Energetics of NH_3 Storage on Zeolite SCR Catalysts

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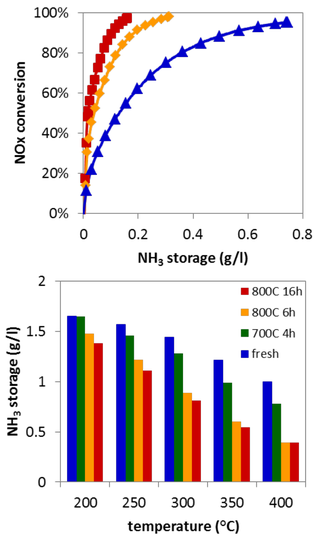
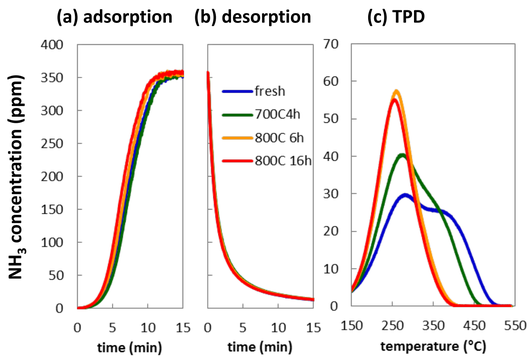
Motivation

- SCR NH_3 inventory must be managed to:
  - maintain high NOx conversion
  - avoid NH_3 slip and wasted reductant
- NH_3 inventory is controlled through reductant dosing
- Dosing strategies are often developed with simulations
- Simulation tools require NH_3 storage models that accurately capture the effects of:
  - catalyst temperature
  - exhaust composition
  - catalyst age
- Typical NH_3 storage measurements [1] rely on transient operating conditions, confounding effects of:
  - thermodynamics
  - adsorption/desorption kinetics
  - transport processes
- SCR catalyst structure/properties and modeling strategies remain uncertain:
  - multiplicity, quantity of storage sites
  - energetics of adsorption at each site
    - Langmuir, Temkin, etc.
  - role of competitive adsorption
  - aging impacts





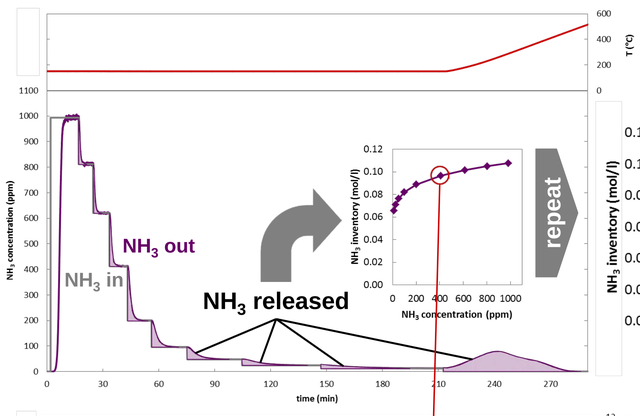
Note: 800 °C 16 h ≈ LD vehicle full useful life [2]

- Confounded experimental data sets and uncertain model structures create too many degrees of freedom for unique parameter estimation
- Better measurement and modeling strategies are needed

