The Effects of Hydrothermal Aging on a Commercial Cu SCR Catalyst

Ja Hun Kwak[1], Diana Tran[1], Maruthi Devarakonda[1], Josh Pihl[2], Stuart Daw[2], Jong Lee[1]

[1]Pacific Northwest National Laboratory

[2]Oak Ridge National Laboratory

Directions in Engine-Efficiency and Emissions Research

Detroit, MI

October 5th, 2011

Motivation

- 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
  - ✓ 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
  - ✓ Zeolite-based transition metal catalyst: Cu, Fe

Approach

- Investigate the nature of active sites using both model and commercial Cu SCR catalysts
- Conduct detailed laboratory reactor evaluation using both model and commercial Cu SCR catalysts
- Develop a Cu SCR catalyst model to extract kinetic parameters

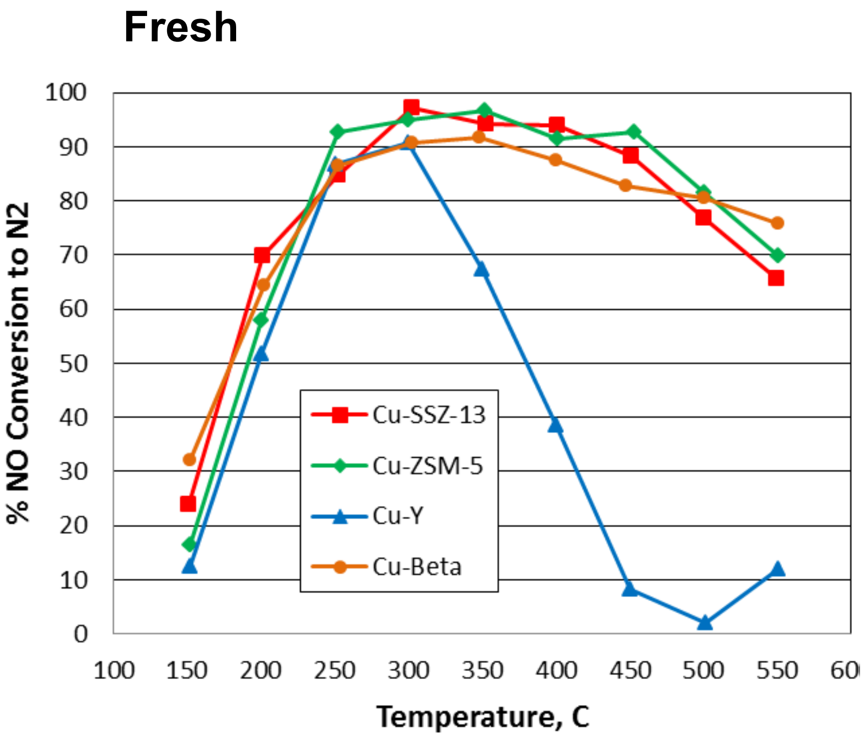
Presentation Outline

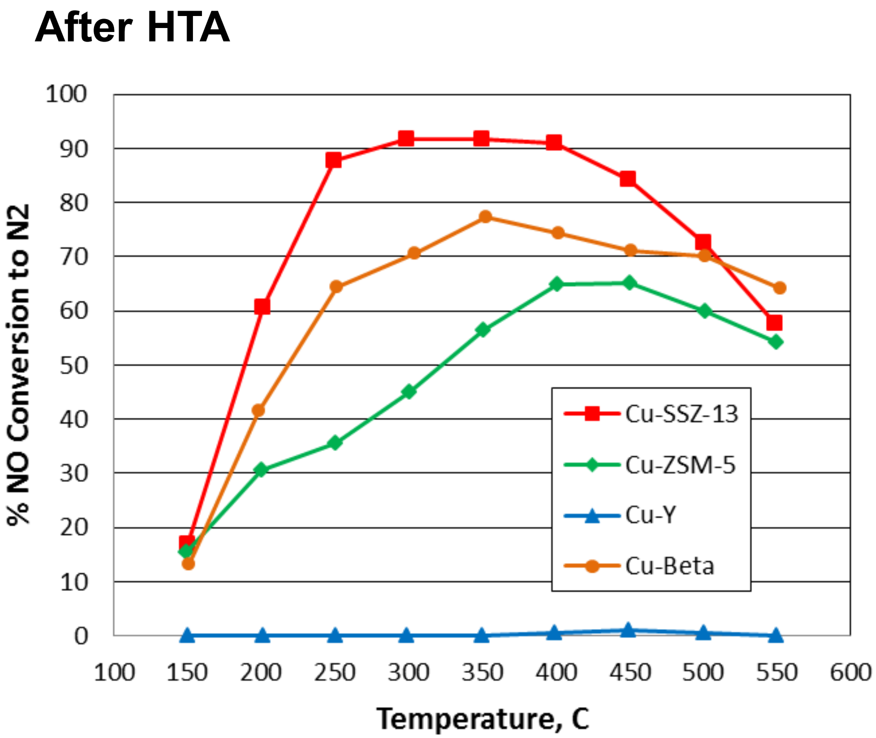
- Model Cu-Zeolite Catalyst
  - ✓ SCR activity
  - ✓ Characterization: XRD, H_2-TPR, Al NMR
- Commercial Cu-Zeolite Catalyst
  - ✓ SCR activity
  - ✓ Characterization
  - ✓ Cu SCR catalyst model
- Conclusions

Model Cu SCR Catalyst Study

- Model Cu-Zeolite SCR Catalyst
  - ✓ Cu-SSZ-13 (Si/Al_2 ~12), Cu-ZSM-5 (Si/Al_2 ~30) Cu-beta (Si/Al_2 ~38), Cu-Y(Si/Al_2 ~5.2)
- Hydrothermal Aging
  - ✓ 10% H_2O in air, 800^{o}C, 16 h
- Lab Reactor Evaluation
  - ✓ 350 ppm NO_x, 350 ppm NH_3, 14% O_2, 10% H_2O in balance N_2
  - ✓ GHSV = 30K h^{-1}
  - ✓ FT-IR (NO, NO_2, NH_3, N_2O)
- Catalyst Characterization
  - ✓ XRD, H_2-TPR, ^{27}Al NMR

