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

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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 also include HC trap studies in October 2010 (beginning for FY11), total budget remained as initially agreed
- Finish – September 2012 (end of FY12)
- The project consisted of two parts that will be discussed separately:
  - Deactivation of zeolite-based urea SCR catalysts
  - Development of Hydrocarbon Adsorber Materials

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

The project consisted of two parts:

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

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

Project Overview

Timeline

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

Budget

- DOE funding for urea SCR studies in FY12: $150K

Barriers

- Discussed on next slide

Partners

- Institute for Integrated Catalysis, PNNL
- Ford Motor Company

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.

Purpose of the Work

- Correlate the performance and characterization of the catalysts aged in the laboratory, on engines and on vehicles.
- Develop an understanding of various specific aging factors identified by Ford and in this work as possibly impacting the long-term performance of urea selective catalytic reduction (SCR) materials in diesel vehicle applications.
- (Ford activity): Use these results to develop realistic laboratory aging protocols, saving experimental time and cost.

Program Summary

Studies performed have focused on a number of critical issues:

1. Measurement of the performance and characterization of the catalysts used for various Ford-developed laboratory aging protocols.
2. Sulfur poisoning of urea SCR catalysts that follow a diesel oxidation catalyst:
   - Studies of sulfur poisoning of urea SCR catalysts had only considered 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. Ford studies showed significantly greater poisoning by SO_3 than with SO_2.
   - PNNL performed detailed studies aimed at characterizing the differing effects of these two sulfur species, and to identify their respective mechanisms of poisoning.
3. Laboratory studies of phosphorus poisoning.

Program Progress

Studies to date have focused on a number of critical issues:

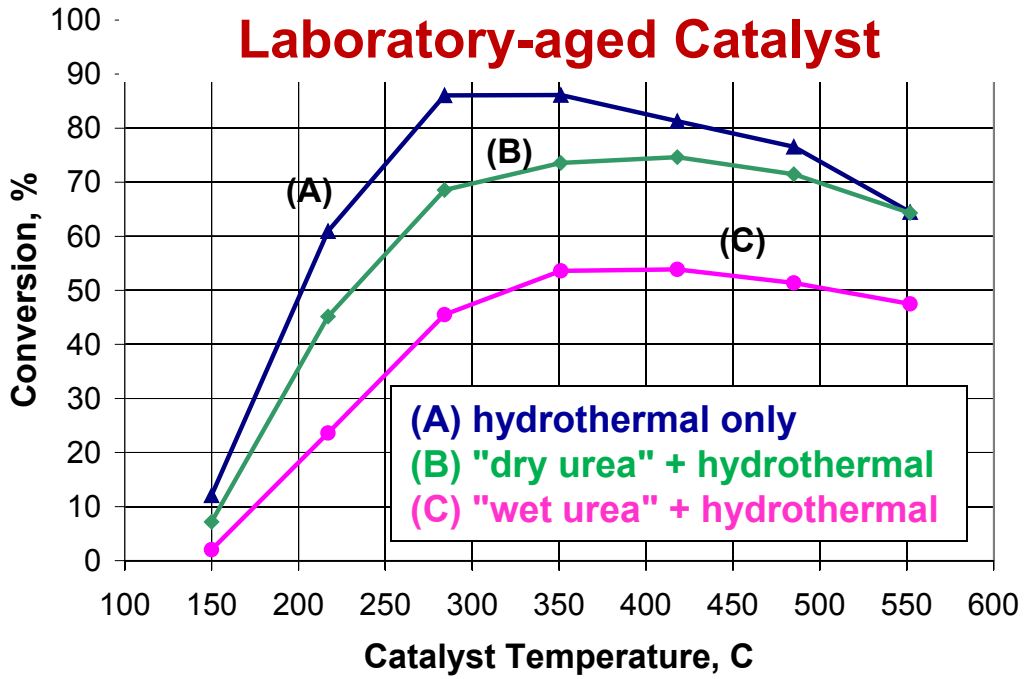
4. Measurement of the performance and materials characterization of engine-aged urea SCR catalysts.

5. 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 some zeolite catalysts, then performed studies of model catalysts aimed at understanding the nature of the active catalyst responsible for the unusual HT behavior.

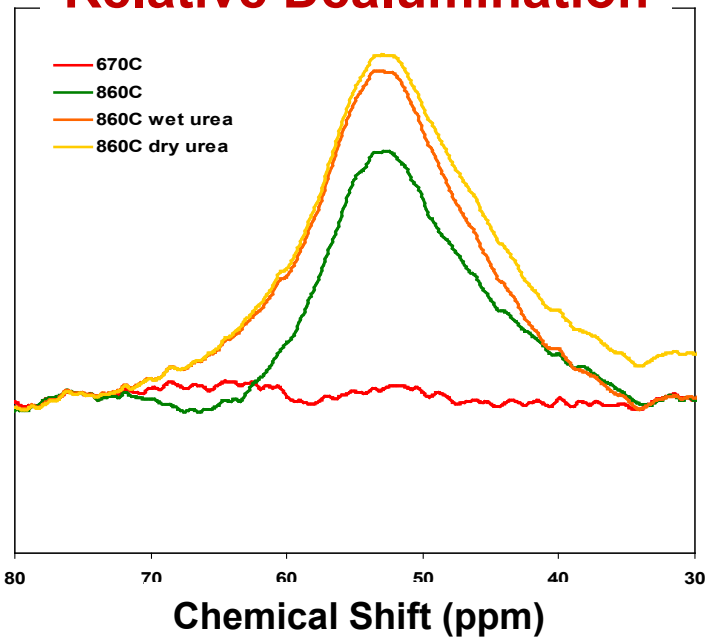
Will present one highlight from each of these areas in the following.

1. Performance and Characterization of Lab-Aged Catalysts

NOx SCR Performance: Laboratory-aged Catalyst



^{27}Al NMR – Relative Dealumination



- First studies carried out when little was known about Cu-zeolite aging in exhaust relevant conditions
- PNNL characterization clearly showed loss of zeolite crystallinity correlated with performance loss measured at Ford.
- Urea may have some influence on catalyst aging.

Y Cheng, J Hoard, CK Lambert, JH Kwak, CHF Peden, *Catalysis Today* **136** (2008) 34-39.

