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

Ja Hun Kwak, Jong Lee,
Chuck Peden, Diana Tran
Institute for Integrated Catalysis
Pacific Northwest National Laboratory

Yisun Cheng, Jason Lupescu,
Giovanni Cavataio, Christine
Lambert, Robert McCabe
Ford Motor Company

Program Managers: Ken Howden and Gurpreet Singh

The work was funded by the U.S. Department of Energy (DOE) Office of FreedomCar and Vehicle Technologies.

May 17, 2012

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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 now 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 now consists 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 consists of two parts:

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

- Development of Hydrocarbon Adsorber Materials - Jong Lee (P.I.) now transitioned to Chuck Peden

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 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.

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

1. Sulfur poisoning of urea SCR catalysts that follow a diesel oxidation catalyst:
   - 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 had shown 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.
2. Laboratory studies of phosphorus poisoning.
3. Measurement of the performance and characterization of the catalysts used for various Ford-developed laboratory aging protocols.

Program Progress

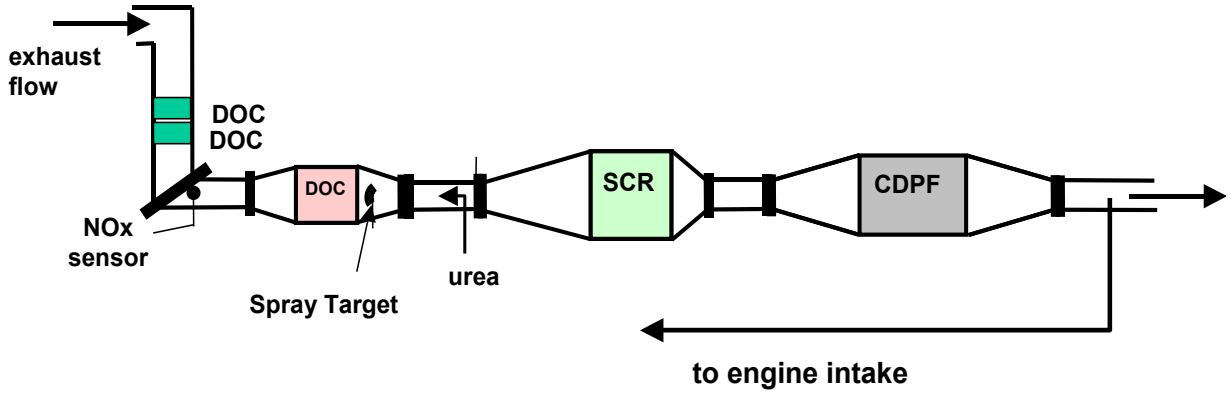
Studies to date have focused on a number of critical issues:

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 highlights from the fourth area in the following.

Vehicle-Aged Catalyst Studies - Introduction

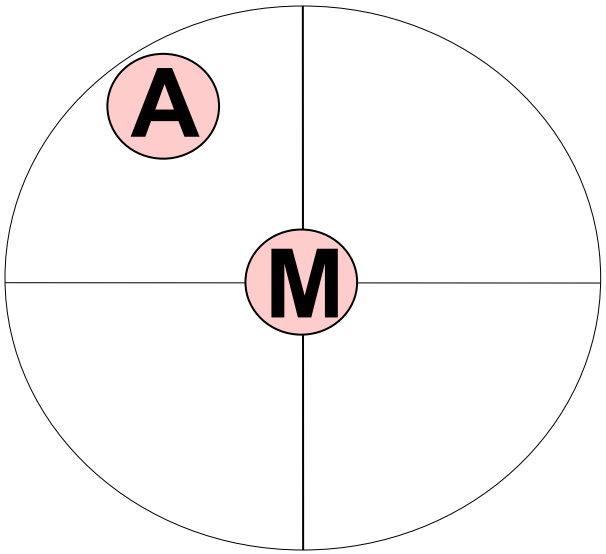


Ford Engine Exhaust System Configuration

- Previous studies
  - Deactivation of engine aged SCR catalysts is not uniform
  - Inlet sections of catalyst bricks generally deactivate more severely
- Our recent studies
  - Aimed at a better understanding of this non uniform aging phenomena in engine aged SCR catalysts
  - Cu/CHA SCR catalysts aged for 50K miles on a Super Duty Diesel truck

