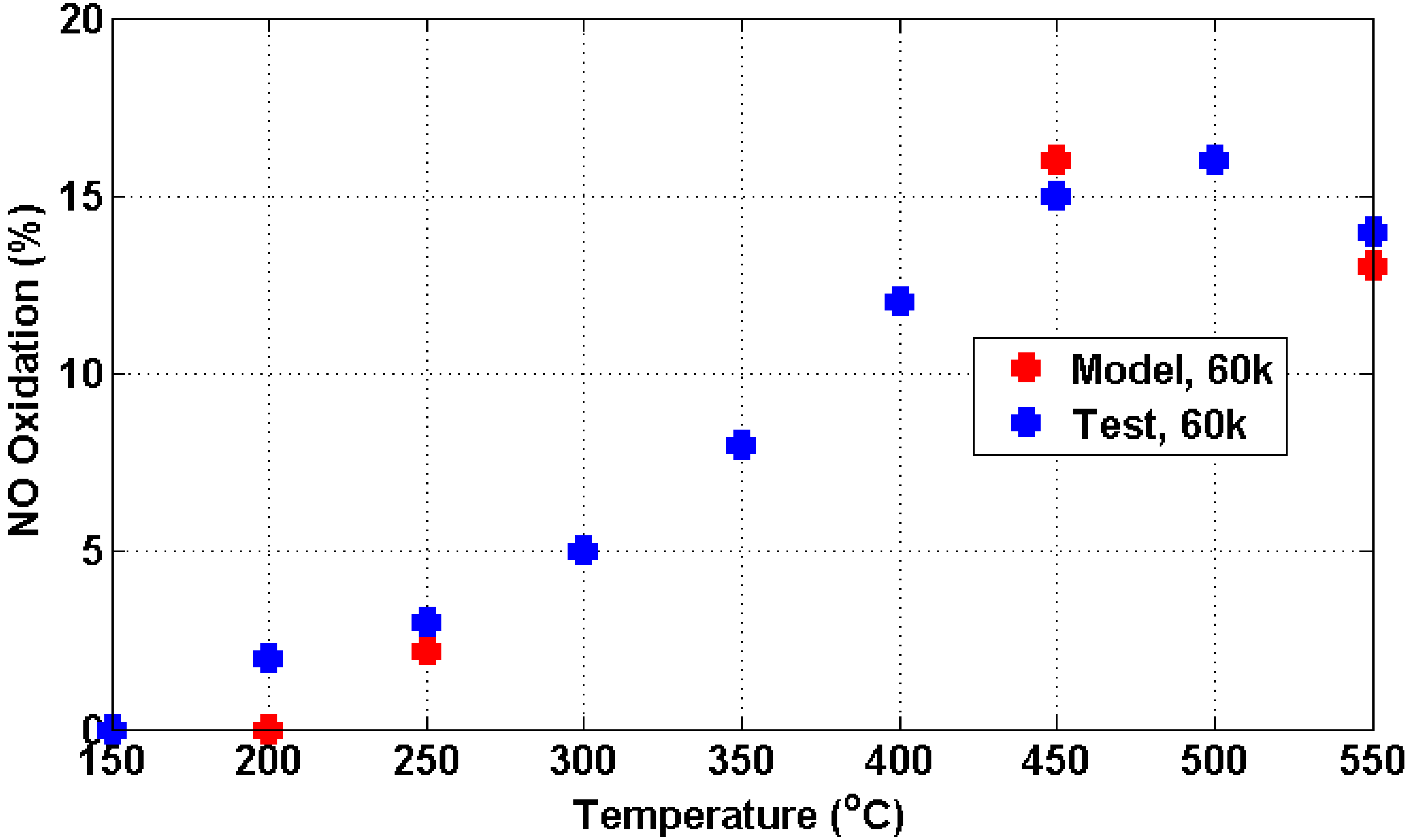
E = 43 kJ/mol

A_{eq} = 9.42E-7

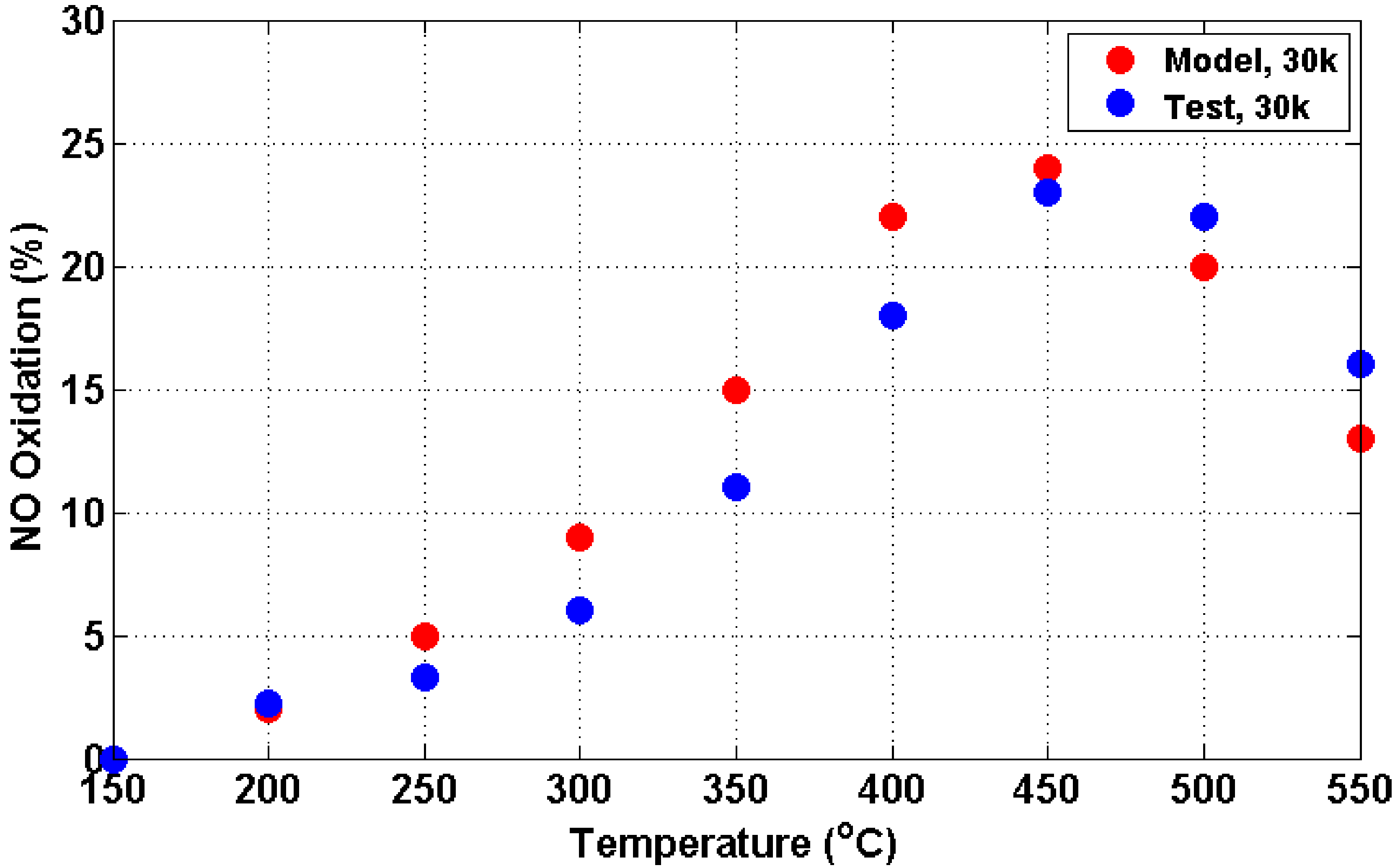
E_{eq} = 58 kJ/mol

- **Parameters identified using 4 data points at 60k/hr and 90k/hr using unconstrained nonlinear minimization function in Matlab (*fminsearch*).**
- **Cost function to be minimized is defined as the average sum of absolute error between the test and simulated NO and NO_2 concentrations.**

$$J = \frac{\sum_{i=1}^{N}\left|(c_{NO.s} - c_{NO,t})\right| + \left|(c_{NO_2,s} - c_{NO_2,t})\right|}{N}$$



20
15
10
5
0
150
200
250
300
350
400
450
500
550
NO Oxidation (%)
Temperature (°C)
Model, 60k
Test, 60k



Model, 30k
Test, 30k
NO Oxidation (%)
30
25
20
15
10
5
0
150
200
250
300
350
400
450
500
550
Temperature (°C)

Standard SCR Model

$$\frac{\partial c_{g,NO}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NO}}{\partial x} - \frac{1}{\varepsilon}(r_{NO,oxi} + \Omega r_{std-scr})$$

$$\frac{\partial c_{g,NO_2}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NO_2}}{\partial x} + \frac{1}{\varepsilon}(r_{NO,oxi})$$

$$\frac{\partial c_{g,NH_3}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NH_3}}{\partial x} + \frac{\Omega}{\varepsilon}(r_{des} - r_{ads})$$

$$\frac{d\theta_{NH_3}}{dt} = r_{ads} - r_{des} - r_{NH_3,oxi} - r_{std-scr}$$

$$\frac{\partial c_{g,O_2}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,O_2}}{\partial x} - \frac{\Omega}{\varepsilon}(\frac{3}{4}r_{NH_3,oxi} + \frac{1}{4}r_{std-scr})$$