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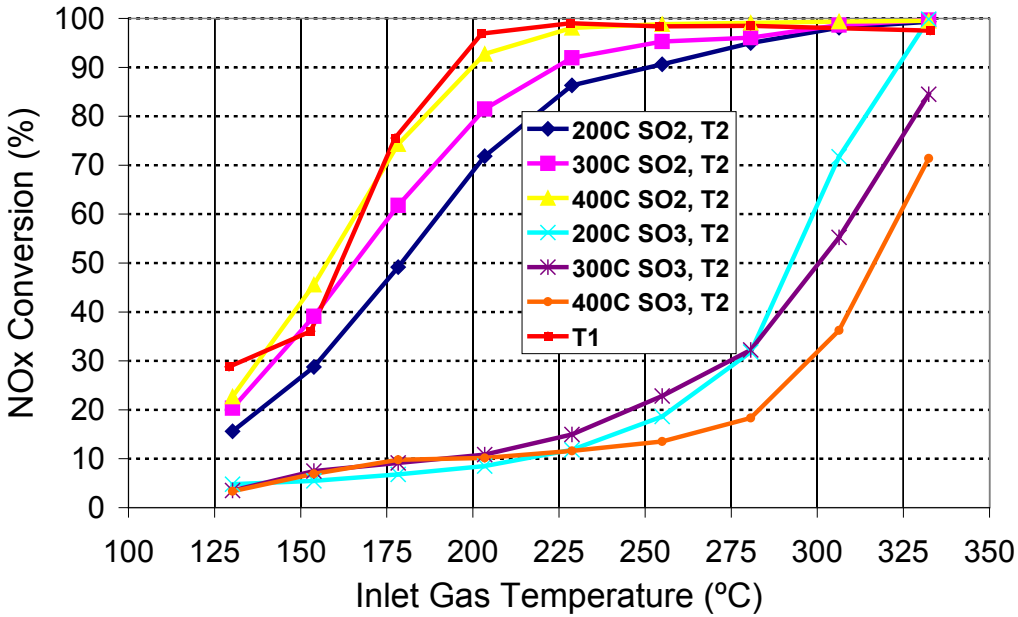
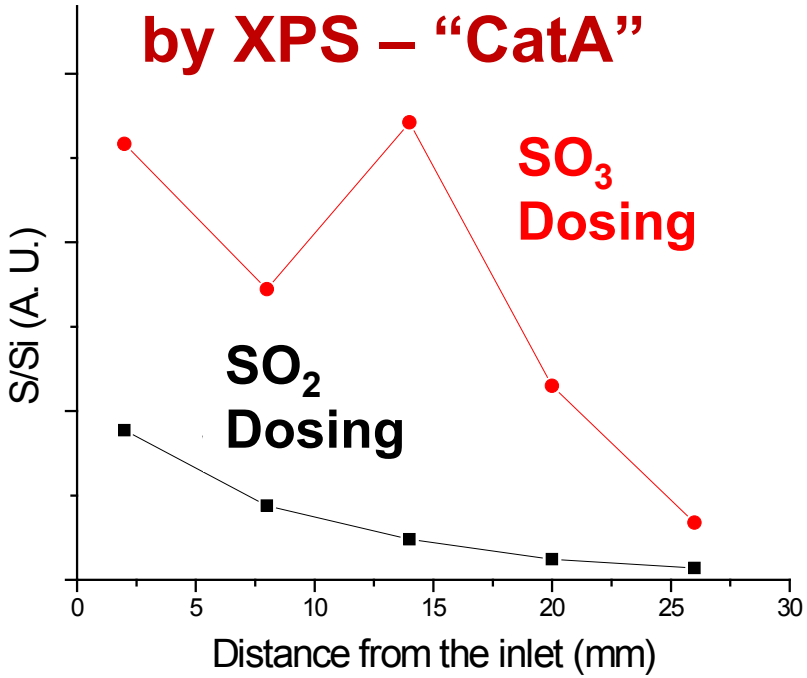
2. Sulfur poisoning of SCR catalysts that follow a diesel oxidation catalyst

Ford SCR Performance Data Exposure to Either SO_2 or SO_3



S Distributions by XPS – "CatA"



- SCR Performance clearly sensitive to whether sulfur present as SO_2 (as in engine exhaust) or SO_3 (as after a DOC).
- PNNL-obtained XPS and EXAFS results verified significantly higher residual sulfur concentrations with SO_3 exposure.
- TPD used to estimate strength of binding of formed S-species.

Y Cheng, CK Lambert, DH Kim, SJ Cho, JH Kwak, CHF Peden, *Catalysis Today* **151** (2010) 266-270.

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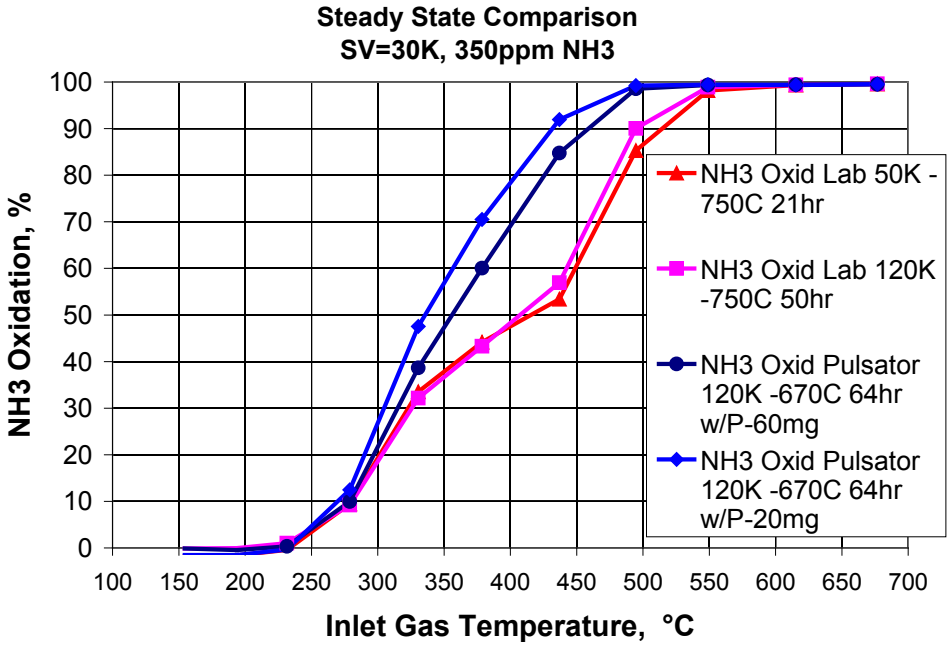
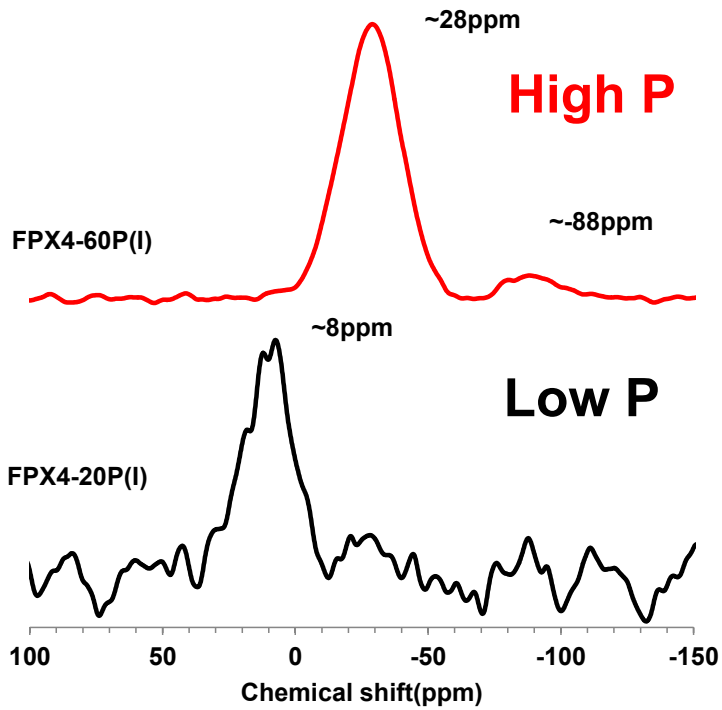
3. Laboratory studies of poisoning phosphorus in the exhaust

Ford NH_3 Oxidation Data With and Without Varying Phosphorus Exposures



^{31}P NMR Data



- SCR performance (not shown) and NH_3 oxidation show some sensitivity to prior exposure to phosphorus.
- Phosphate-like P present at various concentrations via XPS.
- ^{31}P NMR peak shifts with phosphorus loading – why?

Y Cheng, D Dobson, CK Lambert, JH Kwak, CHF Peden, *unpublished results*.

