# Measuring the impacts of catalyst state on $NH_3$ adsorption in copper zeolite SCR catalysts

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presentation to:

2015 DOE Crosscut Lean/Low-temperature Exhaust Emissions Reduction Simulation (CLEERS) Workshop

*Dearborn, MI*

April 27, 2015

ORNL is managed by UT-Battelle
for the US Department of Energy

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# Acknowledgements

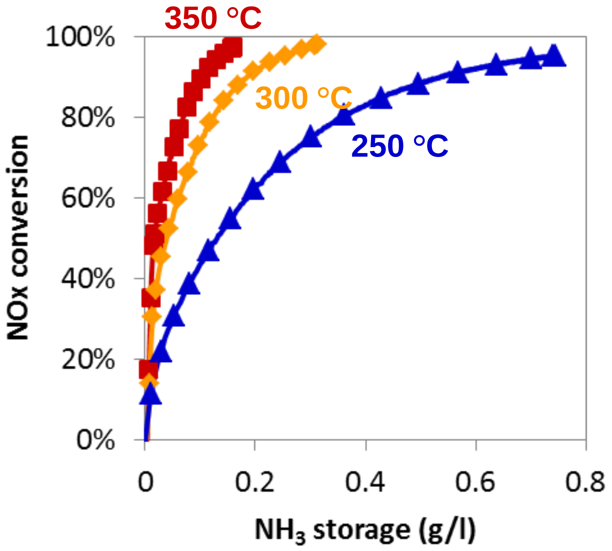
- **Funding from the Department of Energy Vehicle Technologies Office**
  - *Ken Howden, Gurpreet Singh, Leo Breton*

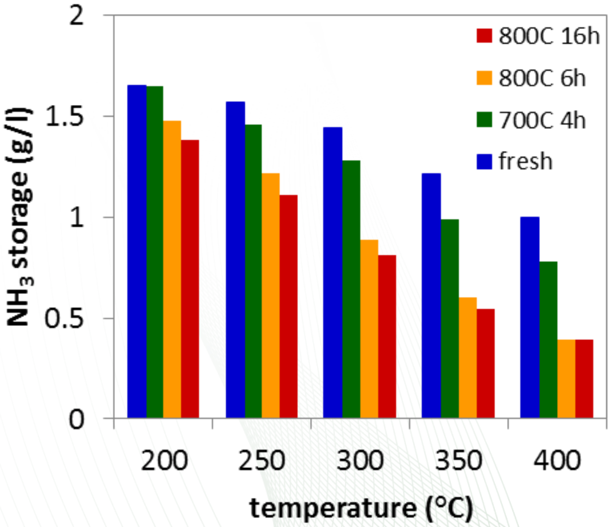
- **Collaboration with Pacific Northwest National Laboratory**
  - *Mark Stewart, George Muntean, Chuck Peden*

- **Interactions with coworkers at Fuels, Engines, and Emissions Research Center**
  - *Todd Toops, Bill Partridge, Jae-Soon Choi, Vitaly Prikhodko, Jim Parks*

# Accurate models of $NH_3$ storage needed to develop high NOx conversion SCR systems

- CLEERS 2013 Industry Priority Survey: $NH_3$ storage, oxidation, and release ranked as a high priority topic
  - #1 of 7 urea SCR topics, 12 NOx control topics
  - #3 of all 32 survey topics
- Catalyst $NH_3$ inventory must be managed:
  - high $NH_3$ coverages required for high NOx conversion
  - excess $NH_3$ leads to slip, wasted reductant
  - critical for approaches based on $NH_3$ production/ consumption cycles (passive SCR, LNT-SCR)
- Inventory managed through dosing/control strategies
  - often built from simulation tools
  - require accurate $NH_3$ storage models
- Challenge: $NH_3$ storage capacity varies significantly with gas composition, temperature, and catalyst age
  - high T capacity drops by half after 16 h at 800 °C (roughly equivalent to LD vehicle full useful life[*])

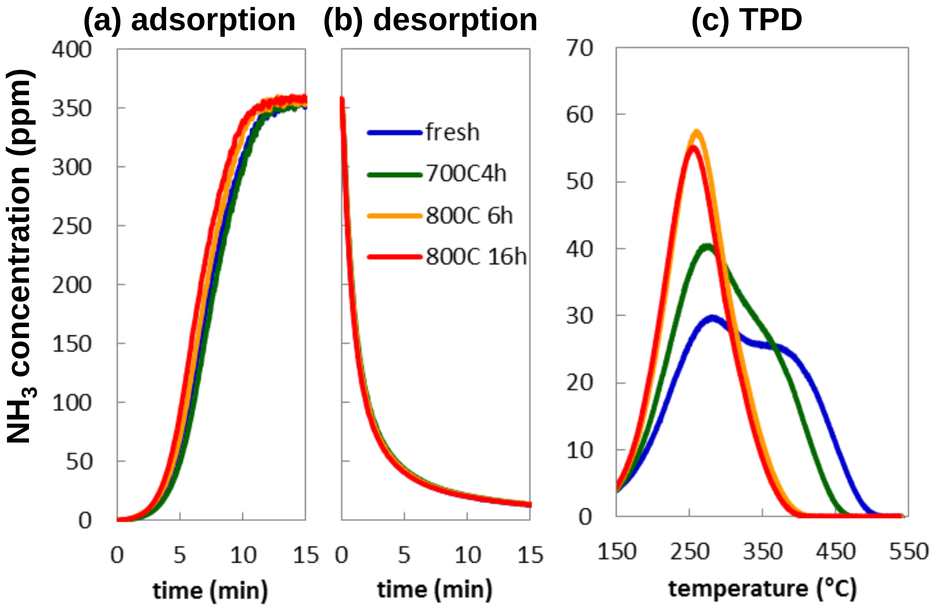


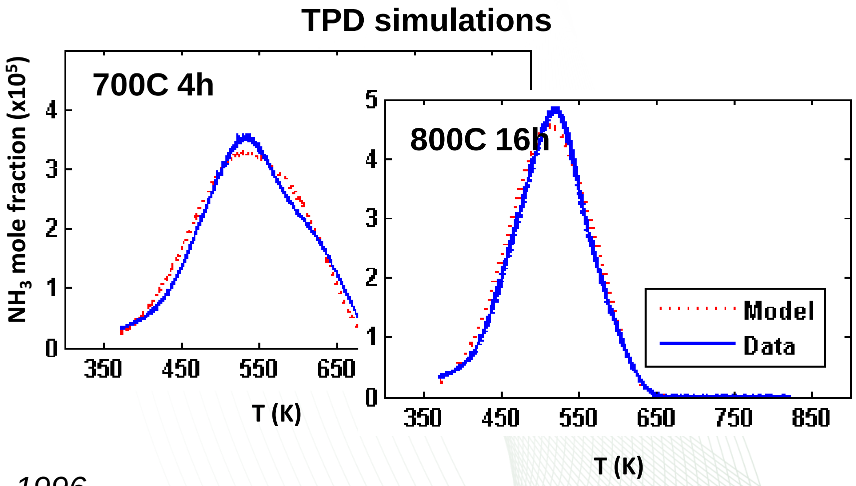


[*] S. Schmieg, S. Oh, C. Kim, D. Brown, J. Lee, C. Peden, D. Kim, *Catal. Today, 184, 252-261, 2011.*

# Common approaches for measuring and modeling $NH_3$ storage create challenges during calibration

- Standard experimental protocols* rely on transient operating conditions, confounding:
  - thermodynamics
  - kinetics
  - transport processes
- Uncertainty regarding model strategies
  - number of $NH_3$ storage sites
  - energetics of adsorption at each site
    - Langmuir, Temkin, Freundlich ...
- Complicated data sets and uncertain model structures generate too many degrees of freedom during parameter estimation
  - easy to generate "reasonable" fits to data
  - resulting parameters neither unique nor globally valid


