Deactivation Mechanisms of Base Metal/Zeolite Urea Selective Catalytic Reduction Materials, and Development of Zeolite-Based Hydrocarbon Adsorber Materials

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May 12, 2011

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

ACE055

Project History

- Initial CRADA signed and project initiated in February 2007
  – Deactivation mechanisms of urea SCR catalysts
- Annual budgets were smaller than planned so some work was de-scoped
- CRADA extended and expanded to now also include HC trap studies in October 2010, total budget remained as initially agreed
- Finish – September 2012
- The project now consists of two parts that will be discussed separately:
  - Deactivation of zeolite-based urea SCR catalysts
    – Chuck Peden (P.I.)
  - Development of Hydrocarbon Adsorber Materials
    – Jong Lee (P.I.)

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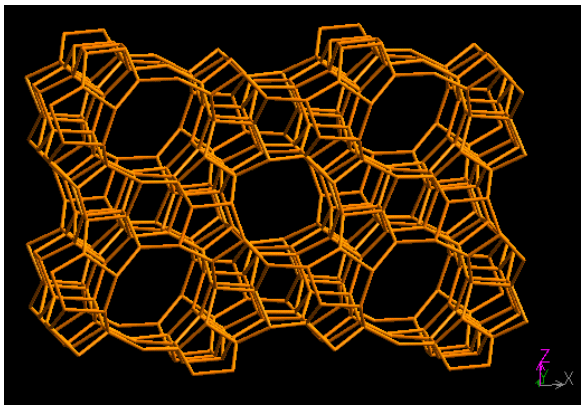
Approach

- Ford tasks:
  - Procure urea SCR catalyst and HC trap materials
    - Commercial materials, model and doped zeolites
  - Laboratory, engine and vehicle aging of materials
  - Laboratory and engine performance testing
  - Provide aged materials for PNNL characterization
  - Develop refined laboratory aging protocols
- PNNL tasks:
  - Use PNNL/IIC's state-of-the-art tools to characterize sets of laboratory- and engine-aged samples provided by Ford.
  - Correlate materials characterization results with performance data (provided by Ford), and with changes in catalyst surface chemical properties as a function of wide array of laboratory and engine aging conditions.
  - Use this information for determining important mechanisms for performance and activity degradation.

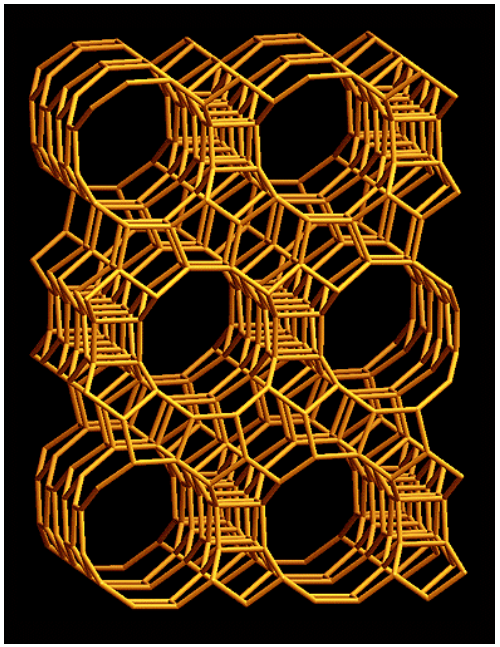
PNNL Catalyst Characterization Facilities

Zeolite Materials are Focus for both Program Elements

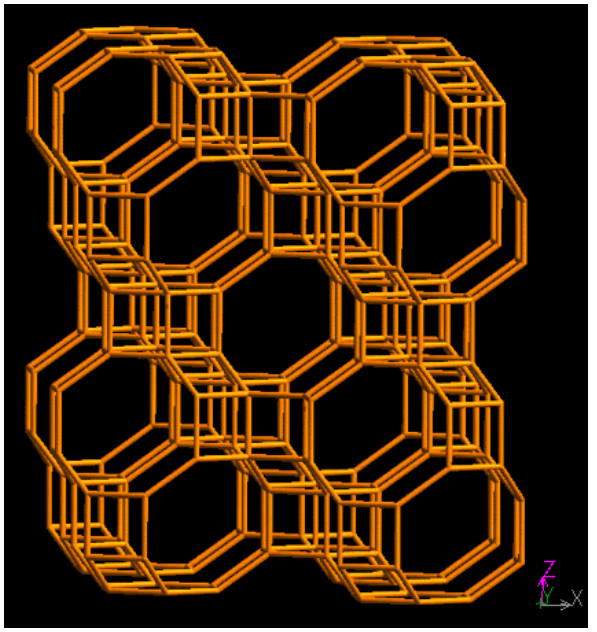
- **Zeolites** are microporous, aluminosilicate minerals
- Widely used as sorbants and catalysts (e.g., petroleum refining)
- ~200 unique zeolite frameworks have been identified, and over 40 naturally occurring zeolite frameworks are known



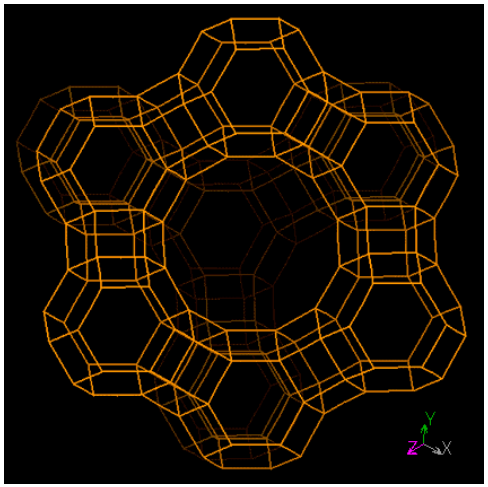
MFI Zeolite (e.g., ZSM-5)



BEA Zeolite (beta)



CHA Zeolite (SAPO-34, SSZ-13)



FAU Zeolite (e.g., Y)

The project consists of two parts:

- Deactivation of zeolite-based urea SCR catalysts – Chuck Peden (P.I.)

- Development of Hydrocarbon Adsorber Materials - Jong Lee (P.I.)

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Project Overview

Timeline

- Start – February 2007
- CRADA extended and expanded (now also includes HC trap studies to be discussed separately) in FY11
- Finish – September 2012

Budget

- DOE funding for urea SCR studies in FY11: $150K

Barriers

- Discussed on next slide

Partners

- Institute for Interfacial Catalysis, PNNL
- Ford Motor Company

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Barriers

- Lean-NOx emission control technologies, including urea selective catalytic reduction (SCR) are needed to enable wider use of fuel-efficient diesel engines.
- Regulations impose challenging requirements for catalyst activity and durability, with durability especially difficult due to a relative lack of experience with this new technology.
- As such, there is a critical need to develop realistic laboratory aging protocols that effectively simulate engine aging induced catalyst deactivation. For this, a fundamental understanding of the deactivation mechanisms is essential.

Purpose of the Work

- Develop an understanding of various aging factors that impact the long-term performance of urea selective catalytic reduction (SCR) materials in diesel vehicle applications.
- Improve the correlation between laboratory and engine aging.
- (Ford activity): Use this fundamental understanding to develop realistic laboratory aging protocols, saving experimental time and cost.

FY 2011 Objectives/Activities

Recent accomplishments in a number of areas:

1. Sulfur poisoning of urea SCR catalysts that follow a diesel oxidation catalyst (DOC):
   - Studies of sulfur poisoning of urea SCR catalysts look at effects of SO_2 since this is the primary S-species in the exhaust.
   - However, DOC's (which typically contain Pt) will oxidize SO_2 to SO_3.
   - Recent Ford work has shown significantly greater poisoning by SO_3 than with SO_2.
   - PNNL has performed detailed studies to develop an understanding of the differing effects of these two sulfur species, and to identify mechanisms of poisoning.