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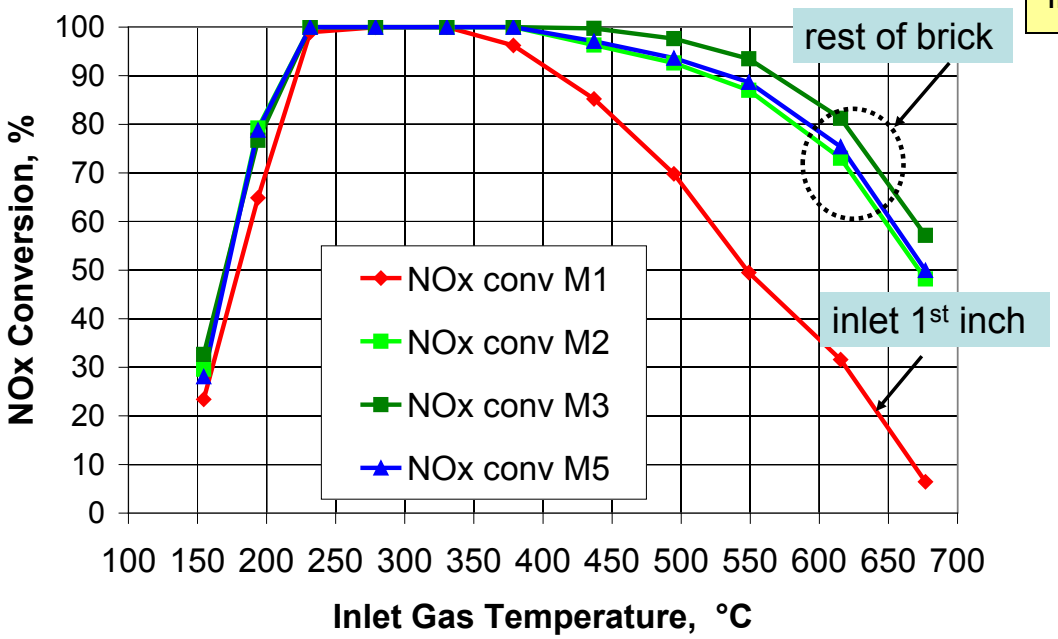
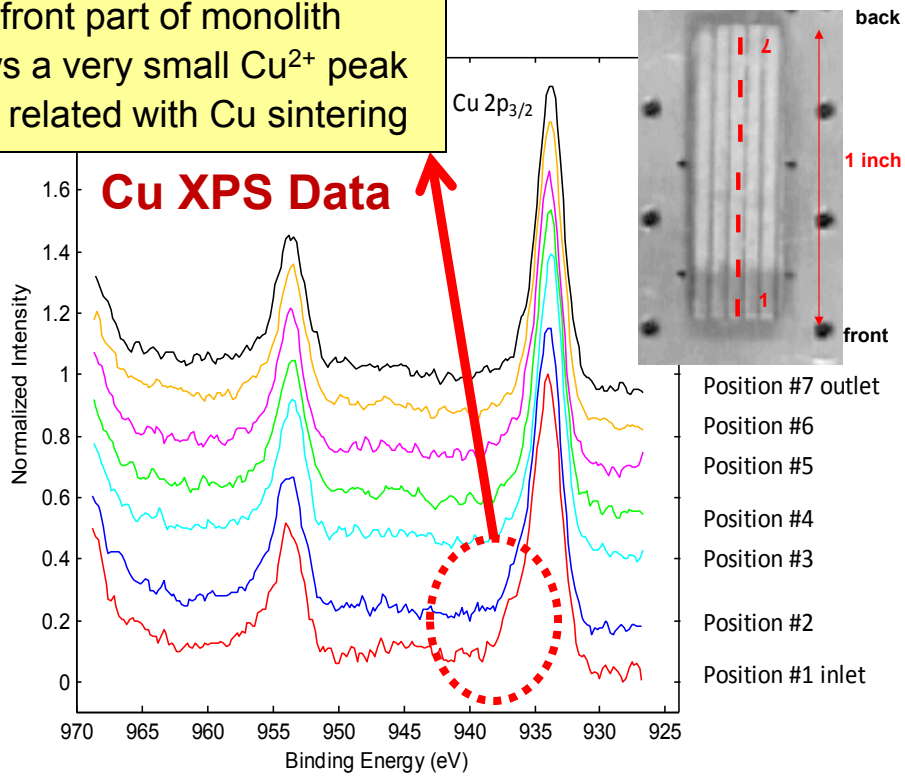
4. Non-Uniform Deactivation of Vehicle-Aged SCR Catalysts

Ford Laboratory SCR Performance Data of Vehicle-Aged SCR Catalyst



Very front part of monolith shows a very small Cu^{2+} peak likely related with Cu sintering

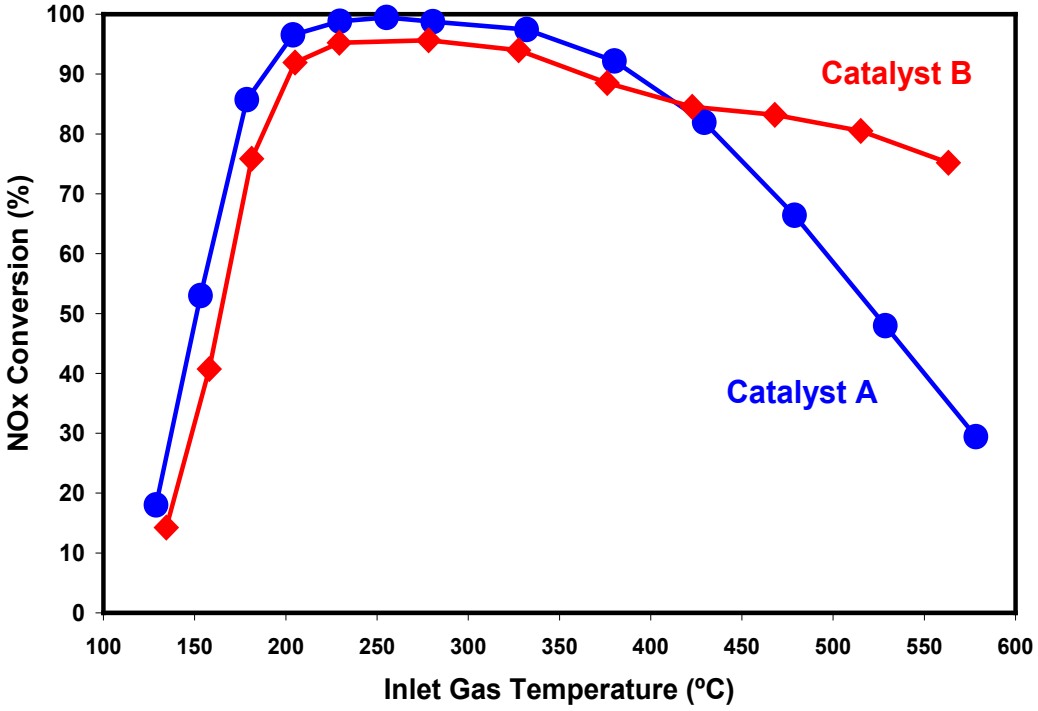


- Fully-formulated Cu/CHA catalyst; 50K miles on Super-Duty Truck
- Steady State NOx-NH_3 SCR, SV=30K, 350ppm NO/350ppm NH_3
- Front end ("M1") only core to show significant deactivation
- Even within this first (M1) core, reactivity is worse at the front end.
- Only very front of catalyst shows contaminants (P,C,Zn but no S), and changes in Cu (TPR and XPS).