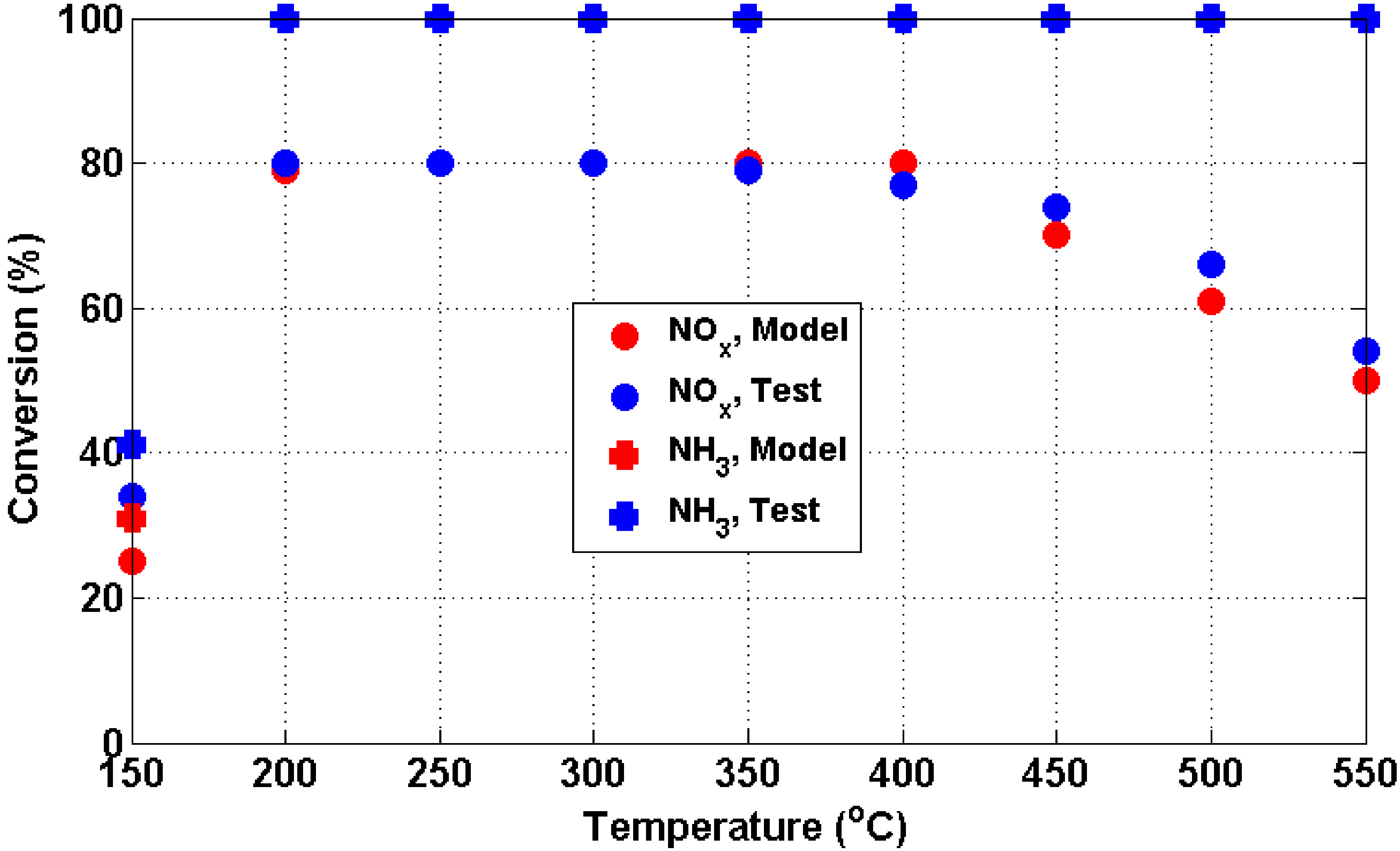
$$4NH_3.S + 4NO + O_2 \rightarrow 4N_2 + 6H_2O + 4S$$

$$r_{std-scr} = A_{std-scr}\, e^{\frac{-E_{std-scr}}{RT}}\, c_{g,NO}\, \theta_{NH_3}$$