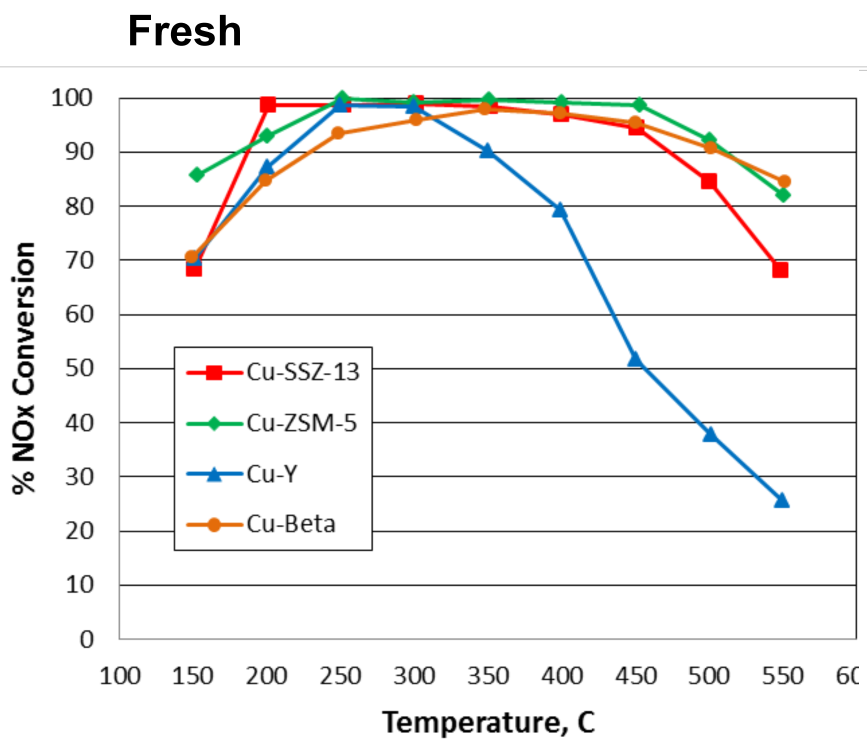
NO SCR over Model Cu Zeolite Catalysts

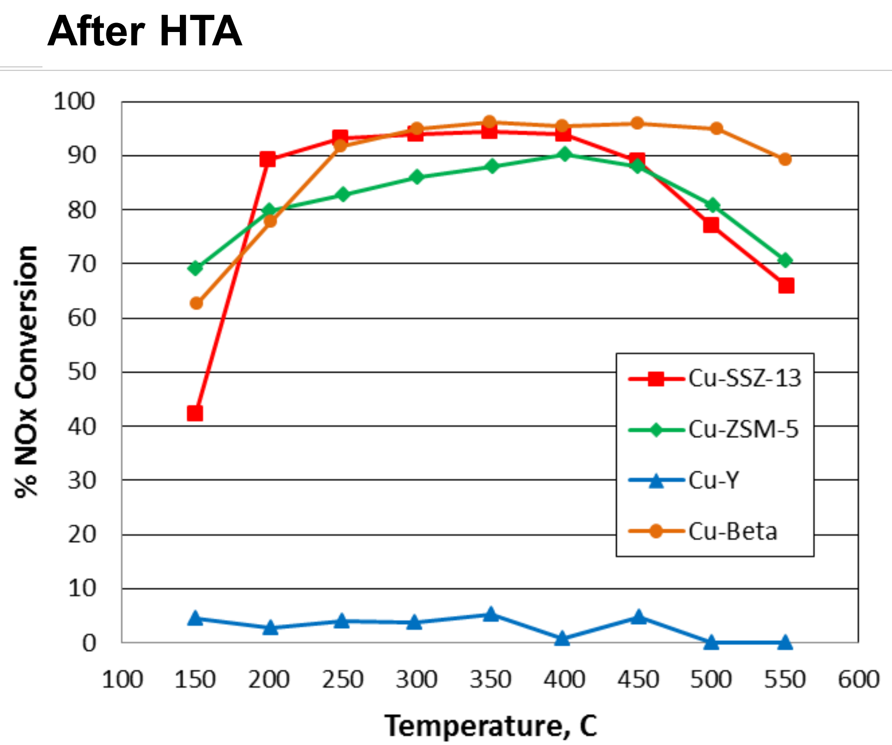




- High NO SCR activity for Cu-SSZ-13 even after HTA
- Significant loss of activity for Cu-ZSM-5, Cu-beta, Cu-Y

Fast SCR ($NO/NO_2 = 1$)