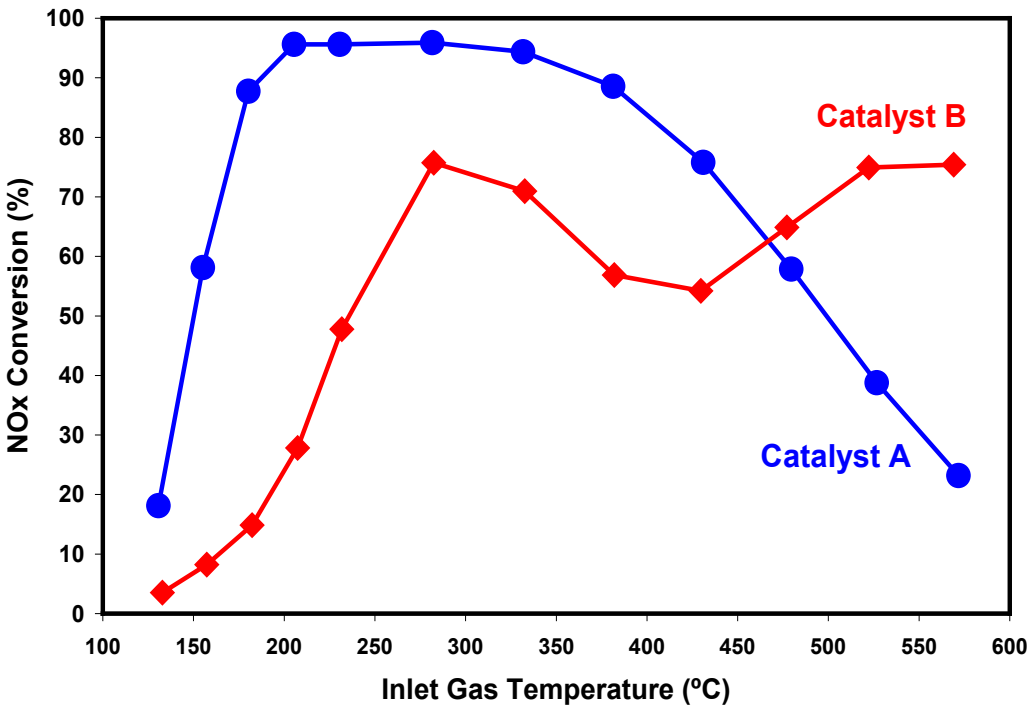
Y Cheng, H Jen, M Jagner, CK Lambert, JH Kwak, DH Kim, CHF Peden, *2010 DEER and 22nd NAM (2011) Presentations*.

5. Unusual Hydrothermal Aging of Urea SCR Catalysts

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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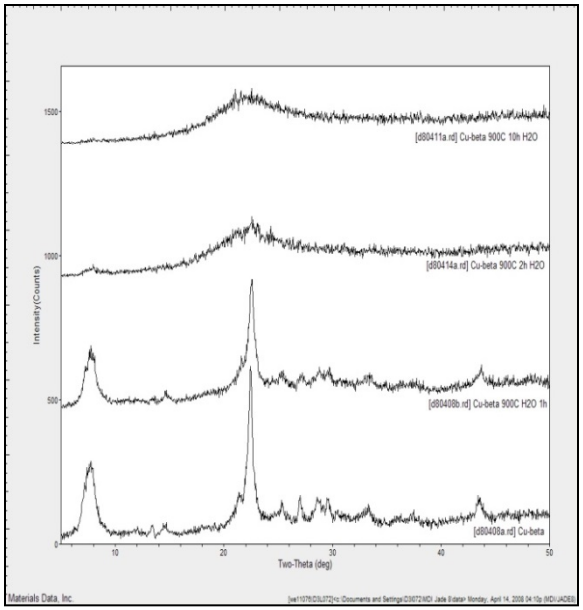
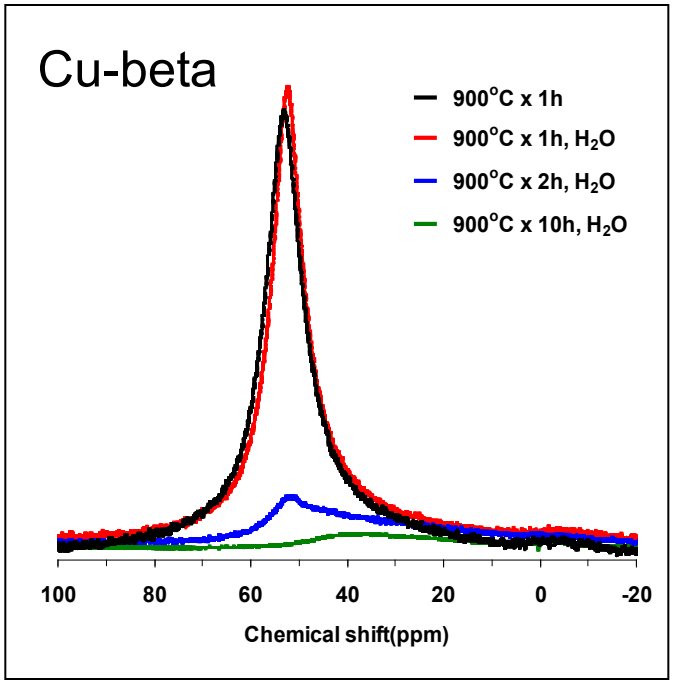
5. Unusual Hydrothermal Aging of Urea SCR Catalysts

Vehicle Technologies Program

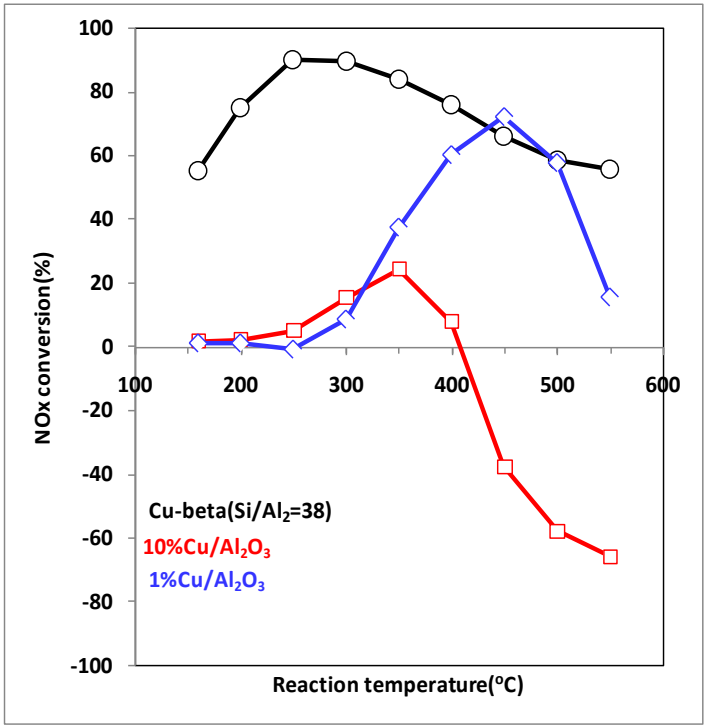
XRD Data



^{27}Al NMR Data



SCR Performance



- XRD shows progressive dealumination of Cu/beta catalyst.
- ^{27}Al NMR also show loss of zeolite crystallinity but no new features.
- Isolated CuO shows significant SCR activity at high temperature.
- CuO clusters at high Cu loading oxidize the NH_3 and produce NO_x.

CHF Peden, JH Kwak, SD Burton, RG Tonkyn, DH Kim, JH Lee, HW Jen, G Cavataio, Y Cheng, CK Lambert, *Catalysis Today* **184** (2012) 245-251.

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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.) then transitioned to Chuck Peden

Overview

Timeline

- Start – October 2010
- Finish – September 2012

Budget

- DOE funding in:
  - FY12: $125K; total funding of $250K for 2 year program.