(a) adsorption (b) desorption (c) TPD


TPD simulations

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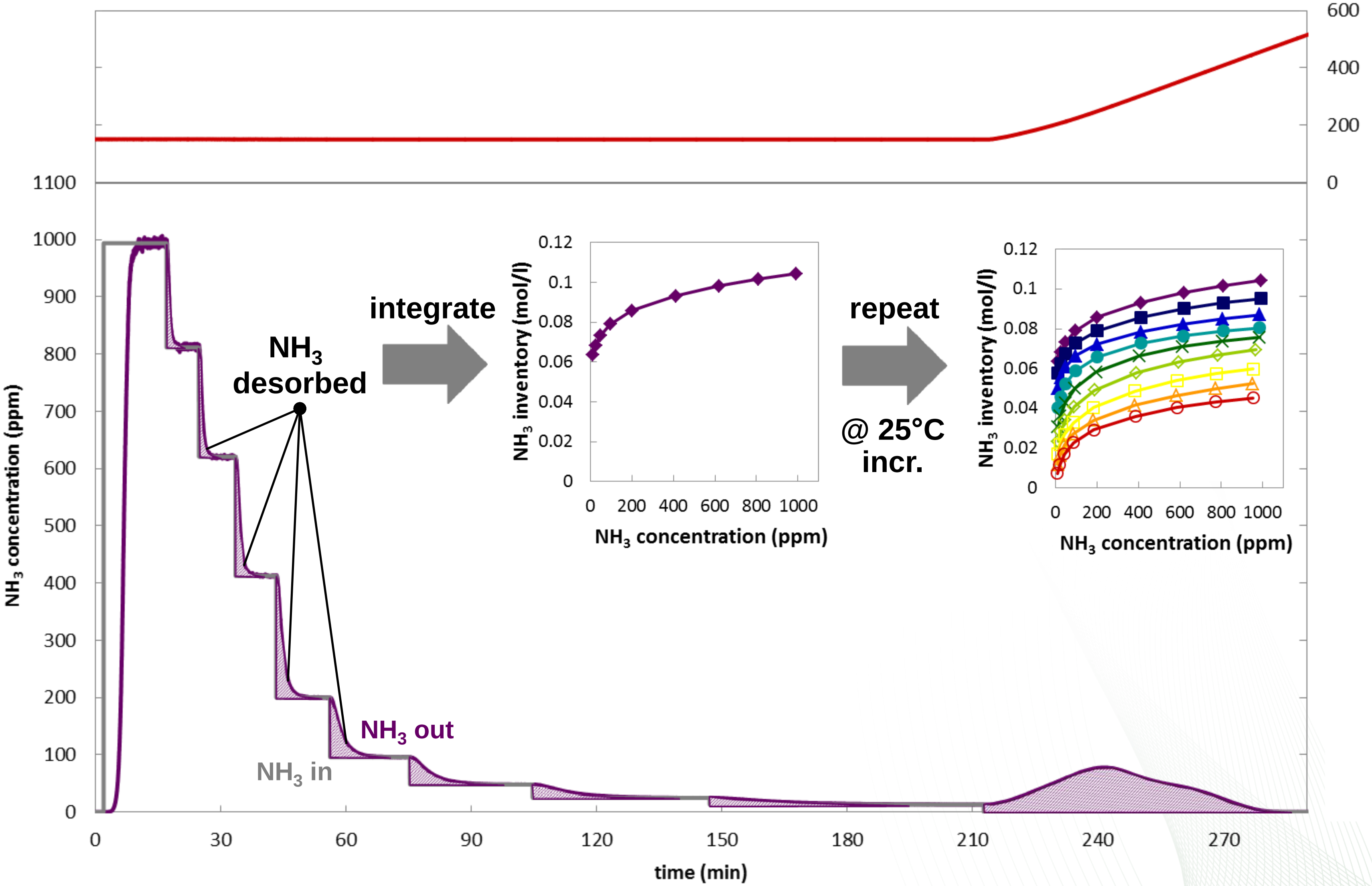
*E. Tronconi, L. Lietti, P. Forzatti, S. Malloggi, Chem. Eng. Sci. 51, 2965, 1996*

# Experiment for measuring equilibrium $NH_3$ adsorption isotherms quantifies $NH_3$ inventories and desorption rates

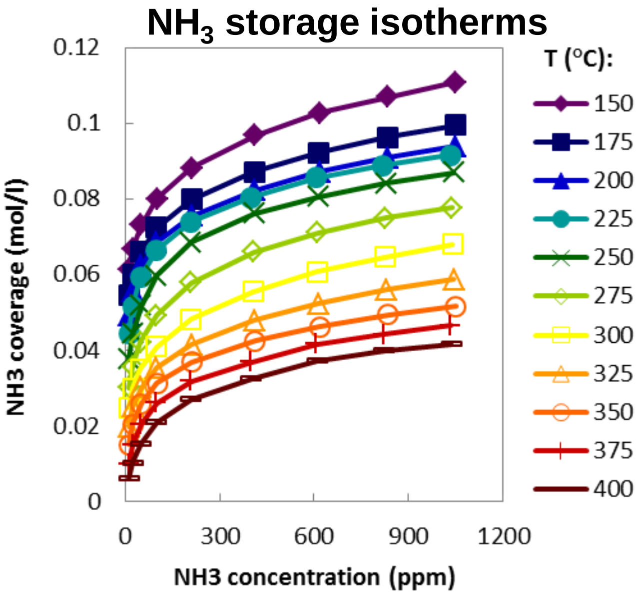


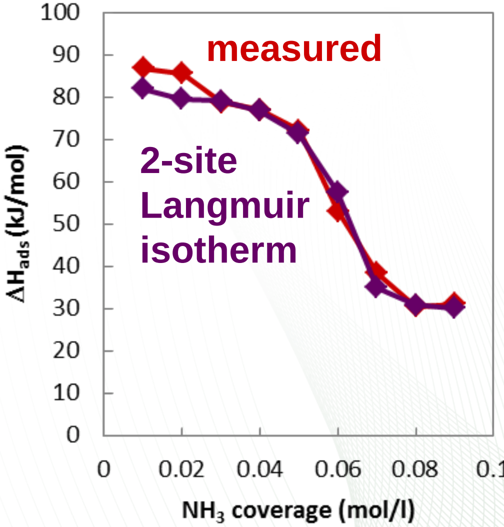
# Steady state isotherms and thermodynamic analysis isolate SCR $NH_3$ adsorption energetics, guide model development

- Measure steady state $NH_3$ adsorption isotherms with stepwise isothermal desorption experiments
- Extract adsorption enthalpies with standard thermodynamic relation (Clausius-Clapeyron)

$$\frac{d\left(\ln P_{NH_3}\right)}{d\left(\frac{1}{T}\right)} = \frac{\Delta H_{ads}}{R}$$

- Use $\Delta H_{ads}$ vs. $NH_3$ coverage to characterize storage sites and identify modeling strategies:
  - number of sites
  - relative abundance of sites
  - energetics of adsorption at each site