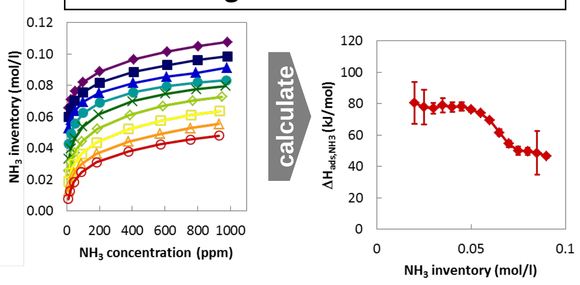
Approach

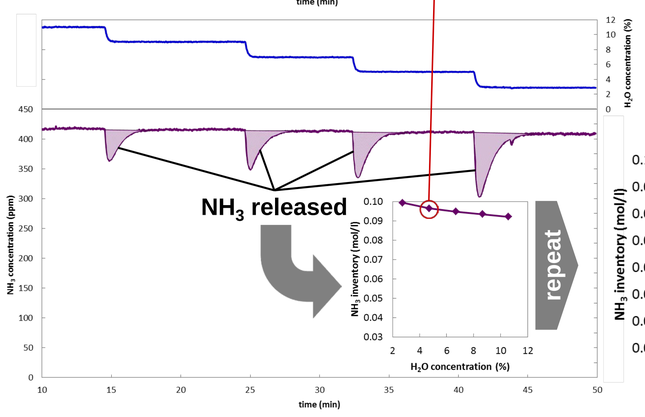
- Use an automated flow reactor to measure steady state NH_3 inventories on core samples cut from commercial SCR catalysts
  - vary NH_3 concentration (isotherms), temperature, H_2O concentration
  - isolates energetics from kinetics and transport
- Extract adsorption enthalpies from isotherms with thermodynamic relation:

Clausius-Clapeyron equation: $\frac{\partial(\ln P_{NH_3})}{\partial(1/T)} = \frac{\Delta H_{ads}}{R}$

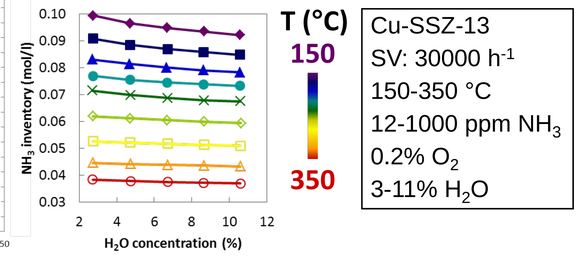


ΔH_{ads} vs. inventory consistent with 2 sites described by Langmuir isotherms





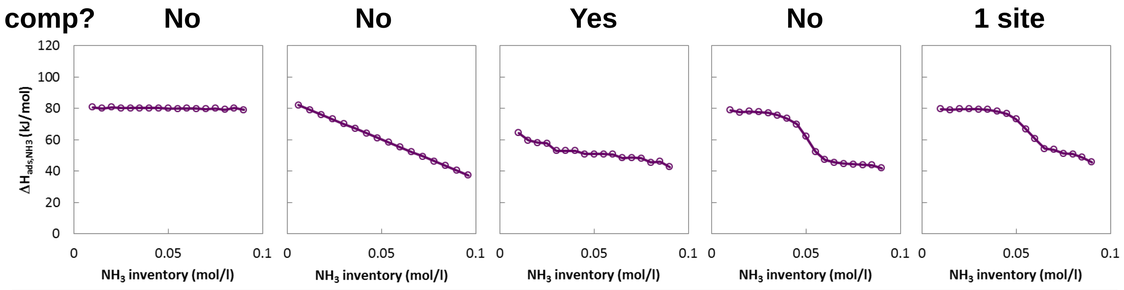
H_2O inhibition of NH_3 storage only significant at low Ts (competes for "low energy" site)



Cu-SSZ-13
SV: 30000 h^{-1}
150-350 °C
12-1000 ppm NH_3
0.2% O_2
3-11% H_2O

Adsorption enthalpy vs. inventory for model isotherms

# sites	1	1	1	2	2
isotherm	Langmuir	Temkin	Langmuir	Langmuir	Langmuir
H2O comp?	No	No	Yes	No	1 site



Adsorption enthalpy vs. inventory curve guides selection of modeling strategies by providing insights into site multiplicity, adsorption energetics