$A_{std-scr}$ = 9.89E8 m^3/mol/s

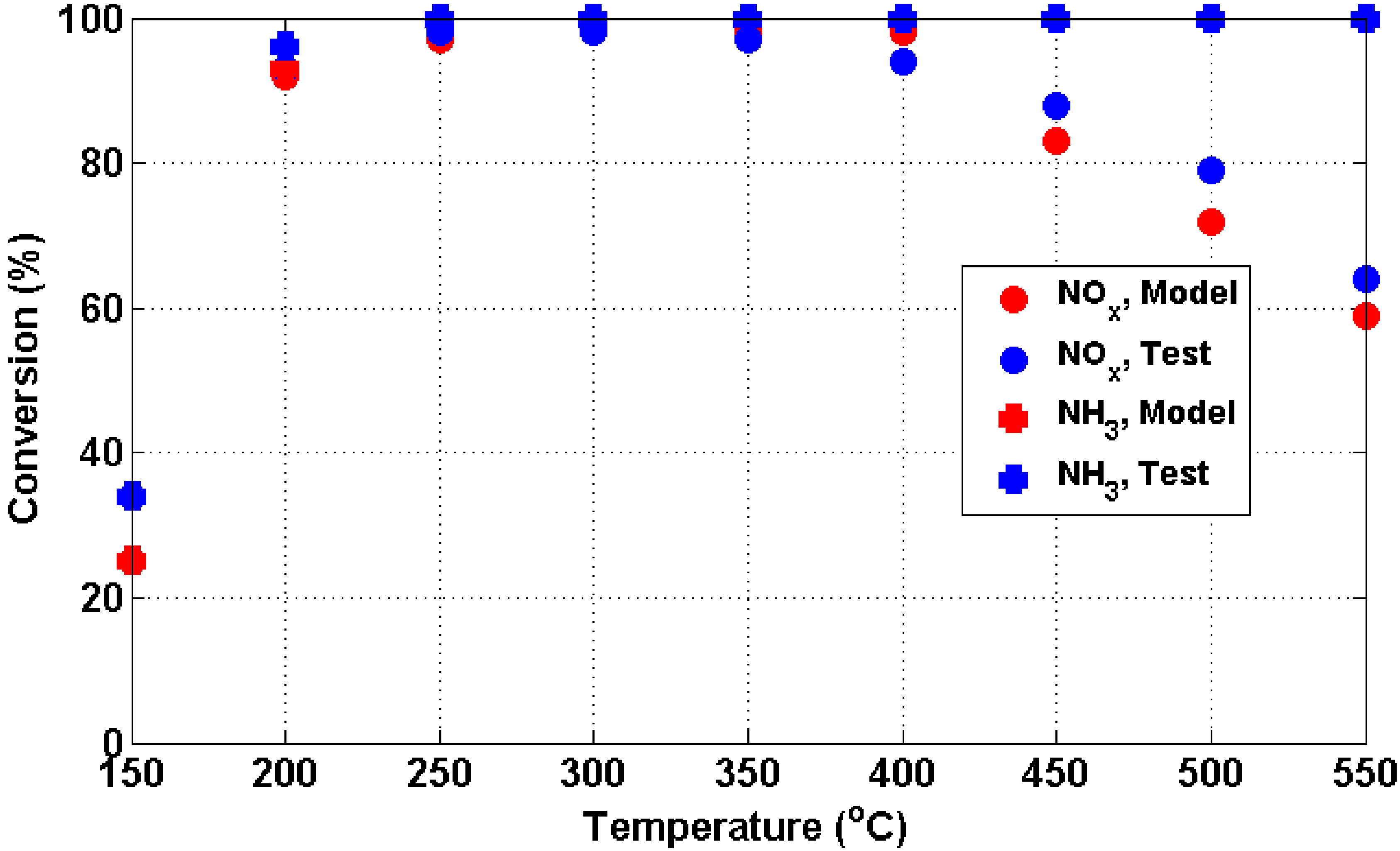
$E_{std-scr}$ = 84.9 kJ/mol

- **Standard SCR pre-exponential was manually adjusted at 150°C, 30k/hr SV and the model was validated at the remaining data points.**
- **Model mismatch in NO_x conversion at T > 450°C was observed at higher space velocities, possibly due to NH_3 oxidation to NO, which is not considered in the model.**



100
80
60
40
20
0
150
200
250
300
350
400
450
500
550
Conversion (%)
Temperature (°C)
NOx, Model
NOx, Test
NH3, Model
NH3, Test

Alpha = 0.8



Conversion (%)
Temperature (°C)
NOx, Model
NOx, Test
NH3, Model
NH3, Test
0
20
40
60
80
100
150
200
250
300
350
400
450
500
550

Alpha = 1.0

Fast SCR Model

$$\frac{\partial c_{g,NO}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NO}}{\partial x} - \frac{1}{\varepsilon}(r_{NO,oxi} + \Omega(r_{std-scr} + 0.5 r_{fast-scr}))$$

$$\frac{\partial c_{g,NO_2}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NO_2}}{\partial x} + \frac{1}{\varepsilon}(r_{NO,oxi} - \Omega(r_{NO_2-scr} + 0.5 r_{fast-scr}))$$

$$\frac{\partial c_{g,NH_3}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NH_3}}{\partial x} + \frac{\Omega}{\varepsilon}(r_{des} - r_{ads})$$

$$\frac{d\theta_{NH_3}}{dt} = r_{ads} - r_{des} - r_{NH_3,oxi} - r_{std-scr} - r_{NO_2-scr} - r_{fast-scr}$$

$$\frac{\partial c_{g,O_2}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,O_2}}{\partial x} - \frac{\Omega}{\varepsilon}(\frac{3}{4} r_{NH_{3,}oxi} + \frac{1}{4} r_{std-scr})$$