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 Integrated Catalysis, PNNL
- Ford Motor Company

Ford

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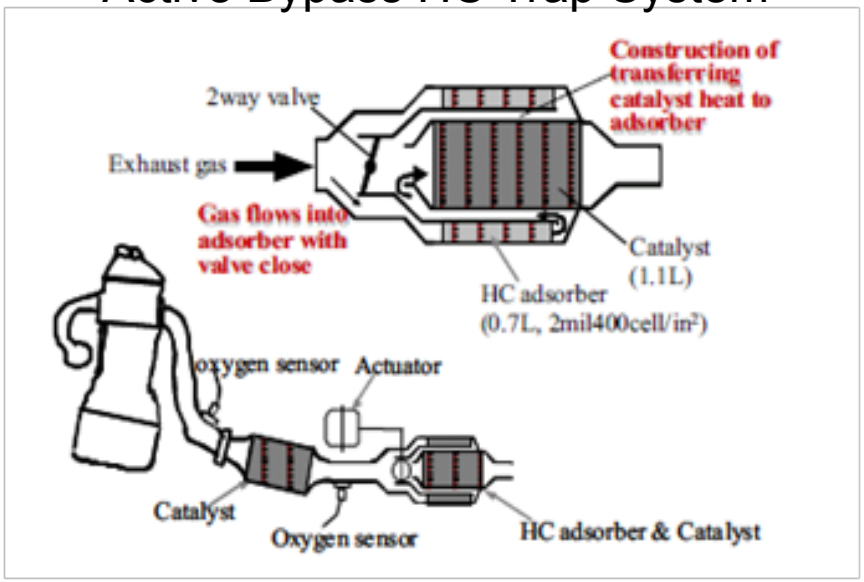
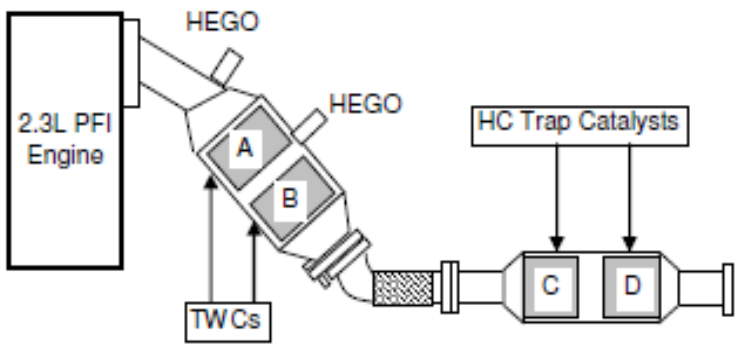
Objectives

- Ford carrying out studies of potential HC adsorber materials for two applications:
  - Diesel cold-start applications
  - E0 and E85 fueled vehicles
- Focus of these Ford studies is on comparative full feed performance with a range of materials that vary:
  - Zeolite type (variations in pore size and shape, acidity (Si/Al ratios), effects of added metals and/or other exchangable cations

Active Bypass HC Trap System



Passive In-line HC Trap System



Objectives for PNNL Work

PNNL studies were aimed at a more fundamental understanding of important HC Trap characteristics by:

- Performance measurements that include single 'model' hydrocarbon components (ethanol, toluene, n-dodecane, propene) in order to isolate varying effects of HC size, degree of unsaturation, and the presence of heteroatoms (notably, oxygen).
- Assessment of the effects of water and CO_2 on performance.
- Use state-of-the-art catalyst characterization facilities to identify modes of deactivation experienced in Ford laboratory studies.
- As in the studies at Ford, catalyst variability was assessed in the more fundamental studies at PNNL:
  1. Effect of Si/Al ratio
     - acidity and hydrophobicity
  2. Effect of zeolite pore size & structure
     - HC size exclusion and limits on diffusion)
  3. Effect of metals and/or other exchanged cations
     - Possible oxidation reactions and pore size modifications

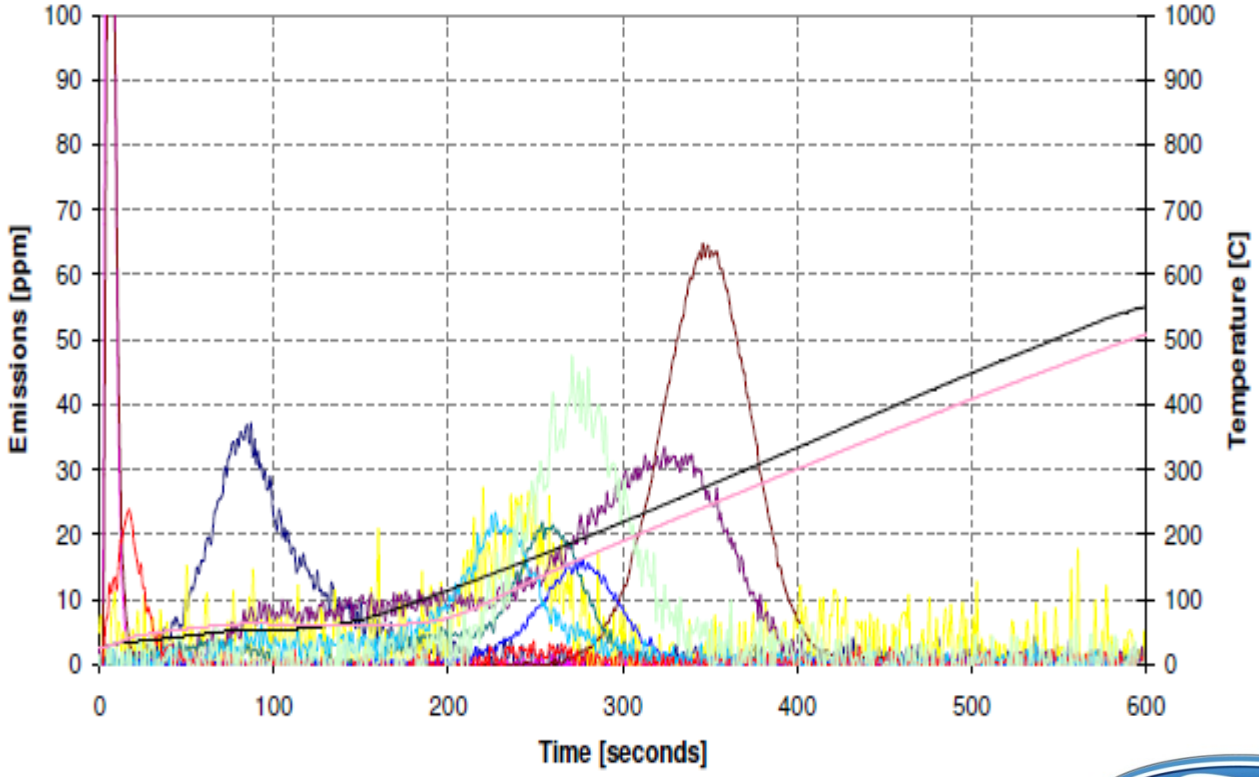
Example of Recent Results from Studies at Ford

HC Trap for LEV-III Application — Chemical Engineering

Project 2: Evaluate best E0 zeolites for E85

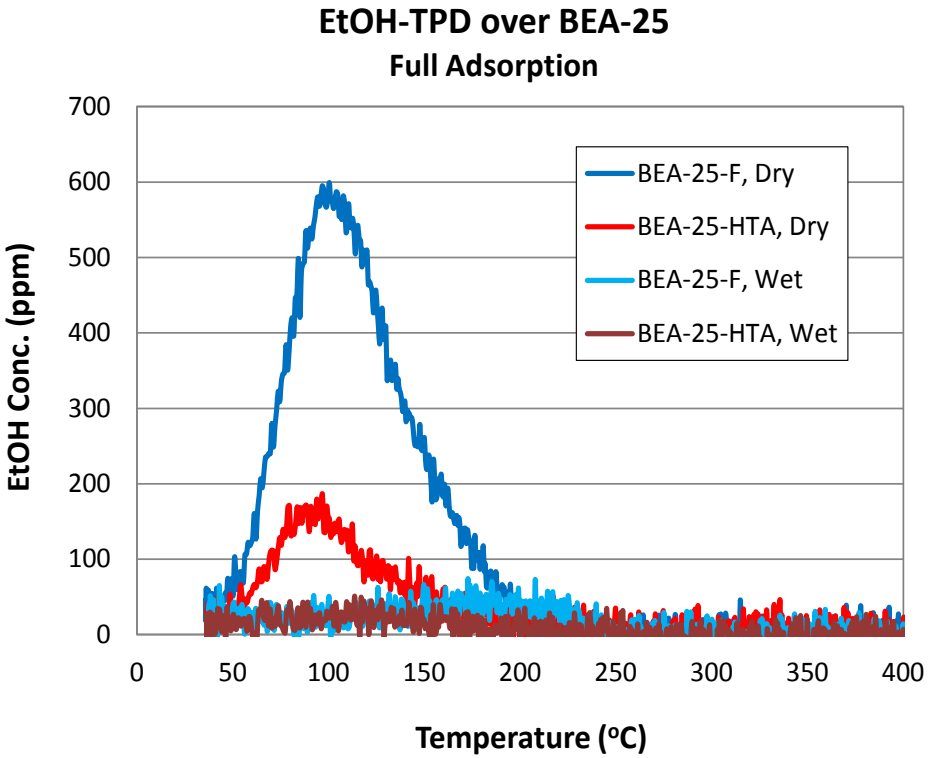
- Evaluate with 10-part HC blend that mimics E85
- Observe whether E0 trends hold for E85