Equilibrium storage model equations

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

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

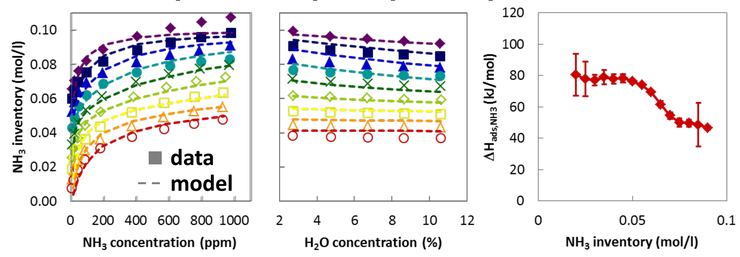
$$\theta_{2,NH3} = \frac{K_{2,NH_3} P_{NH_3}}{1 + K_{2,NH_3} P_{NH_3} + K_{2,H_2O} P_{H_2O}}$$

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

- two distinct storage sites
- site 1: Langmuir isotherm
- site 2: Langmuir isotherm with H_2O competitive adsorption
- both sites: constant adsorption enthalpies (no coverage dependence)

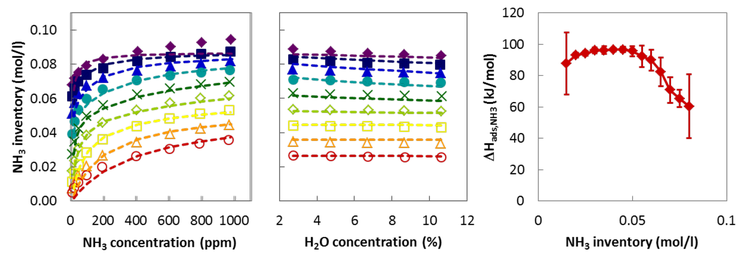
Zeolite composition effects on NH_3 storage

Cu-SSZ-13 (2010 GM pickup truck)



site	1	2
ω (mol/l)	0.050	0.050
$K_{i,NH3,0}$	1.8E-3	3.0E-5
$\Delta H_{i,NH3}$ (kJ/mol)	-80	-79
$K_{i,H2O,0}$	--	9.4E-4
$\Delta H_{i,H2O}$ (kJ/mol)	--	-42