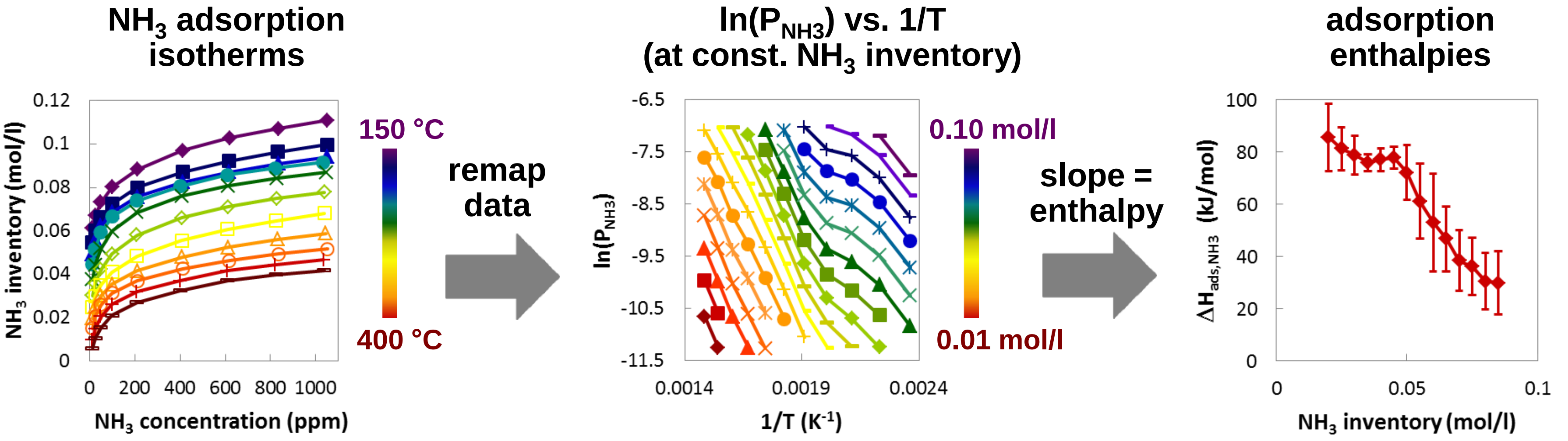




*Cu-SSZ-13*
*degreened*
*700 °C 4 h*

*60000 $h^{-1}$*
*150-400 °C*
*variable $NH_3$*
*5% $H_2O$*

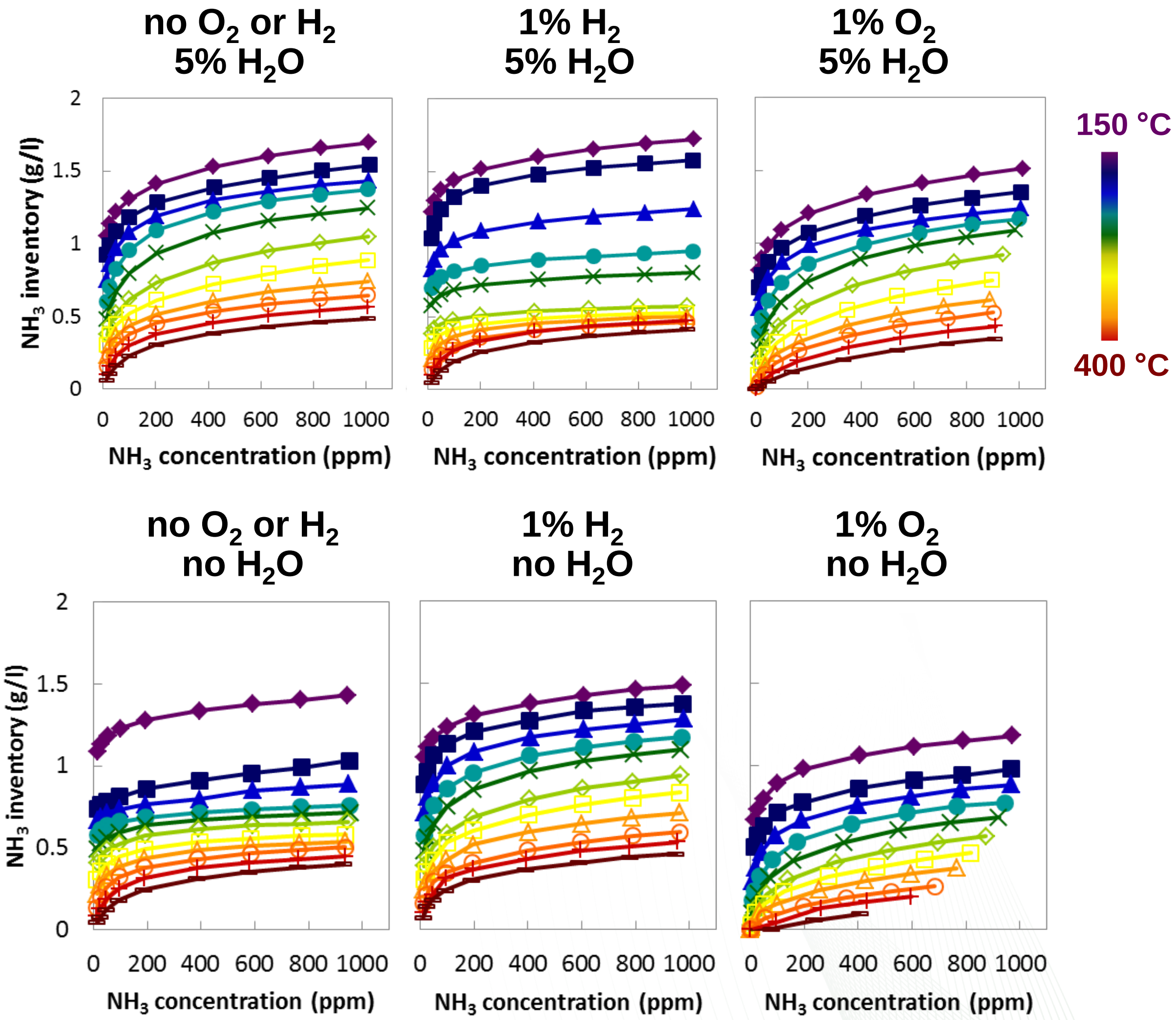
# Estimation of uncertainty in calculated adsorption enthalpy highlights need for improvements in experimental protocol



- Adsorption enthalpy calculated from slope of $\ln(P_{NH3})$ vs. 1/T
  - note: simple isotherms predict straight lines
- 95% confidence intervals estimated from error on linear regression slope
  - nonlinearity increases uncertainty in estimated enthalpies & modeling approach
- Potential sources of nonlinearity/uncertainty:
  - changes in catalyst oxidation state
  - $H_2O$ competitive adsorption

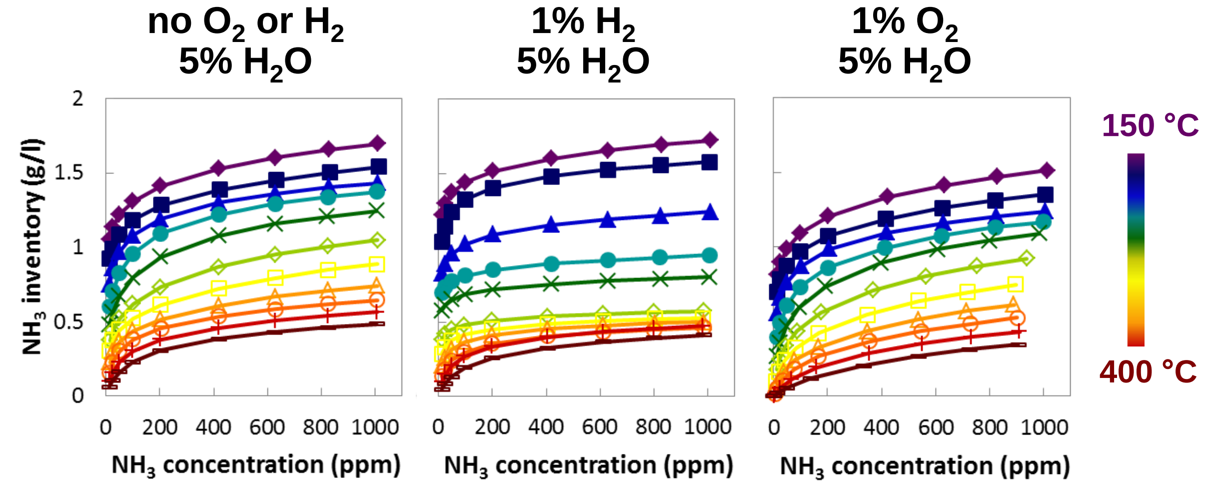
# Controlling catalyst oxidation state is critical in quantifying $NH_3$ adsorption properties