Materials and Methods

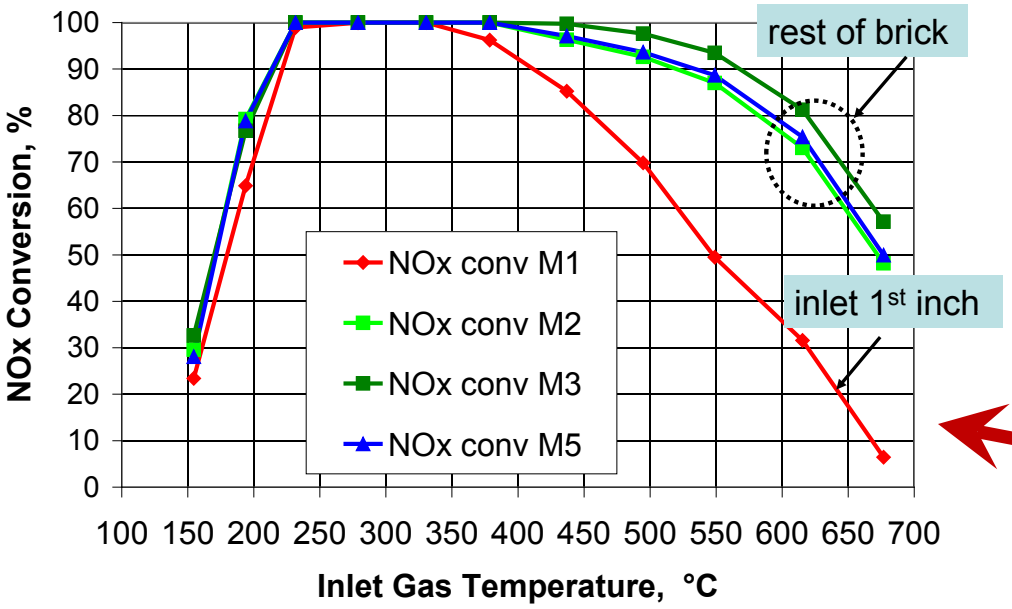
- Fully formulated monolith Cu/CHA catalyst
  - Washcoat loading was 2.7 g/in3
  - Cu loading was 71 g/ft3
  - Aged for 50K miles on a Super Duty Diesel truck
- Postmortem analysis
  - Steady state NOx-NH_3 SCR performance
  - Catalyst characterization: BET surface area, TPR, XRF, XPS and TEM.