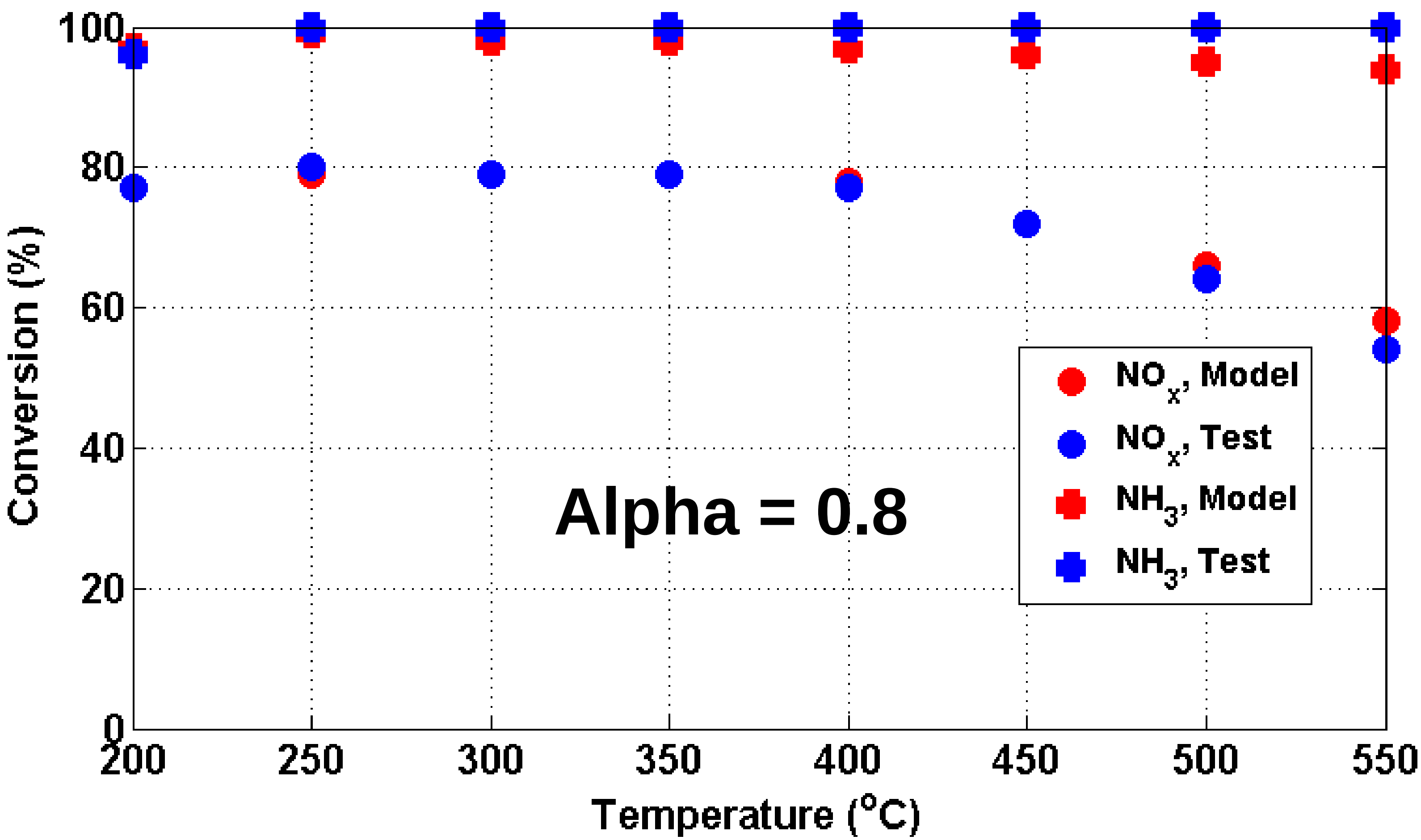
$$4NH_3.S + 2NO + 2NO_2 \rightarrow 4\,N_2 + 6H_2O + 4S$$

$$r_{fast-scr} = A_{fast-scr} e^{\frac{-E_{fast-scr}}{RT}} c_{g,NO} c_{g,NO_2} \theta_{NH_3}$$