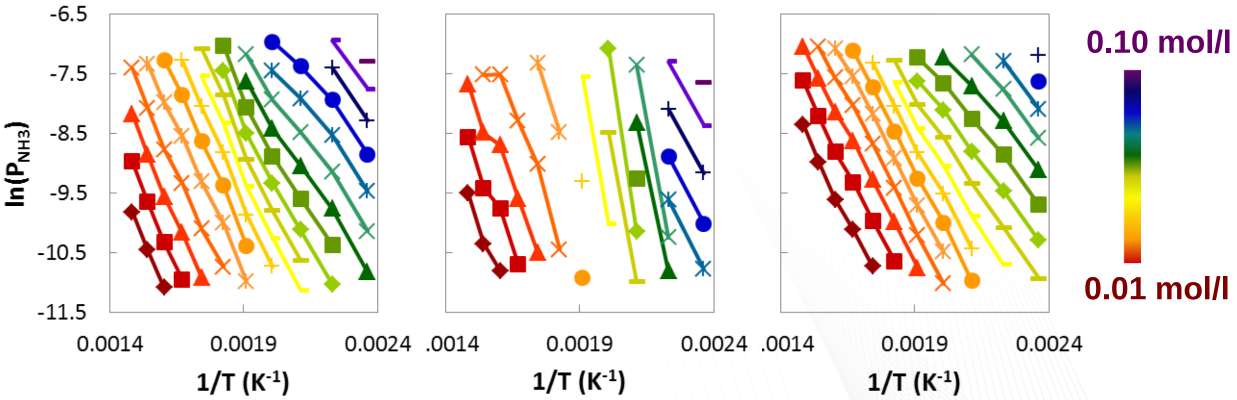
- $NH_3$ adsorption controlled by complex interactions between redox environment and humidification



# Controlling catalyst oxidation state is critical in quantifying $NH_3$ adsorption properties

- $NH_3$ adsorption controlled by complex interactions between redox environment and humidification
- Reducing conditions result in very different $NH_3$ adsorption behavior
  - potential implications for LNT or TWC + SCR
  - simple isotherm analysis breaks down
- Oxidizing conditions yield expected linear behavior for ln($P_{NH3}$) vs. 1/T
  - most relevant conditions for urea SCR
  - used for subsequent investigations



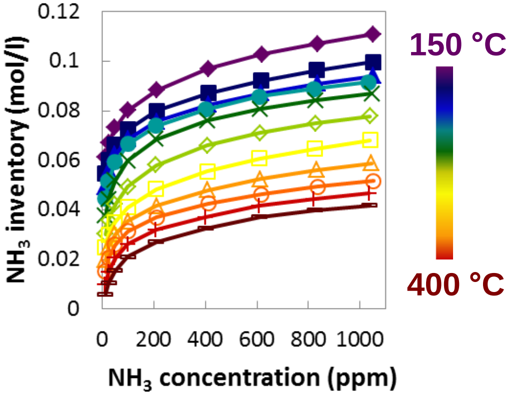


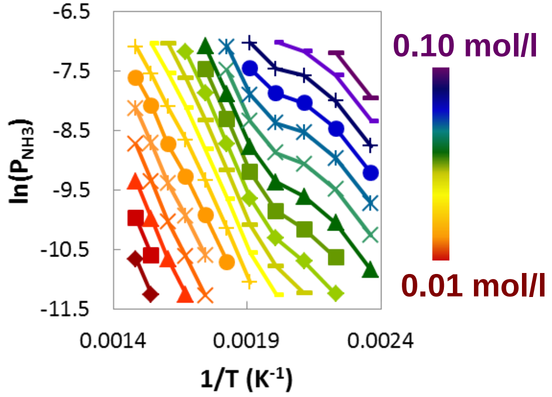
# Controlling catalyst oxidation state increases confidence in adsorption enthalpy estimates & modeling approach