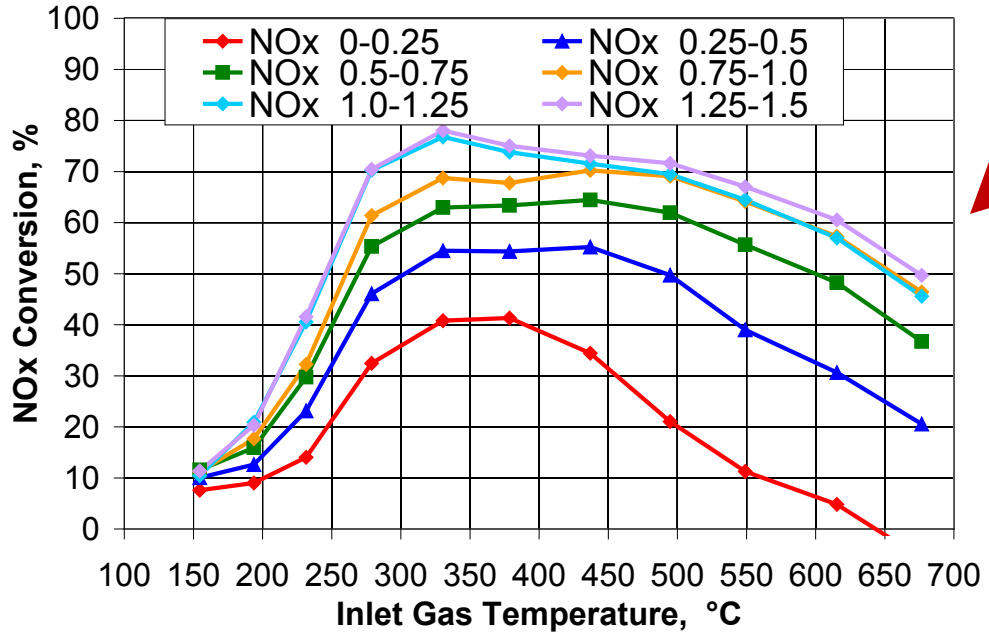


Exhaust Gas Flow Direction

M1	M2	M3	M4	M5	M6

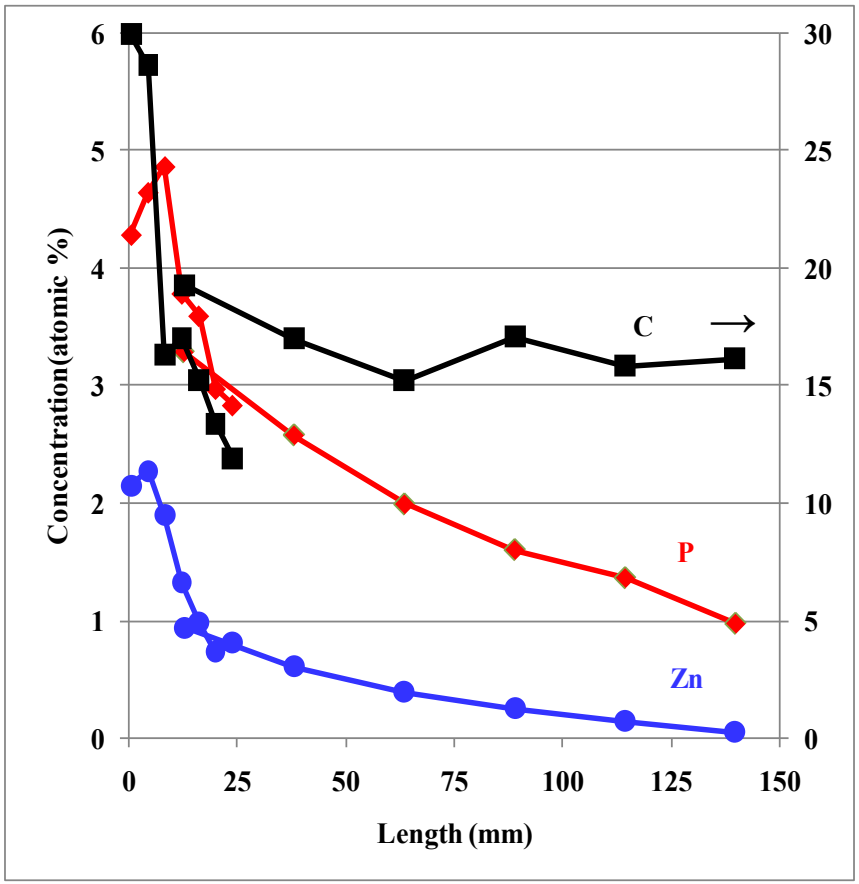
Non-uniform NOx Conversion





- 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.
- Changes in performance not due to surface area loss in front section.