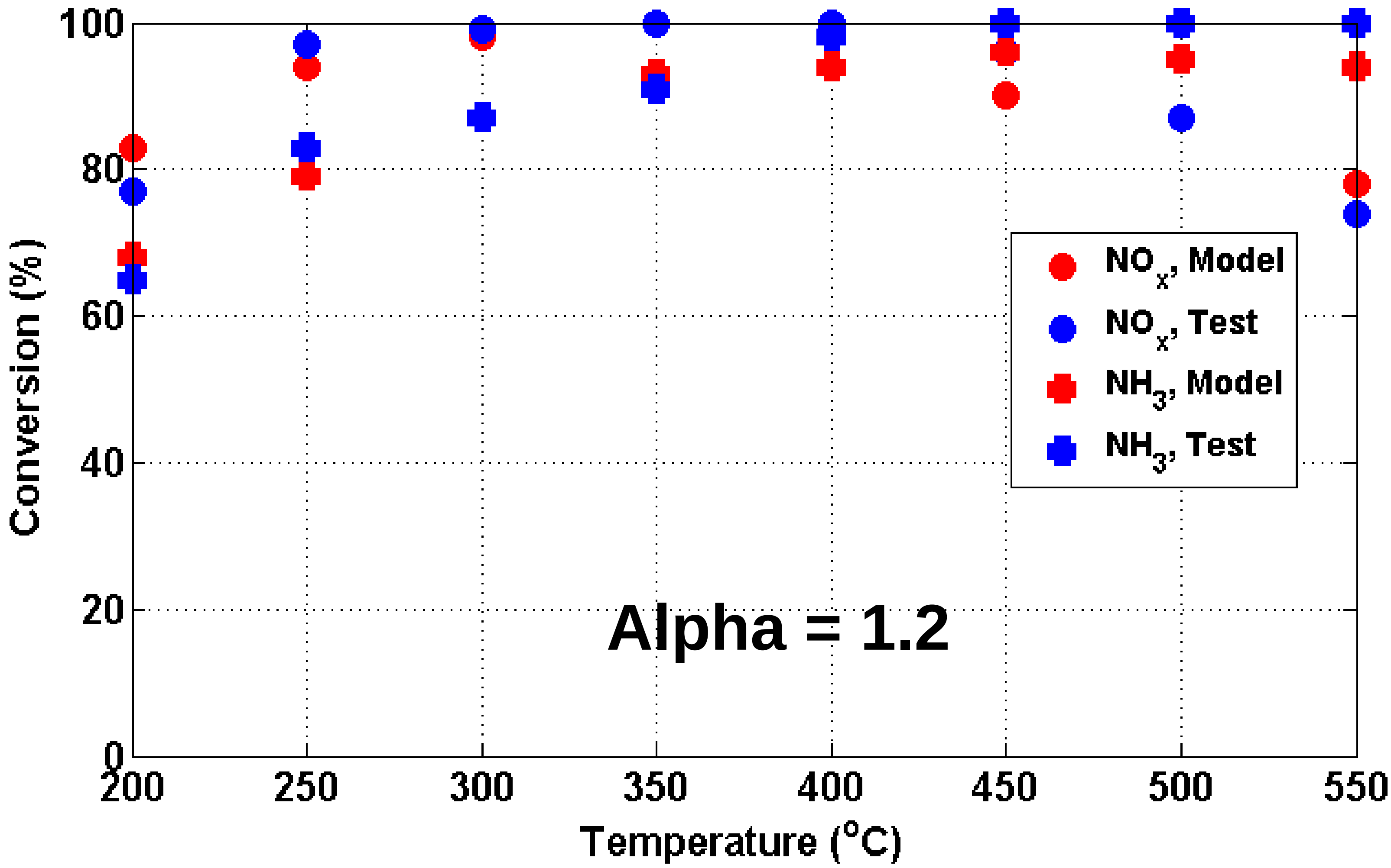
$A_{fast-scr}$ = 1.9E12 m^3/mol/s

$E_{fast-scr}$ = 85.1 kJ/mol

- **Model validation shown only for T > 150^{o}C due to poor model match with the test data at lower temperatures. Mis-match possibly due to the absence of nitrate formation kinetics, etc in the model.**
- **NO_2-SCR kinetic model included for better match at low temperatures. At high temperatures NO_2-SCR can be neglected.**
- **No parameter tuning was done – Fast SCR & NO_2-SCR parameters from Olsson et al., (2008) on Cu-Z SCR model were used in the model directly.**