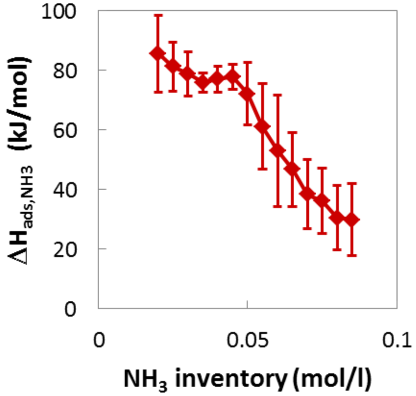
**$NH_3$ adsorption isotherms**

**$\ln(P_{NH3})$ vs. 1/T (at const. $NH_3$ inventory)**

**adsorption enthalpies**



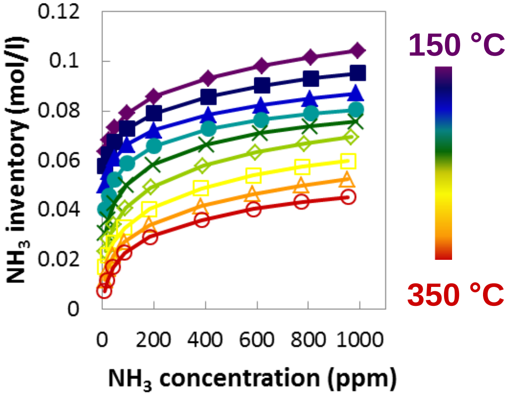


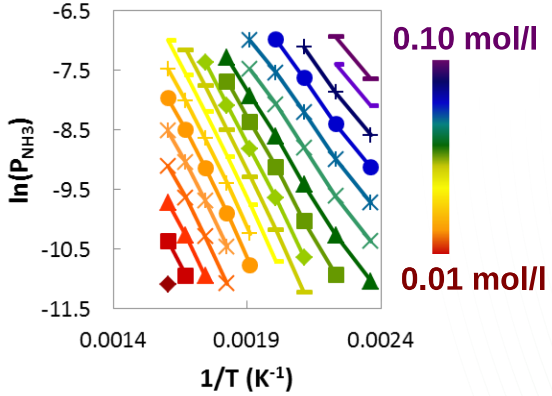


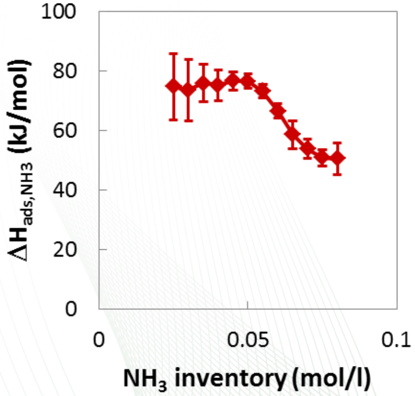
**include 0.2% $O_2$**

**eliminates slope discontinuities**

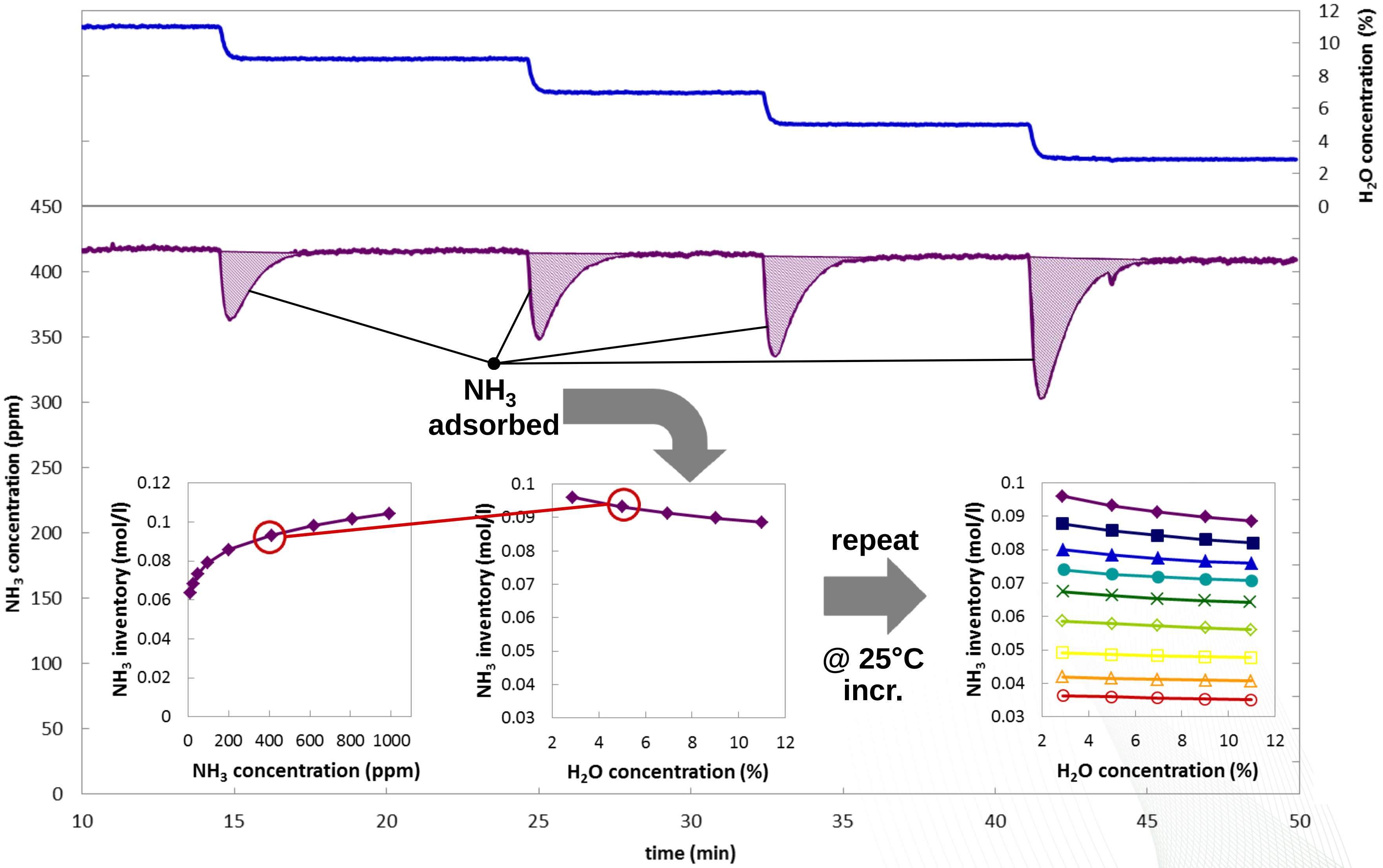
**reduces uncertainty**





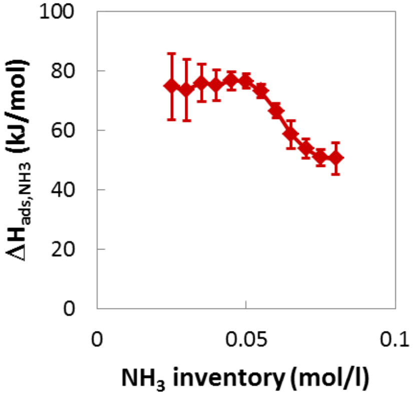


# Measuring the impact of $H_2O$ competitive adsorption on equilibrium $NH_3$ storage

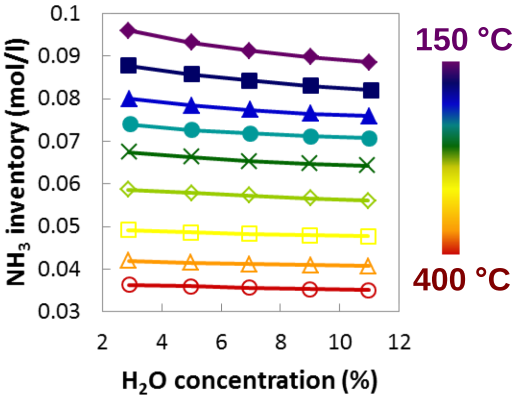


# $NH_3$ storage model structure selected based on adsorption enthalpy trends, $H_2O$ competition measurements

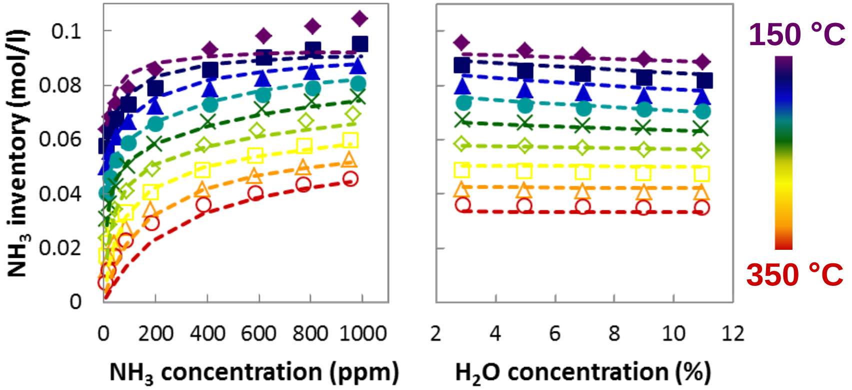
**$NH_3$ adsorption enthalpy vs. inventory**



**$H_2O$ competition with $NH_3$ (measured)**



**full $NH_3$ adsorption data set (points)**



**model structure:**

- 2 sites
- Langmuir isotherms

**$H_2O$ competition:**

- low energy site only

**parameter estimation:**

- fit model (dashed lines) to data
- initial guesses from enthalpy curve

$$I_{NH_3} = \omega_1 \theta_{1,NH_3} + \omega_2 \theta_{2,NH_3}$$

$$\theta_{1,NH3} = \frac{K_{1,NH_3} P_{NH_3}}{1 + K_{1,NH_3} P_{NH_3}}$$

$$\theta_{2,NH3} = \frac{K_{2,NH_3} P_{NH_3}}{1 + K_{2,NH_3} P_{NH_3} \boxed{+ K_{2,H_2O} P_{H_2O}}}$$

