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Global Kinetic SCR Model with Two Ammonia Storage Sites

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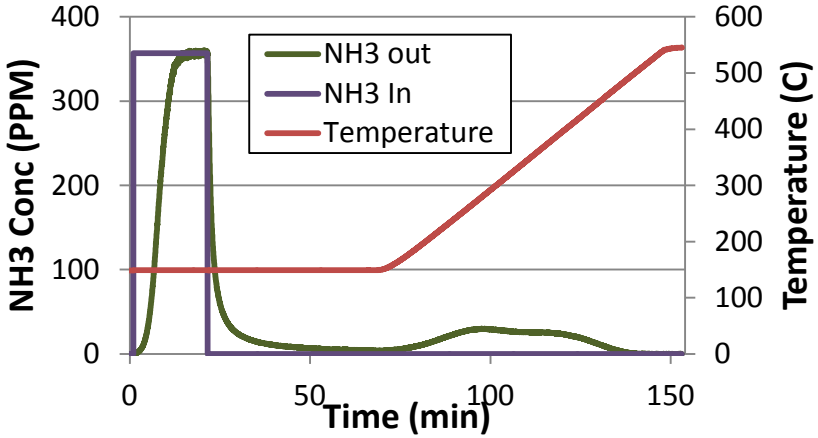
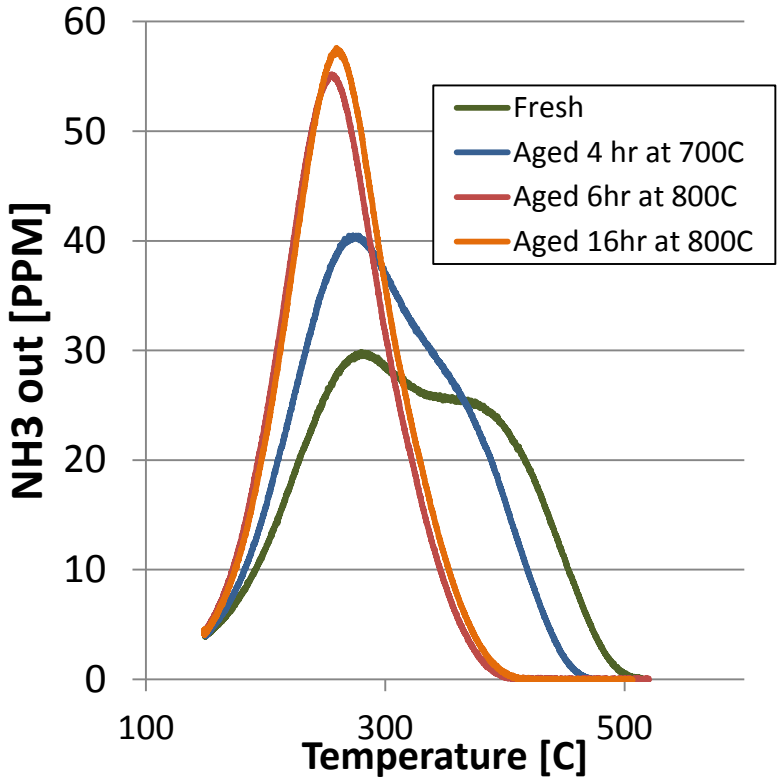
Two-site storage suggested by ORNL experiments



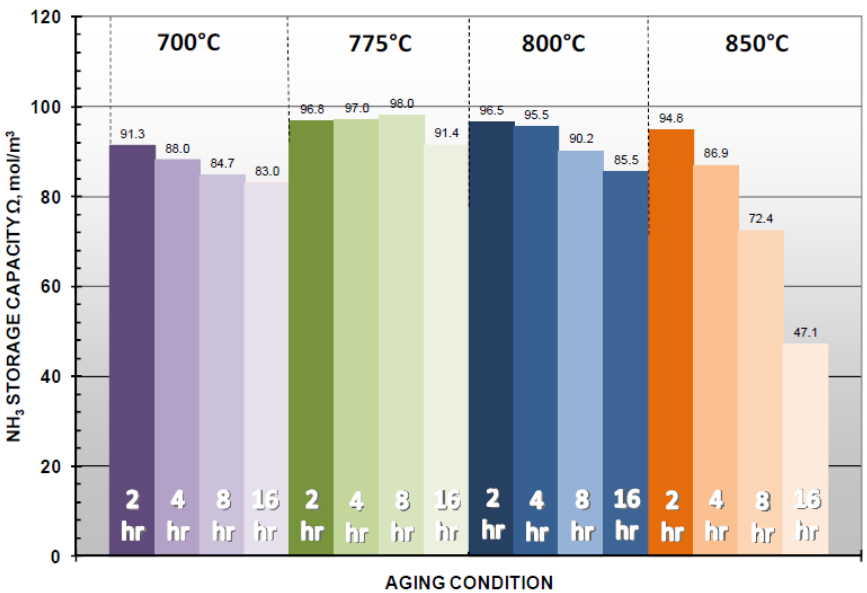


- ORNL kinetics experiments with current Cu-CHA SCR catalyst using TPD and the CLEERS transient SCR protocol
- TPD experiments with fresh and hydrothermally aged samples suggest two types of NH_3 storage sites
- Similar behavior has been observed with other SCR catalysts[1]
- During hydrothermal aging capacity seems to shift from one type of site the other
- A two site model was developed to describe observed changes in performance

[1] Olsson, L., H. Sjövall, and R.J. Blint, "A kinetic model for ammonia selective catalytic reduction over Cu-ZSM-5". *Applied Catalysis B: Environmental*, 2008. 81(3–4): p. 203-217 DOI: 10.1016/j.apcatb.2007.12.011.

Catalyst aging

- We are focusing on mild to moderate aging phenomena that happen between fresh catalyst, through de-greening, and up to 6 hr at 800°C
- Studies with GM have suggested that 16 hr hydrothermal aging at 800°C is representative of 135,000 miles on vehicle [2]
- This may be a separate effect from the reduction in total storage capacity observed by others under more severe aging conditions



[2] Schmieg, S.J., S.H. Oh, C.H. Kim, D.B. Brown, J.H. Lee, C.H.F. Peden, and D.H. Kim, "Thermal durability of Cu-CHA NH3-SCR catalysts for diesel NOx reduction". *Catalysis Today*, 2012. 184(1): p. 252-261 DOI: 10.1016/j.cattod.2011.10.034.