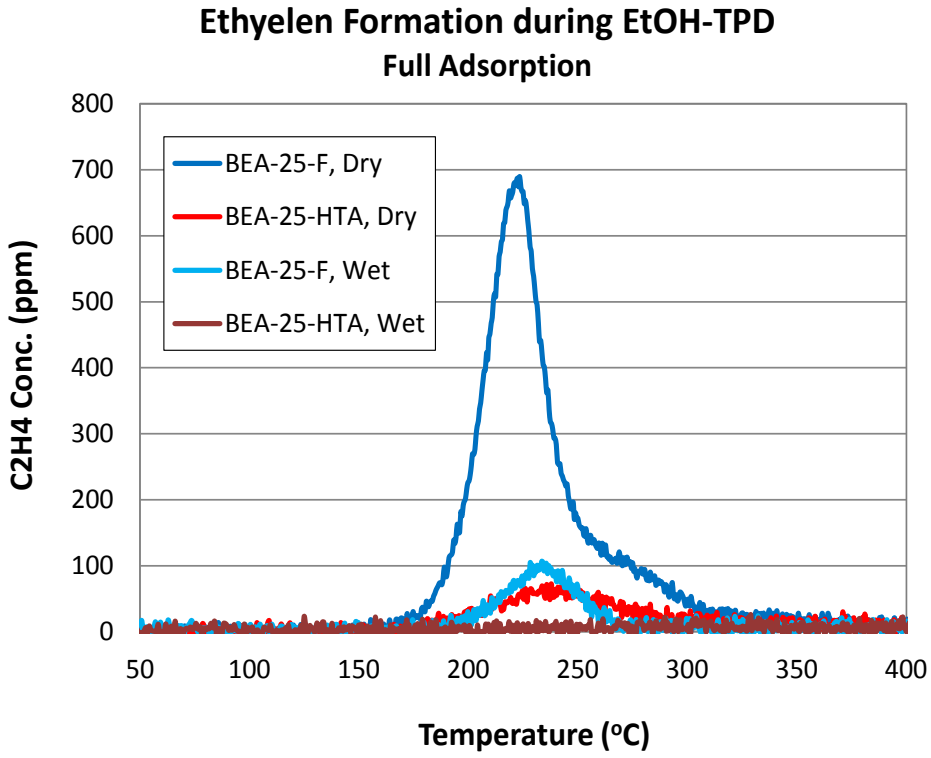
Jason Lupescu, CRADA Conference Call Data



- Complex hydrocarbon feed includes ***ethanol***, branched and straight-chain paraffins and unsaturated HCs, aromatics, and aldehydes
- Data used to compare performance of different zeolites for these mulitple HCs.

Beta-25 Zeolite: Effects of Aging & H_2O





- Ethanol desorption at <200°C, ethylene desorption at >200°C
- Significant loss of ethanol adsorption & dehydration with 3.5% H_2O
- Practically no adsorption of ethanol with H_2O after HTA
- Blocking of pores by H_2O?

Technical Summary

A number of studies of zeolite-based SCR catalysts were completed including:

- Initial studies focused on the relevance of various laboratory aging conditions (Catal. Today **136** (2008) 34).
- Comparative poisoning by SO_2 and SO_3 (Catal. Today **151** (2010) 266).
- Mechanism of poisoning by phosphorus species (unpublished work).
- Detailed studies of engine and vehicle aged SCR catalysts (2010 DEER and 22nd NAM (2011) presentations).
- Nature of a high-temperature active phase formed upon HTA of zeolite-based SCR catalysts (Catal. Today **184** (2012) 245).

For last two years of this CRADA, studies aimed at providing fundamental insights into the performance of zeolite-based HC Trap materials were performed:

- Identification of optimum properties including zeolite pore size and structure, acidity, and incorporation of metals and/or other exchangeable cations, including:
  - Studies of ethanol adsorption and reaction as a function of zeolite structure, hydrothermal aging, and the presence of water.

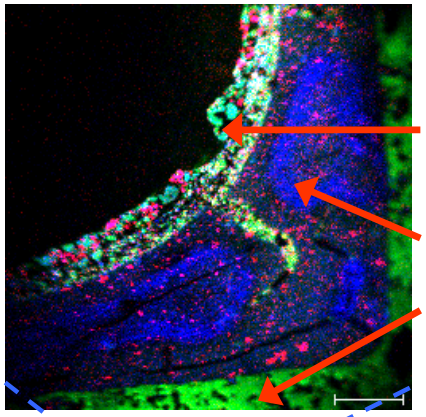
Future Work

No future work is planned; this program has been completed.

Extra Data Slides

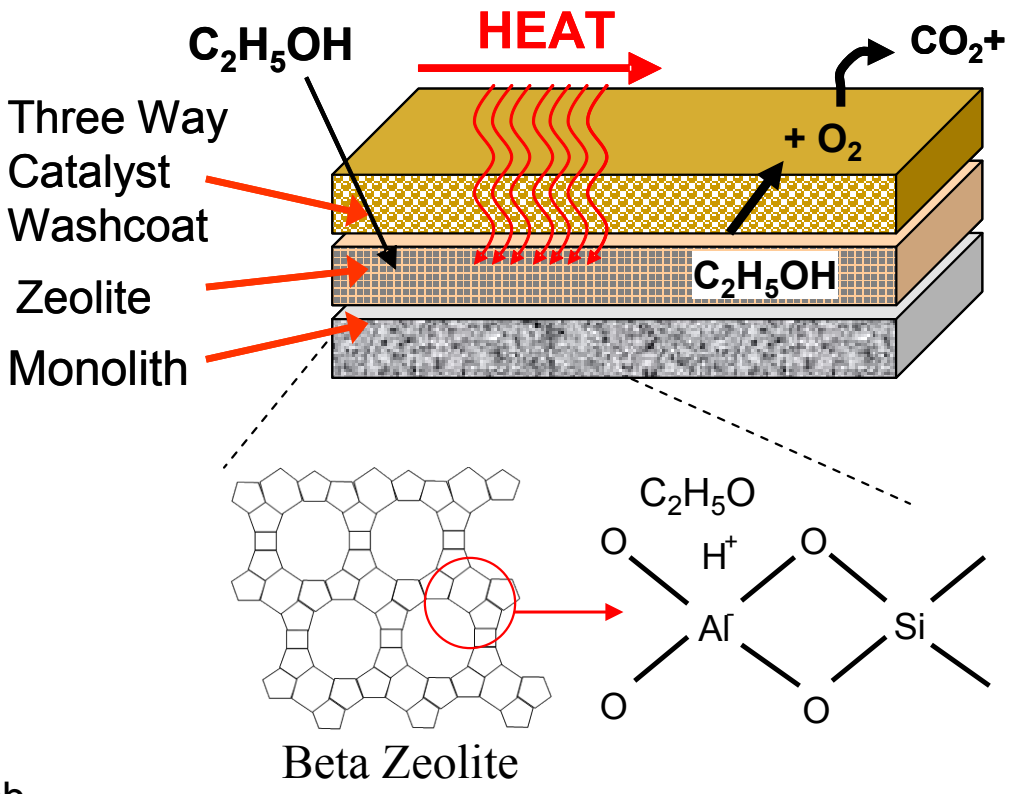
How Does a Hydrocarbon Trap Work?