FY 2011 Objectives/Activities

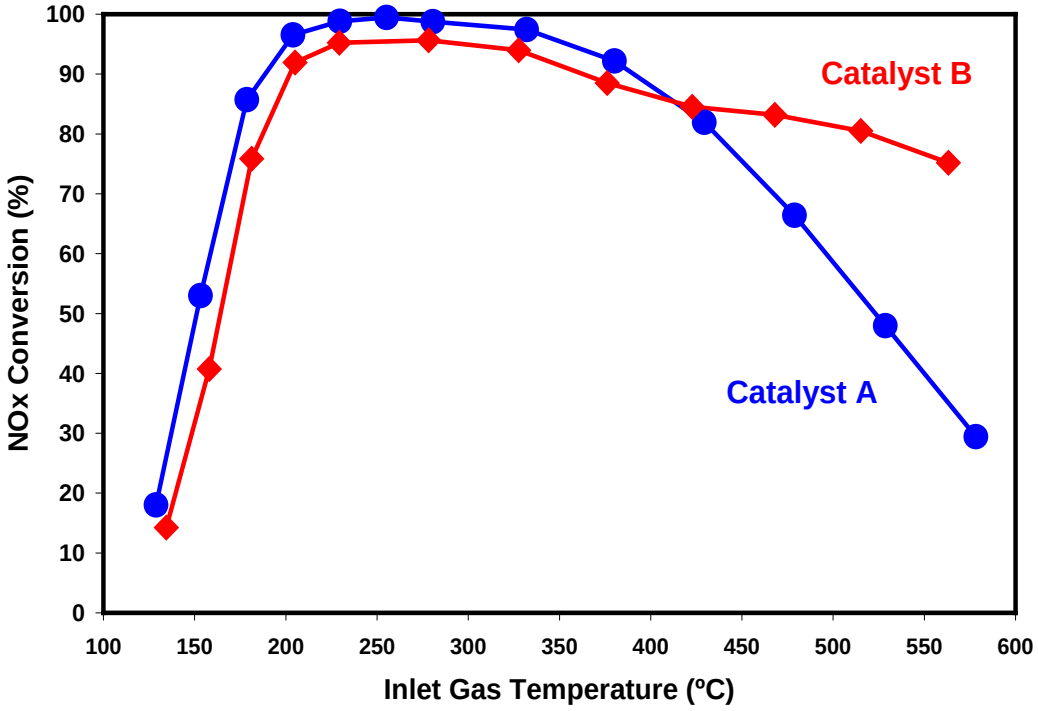
Recent accomplishments in a number of areas:

2. Characterize the nature and distribution of phosphorus deposits observed on engine-aged urea SCR catalysts.
3. Develop a detailed understanding of unusual hydrothermal aging of urea SCR catalysts observed at Ford:
   - Initial results published in SAE paper by Ford researchers (Cavataio, et al.) that suggested possible way to obtain better HT performance.
   - PNNL reproduced the Ford results in early FY10 on model catalysts.
   - PNNL performed a considerable number of experiments over the last year to try to understand the nature of the active catalyst responsible for the unusual HT behavior.

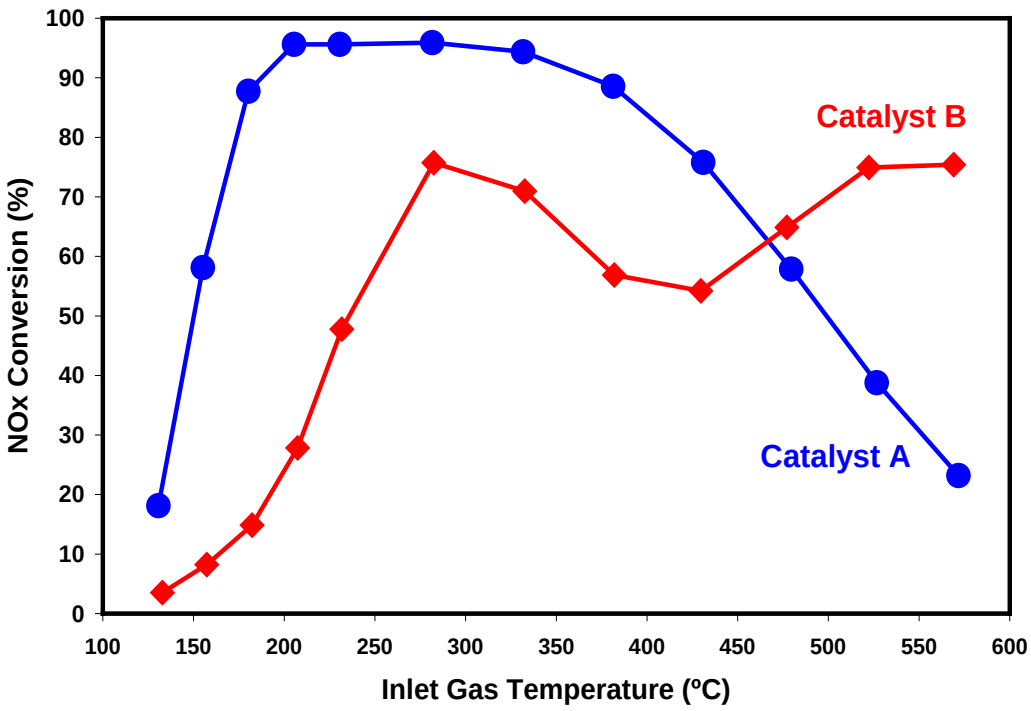
Will present highlights from the third area in the following.

NOx Conversion After Hydrothermal Aging

HTA 64hrs/670°C



HTA 1hr/900°C



Under moderate aging conditions, large differences in SCR NOx performance is observed above 400°C.

Under severe aging conditions, Catalyst B retains high temp. performance but low temp. activity is now unacceptable.

G Cavataio, H-W Jen, JR Warner, JW Girard, JY Kim, CK Lambert, SAE 2008-01-1025

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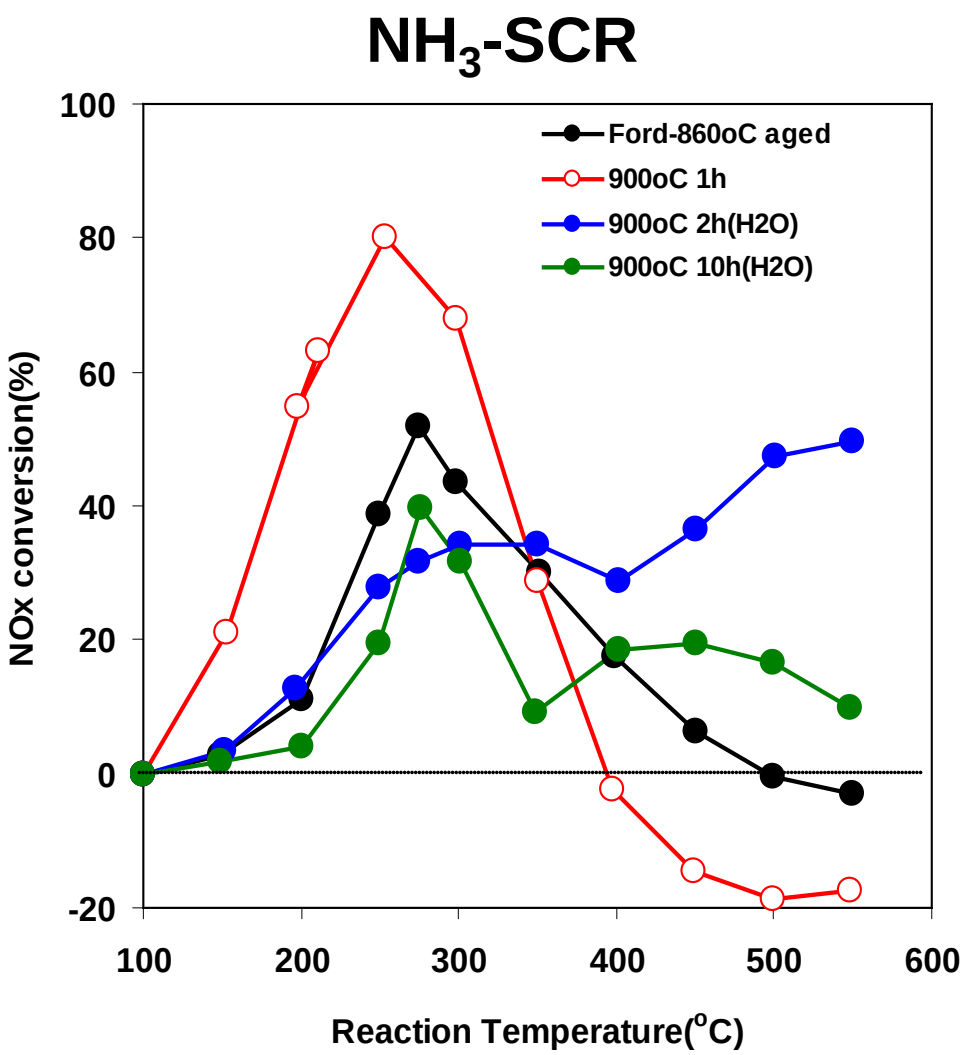
Reaction Conditions and Samples