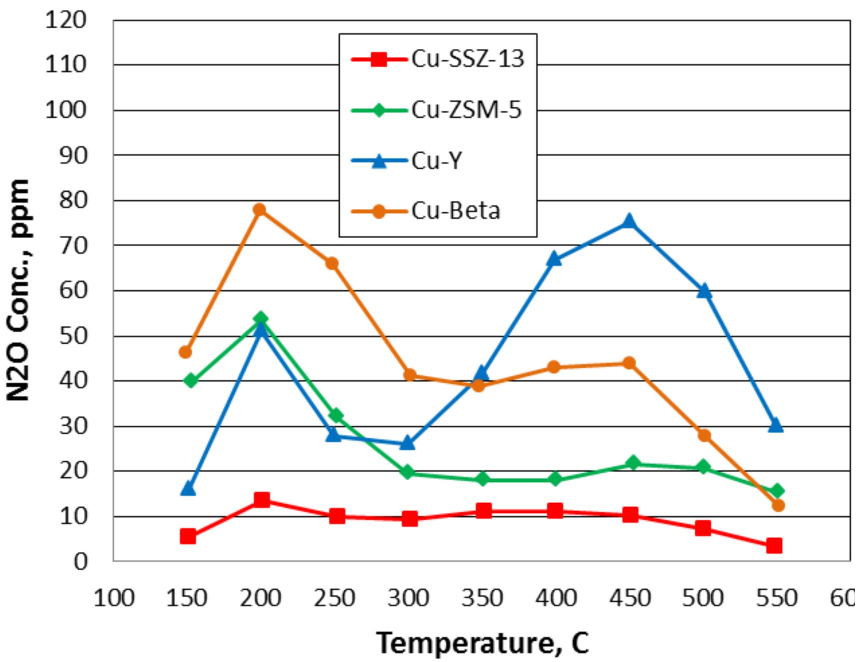




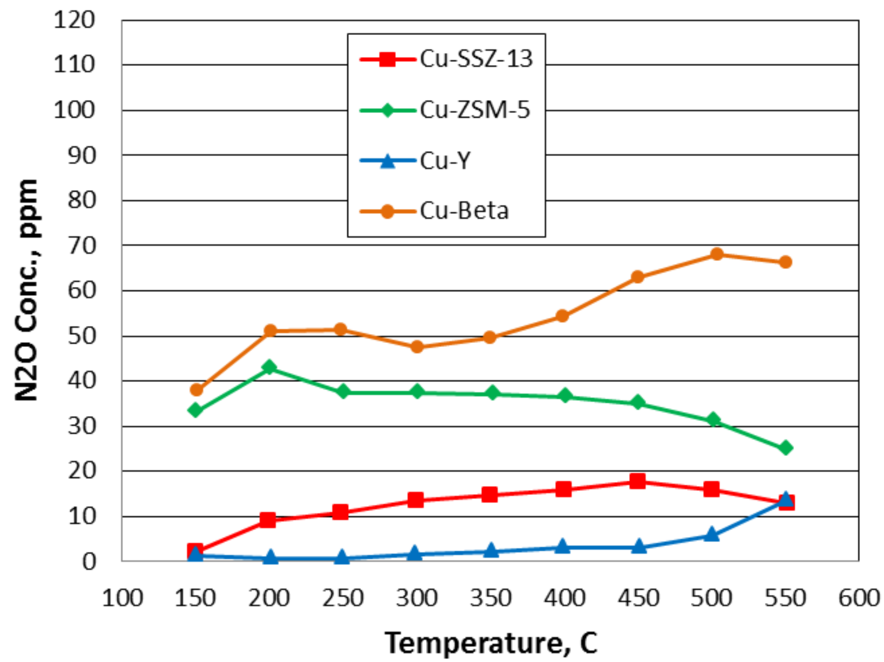
- Significant loss of activity for Cu-Y
- High SCR activity maintained for Cu-ZSM-5, Cu-beta, Cu-SSZ-13

N_2O Formation during Fast SCR

Fresh



After HTA



- Significant N_2O formation during “fast” SCR
- Little N_2O formation on Cu-SSZ-13

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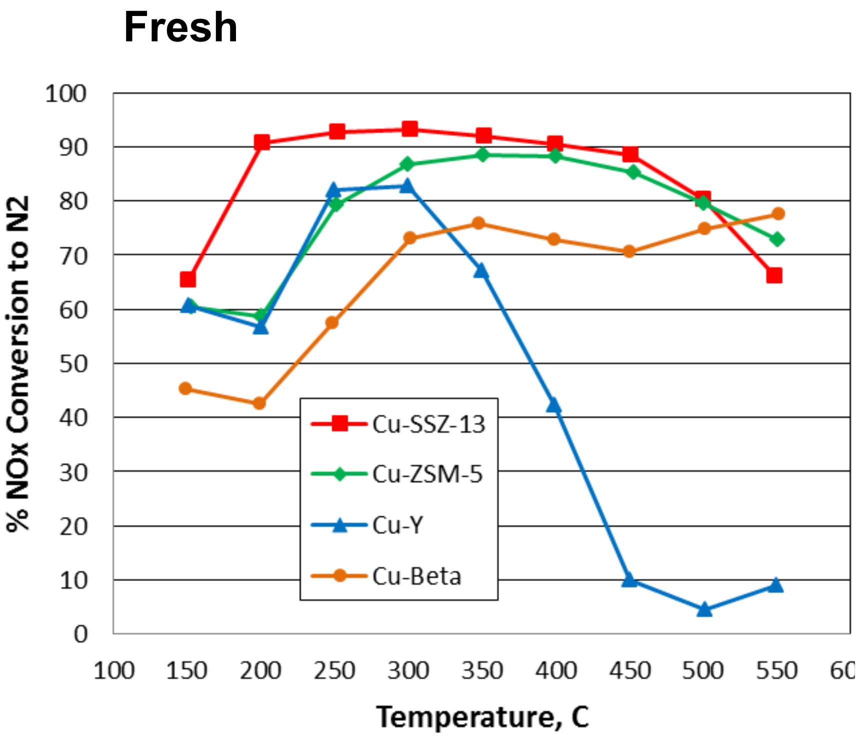
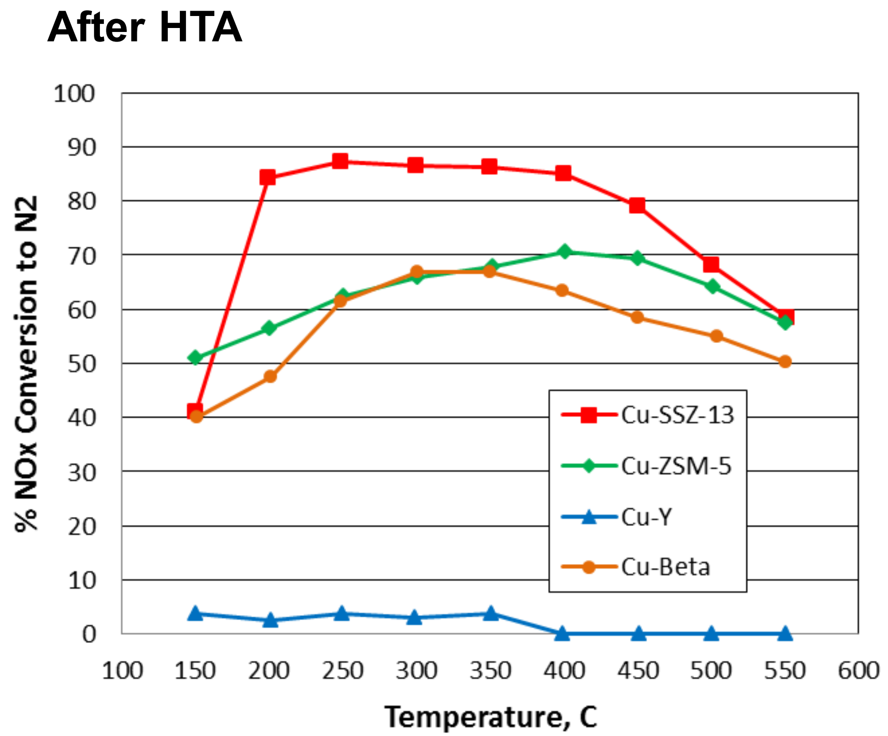
Fast SCR ($NO/NO_2 = 1$)

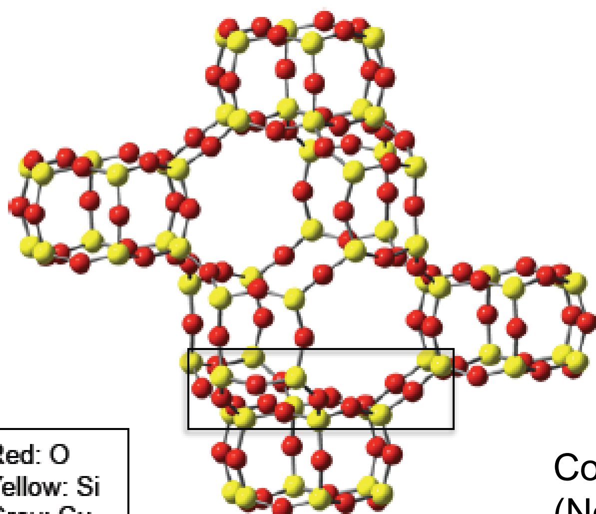




- High NO SCR activity for Cu-SSZ-13 even after HTA
- Significant loss of activity for Cu-ZSM-5, Cu-beta, Cu-Y