New Cu-zeolite aging data
Gordon Bartley, SWRI
2012 CLEERS Workshop

Modeling approach

- Several previously published models have tracked multiple adsorbed species and intermediates, and included fundamental reaction steps [3,4]
- Our goal was a simpler global kinetic model [1] where most of the rates represent overall reactions, combining intermediate steps
- Only ammonia storage sites were included in the model, and only NH_3 coverages were tracked
- Two NH_3 storage sites were included, using a storage model similar to that proposed by Colombo et al, 2012 [5]
- Kinetic parameters for storage are a compromise between fresh and aged datasets
- In general, our goal was the simplest model that would adequately describe data

[3] Sjövall, H., R.J. Blint, and L. Olsson, "Detailed kinetic modeling of NH3 SCR over Cu-ZSM-5". *Applied Catalysis B: Environmental*, 2009. 92(1–2): p. 138-153 DOI: http://dx.doi.org/10.1016/j.apcatb.2009.07.020.
[4] Colombo, M., I. Nova, and E. Tronconi, "Detailed kinetic modeling of the NH3-NO/NO2 SCR reactions over a commercial Cu-zeolite catalyst for Diesel exhausts after treatment". *Catalysis Today*, 2012. 197(1): p. 243-255 DOI: 10.1016/j.cattod.2012.09.002.
[5] Colombo, M., G. Koltsakis, I. Nova, and E. Tronconi, "Modelling the ammonia adsorption-desorption process over an Fe-zeolite catalyst for SCR automotive applications". *Catalysis Today*, 2012. 188(1): p. 42-52 DOI: 10.1016/j.cattod.2011.09.002.

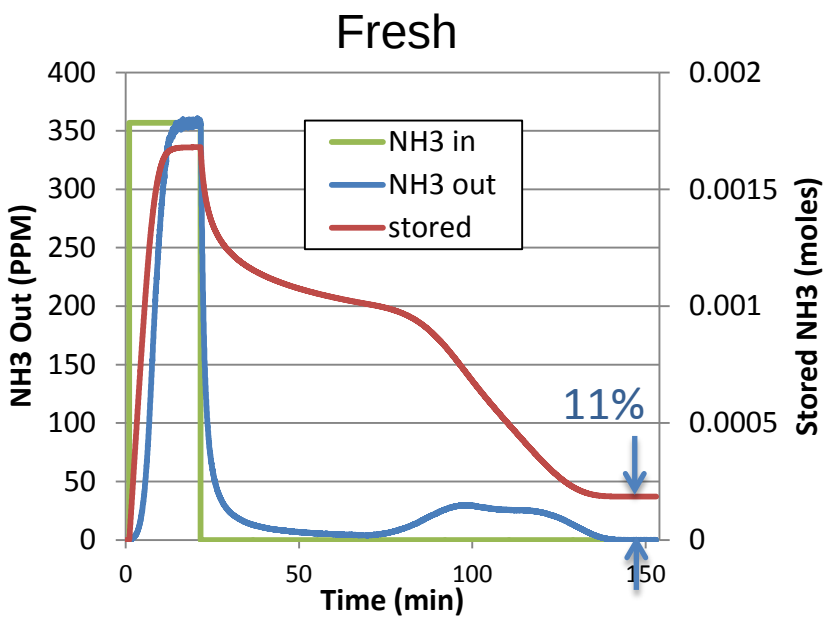
Model implementation

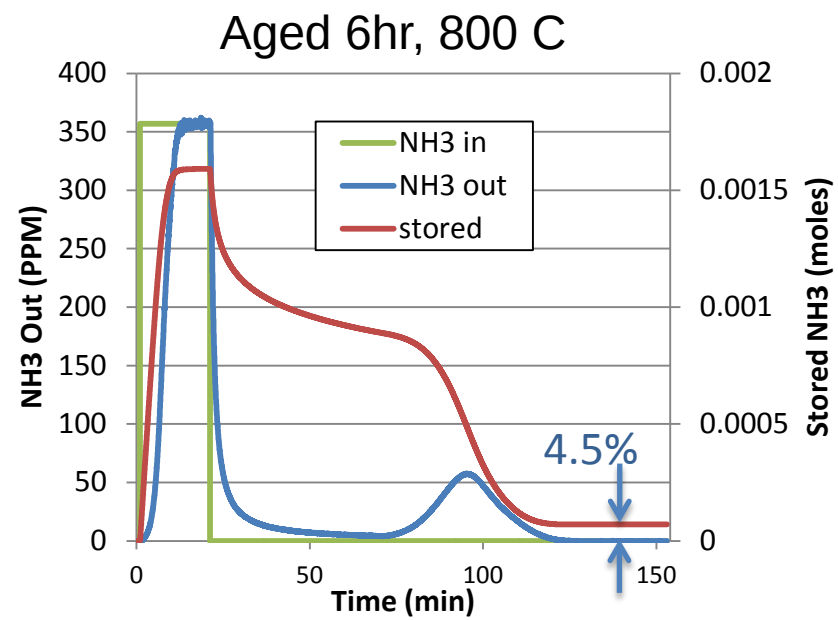
- As in most previous SCR models, PDEs are converted to ODEs using the Method of Lines and approximating the spatial derivatives
- Upwind differencing is used for advective terms
- Mat Lab is used to solve the resulting system of ODEs
- 40 axial nodes were used to model the small core in the results shown
- O_2 concentration is considered constant
- Our current model does not include transport resistances – either film resistance between channel and catalyst or resistance within the washcoat

Experimental

- Experiments conducted by Josh Pihl at ORNL using the latest CLEERS transient SCR protocol
- Monolith coated with commercial Cu-CHA catalyst taken from a new vehicle
- Cores cut from monolith - 2 cm diameter by 5 cm long
- 60,000 1/hr space velocity
- NO_X inlet concentration: 350 PPM
- NH_3/NO_X ratio for data shown: 1.0

NH_3 balance issues





- When outlet NH_3 concentration is integrated, some of the NH_3 originally absorbed is unaccounted for
- No O_2 present during storage experiments, so this can't be explained by the reactions in our simple model
- Loss of NH_3 was also observed recently by Colombo et al, 2012 [3]
- Since their experiment was run in Argon, they could see some of the NH_3 coming off as N_2 at the beginning of the TPD
- There is likely some oxidation by O_2 stored while cleaning the catalyst prior to the NH_3 storage experiment