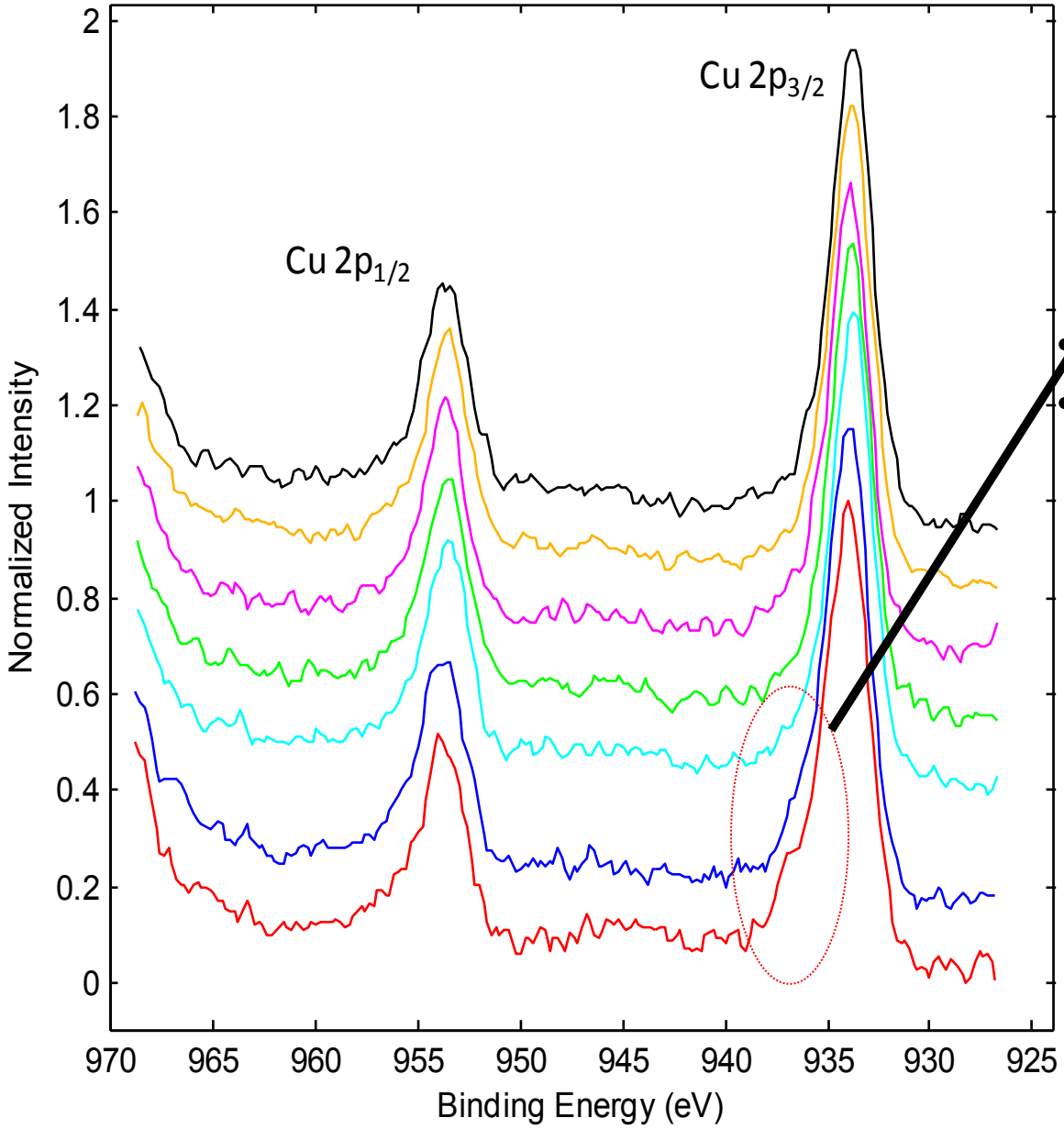
XPS and XRF – 1st inch contains C, S, P, Zn



- Significant carbon deposition of front side(~ 7 % for fresh sample and ~ 1 % for lab aged sample).
- Carbon deposition may account for some activity loss, especially 1st run.
- P and Zn deposition on the inlet end of the monolith.
- Practically no sulfur in the samples.