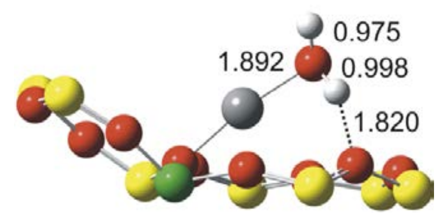
Effects of Hydrothermal Aging

1. Zeolite structure change
2. Dealumination of zeolite structure
3. Formation of different Cu species (e.g. CuO)



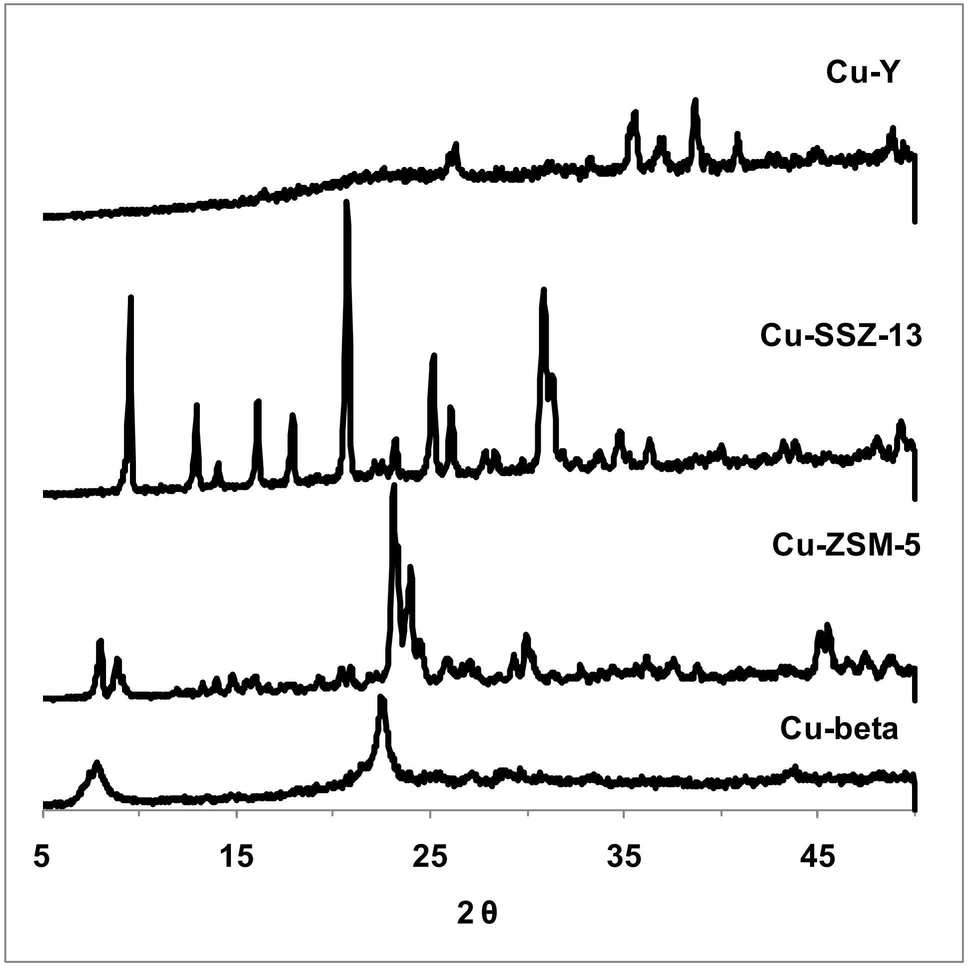
Red: O
Yellow: Si
Grey: Cu
Green: Al
White: H

periodic DFT



Courtesy of Prof. Bill Schneider (Notre Dame)

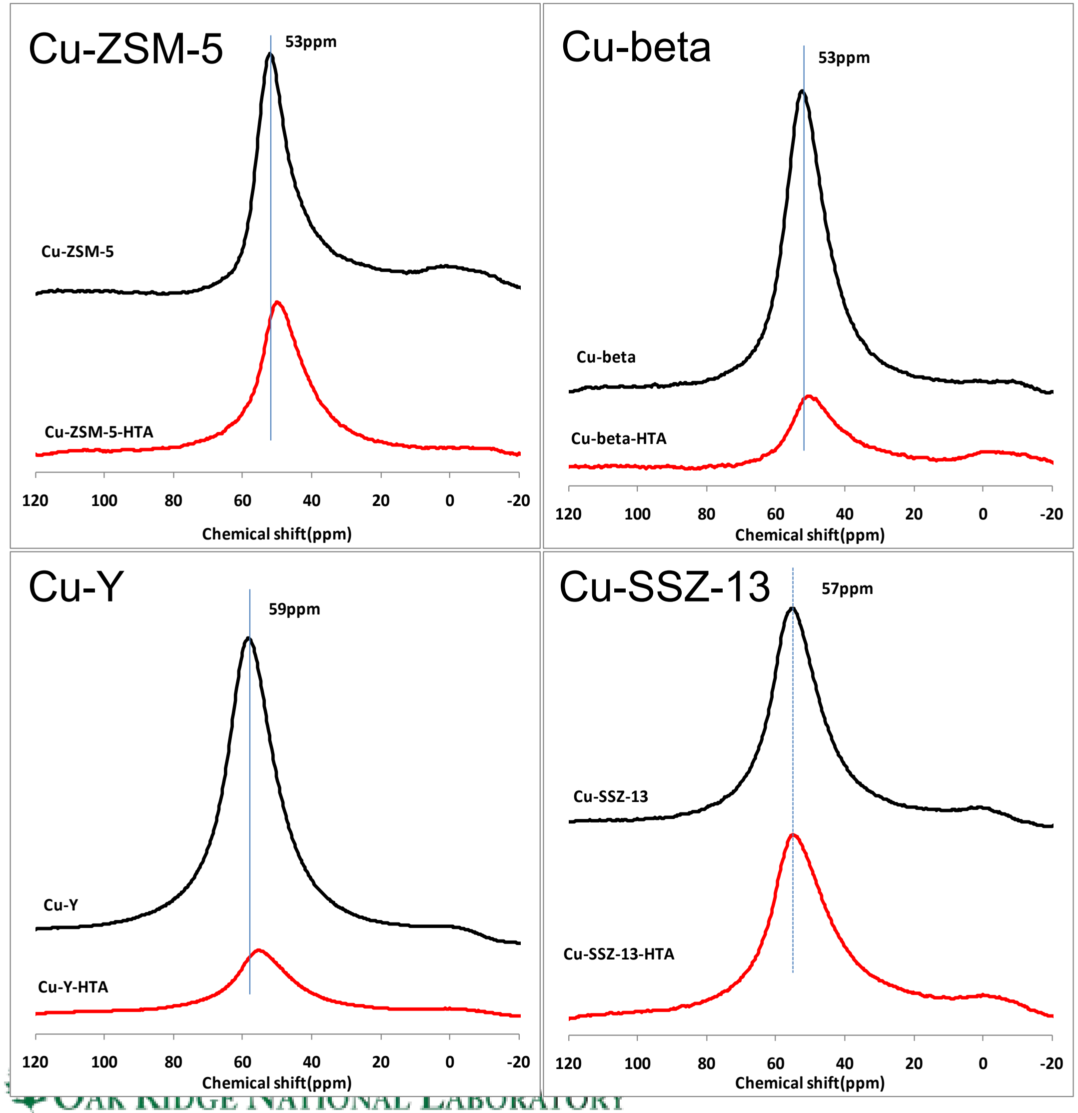
Structural Integrity by XRD



- Total collapse of zeolite structure for Cu-Y
- Little changes noticed for Cu-SSZ-13, Cu-ZSM-5, Cu-beta