Short-term solution to imbalance issue: simple decomposition reaction

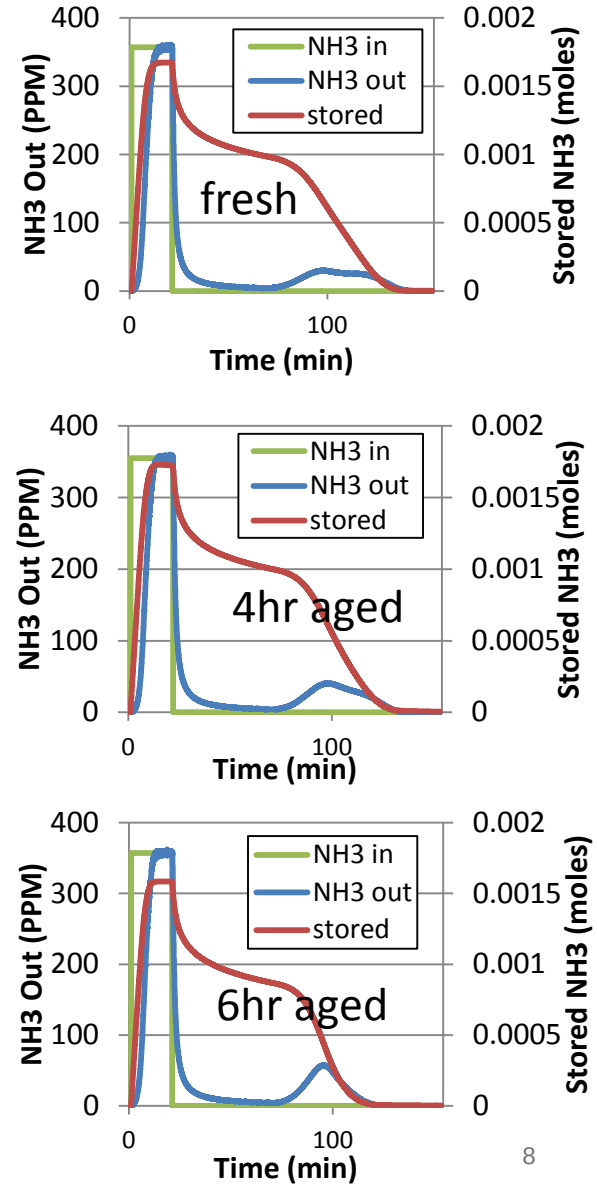
- Anaerobic decomposition of NH_3 over zeolite supported base-metal catalysts has been explored for hydrogen production (Choudhary et al, 2001 [6])
- Simple NH_3 decomposition model was used to account for the loss to enable modeling
- Current approach uses same kinetic parameters for all aging states
- Aged samples decompose less NH_3 because less remains adsorbed at high temperatures
- This reaction was **only** included in simulation of anaerobic storage experiments

NH_3 decomposition $\quad 2NH_3 \rightarrow N_2 + 3H_2$

$$r_{decomp,s1} = A_{decomp} e^{\frac{-E_{decomp}}{RT}} \theta_{NH_3,s1}$$

$$r_{decomp,s2} = A_{decomp} e^{\frac{-E_{decomp}}{RT}} \theta_{NH_3,s2}$$

Parameter	Units	Value
A_{decomp}	1/s	0.45
e_{decomp}	kJ/mol	40



[6] Choudhary, T.V., C. Sivadinarayana, and D.W. Goodman, "Catalytic ammonia decomposition: COx-free hydrogen production for fuel cell applications". *Catalysis Letters*, 2001. 72(3-4): p. 197-201 DOI: 10.1023/a:1009023825549.

Two site NH_3 storage model

$$\frac{\partial c_{g,NH_3}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NH_3}}{\partial x} + \frac{\Omega_1}{\varepsilon}(r_{des,s1} - r_{ads,s1}) + \frac{\Omega_2}{\varepsilon}(r_{des,s2} - r_{ads,s2})$$

$$\frac{d\theta_{NH_{3,s1}}}{dt} = r_{ads,s1} - r_{des,s1}$$

$$\frac{d\theta_{NH_{3,s2}}}{dt} = r_{ads,s2} - r_{des,s2}$$

Form of storage model similar to Colombo et al, 2012 [4]

Parameter	Units	Site 1	Site 2
$A_{ads,s}$	m^3/mol/s	1.4	1.0
$A_{des,s}$	1/s	8.536E+3	2.4E+4
$e_{ads,s}$	kJ/mol	69.0	93.0
γ		0.216	0.080

Site 1 (Weakly Adsorbed)

$$r_{ads,s1} = A_{ads,s1} c_{g,NH_3}(1-\theta_{NH_3,s1})$$

$$r_{des,s1} = A_{des,s1} e^{\frac{-E_{des,s1}(1-\gamma_1\theta_{NH_3,s1})}{RT}} \theta_{NH_3,s1}$$

Site 2 (Strongly Adsorbed)

$$r_{ads,s2} = A_{ads,s2} c_{g,NH_3}(1-\theta_{NH_3,s2})$$

$$r_{des,s2} = A_{des,s2} e^{\frac{-E_{des,s2}(1-\gamma_2\theta_{NH_3,s2})}{RT}} \theta_{NH_3,s2}$$

- As in most previously published models, we assume an un-activated adsorption reaction
- We gave ourselves the ability to include a small coverage dependence on the strongly adsorbed site