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

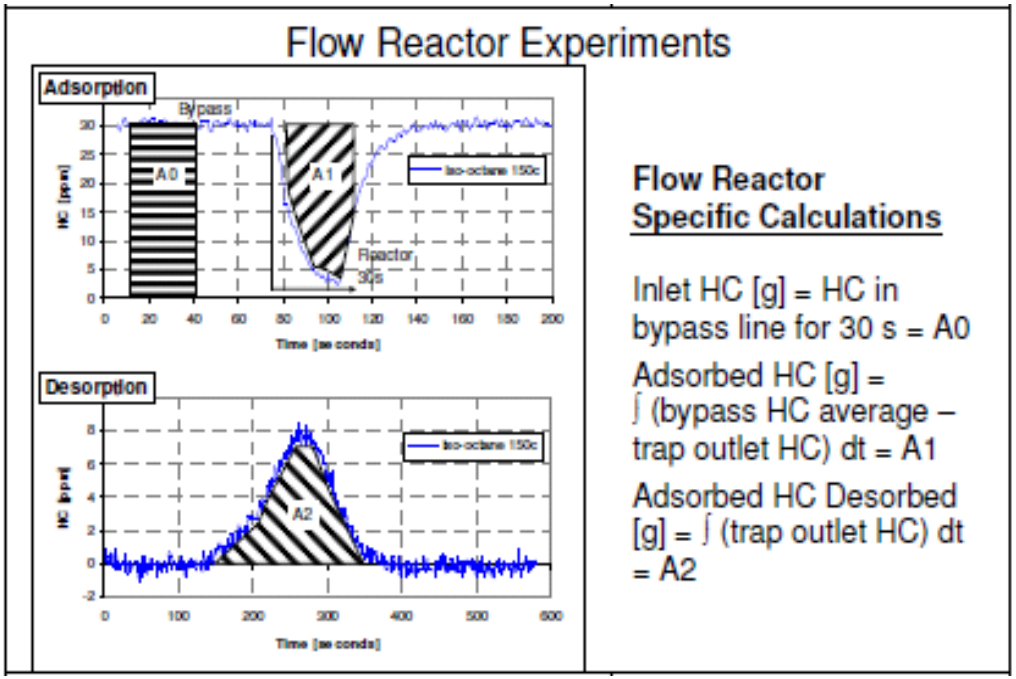
Zeolite cage structure traps and holds hydrocarbon molecules at metal ion sites (Al^{-1}) until precious metal catalyst in washcoat is hot enough to oxidize them.

Brief Summary of Recent PNNL Studies

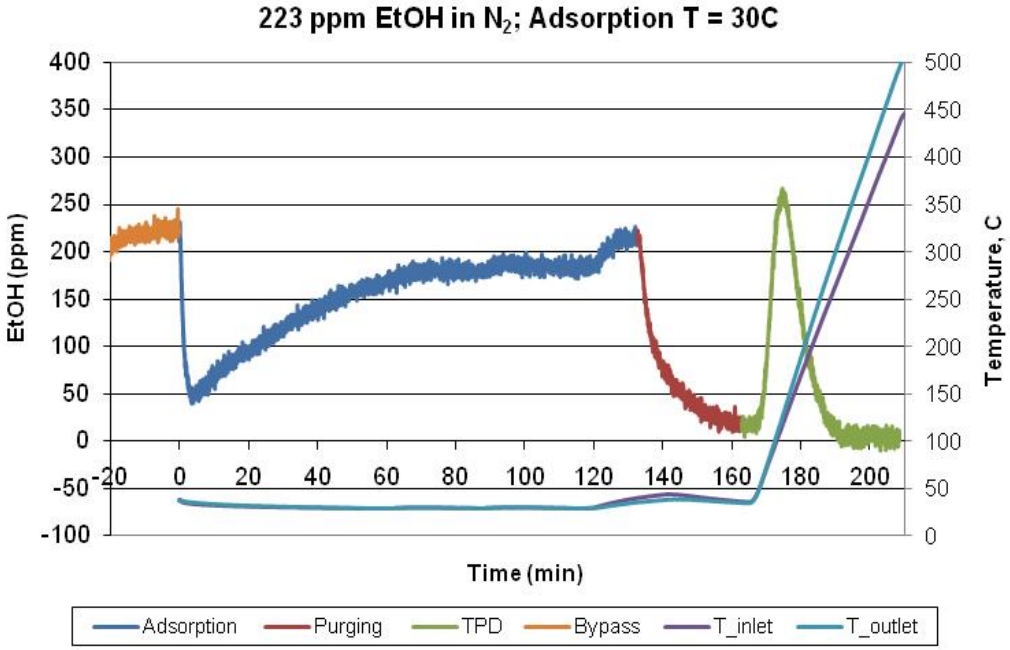
- Obtained model zeolite samples relevant to studies being carried out at Ford and designed to probe the effects of various zeolite properties on HC adsorber performance and durability.
- Examined the effects of HTA of the model zeolites on their physical properties
  - Determined when loss of crystallinity, and loss of surface area and acidity occurs as a function of some hydrothermal aging conditions.
- Evaluated adsorption & desorption characteristics of various individual hydrocarbons with respect to Si/Al ratio, HTA, and the presence of water.
  - Ethanol dehydration to ethylene during ethanol-TPD
  - Ethanol desorption at <200ºC, ethylene desorption at >200ºC
  - Significant loss of ethanol adsorption after HTA
  - Very little adsorption in the presence of H_2O
  - Improved ethanol adsorption with H-ZSM-12

HC Adsorption/Desorption Testing

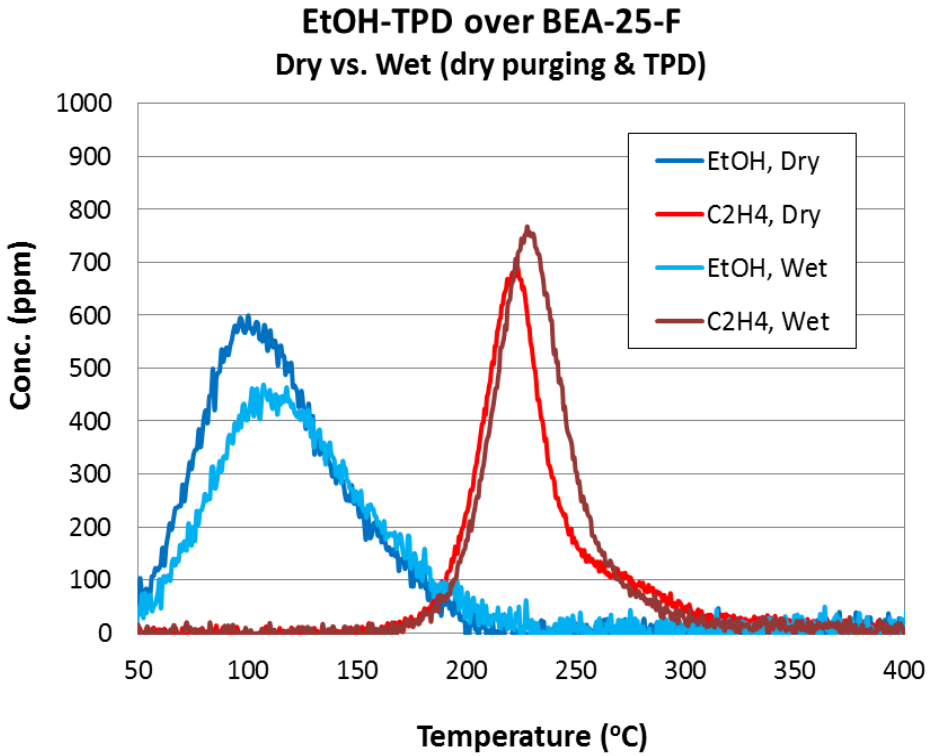
- Reactor setup and test procedures established with a commercial sample
  - Reactor system to handle both monolith and powder samples
- For ethanol adsorption/desorption studies :
  - Temporal exposure to ethanol at room temperature, followed by TPD
  - Effects of H_2O, aging, Si/Al ratio, etc.