- Base zeolite: beta zeolite (Si/Al_2 = 38) from Zeolyst
- Cu ion exchange: solution ion exchange twice
- Heat treatment: 900°C with and without H_2O
- Reaction tests:
  - NH_3-SCR
    - Catalyst: 0.11g
    - total flow rate: 500 sccm (~350 ppm NO, ~350 ppm NH_3 14% O_2, 4%H_2O in He)
  - NH_3-oxidation
    - Catalyst: 0.11 g
    - Total flow rate: 500 sccm (~350 ppm NH_3, 14% O_2, 4% H_2O in He)
  - Product analysis with FTIR

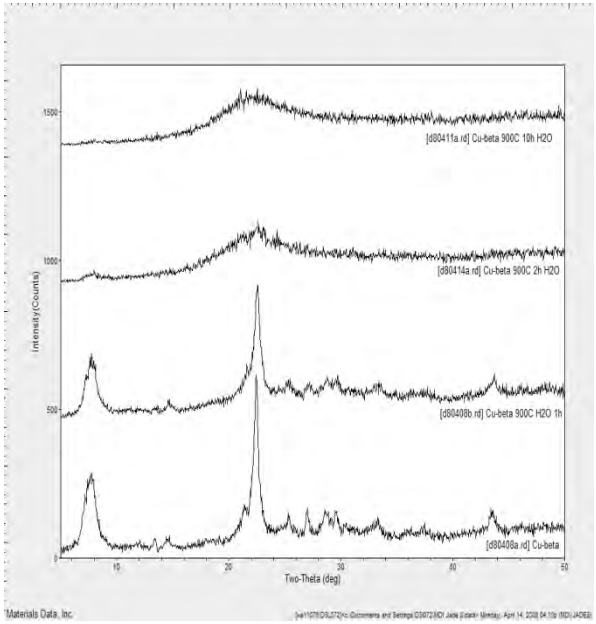
Summary of Reaction Data – NH_3 SCR



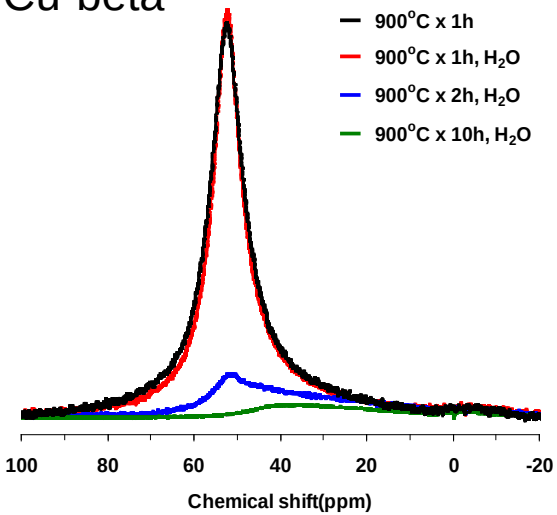
- Catalyst treated at 900°C for 1 hr without H_2O shows highest activity at ~ 250°C, but performance drops at higher temperature and even makes NO_x above 400°C.
- Sample treated at 900°C for 2 hrs with 2% H_2O shows very similar behavior with Ford's high temperature aged sample.
- Even more severely (10 hr) treated sample shows similar behavior but significantly lower activity.
- This behavior has some correlation with residual zeolite structure.

Characterization of High-Temp Calcined Cu-Beta by XRD, TEM and NMR

XRD



Cu-beta



XRD and TEM

- Zeolite structure was maintained after calcination at 900°C for 1 hour under air flow with 2% H_2O.
- However, most of the structure was collapsed after a 2 hour treatment using the same conditions.
- No evidence for bulk-like Cu species in XRD or TEM.

NMR

- Tetrahedral aluminum NMR peak 900°C 1h treated sample does not change.
- Sample treated at 900°C for 2h with water loses significant amounts of tetrahedral aluminum, consistent with XRD and TEM results.
- However, a peak due to octahedral aluminum does not form which may mean that Cu strongly interacts with the produced aluminum species.

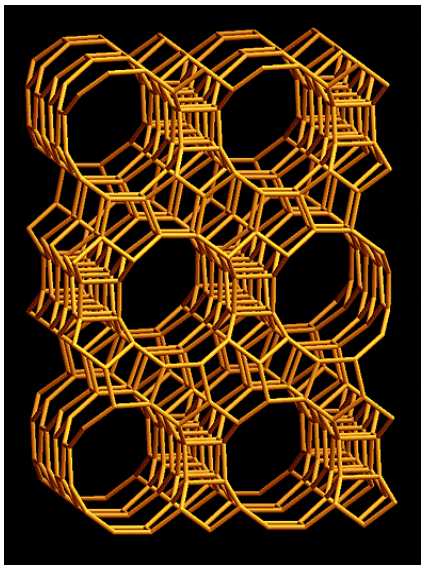
Solid-State ^{27}Al NMR

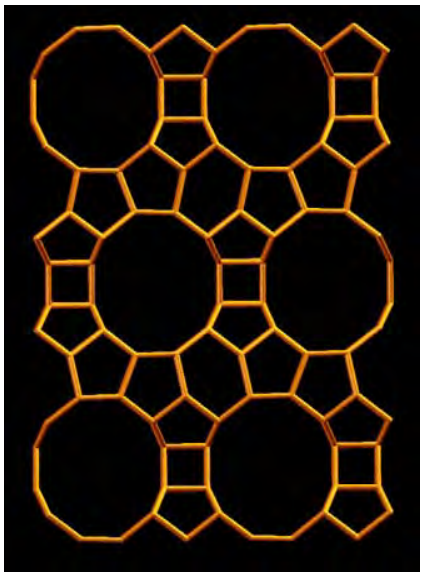
Summary of Initial Studies

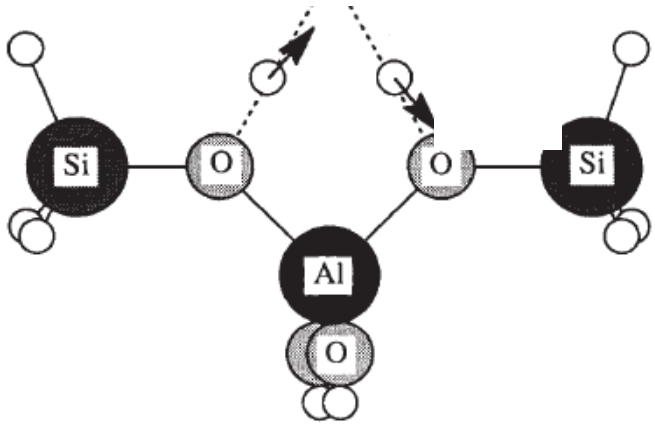
- Cu-beta treated at 900°C for 2 hours with H_2O shows similar reaction profiles with Ford's high-temperature aged sample.
- Partially collapsed structure seems to account for the unique NH_3-SCR activity behavior of these intermediately aged samples.
- No evidence in TEM and XRD for bulk-like Cu species.
- NMR results indicate a strong interaction between Cu and Al in the aged catalysts that show good high-temperature NH_3-SCR performance.

What may be occurring during hydrothermal deactivation of zeolites?