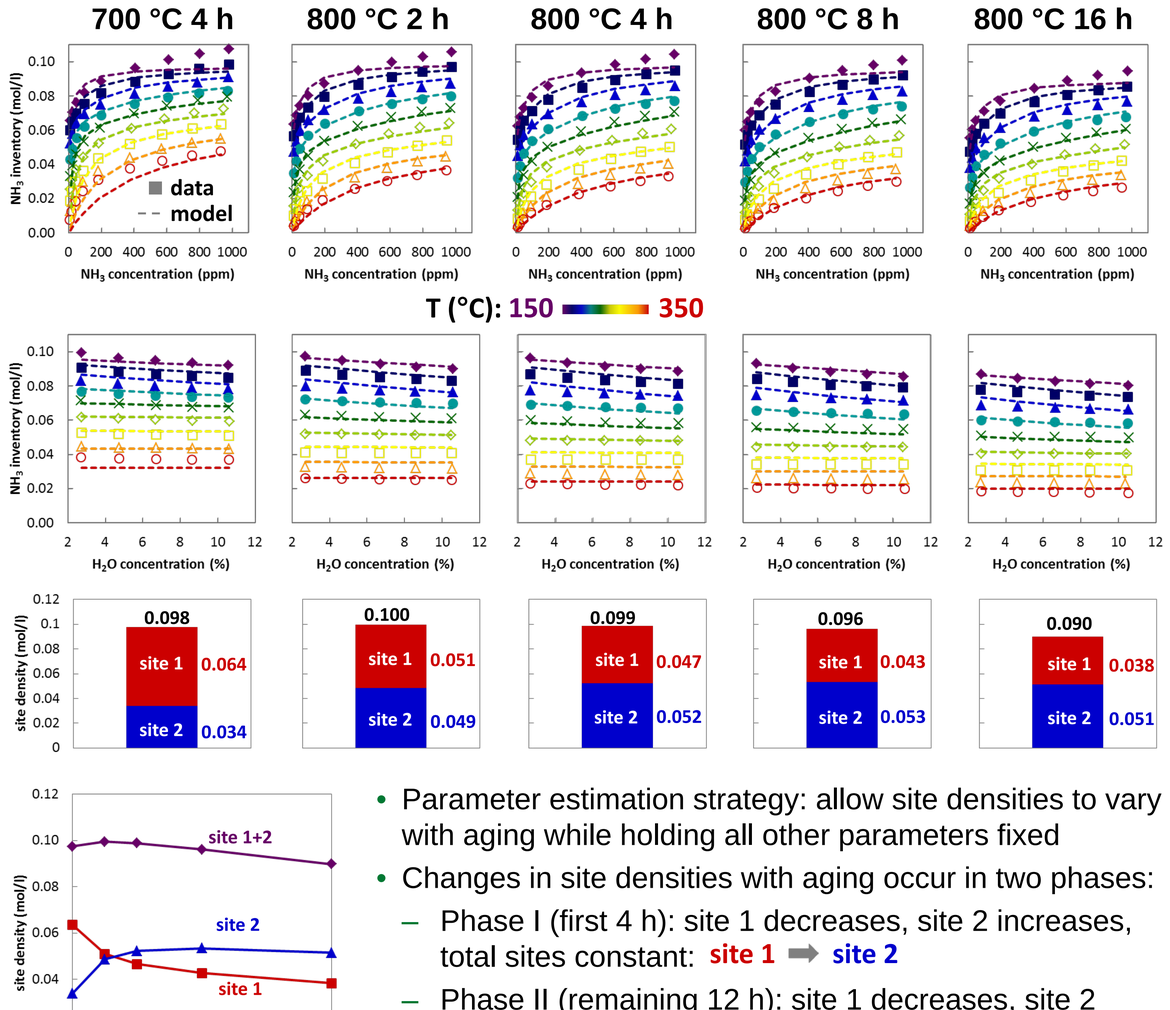
Cu-SAPO-34 (2010 Cummins ISB engine)



site	1	2
ω (mol/l)	0.050	0.037
$K_{i,NH3,0}$	2.7E-5	9.9E-8
$\Delta H_{i,NH3}$ (kJ/mol)	-95	-102
$K_{i,H2O,0}$	--	2.3E-5
$\Delta H_{i,H2O}$ (kJ/mol)	--	-55

2 site model with constant adsorption enthalpies and H_2O competition at one site effectively captures NH_3 storage behavior on two commercial small pore copper zeolites with very different compositions

Hydrothermal aging effects on NH_3 storage over Cu-SSZ-13



- Parameter estimation strategy: allow site densities to vary with aging while holding all other parameters fixed
- Changes in site densities with aging occur in two phases:
  - Phase I (first 4 h): site 1 decreases, site 2 increases, total sites constant: **site 1** ➡ **site 2**
  - Phase II (remaining 12 h): site 1 decreases, site 2 ~stable, total sites constant: loss of **site 1**

Equilibrium NH_3 storage model can be adapted to account for catalyst aging by adjusting site densities

Conclusions

- Measuring NH_3 adsorption isotherms and calculating adsorption enthalpy as a function of NH_3 inventory provides unique insights that guide model strategy development
- A two site adsorption equilibrium model with constant adsorption enthalpies and H_2O competitive adsorption at one site accurately captures the NH_3 storage behavior of commercial Cu-SSZ-13 and Cu-SAPO-34 SCR catalyst formulations
- Hydrothermal aging impact on NH_3 storage over anticipated light duty vehicle life can be modeled by adjusting only site densities

Future Work

- Implement model structure and parameters in fully transient SCR model
- Extend approach to model catalysts to identify physical sites corresponding to sites 1, 2

References

[1]E. Tronconi et. al, Chem. Eng. Sci. 51, 2965, 1996

[2]S. Schmieg et. al, Catal. Today, 184, 252-261, 2011