→ Structure mostly intact after 800C for 16 h

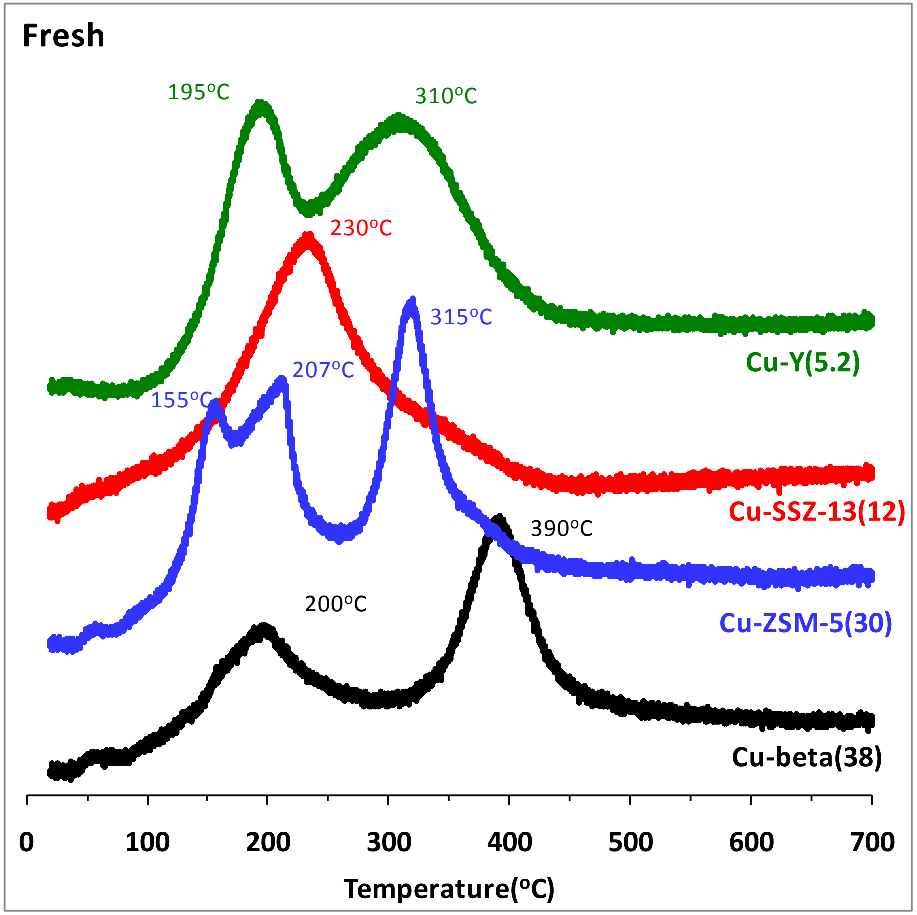
Dealumination by Solid State ^{27}Al NMR

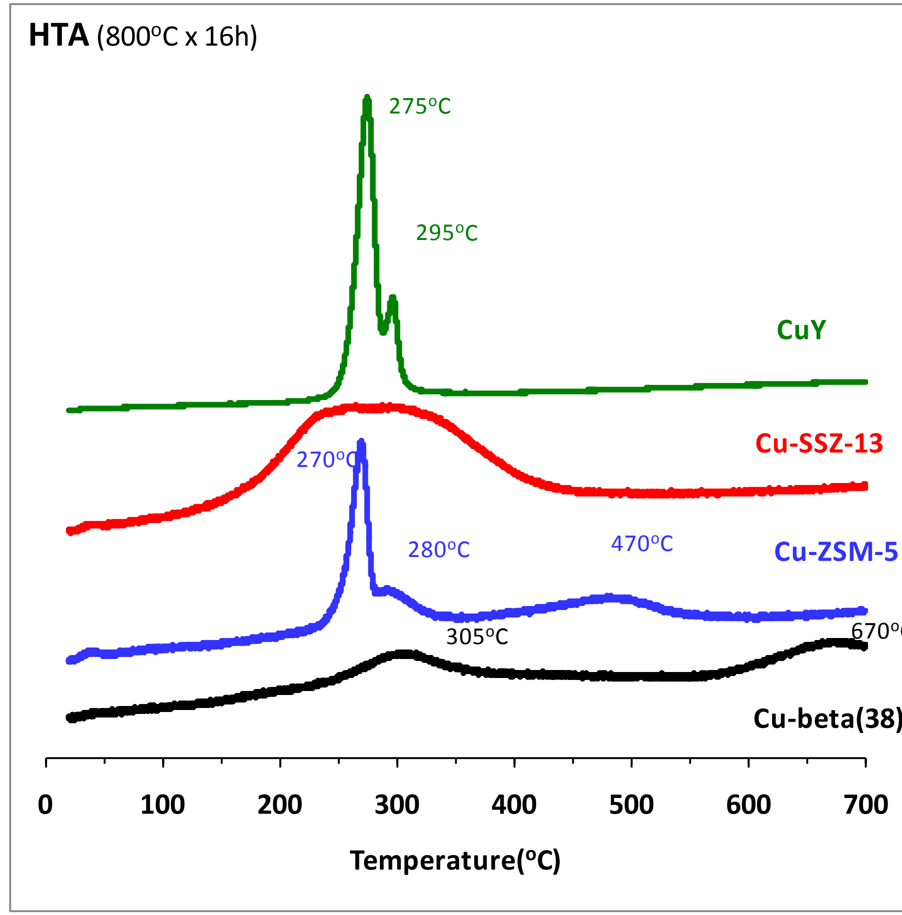


- With dealumination, tetrahedral Al becomes octahedral
- Cu-SSZ-13: no change
- Cu-ZSM-5, Cu-beta, Cu-Y: loss of tetrahedral Al, but no octahedral Al