BEA Zeolite (Viewed along [100])





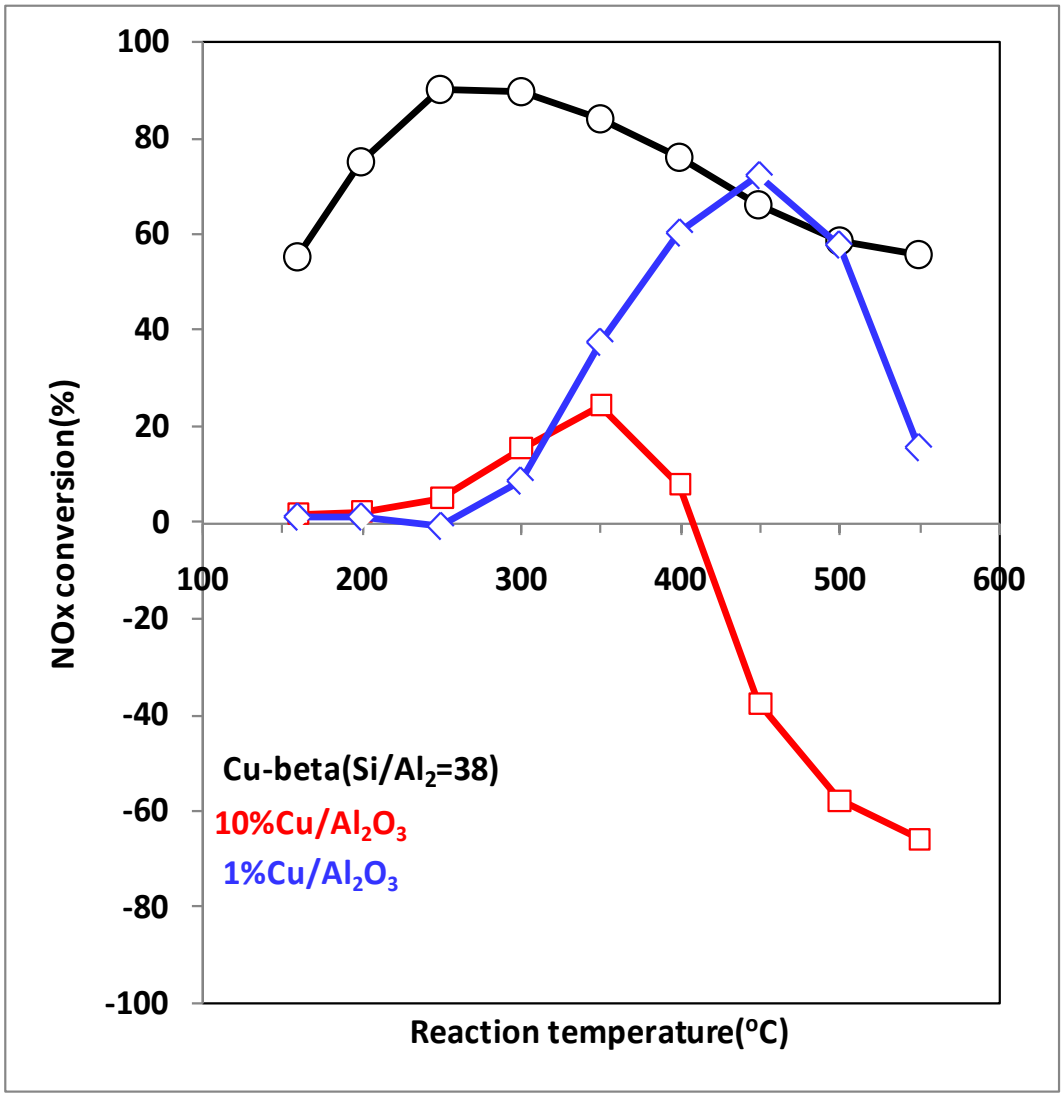


Hydrolysis of Si-O-Al bonds results in removal of Al species from the zeolite framework.

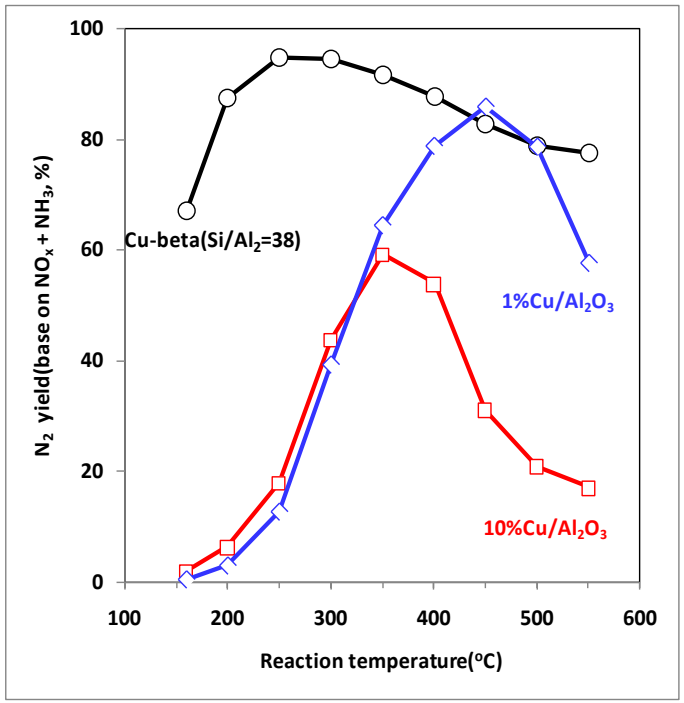
Possible Candidate Catalyst Structures

- A series of Cu on gamma-alumina with various loadings of Cu (e.g., see Kwak, J.H.; Hu, J.Z.; Mei, D.; Yi, C. W.; Kim, D.H.; Peden, C.H.F.; Allard, L.F.; Szanyi, J. *Science* 2009, ***325***, 1670-1673).
- De-aluminate a beta zeolite first and then impregnate Cu to various loadings.
- Impregnate various loadings of Cu on our monolayer alumina/MCM-41 or /SBA-15 materials.(e.g., see Herrera, J.E.; Kwak, J.H.; Hu, J.Z.; Wang, Y.; Peden, C.H.F., J. *Topics in Catalysis* 2006, ***39***, 245-255) – ***See Extras***.

NH_3 SCR on Cu/alumina



- Isolated CuO shows significant SCR activity at high temperature.
- CuO clusters at high Cu loading oxidize the NH_3 and produce NO_x.



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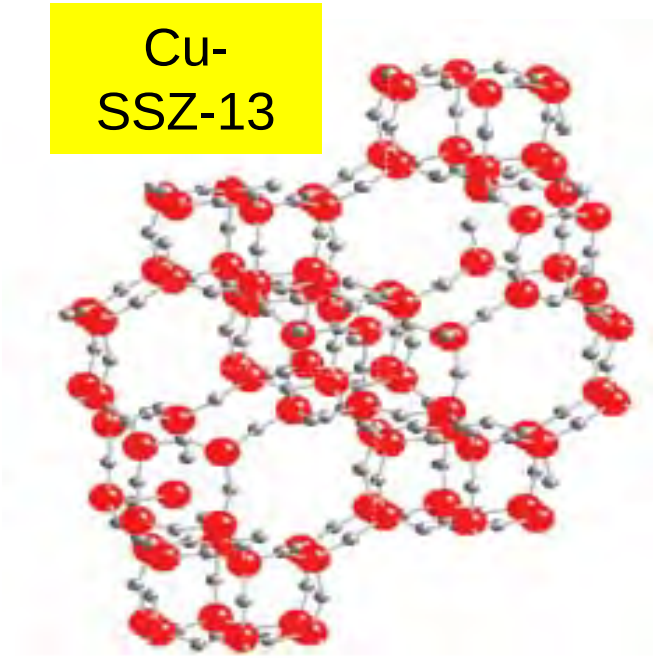
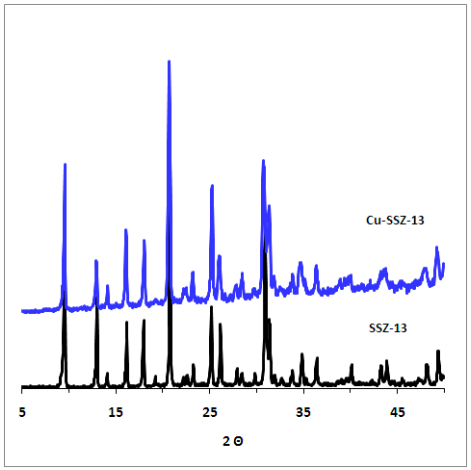
Activities for Next Fiscal Year

- Complete mechanistic studies of phosphorus deactivating effects .
- Detailed studies of hydrothermal dealumination in Cu-SSZ-13 (CHA).
- Preparing additional CHA zeolite for joint Ford/PNNL studies of Cu loading effects (aimed at HT performance).
- Some new focus on:
  - SCR degradation mechanisms due to upstream LNT;
  - SCR deactivation due to use of biofuels.