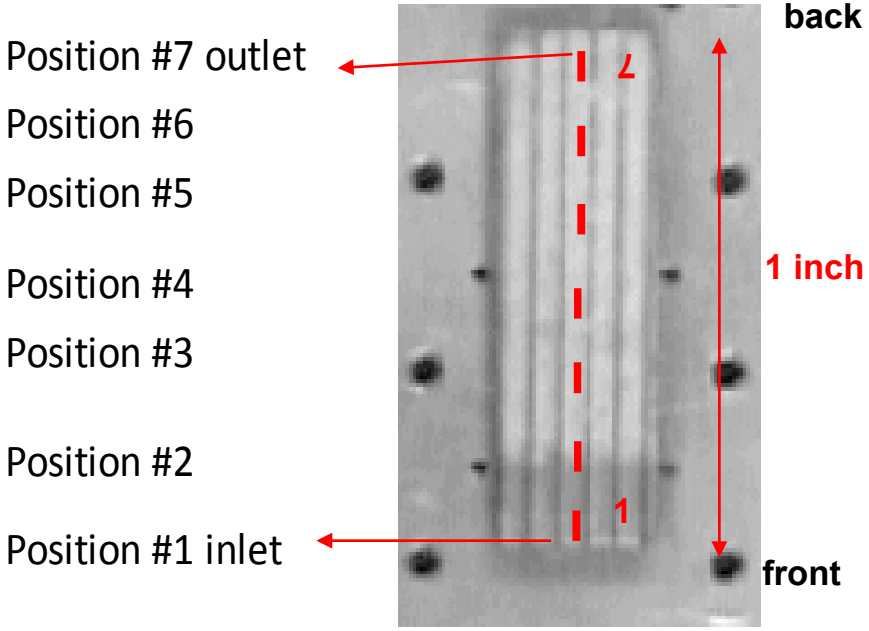
XRF	1st	2nd	3rd	4th	5th	6th
P	0.043	0.020	0.015	0.010	0.009	0.006
S	0.006	0.006	0.005	0.005	0.005	0.004
Zn	0.008	0.003	0.003	0.002	0.002	0.002