Current best fits of storage data

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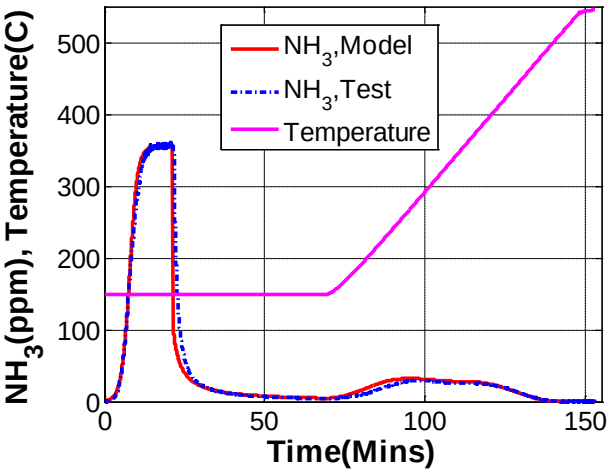
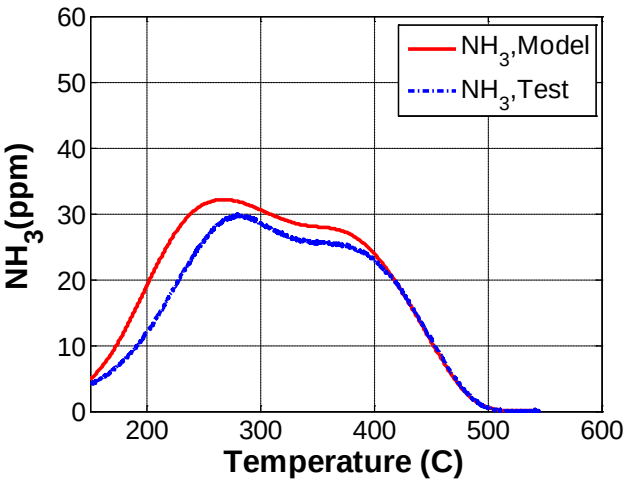
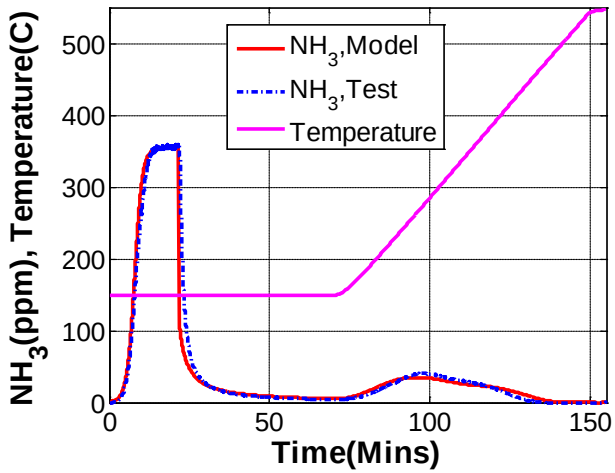
fresh