Summary

- PNNL has been carrying out a CRADA program with Ford Motor Company to study deactivation mechanisms in zeolite-based urea SCR catalysts. A specific goal of this work is to use this fundamental information to develop realistic laboratory aging protocols.
- Technical progress to date has included correlation of catalyst characterization with performance of laboratory- and field-aged samples, studies of the variable effects of SO_2 versus SO_3 poisoning, and deactivation due to phosphorus.
- Hydrothermal aging of zeolite-based SCR catalyst shown to provide possible route to achieve high-temperature performance.

The project consists of two parts:

- Deactivation of zeolite-based urea SCR catalysts – Chuck Peden (P.I.)

- Development of Hydrocarbon Adsorber Materials - Jong Lee (P.I.)

Overview

Timeline

- Start – October 2010
- Finish – September 2012

Budget

- DOE funding in:
  - FY11: $125K

Barriers

- Upcoming stringent hydrocarbon emission standards
- Increased HC emissions from advanced combustion, vehicle electrification & biofuel (E85)
- Better understanding of the HC adsorber materials for improved performance and durability

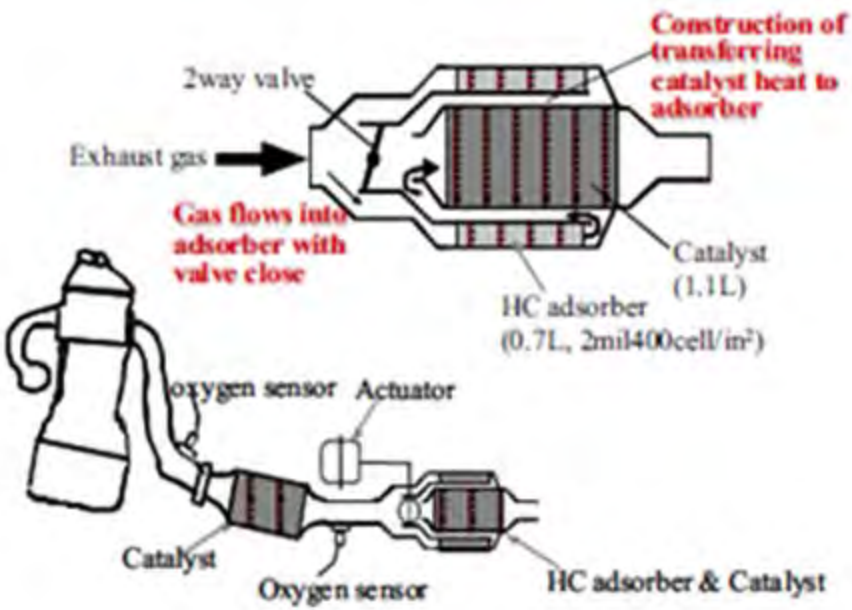
Partners

- Institute for Interfacial Catalysis, PNNL
- Ford Motor Company

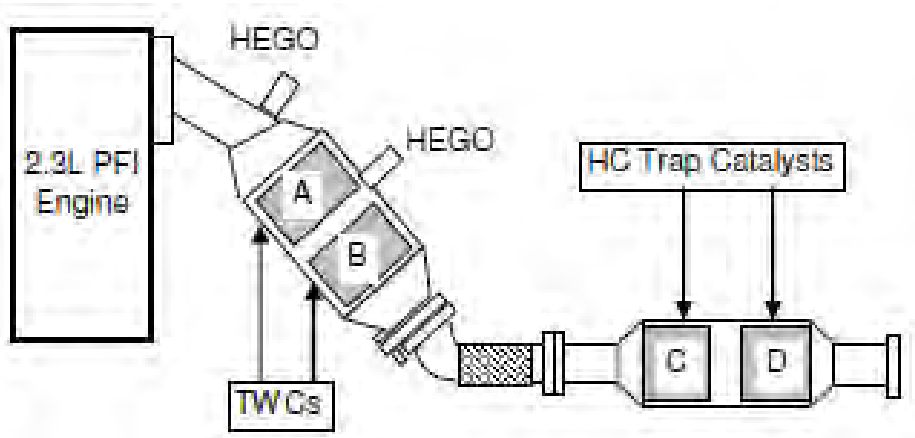
Objectives

- Help fuel-efficient advanced combustion engines meet the current and future HC emission standards with effective, inexpensive and reliable HC adsorber technologies
- Improve the understanding of interaction between engine-out HCs and HC adsorber materials during the cold-start and the catalyst warm-up periods

Active Bypass HC Trap System

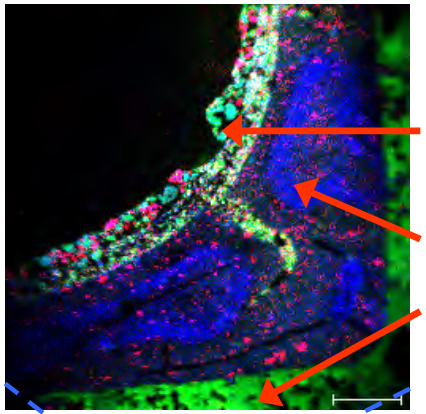


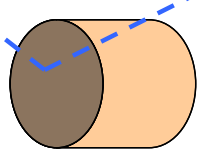
Passive In-line HC Trap System



How Does a Hydrocarbon Trap Work?

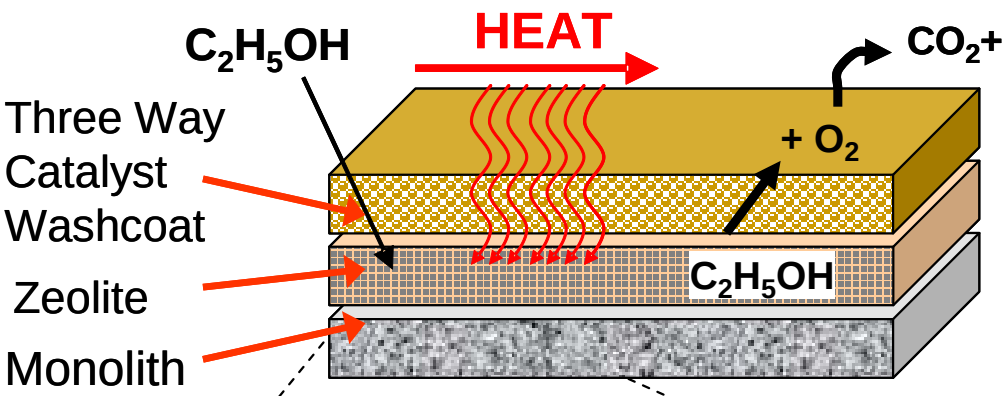
Square channels on front face of HC Trap brick

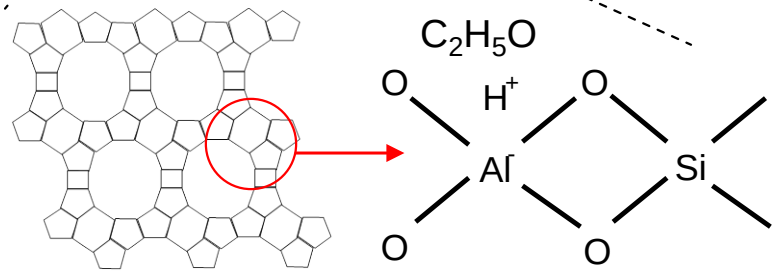




Catalyzed HC trap washcoats on ceramic honeycomb monolith

1. Adsorption of Hydrocarbon into zeolite
2. Warm-up of bulk exhaust stream
3. Desorption of Hydrocarbon from zeolite
4. Hydrocarbon oxidation over catalyzed washcoat with Oxygen





Beta Zeolite

Ford Research and Advanced Engineering

Zeolite cage structure traps and holds hydrocarbon molecules at metal ion sites (Al^{-1}) until precious metal catalyst in washcoat is hot enough to oxidize them.