1st inch XPS - Cu



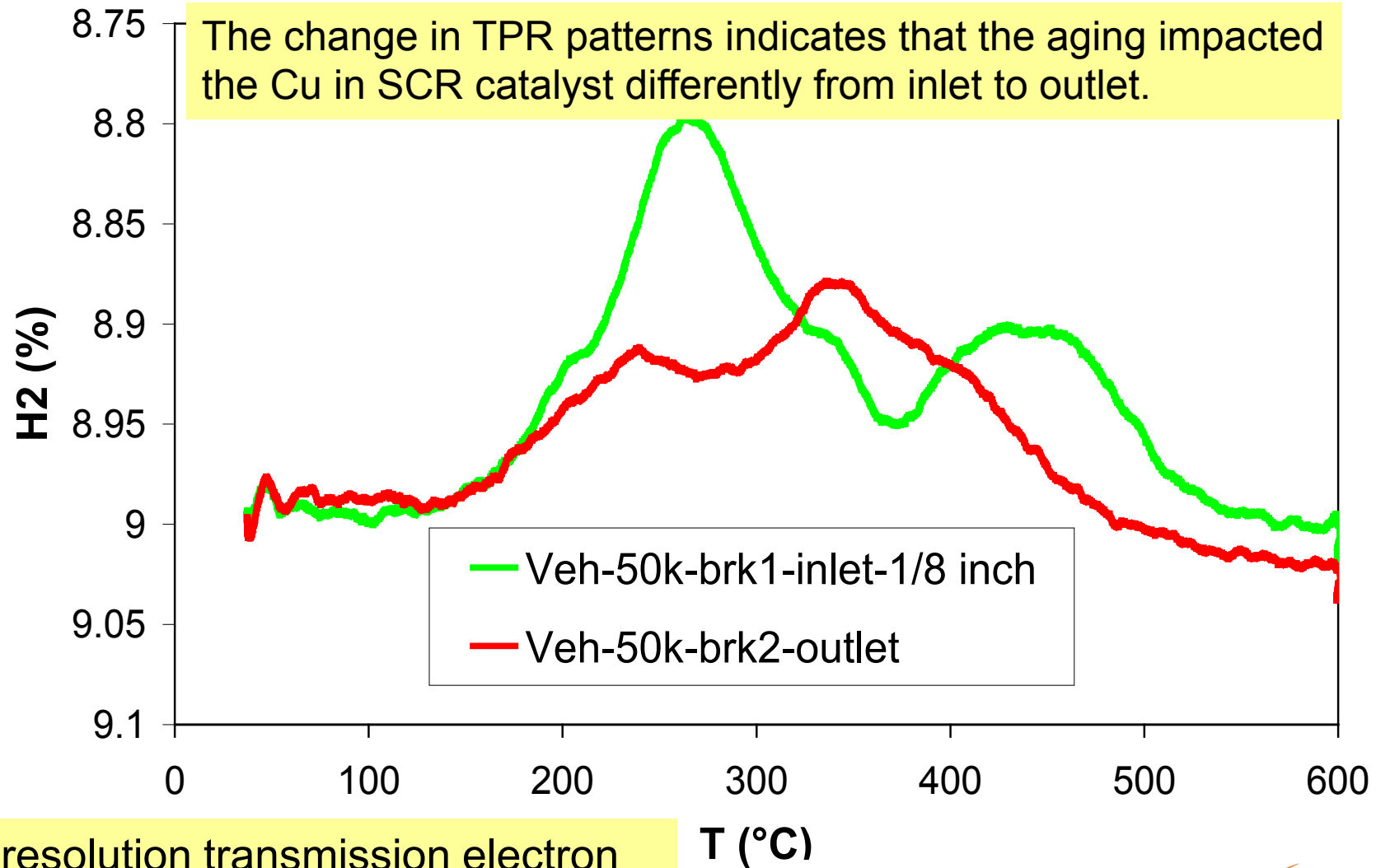
- Very front part of monolith shows a very small Cu^{2+} peak likely related with Cu sintering

- **#1 located 0.5 mm from front end**
- **Each spot spaced by 4 mm**



Temperature Programmed Reduction

TPR with 10°C/min to 600°C using 9%H2/Ar



High resolution transmission electron microscopy (TEM) consistent with these results

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

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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