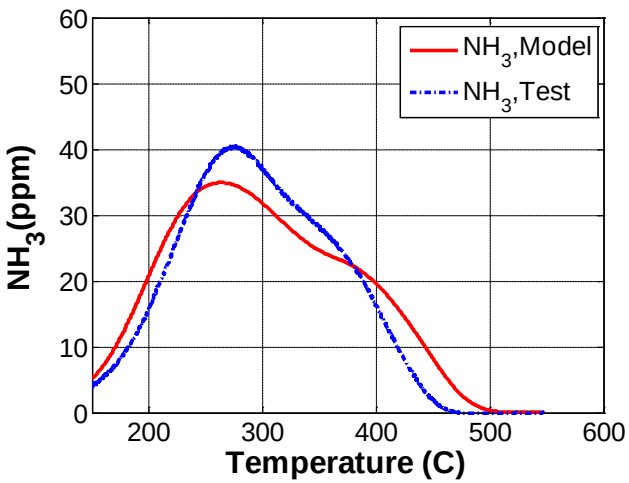




Max stored: 111 mol/m3
Decomposed: 11.5%

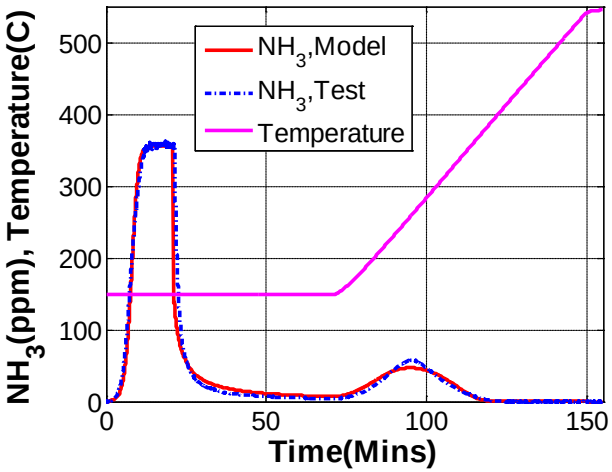
4 hr at 700 C

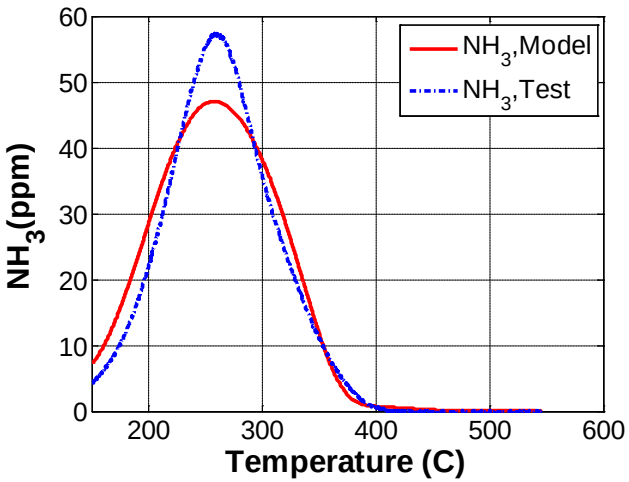




Max stored: 111 mol/m3
Decomposed: 9.7%

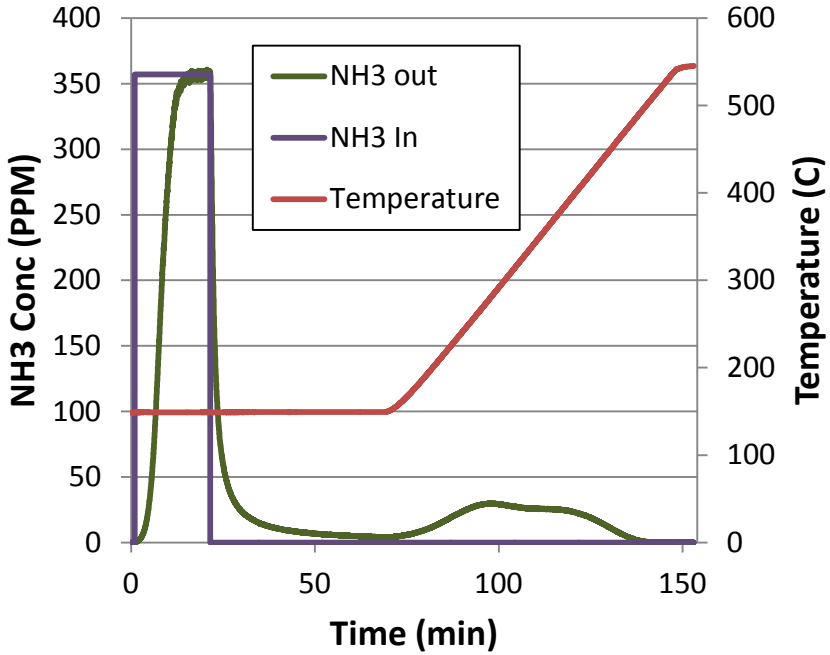
6 hr at 800 C

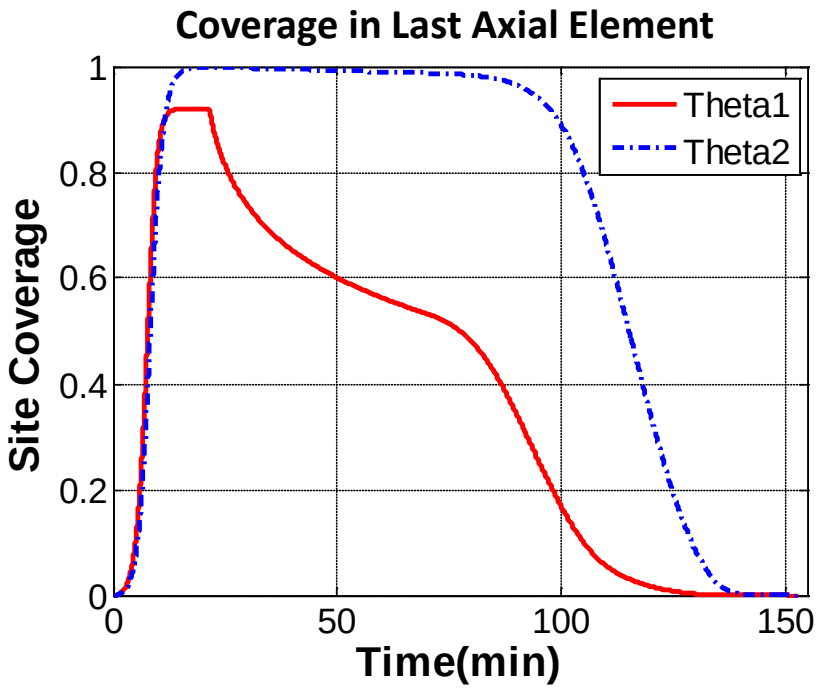




Max stored: 114 mol/m3
Decomposed: 3.8%

Coverage on two sites as a function of time - fresh catalyst





- Theta 1 does not reach 100% because of coverage dependence
- Much of the NH_3 weakly adsorbed on the type 1 site is released when the inlet concentration drops to zero
- NH_3 strongly bound on the type 2 site remains until TPD

Current best fits of storage data

$$\Omega_1 + \frac{\Omega_2}{0.92} = const$$

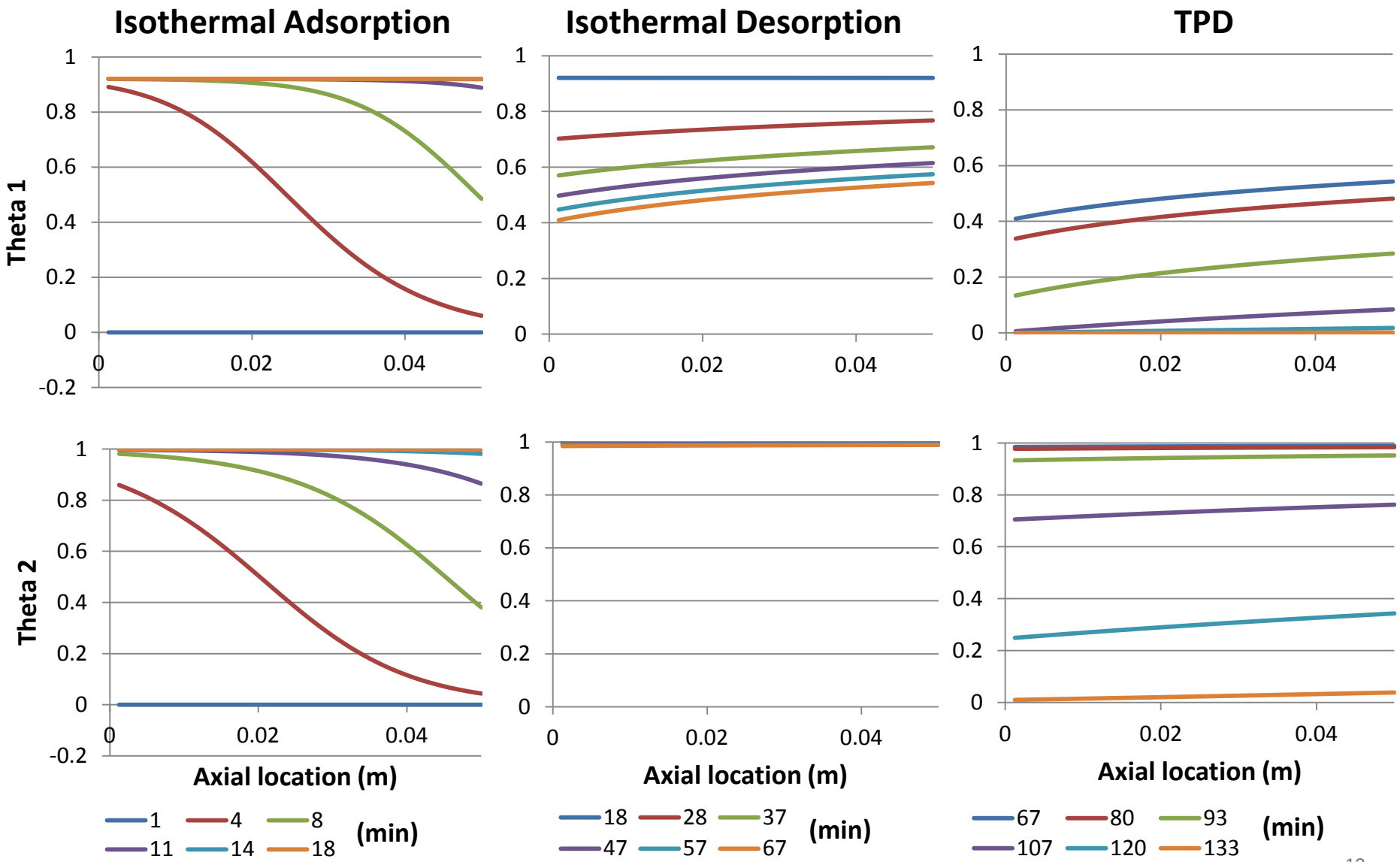
- 0.92 is the approximate coverage of the type 2 sites at saturation (<1.0 because of coverage dependence)