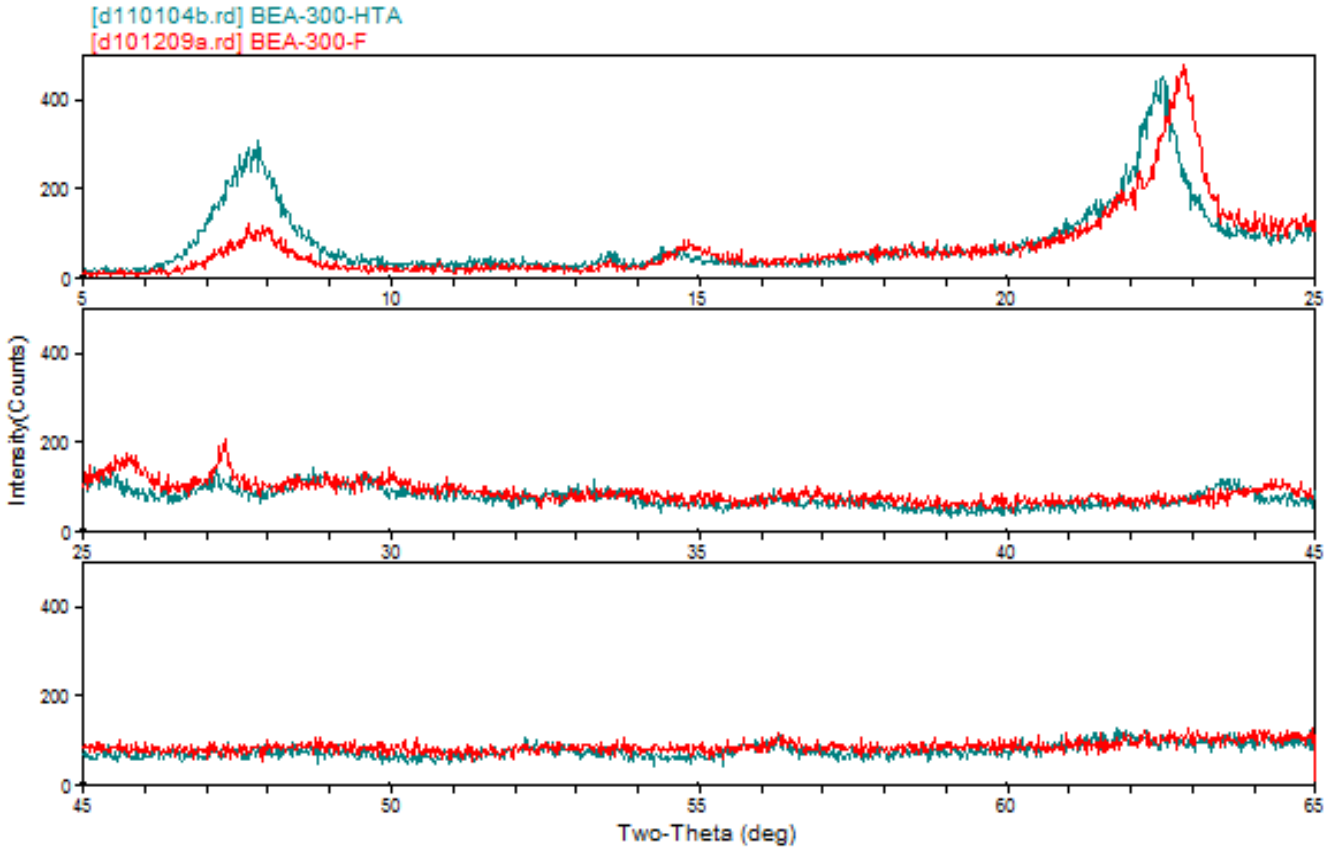
FY10/11 Activities at PNNL

Evaluate HC adsorption/desorption with single HC species

- Fuel-component (ethanol, toluene, n-dodecane), combustion products (propene) with/without H_2O

1. Effect of Si/Al ratio
   - ZSM-5, BEA
   - Hydrophobicity on total HC adsorption capacity
2. Effect of pore size & structure
   - Beta (Large 3D), ZSM-5 (Medium 3D), ZSM-12 (Large 1D)
   - Size & shape selectivity, diffusion under transient conditions
3. Effect of metals
   - Ag, Pd, Cu, Fe, Ba
   - HC chemisorption & reactions (partial oxidation, oligomerization)