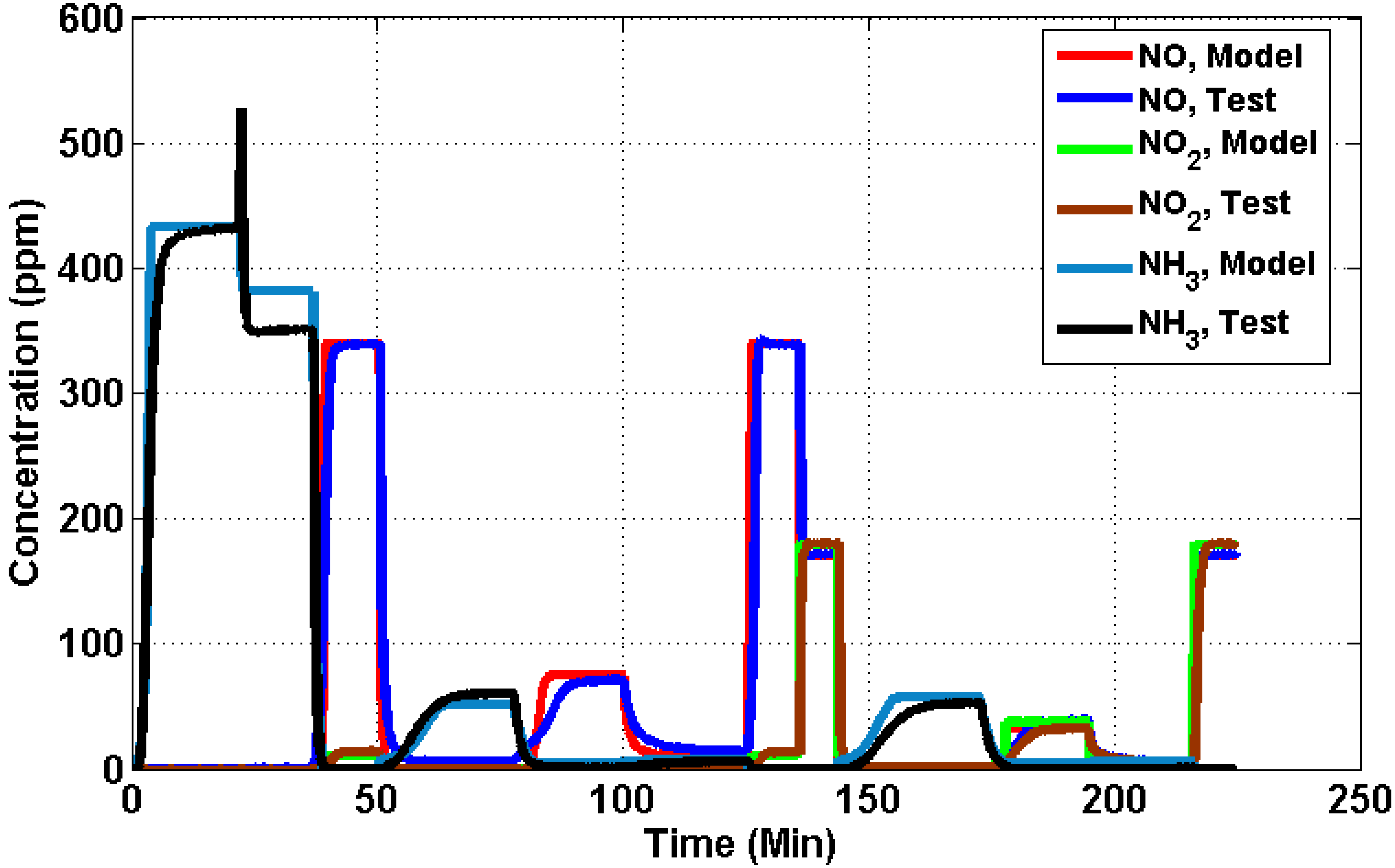


Alpha = 0.8
NO$_x$, Model
NO$_x$, Test
NH$_3$, Model
NH$_3$, Test
Conversion (%)
Temperature (°C)
0
20
40
60
80
100
200
250
300
350
400
450
500
550