- Current compromise actually results in slight increase in storage instead of decrease during aging
  - Could change conversion rules so that total capacity decreases, but that would make the aged TPD peak even shorter
  - Hard to make the aged TPD peak narrower while still providing a good match to isothermal desorption
- Note that Ω sometimes denotes total storage - here it is maximum potential storage for a given site
- Better fits may still be possible with this scheme

State	Ω_1	Ω_2
fresh	75.6	39.6
aged 4 hr at 700 C	84.4	31.5
aged 6 hr at 800 C	117.5	1.0

Ω values are given in mol/m^3 monolith

Transient coverage along axial length - fresh catalyst



Modeling reactions relevant to SCR

- Two-site kinetic models were also developed for various reactions which determine SCR performance – tuned from steady state conversions at various temperatures
- Values of kinetic parameters for the two sites are kept the same for all aging states – only the proportions of the two sites change
- The proportions of the two sites are essentially used as an index to describe various changes in surface processes that may happen over the course of mild aging
- So far, the kinetic parameters have been tuned against the data from fresh and 6 hr aged data. They have not yet been checked against reaction data from the sample aged 4 hrs at 700°C.

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

- The current simple model does not include:
  - N_2O formation
  - NO formation by NH_3 oxidation
  - NH_4NO_3 formation or decomposition
  - NO_2 SCR

NH_3 oxidation reaction

$$\frac{\partial c_{g,NH_3}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NH_3}}{\partial x} + \frac{\Omega_1}{\varepsilon}(r_{des,s1} - r_{ads,s1} - r_{NH_3oxi,g1}) + \frac{\Omega_2}{\varepsilon}(r_{des,s2} - r_{ads,s2} - r_{NH_3oxi,g2})$$

$$\frac{d\theta_{NH_{3,s1}}}{dt} = r_{ads,s1} - r_{des,s1}$$

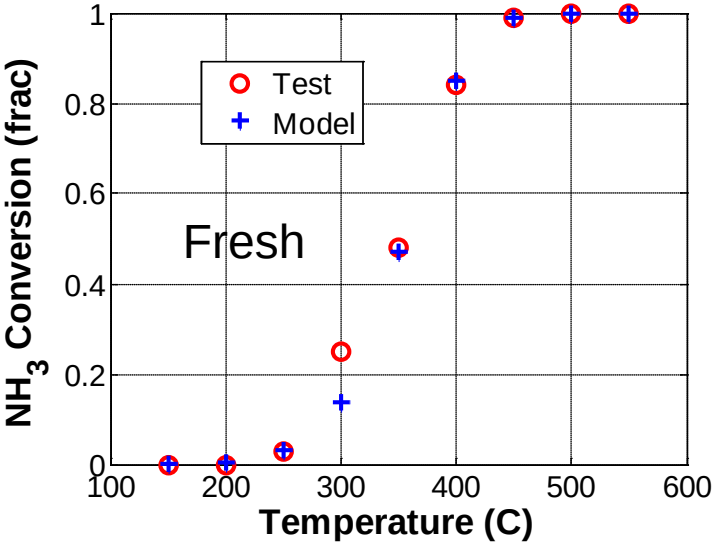
$$\frac{d\theta_{NH_{3,s2}}}{dt} = r_{ads,s2} - r_{des,s2} - r_{NH_3oxi,s2}$$

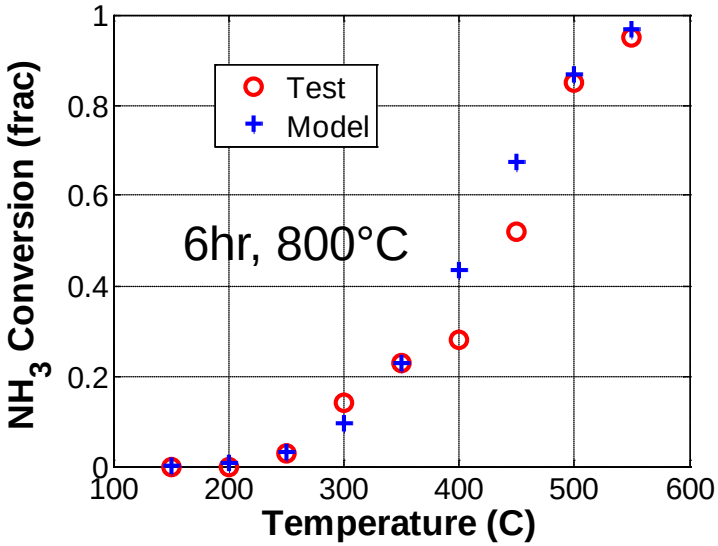
$$r_{NH_3oxi,g1} = k_{NH_3oxi,g1} c_{g,O_2} c_{g,NH_3}$$

$$r_{NH_3oxi,s2} = k_{NH_3oxi,s2} c_{g,O_2} \theta_{NH_3,s2}$$

$$r_{NH_3oxi,g2} = k_{NH_3oxi,g2} c_{g,O_2} c_{g,NH_3}$$

- Because of very low surface coverages, at high temperatures, we found it necessary to include rates based on gas concentrations as in Sjövall et al, 2010 [6]
- Ability of model to match standard SCR experiments also depends upon the form of the NH_3 oxidation model





[6] Sjövall, H., R.J. Blint, A. Gopinath, and L. Olsson, "A Kinetic Model for the Selective Catalytic Reduction of NOx with NH3 over an Fe-zeolite Catalyst". *INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH*, 2010. 49(1): p. 39-52 DOI: 10.1021/ie9003464.