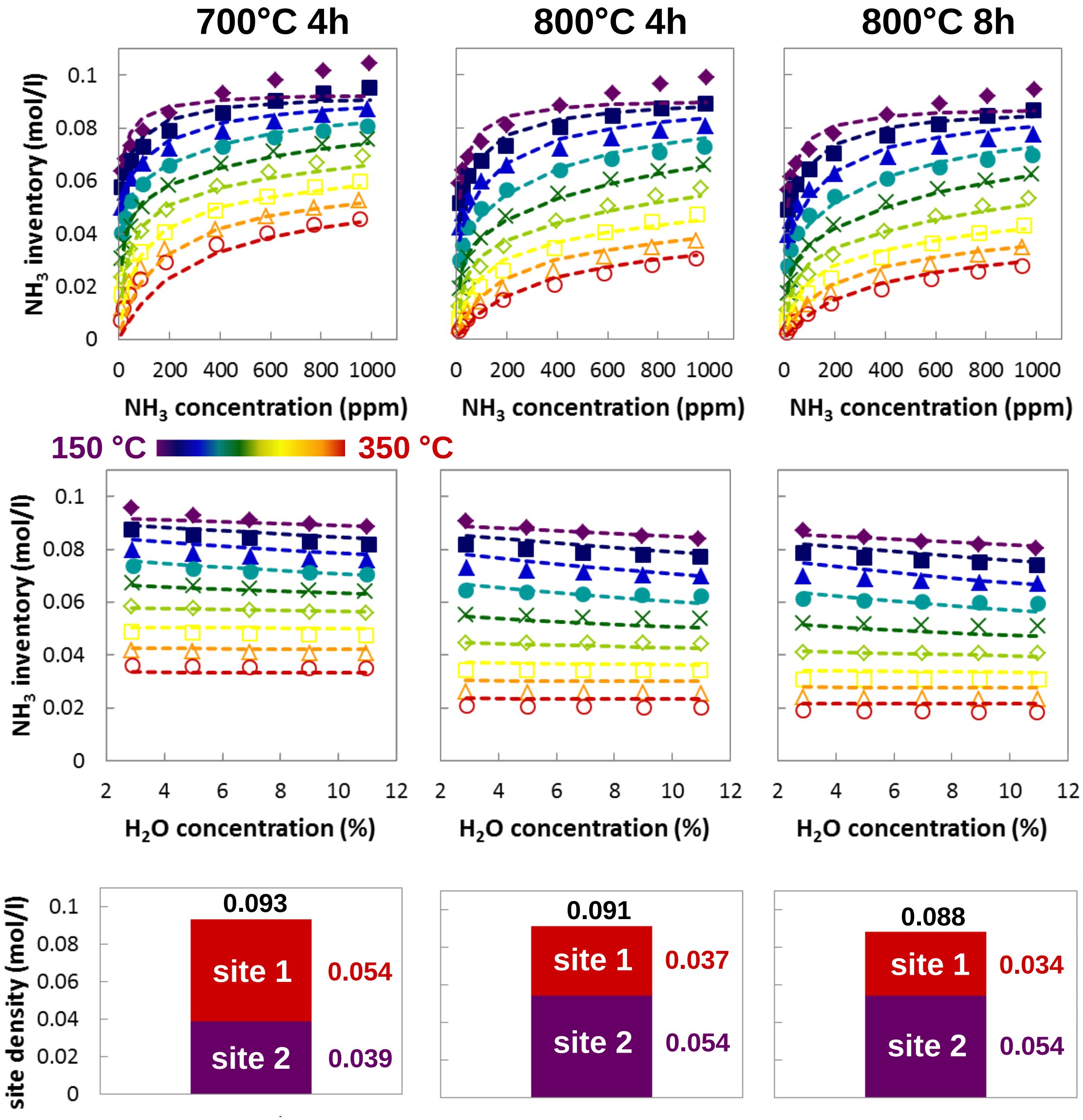
$$K_{i,a} = K_{i,a,0} e^{-\Delta H_{i,a}/RT}$$

***$NH_3$ equilibrium adsorption model incorporates:***

- ***temperature***
- ***$NH_3$ concentration***
- ***$H_2O$ concentration***
- ***aging?***

| site | 1 | 2 |
|---|---|---|
| ω (mol/l) | 0.054 | 0.039 |
| $K_{i,NH3,0}$ | 3.1E-3 | 5.2E-6 |
| $\Delta H_{i,NH3}$ (kJ/mol) | -84 | -85 |
| $K_{i,H2O,0}$ | -- | 2.9E-4 |
| $\Delta H_{i,H2O}$ (kJ/mol) | -- | -44 |

# Impact of hydrothermal aging captured by changing site densities while holding other parameters fixed



- Re-measured $NH_3$ isotherms after stepwise 800 °C HTA
- Model calibration strategy:
  - fit model to all data points
  - vary site densities w/ aging
  - hold other parameters fixed
- Changes in site density:
  - site 1: decreases
  - site 2: increases
  - total sites: ~constant

| site | 1 | 2 |
|---|---|---|
| ω (mol/l) | f(age) | f(age) |
| $K_{i,NH3,0}$ | 3.1E-3 | 5.2E-6 |
| $\Delta H_{i,NH3}$ (kJ/mol) | -84 | -85 |
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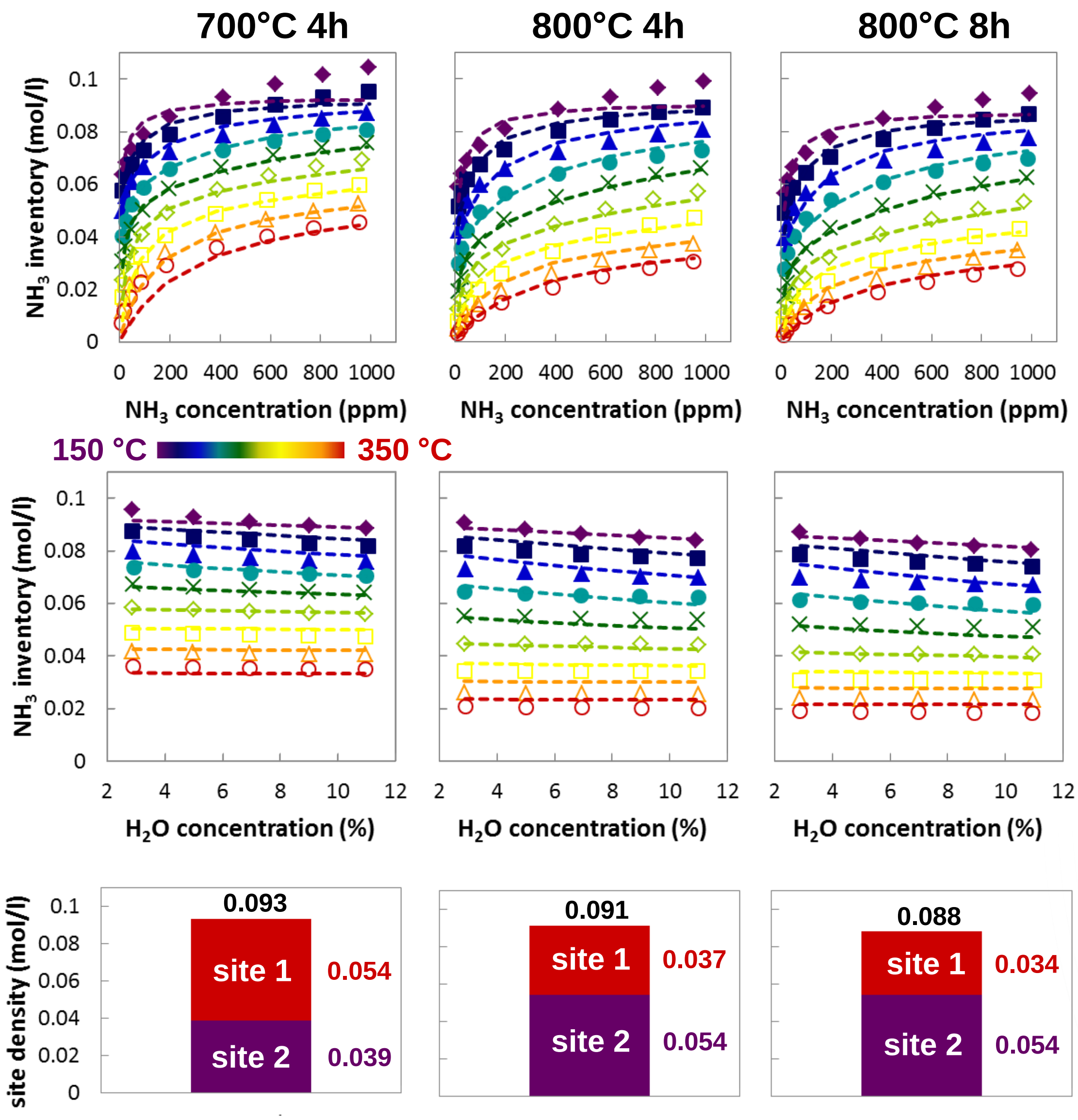