→ Isolated Cu species in strong contact with alumina in Cu-ZSM-5, Cu-beta

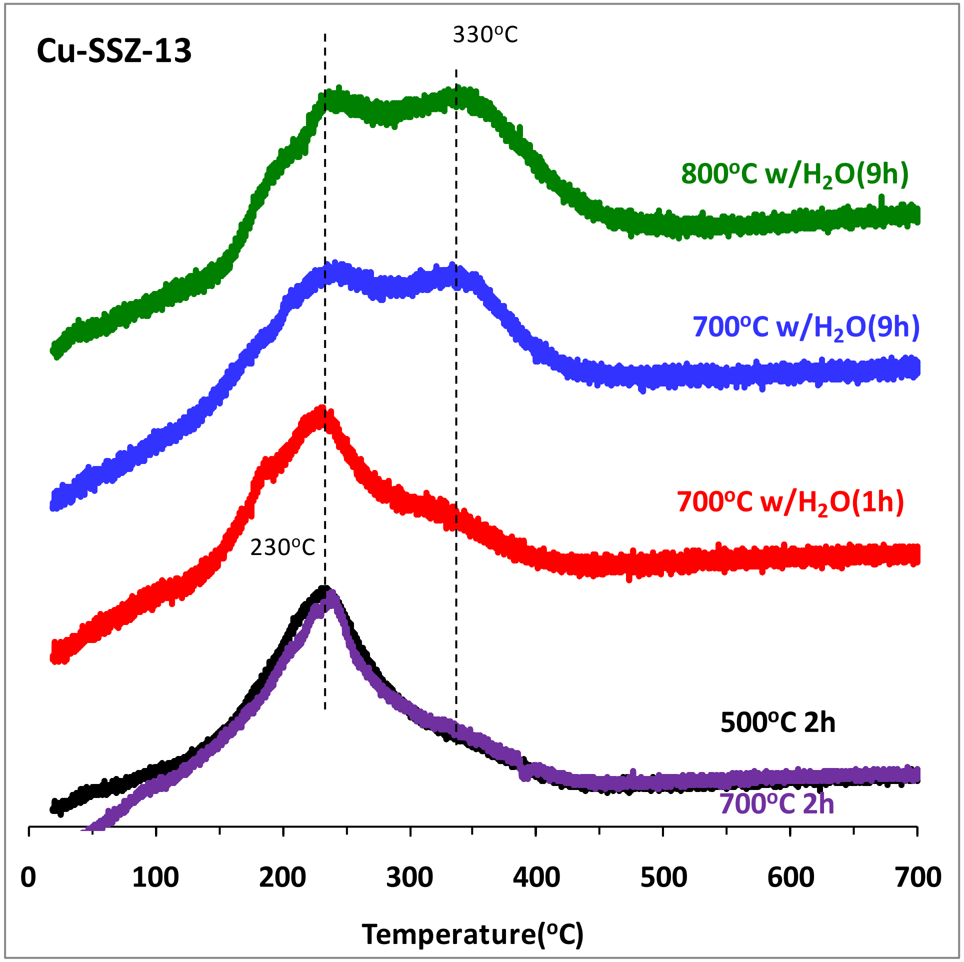
Cu Reducibility by H_2-TPR



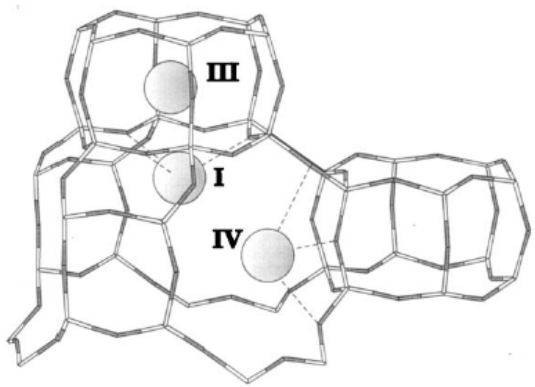


- Reduced amount of "zeolytic" Cu over aged Cu-ZSM-5, Cu-beta
- Same amount, but different ratios of two peaks over Cu-SSZ-13

Cu Species in Cu-SSZ-13



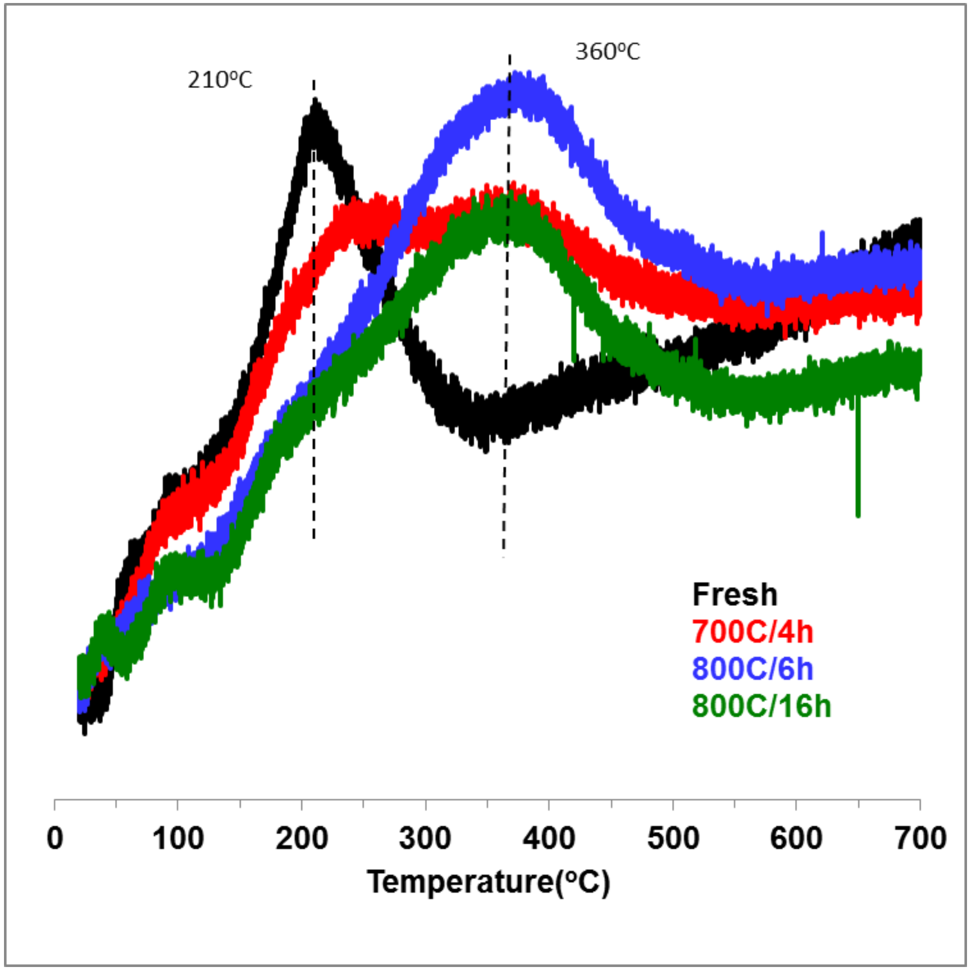
Cationic sites in dehydrated CHA



J. Dědeček et al. / Microporous and Mesoporous Materials 32 (1999) 63–74

Change in distribution of Cu species after HTA!