NO oxidation reaction

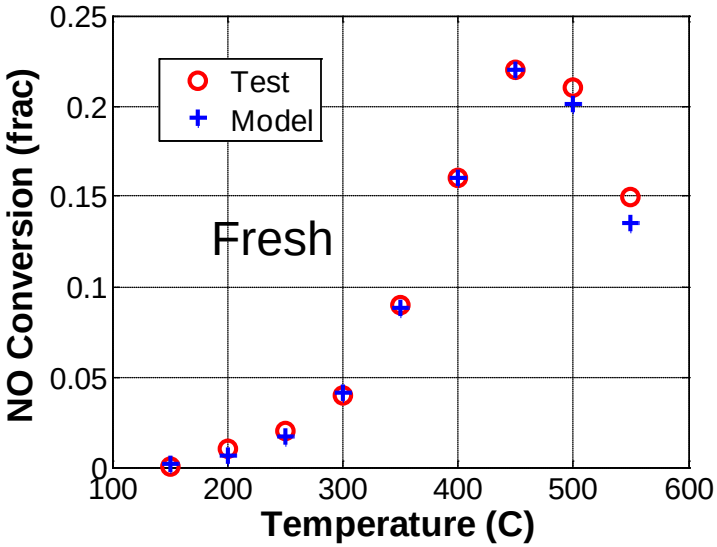
$$\frac{\partial c_{g,NO}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NO}}{\partial x} - \frac{\Omega_1}{\varepsilon}(r_{NO-oxi,g1}) - \frac{\Omega_2}{\varepsilon}(r_{NO-oxi,g2})$$

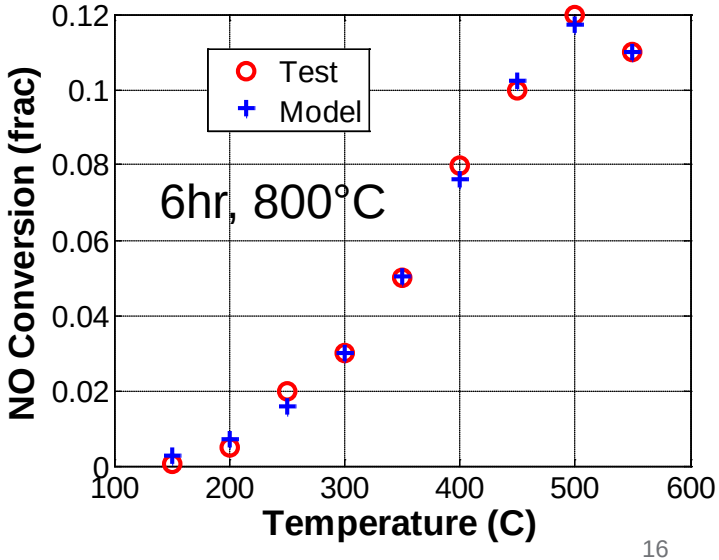
$$\frac{\partial c_{g,NO_2}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NO_2}}{\partial x} + \frac{\Omega_1}{\varepsilon}(r_{NO-oxi,g1}) + \frac{\Omega_2}{\varepsilon}(r_{NO-oxi,g2})$$

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

- NO oxidation model assumes no NO_2 inhibition

Parameter	Units	Site 1	Site 2
$A_{NH3oxi,s}$	$m^3/mol/s$		2.118E+6
$e_{NH3oxi,s}$	kJ/mol		108.07
$A_{NH3oxi,g}$	$m^6/mol^2/s$	2.150E+4	3.244E+9
$e_{NH3oxi,g}$	kJ/mol	71.95	126.25
$A_{NO-oxi,g}$	$m^{9/2}/mol^{3/2}/s$	21.63	1.449E+4
$e_{NO-oxi,g}$	kJ/mol	38.93	66.00





Kinetic models including SCR reactions

$$\frac{\partial c_{g,NH_3}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NH_3}}{\partial x} + \frac{\Omega_1}{\varepsilon}(r_{des,s1} - r_{ads,s1} - r_{NH_3oxi,g1}) + \frac{\Omega_2}{\varepsilon}(r_{des,s2} - r_{ads,s2} - r_{NH_3oxi,g2} - r_{std-scr,g2})$$

$$\frac{\partial c_{g,NO}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NO}}{\partial x} + \frac{\Omega_1}{\varepsilon}(-r_{NO-oxi,g1} - r_{std-scr,s1} - \frac{1}{2}r_{fast-scr,s1}) + \frac{\Omega_2}{\varepsilon}(-r_{NO-oxi,g2} - r_{std-scr,s2} - r_{std-scr,g2} - \frac{1}{2}r_{fast-scr,s1})$$

$$\frac{\partial c_{g,NO_2}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NO_2}}{\partial x} + \frac{\Omega_1}{\varepsilon}(r_{NO-oxi,g1} - \frac{1}{2}r_{fast-scr,s1}) + \frac{\Omega_2}{\varepsilon}(r_{NO-oxi,g2} - \frac{1}{2}r_{fast-scr,s1})$$

$$\frac{d\theta_{NH_{3,s1}}}{dt} = r_{ads,s1} - r_{des,s1} - r_{std-scr,s1} - r_{fast-scr,s1}$$

$$\frac{d\theta_{NH_{3,s2}}}{dt} = r_{ads,s2} - r_{des,s2} - r_{NH_3oxi,s2} - r_{std-scr,s2} - r_{fast-scr,s2}$$

$$r_{std-scr,s1} = A_{std-scr,s1} e^{\frac{-E_{std-scr,s1}}{RT}} c_{g,NO}\theta_{NH_3,s1}$$

$$r_{std-scr,s2} = A_{std-scr,s2} e^{\frac{-E_{std-scr,s2}}{RT}} c_{g,NO}\theta_{NH_3,s2}$$

$$r_{std-scr,g2} = A_{std-scr,g2} e^{\frac{-E_{std-scr,g2}}{RT}} c_{g,NO}c_{g,NH_3}$$

$$r_{fast-scr,s1} = A_{fast-scr,s1} e^{\frac{-E_{fast-scr,s1}}{RT}} c_{g,NO}c_{g,NO_2}\theta_{NH_3,s1}$$