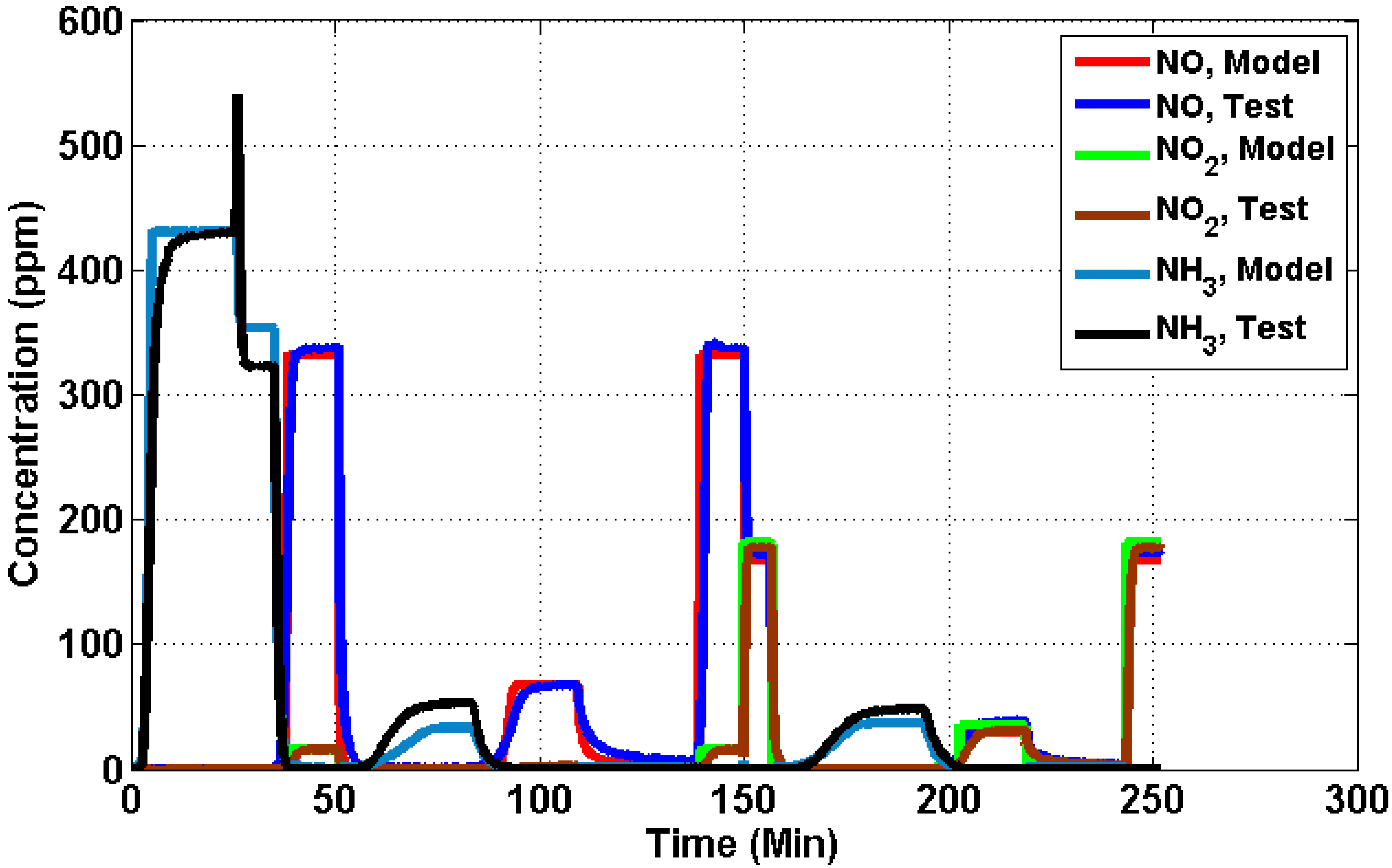


Conversion (%)
100
80
60
40
20
0
200
250
300
350
400
450
500
550
Temperature (°C)
NOx, Model
NOx, Test
NH3, Model
NH3, Test
Alpha = 1.2

Model Validation I: Protocol Run – 300ºC (90k/hr SV)



Model Validation II: Protocol Run – 300°C (60k/hr SV)



Rate Parameter Comparison

Reaction	E (kJ/mol)	E (kJ/mol) from Published Literature	Reference
✓**NH_3 Desorption**	180.2	181.5	Olsson, 2008
✓**NH_3 Oxidation**	74	68.7±6.3[1]	Kamasamudram, 2010
✓**NO Oxidation**	39	43	Chakravarthy, 2007
Standard SCR	84.9	84.9	Olsson, 2008
Fast SCR	85.1	85.1	Olsson, 2008

[1]Parameter reported on Fe-Z by Kamasamudram et al., Catalysis Today 151 (2010) 212-222

Summary

- Fresh commercial Cu zeolite shows:
  - wide operating window
  - SCR performance limited by NH_3 oxidation at high temperatures
  - low sensitivity to NO_2/NOx in feed
- Protocol transients generate vital information for model-based control design:
  - target NH_3 coverage for high NOx conversion
  - “usable” NH_3 storage
  - fractional catalyst utilization
- Baseline SCR model developed and validated against the reactor data for $0.8 \leq NH_3/NOx \leq 1.2$ and $30k \leq SV \leq 90k$
- Low temperature performance needs to be improved by incorporating global nitrate formation kinetics, N_2O formation and NO_2-SCR reaction

Next Steps

- Improve the baseline Cu SCR model prediction at lower temperatures
- Investigate the competitive adsorption kinetics on a model Cu/beta SCR catalyst through experiments and modeling
- Determine need for incorporating NO_2 SCR in protocol
- Investigate the effects of catalyst aging on the kinetic parameters and physicochemical properties of Cu SCR catalyst
- Identify critical rate/model parameters that need to be adapted for catalyst aging/deactivation and develop maps/math expressions to support model-based controls
- Incorporate the Cu SCR model into Autonomie for system-level performance simulation

Acknowledgments

- Ken Howden and Gurpreet Singh, DOE-OVT
- CLEERS Team
- Sanath Kumar and Pat Burks, BASF
- Giovanni Cavataio, Ford

Pacific Northwest NATIONAL LABORATORY | Institute for INTERFACIAL CATALYSIS

DEPARTMENT OF ENERGY • UNITED STATES OF AMERICA

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

CLEERS