- Re-measured $NH_3$ isotherms after stepwise 800 °C HTA
- Model calibration strategy:
  - fit model to all data points
  - vary site densities w/ aging
  - hold other parameters fixed
- Changes in site density:
  - site 1: decreases
  - site 2: increases
  - total sites: ~constant
  - conceptual model:

**site 1** (high energy) → **site 2** (low energy)

***$NH_3$ equilibrium adsorption model accounts for:***

- ***temperature***
- ***$NH_3$ concentration***
- ***$H_2O$ concentration***
- ***hydrothermal aging***

# Mapping of equilibrium adsorption model parameters to reaction rate expressions for a transient model

### Equilibrium model equations

$$\theta_{1,NH3} = \frac{K_{1,NH_3}P_{NH_3}}{1 + K_{1,NH_3}P_{NH_3}}$$

$$K_{1,NH3} = K_{1,NH3,0}e^{-\Delta H_{1,NH3}/RT}$$

$$\theta_{2,NH3} = \frac{K_{2,NH_3}P_{NH_3}}{1 + K_{2,NH_3}P_{NH_3} + K_{2,H_2O}P_{H_2O}}$$

$$K_{2,NH3} = K_{2,NH3,0}e^{-\Delta H_{2,NH3}/RT}$$

$$K_{2,H2O} = K_{2,H2O,0}e^{-\Delta H_{2,H2O}/RT}$$

### Transient model rate equations

$$NH_3 + S_1 \leftrightarrow S_1\text{-}NH_3 \qquad r_{1,f} = k_{1,f}P_{NH3}\theta_{1,v} \qquad k_{1,f} = K_{1,NH3,0}A_{1,b}$$

$$r_{1,b} = k_{1,b}\theta_{1,NH3} \qquad k_{1,b} = A_{1,b}e^{-\Delta H_{1,NH3}/RT}$$

$$NH_3 + S_2 \leftrightarrow S_2\text{-}NH_3 \qquad r_{2,f} = k_{2,f}P_{NH3}\theta_{2,v} \qquad k_{2,f} = K_{2,NH3,0}A_{2,b}$$

$$r_{2,b} = k_{2,b}\theta_{2,NH3} \qquad k_{2,b} = A_{2,b}e^{-\Delta H_{2,NH3}/RT}$$

$$H_2O + S_2 \leftrightarrow S_2\text{-}H_2O \qquad r_{3,f} = k_{3,f}P_{H2O}\theta_{2,v} \qquad k_{3,f} = K_{2,H2O,0}A_{3,b}$$

$$r_{3,b} = k_{3,b}\theta_{2,H2O} \qquad k_{3,b} = A_{3,b}e^{-\Delta H_{2,H2O}/RT}$$

### Derivation of transient rate expressions for site 1

at equilibrium: $r_{1,f} = r_{1,b}$

$$\frac{k_{1,f}}{k_{1,b}} = \frac{\theta_{1,NH3}}{P_{NH3}\theta_{1,v}} = K_{1,NH3}$$

$$\frac{A_{1,f}e^{-E_{a,1,f}/RT}}{A_{1,b}e^{-E_{a,1,b}/RT}} = K_{1,NH3,0}e^{-\Delta H_{1,NH3}/RT}$$

$$\frac{A_{1,f}}{A_{1,b}} = K_{1,NH3,0} \qquad -E_{a,1,f} + E_{a,1,b} = -\Delta H_{1,NH3}$$

assuming non-activated adsorption: $E_{a,1,b} = -\Delta H_{1,NH3}$

- 6 of the 9 parameters in the transient model rate equations can be calculated directly from the equilibrium storage model parameters
- The remaining 3 parameters ($A_{1,b}$, $A_{2,b}$, $A_{,3,b}$) must be fit to transient data, such as the $NH_3$ concentration profiles between steps of the isotherm experiments

# Next steps

- Conclusions:
  - Controlling oxidation state important when measuring $NH_3$ adsorption
  - Equilibrium $NH_3$ adsorption model captures effects of temperature, $NH_3$ concentration, $H_2O$ concentration, hydrothermal aging
    - 2 sites: Langmuir isotherms at both, with $H_2O$ inhibition at second site
    - hydrothermal aging captured by changing site densities only
- Next steps:
  - Complete hydrothermal aging study (12 h, 16 h)
  - Post adsorption isotherm data sets on CLEERS website
  - Work with PNNL to translate equilibrium adsorption results to a fully transient model
  - Extend approach to other SCR materials
    - commercial Cu-SAPO-34 (later this year)
    - model Cu-SSZ-13
    - others? (Fe, Cu-Fe, V, ...)
  - Apply similar approach to HC adsorption on zeolites for low temperature traps