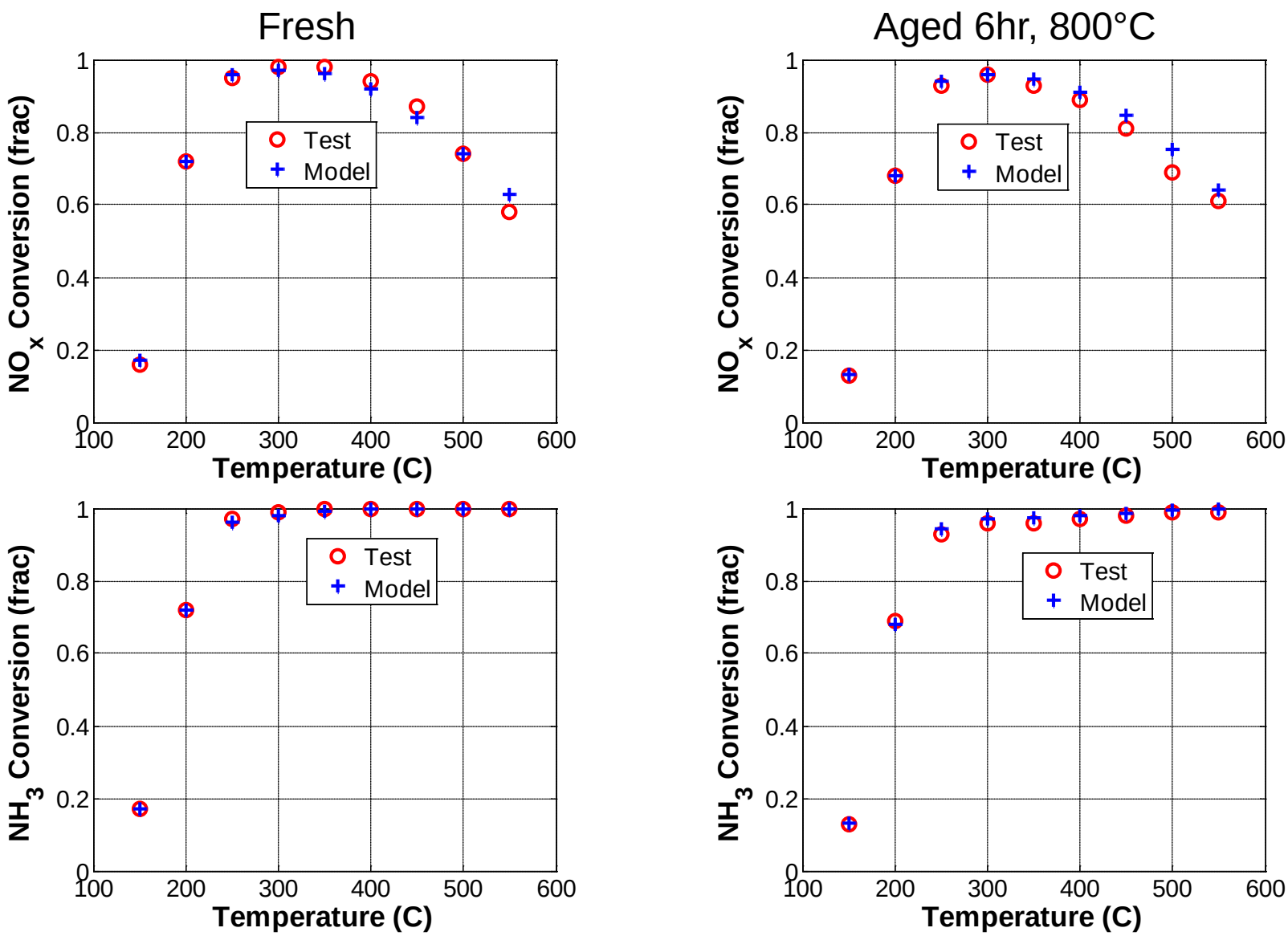
$$r_{fast-scr,s2} = A_{fast-scr,s2} e^{\frac{-E_{fast-scr,s2}}{RT}} c_{g,NO}c_{g,NO_2}\theta_{NH_3,s2}$$

Parameter	Units	Site 1	Site 2
$A_{std\text{-}scr,s}$	$m^3/mol/s$	1.796E+9	2.565E+16
$e_{std\text{-}scr,s}$	kJ/mol	89.93	153.9
$A_{std\text{-}scr,g}$	$m^6/mol^2/s$		2.648E+8
$e_{std\text{-}scr,g}$	kJ/mol		61.56
$A_{fast\text{-}scr,s}$	$m^6/mol^2/s$	1.9E+12	1.9E+12
$e_{fast\text{-}scr,s}$	kJ/mol	85.0	85.0

Kinetic models including SCR reactions

- As with the NH_3 oxidation reactions, some standard SCR rates are a function of gas phase NH_3 concentrations after Sjövall et al, 2010 [6]
- Where a reaction rate depends upon a surface concentration, moles consumed are removed from the respective site
- Where rates depend upon gas phase concentrations, moles consumed are removed from the gas
- Note that all changes to gas phase concentrations are keyed to Ω values for one site or the other, even where rate equations do not depend upon surface coverages
  - Ωs serve to quantify the amount of catalyst present
  - For reactions that take place on other sites, we are essentially assuming a fixed ratio between the reaction sites and NH_3 storage sites
- Although the fast SCR reaction was included in modeling of the standard SCR experiments, the kinetic parameters were not tuned – instead, parameter values from Olsson et all, 2008 [1] were used for both sites

Results for standard SCR reaction



Kinetic from gas and surface concentrations

- Various combinations were tried for reactions based on surface and gas concentrations
- The set shown gave us the best match for our data sets
- Generality of this scheme must be verified using additional validation experiments
- The model could be further simplified at the expense of lower accuracy across the temperature range
- Alternately, perhaps the addition of other reactions would allow elimination of some of those used and provide a more realistic structure

Reaction	Site	Surface	Gas
NO oxidation	1		●
	2		●
NH3 oxidation	1	●	●
	2		●
Standard SCR	1	●	
	2	●	●

Summary

- A two-site global kinetic model has been developed to describe NH_3 storage and SCR reactions on fresh to moderately aged samples of a current commercial Cu-CHA catalyst
- The model can describe the basic shapes of isothermal adsorption/desorption curves and TPD peaks
- Kinetic parameters were fit to describe NH_3 oxidation, NO oxidation, and standard SCR reactions
- The current model could be useful for some applications with little NO_2 present
- It may be possible to extend the modeling approach to a broader range of aging states and conditions including NO_2

Future steps

- Try adapting model to describe Fast SCR, NO_2 SCR experiments
- Consider adding other reactions
  - NH_4NO_3 formation
  - N_2O formation
- Evaluate model conversion predictions against CLEERS SCR protocol data from 'de-greened' sample aged 4 hrs at 700°C
- Try to extend model to fit data from more sample more severely aged at 800°C for 16 hrs
- Add option for film resistance
- Evaluate model against transient data from CLEERS SCR protocol
- Consider running additional experiments for validation
  - Vary space velocity
  - Vary NH_3/NO_X ratio
  - SpaciMS could be used to compare concentrations along the channels to model predictions
- Improve fidelity of method to account for loss of NH_3 during storage experiments (decomposition/oxidation)

Questions for the audience

- Should we be concerned with changes in NH_3 storage behavior that happen over the first ~50,000 miles of a vehicle's life?
- What if these changes in storage behavior are not attended by dramatic changes in steady state NO_X reduction performance?
- Are changes in NH_3 oxidation rates (measured without NO_X present) important, even if they don't seem to significantly impact steady state NO_X reduction?