Cu Species in Commercial Catalyst

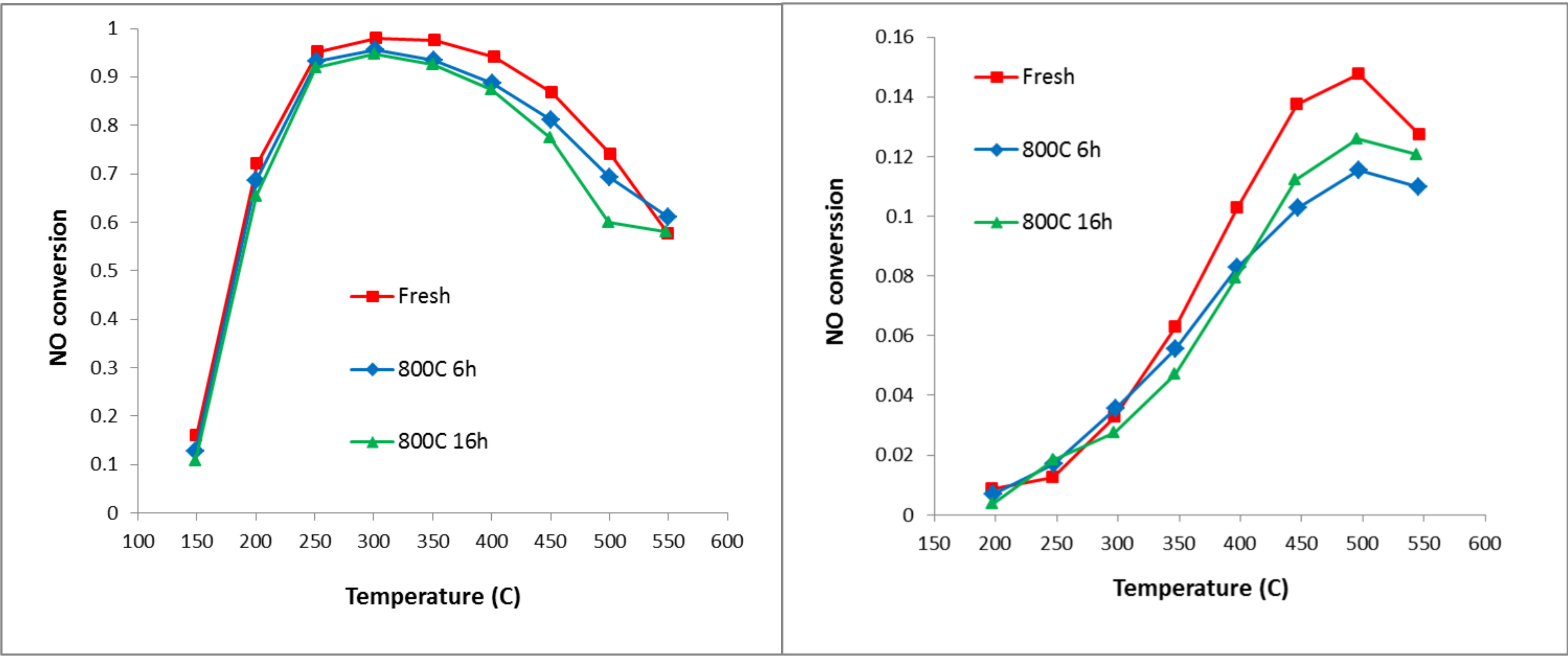


- Hydrothermal aging of Commercial Cu SCR: 700C/4h, 800C/6, 800C/16
- 210ºC and 360ºC peaks

→ Change in distribution of Cu species after HTA?

→ Formation of different Cu species?

NO SCR over Commercial Catalyst



- Progressive deterioration of SCR activity at high temperatures
- Changes in Cu location/species? Changes in kinetics?

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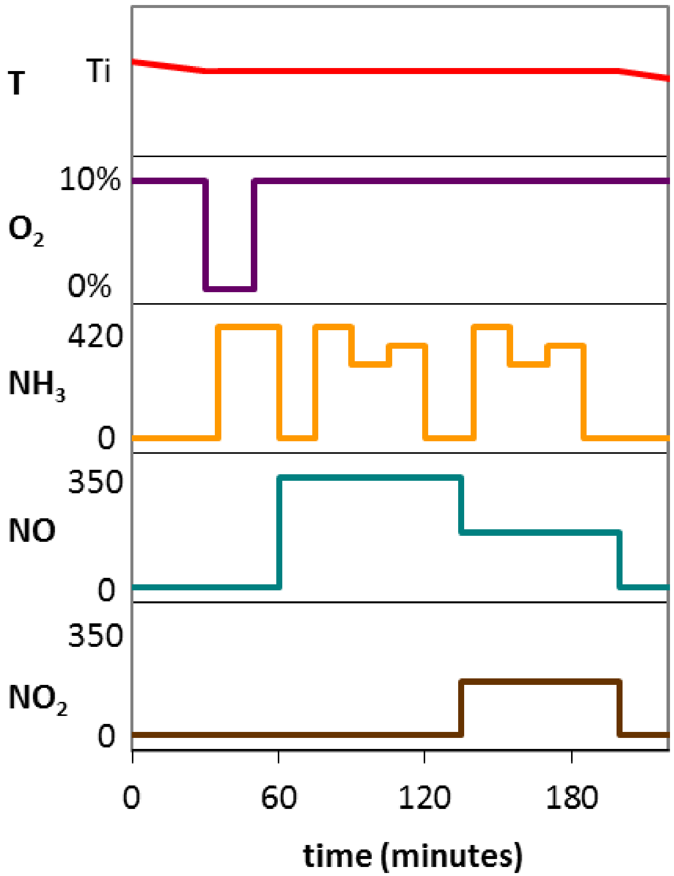
Commercial Cu SCR Catalyst Evaluation

- CLEERS SCR Transient Reactor Protocol designed to generate data needed for model calibration and performance evaluation
  - ✓ Steady state & transient 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

- Experiments conducted on commercial core samples
  - ✓ 150-550°C
  - ✓ 30k, 60k, 90k h^{-1}
  - ✓ 350 ppm NOx