Effects of Hydrothermal Aging

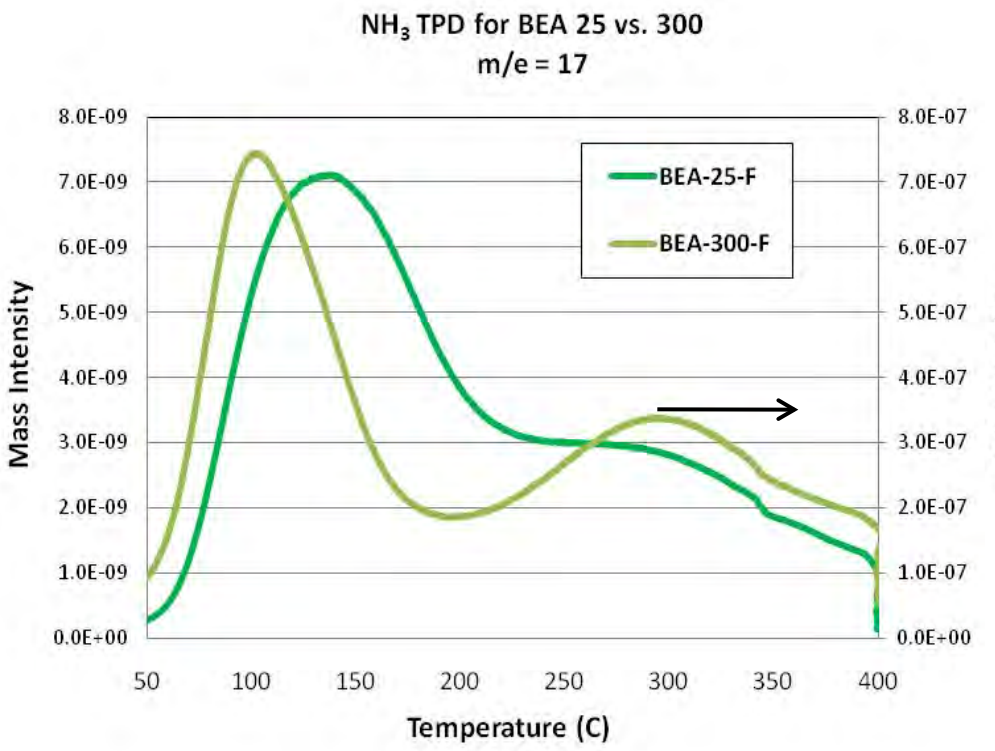


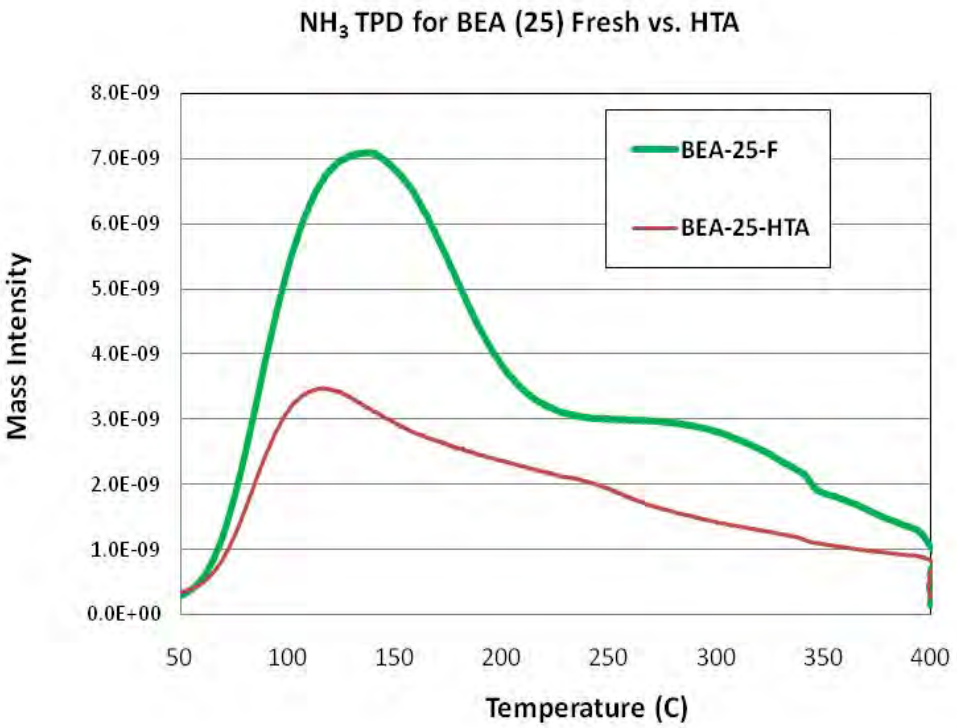
*<u>HTA:</u>

- 10% H_2O in air
- 800°C/80h

- After HTA, little change seen in XRD patterns
- However, loss of BET surface area (estimate only) despite lack of change in XRD results
- Mesopores seen in BEA (30), ZSM-5 (280)

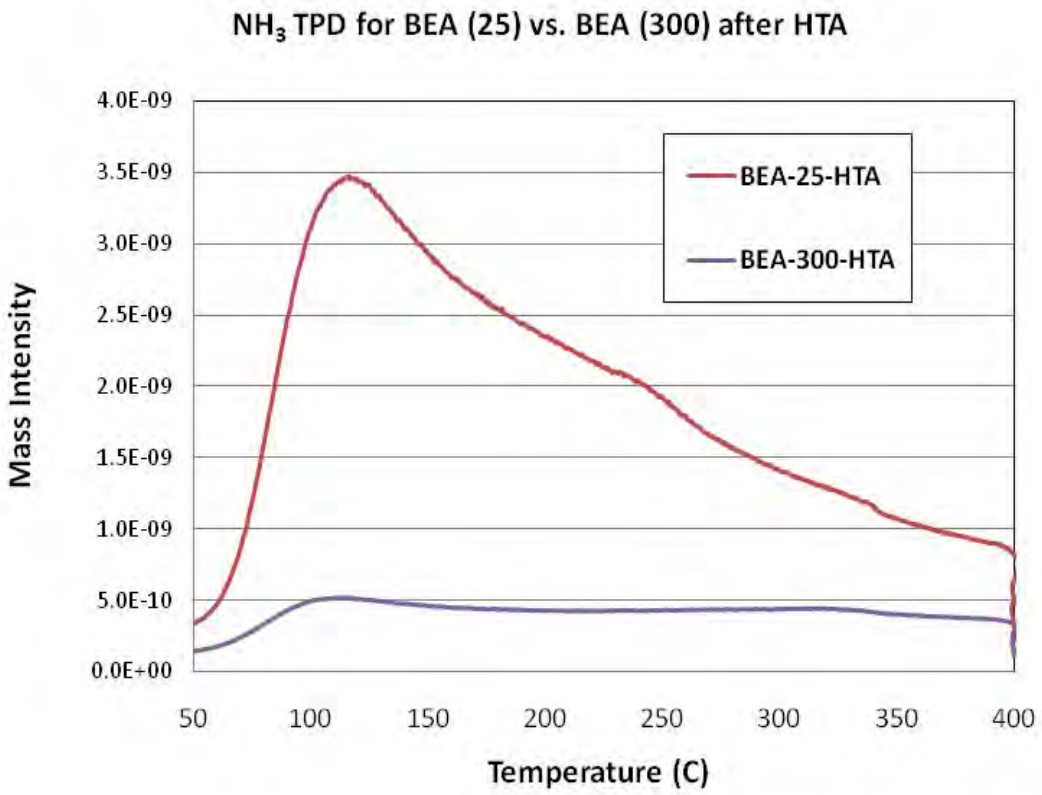
Effects of Hydrothermal Aging





- LT peak assigned to Lewis acid sites, HT peak to Brönsted acid sites
- Loss of acid sites and strength after HTA at 800ºC/80h

Effects of Si/Al Ratio



Adsorbent	NH3 Adsorption capacity (mL STP NH3/g adsorbent)	NH3 Adsorption capacity (mol NH3/g adsorbent)
BEA-25-F	49.89603	2.228E-03
BEA-25-HTA	6.51759	2.910E-04
BEA-300-F	10.0797	4.500E-04
BEA-300-HTA	1.46575	6.544E-05

- Lower number of acid sites with high Si/Al samples
- Significantly reduced number of acid sites after HTA, compared to surface area
- Only ~10% lower surface area for BEA-300-HTA

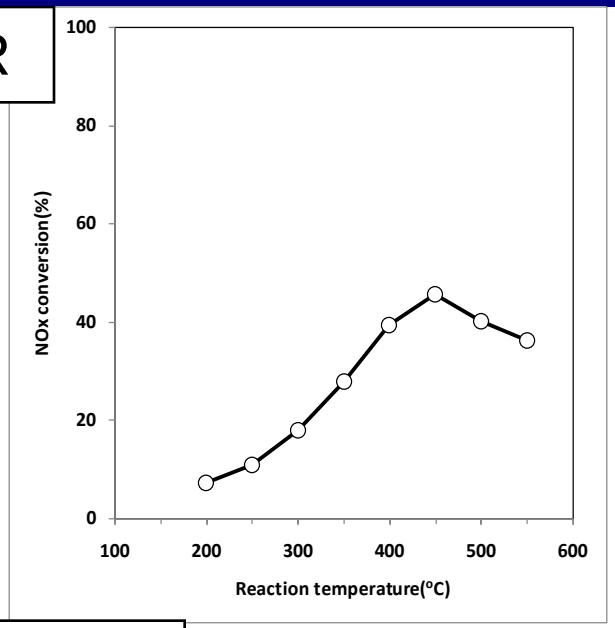
Summary & Future Work

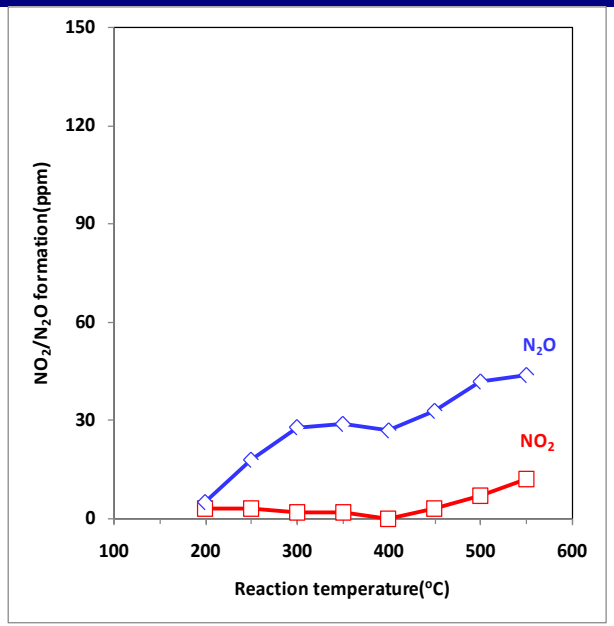
- Model zeolite samples were obtained/prepared to study the effects of physicochemical properties on HC adsorber performance and durability.
- Loss of surface area and crystallinity were observed in select zeolite samples.
- Initial NH_3/Py-TPD and lab reactor testing results indicate, despite lower hydrophobicity, lower Si/Al ratio zeolites appear more effective for HC adsorption and desorption.
- Complete characterization and performance evaluation of the first round model zeolite samples.
- Investigate the effects of pore size and connectivity on HC desorption, and the effects of metals on HC chemisorption and reactions.