Commercial HC Trap Sample on a Monolith

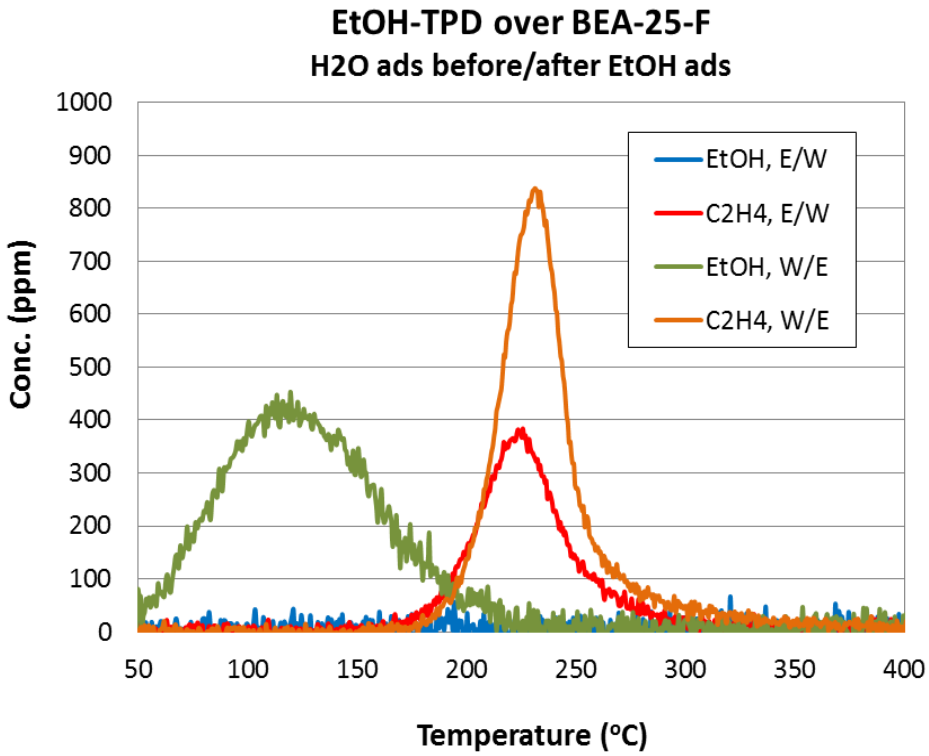


Interaction between Ethanol and Water



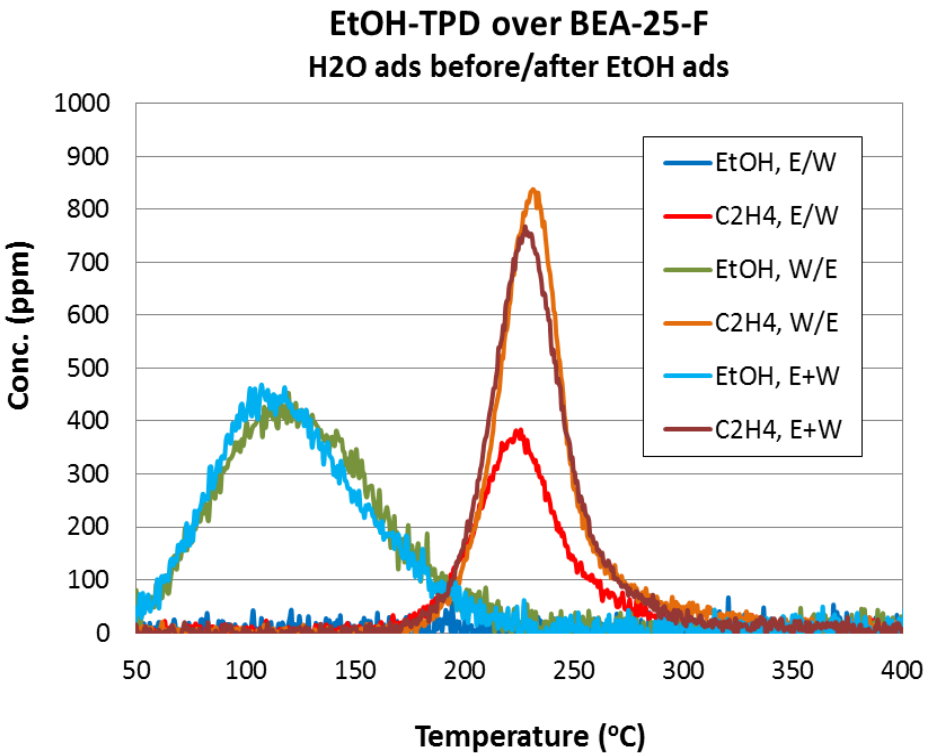
- Ethanol adsorption with/without H_2O, followed by TPD without H_2O (previously TPD with H_2O/N_2)
- Slight reduction in C_2H_5OH ads, but no effect on C_2H_4 formation
- No evidence of pore blocking during co-adsorption of ethanol & water

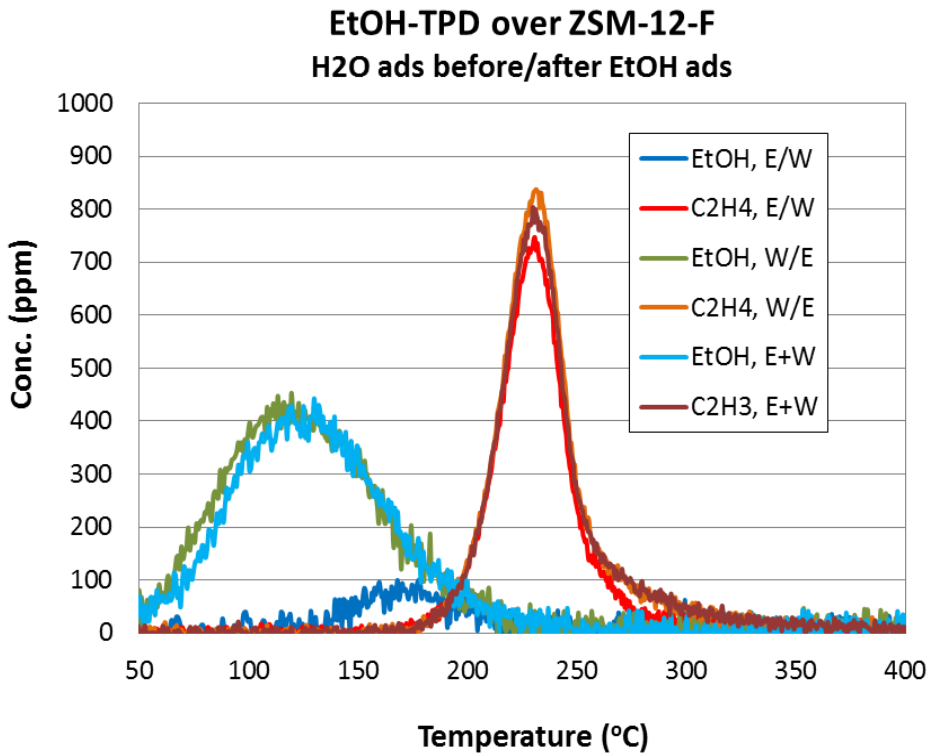
Interaction between Ethanol and Water



- Ethanol adsorption before/after H_2O adsorption, followed by dry-TPD
  - ✓ Ethanol displacement by H_2O during H_2O adsorption (E/W)
  - ✓ H_2O displacement by ethanol during ethanol adsorption (W/E)
- Significant reduction in ethanol and C_2H_4 due to ethanol displacement by H_2O (E/W)!

Comparative Behavior of Different Zeolites





- No evidence of pore blocking during co-adsorption of ethanol & water
- Water replaced by ethanol (W/E)
- Weakly adsorbed ethanol easily replaced by H_2O (E/W)
  - ✓ More ethanol retained and dehydrated over H-ZSM-12 despite higher Si/Al_2 ratio! → Effect of pore connectivity?