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# Backup Slides

# $\Delta H_{ads}$ vs. coverage trends for simple (single site) isotherms guide selection of modeling strategy

## Measured

$$\Delta H_{ads} = f(\theta)$$

## Langmuir

$$K_0 e^{(-\Delta H^0{}_{ads}/RT)} P = \frac{\theta}{(1-\theta)}$$

$$\Delta H_{ads} = \Delta H^0{}_{ads}$$

## Temkin

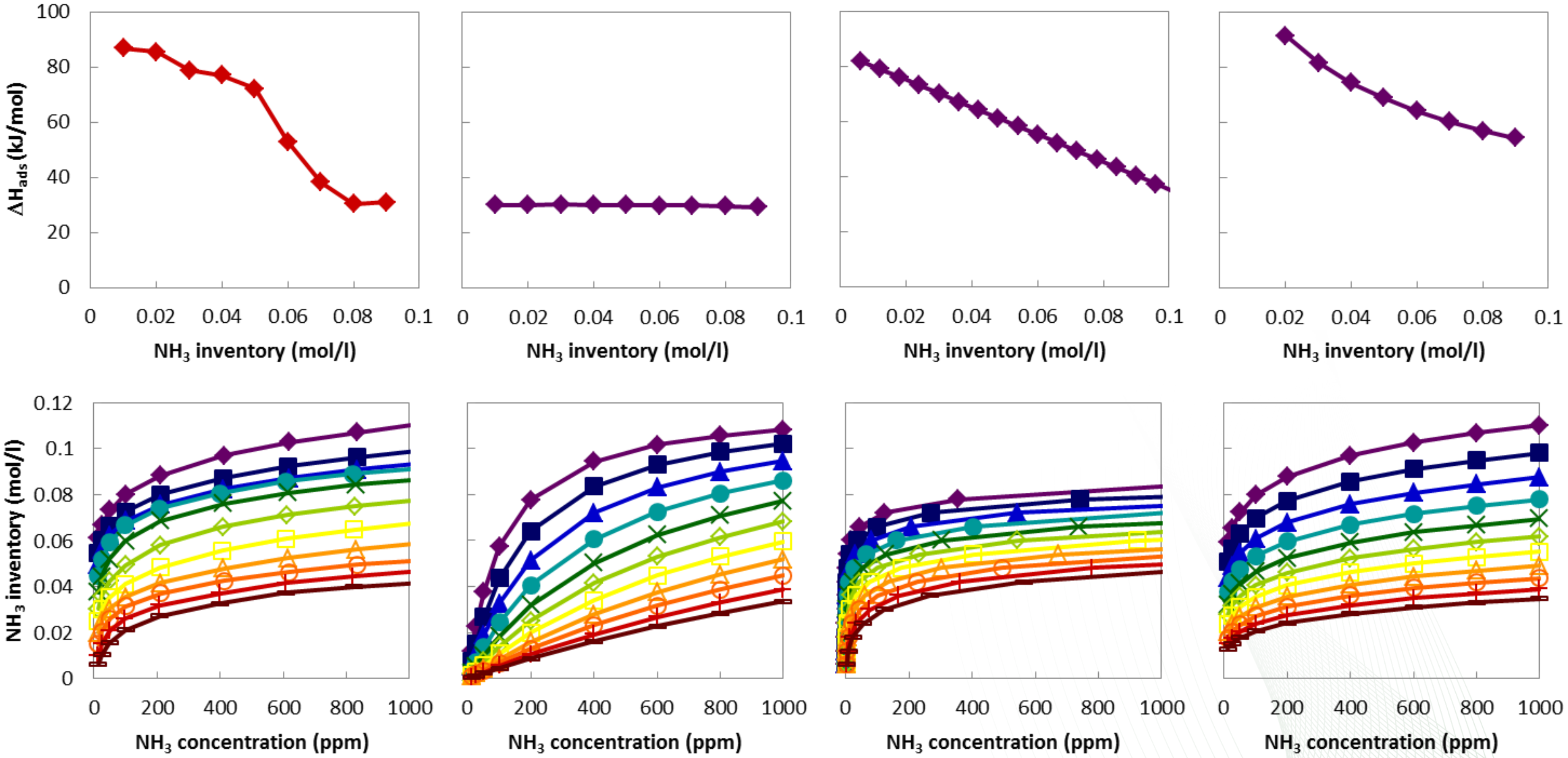
$$K_0 e^{(-\Delta H^0{}_{ads}(1-\alpha\theta)/RT)} P = \frac{\theta}{(1-\theta)}$$

$$\Delta H_{ads} = \Delta H^0{}_{ads}(1-\alpha\theta)$$

## Freundlich

$$K_0 e^{(-\alpha RT/\Delta H^0{}_{ads})} P^{(RT/\Delta H^0{}_{ads})} = \theta$$

$$\Delta H_{ads} = \Delta H^0{}_{ads} \ln\frac{\theta}{K_0}$$



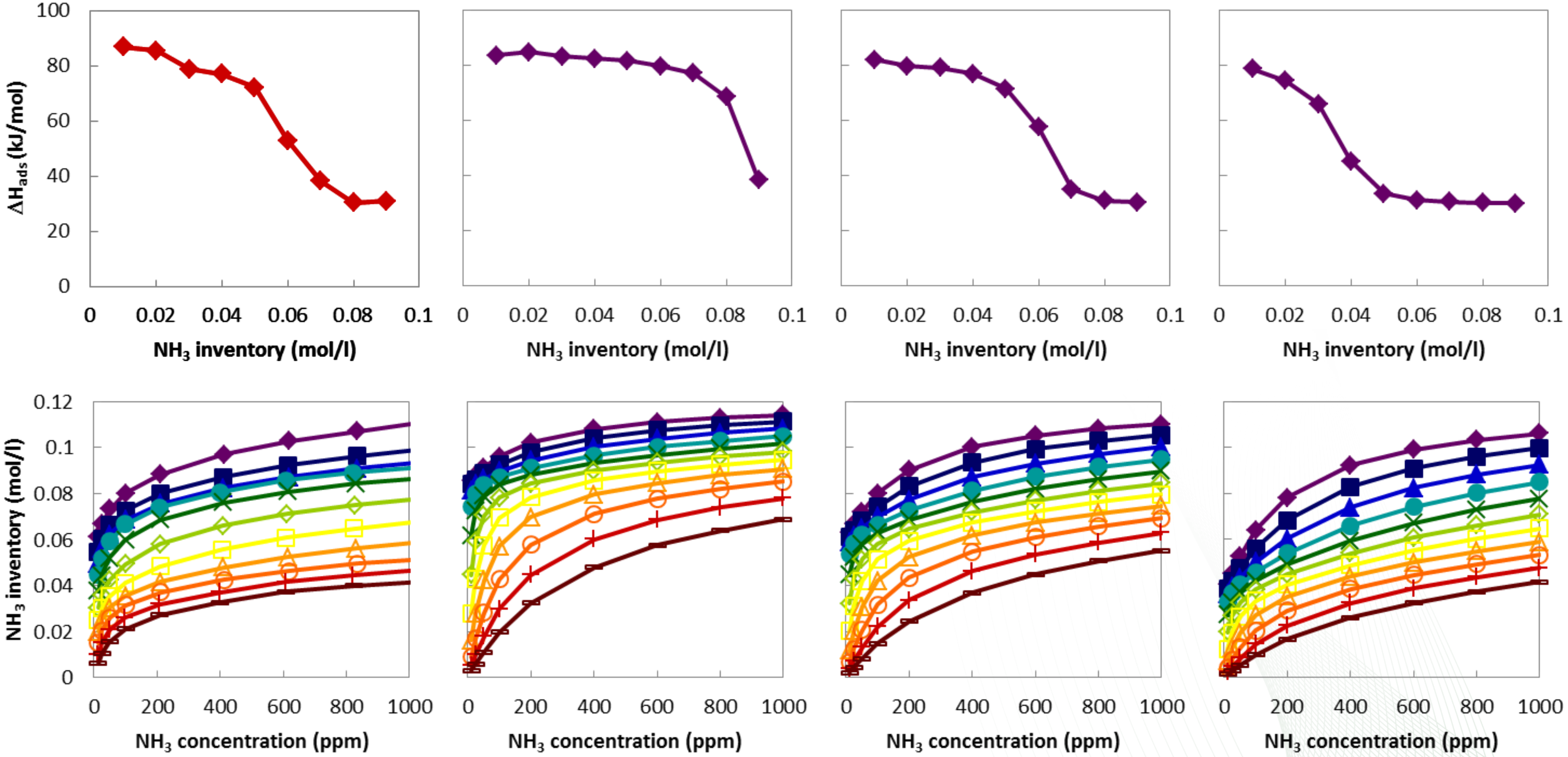
# $\Delta H_{ads}$ vs. coverage trends for simple (two site) isotherms guide selection of modeling strategy

**Measured**

**2 site Langmuir isotherms**

**$\Delta H_{ads,1}$ = -85 kJ/mol; $\Delta H_{ads,2}$ = -30 kJ/mol**

**$N_1/N_{total}$: 0.7** **0.5** **0.3**



# Strategy: develop new measurement and analysis techniques that isolate $NH_3$ adsorption energetics

- Conduct experiments with Cu-SSZ-13 SCR catalyst from GM diesel pickup truck
- Use automated flow reactor to measure $NH_3$ inventories under steady state conditions
  - minimize impacts of mass transport, kinetics
- Develop analysis approach for extracting adsorption energetics
  - build on techniques used for adsorber materials
  - focus on energetics due to exponential dependence in equilibrium constants and rate parameters
  - goal: generate insights into fundamental material properties and appropriate modeling strategies
- Create model for equilibrium $NH_3$ adsorption on SCR catalyst