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Cu SCR Model Development

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

Cu SCR Model Development

- All SCR models developed in Matlab/Simulink using a variable step solver (ode23tb)
- First order Euler integration in space – 100 elements (cells) along the axis
- Nonlinear constrained minimization (fmincon) used to identify rate parameters using Matlab's Optimization toolbox

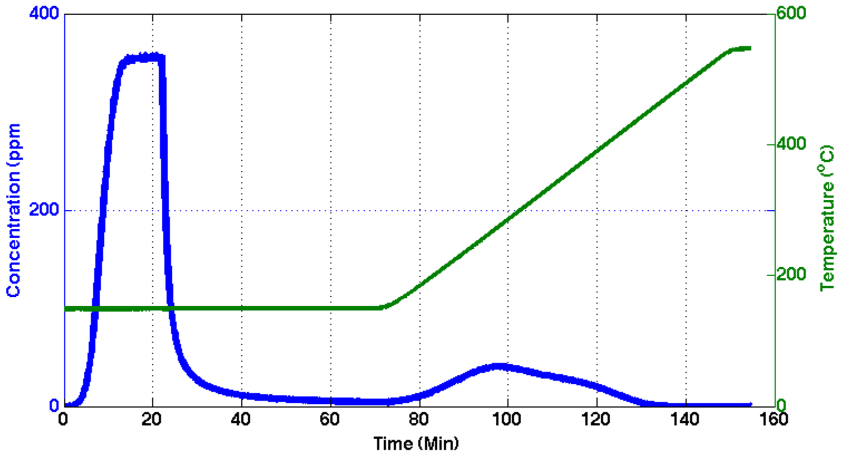
$$\frac{\partial c_{g,NH_3}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NH_3}}{\partial x} + \frac{\Omega}{\varepsilon}(r_{des} - r_{ads})$$

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

NH_3 adsorption and desorption

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

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



SCR Reactions

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

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

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

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

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

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

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

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

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

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

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

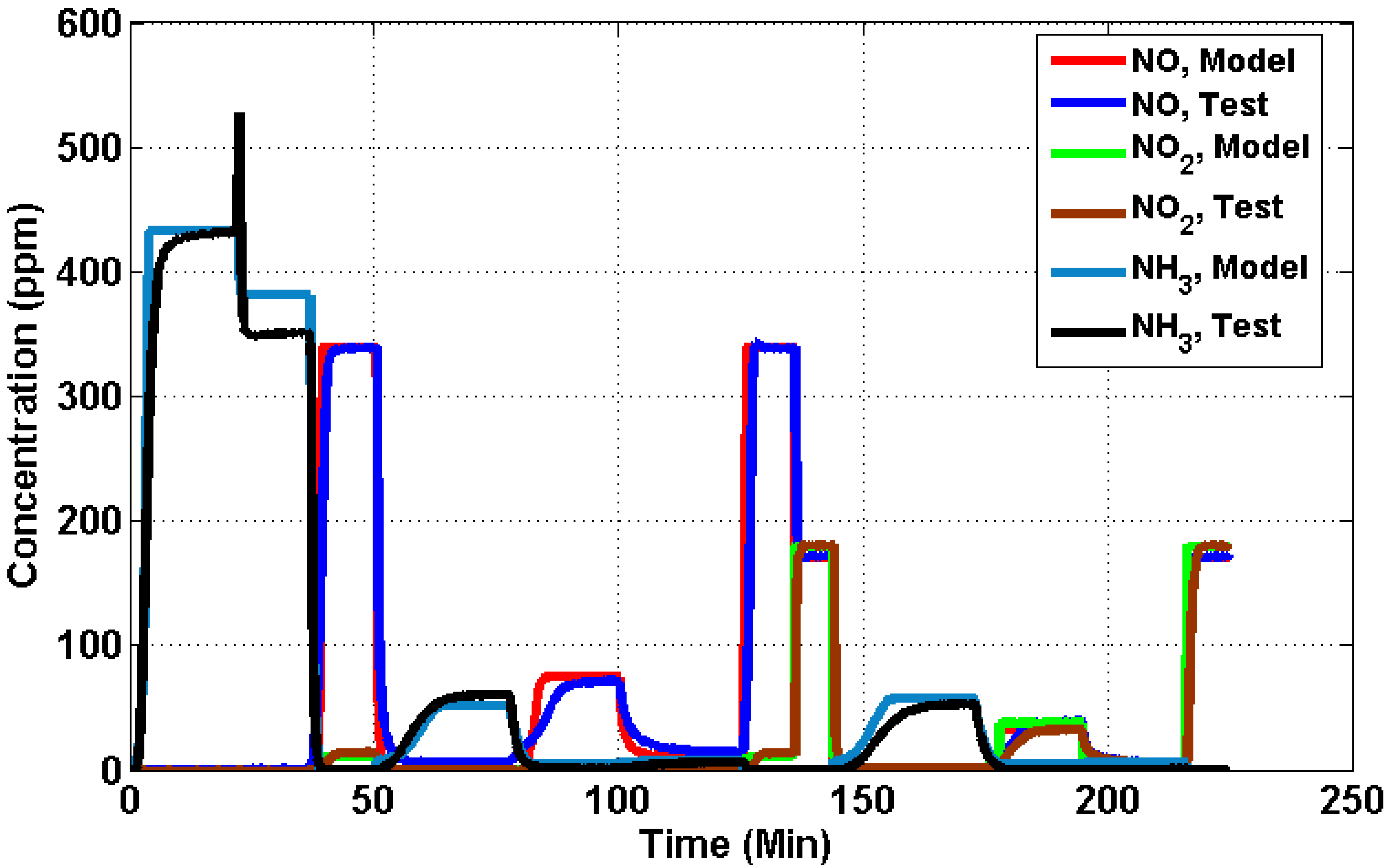
$$\frac{\partial c_{g,NH_3}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NH_3}}{\partial x} + \frac{\Omega}{\varepsilon}(r_{des} - r_{ads})$$

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

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

- Cost function to be minimized is defined as the average sum of absolute error between the test and simulated concentrations.

Model Validation



Rate Parameters

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	Kamasamudram, 2010
NO Oxidation	39	43	Chakravarthy, 2007
Standard SCR	84.9	84.9	Olsson, 2008
Fast SCR	85.1	85.1	Olsson, 2008

- Changes in rate parameters induced by hydrothermal aging to be monitored with respect to changes in Cu species, etc.

Conclusions

- Investigated the effects of hydrothermal aging on the activity and physicochemical properties of model and commercial Cu SCR catalysts.
- Small pore zeolite-based commercial Cu and model Cu-SSZ-13 are highly active, selective, and durable.
  - ✓ Little changes in zeolite structure after 800^{o}C/16h
  - ✓ Isolated Cu ion species (not Cu-aluminate-like species)
- Developed Cu SCR catalyst model to monitor the changes in kinetic parameters induced by catalyst aging.

Acknowledgments

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