Technical Backup Slides

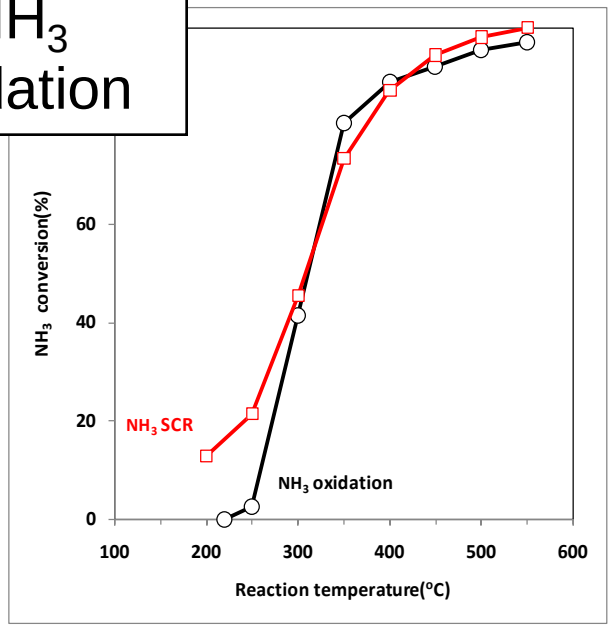
NH_3 SCR on 1% Cu/Al-SBA-15

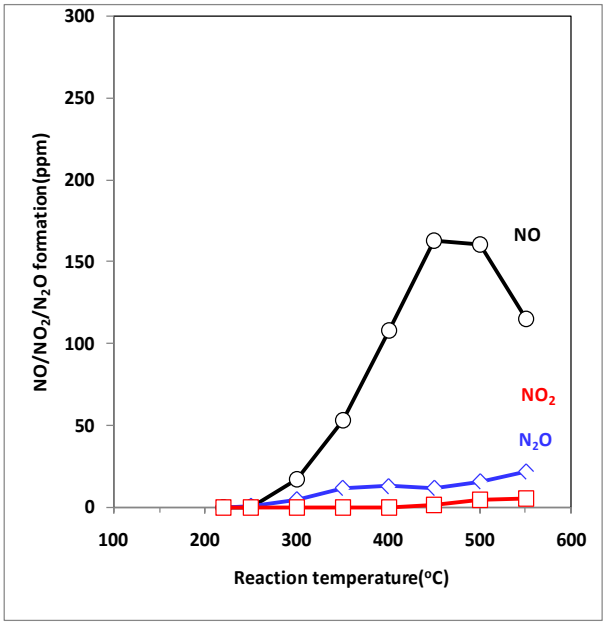
SCR





NH_3 oxidation





- Some amount of SCR activity at high temperatures, but lower than 1% Cu/alumina.
- Relatively low level of NO_2 production than alumina-based catalysts.

- Similar reaction behavior as 1% Cu/alumina.
- Significant amount of NO production.

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Effects of Aging on Surface Area

Sample	BET SA (m2/g)	Pore Size (A)
BEA (25)	700	<10
BEA (25) HTA	560	<10
BEA (300)	708	<10, 50
BEA (300) HTA	505	<10, 80
ZSM-5 (23)	400	<10
ZSM-5 (23) HTA	360	<10, 27(?)
ZSM-5 (280)	404	<10, 18
ZSM-5 (280) HTA	370	<10, 21
ZSM-12 (66)	330	<10
ZSM-12 (66) HTA	75	<10

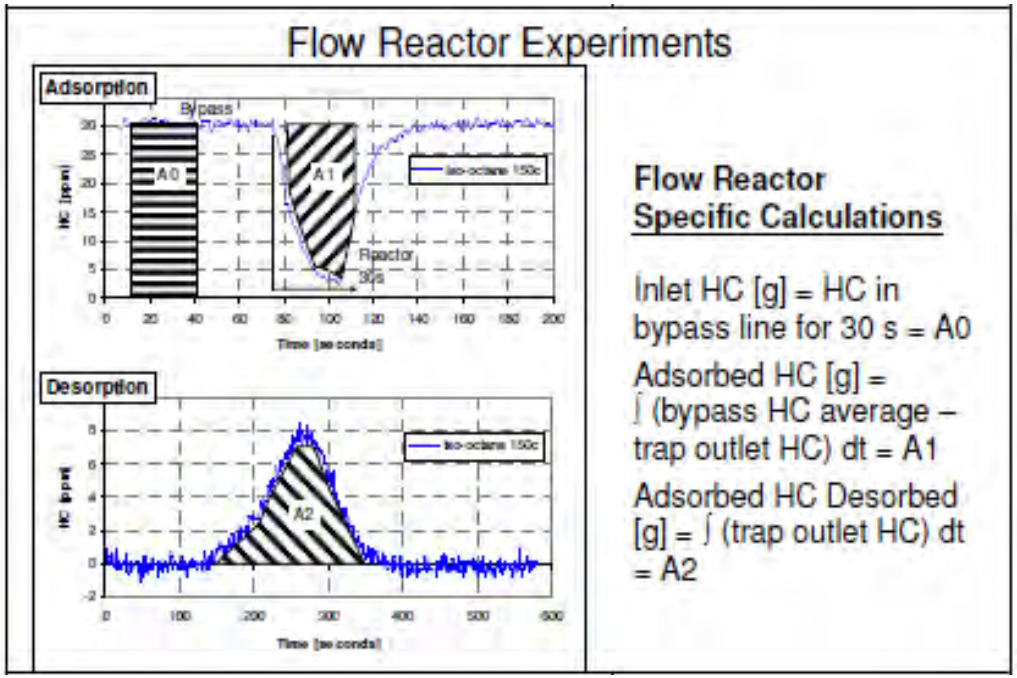
*HTA:

- 10% H_2O in air
- 800°C/80h

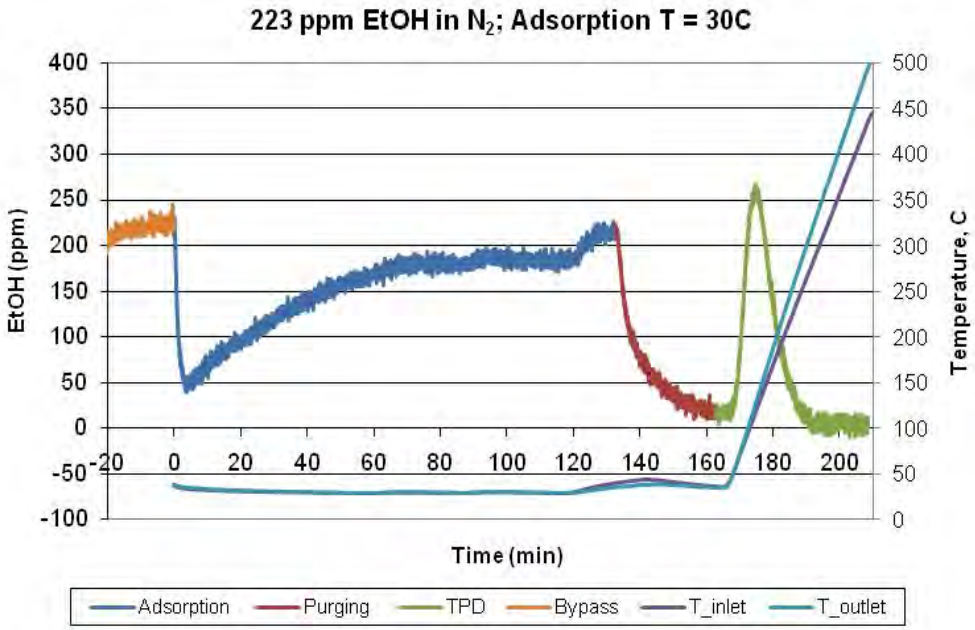
- Loss of BET surface area (estimate only) despite little changes in XRD
- Mesopores seen in BEA (30), ZSM-5 (280)

HC Adsorption/Desorption Testing

- Reactor setup and test procedure with a commercial sample
  - Reactor system to handle both monolith and powder samples
- Ethanol adsorption/desorption (in progress)
  - Temporal exposure to ethanol, followed by TPD
  - Effects of H_2O, aging, Si/Al ratio, etc.



2001 Nissan Sentra PZEV



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