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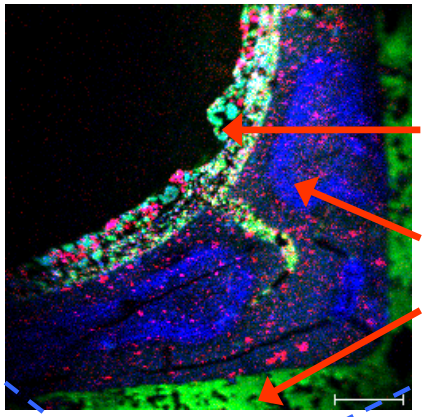
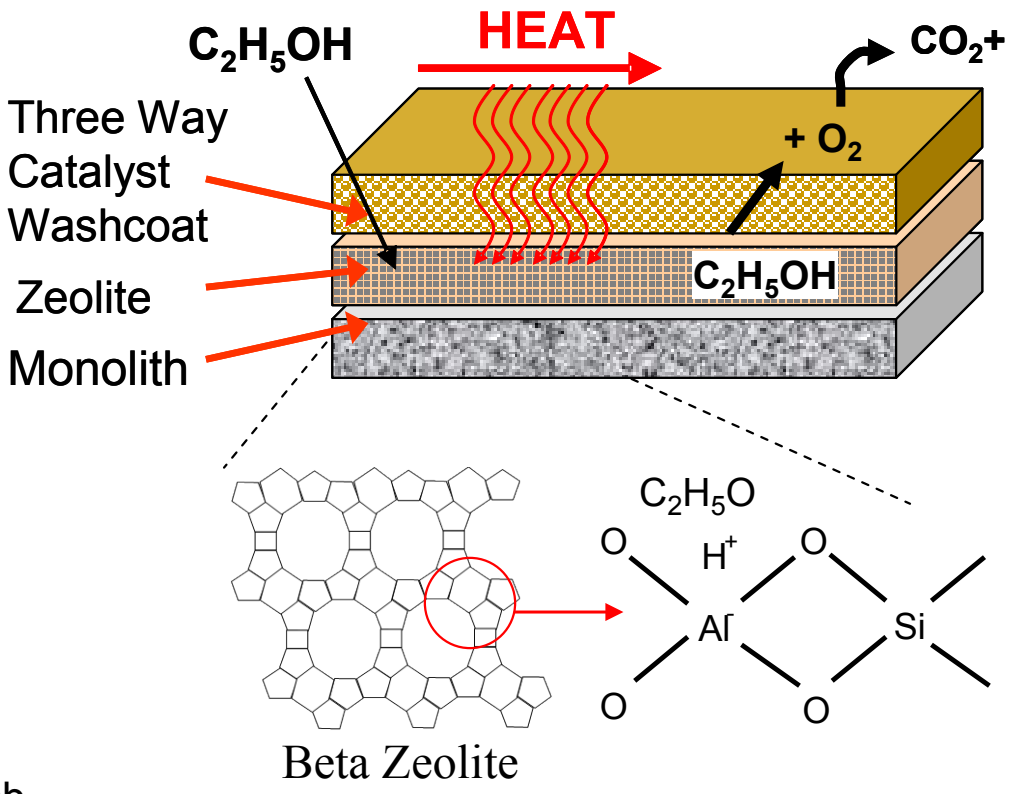
How Does a Hydrocarbon Trap Work?

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

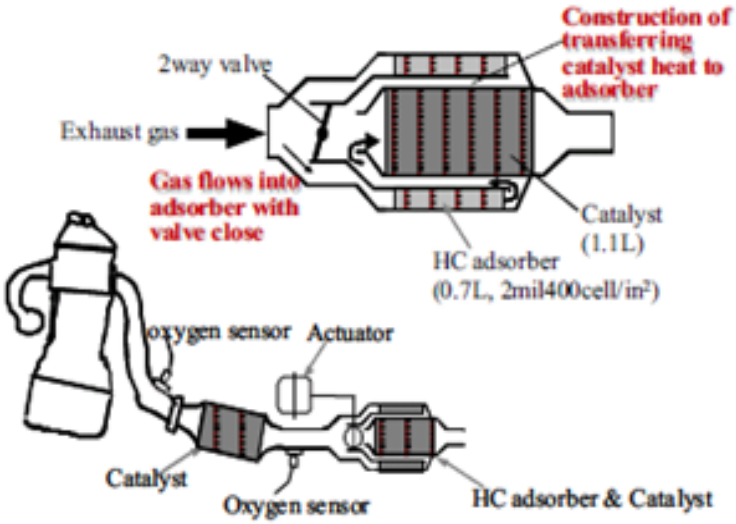
Ford Research and Advanced Engineering

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.

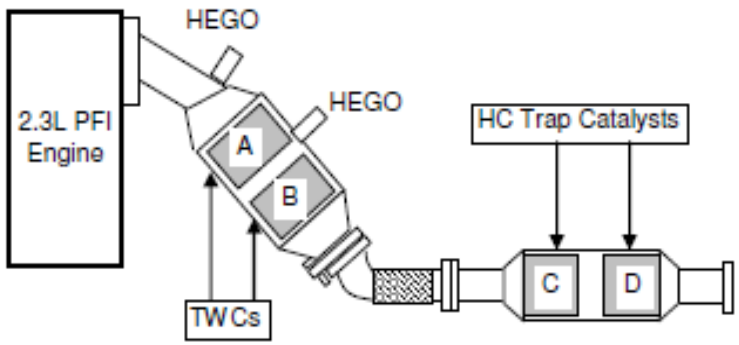
Objectives

- 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 will provide 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 is being 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

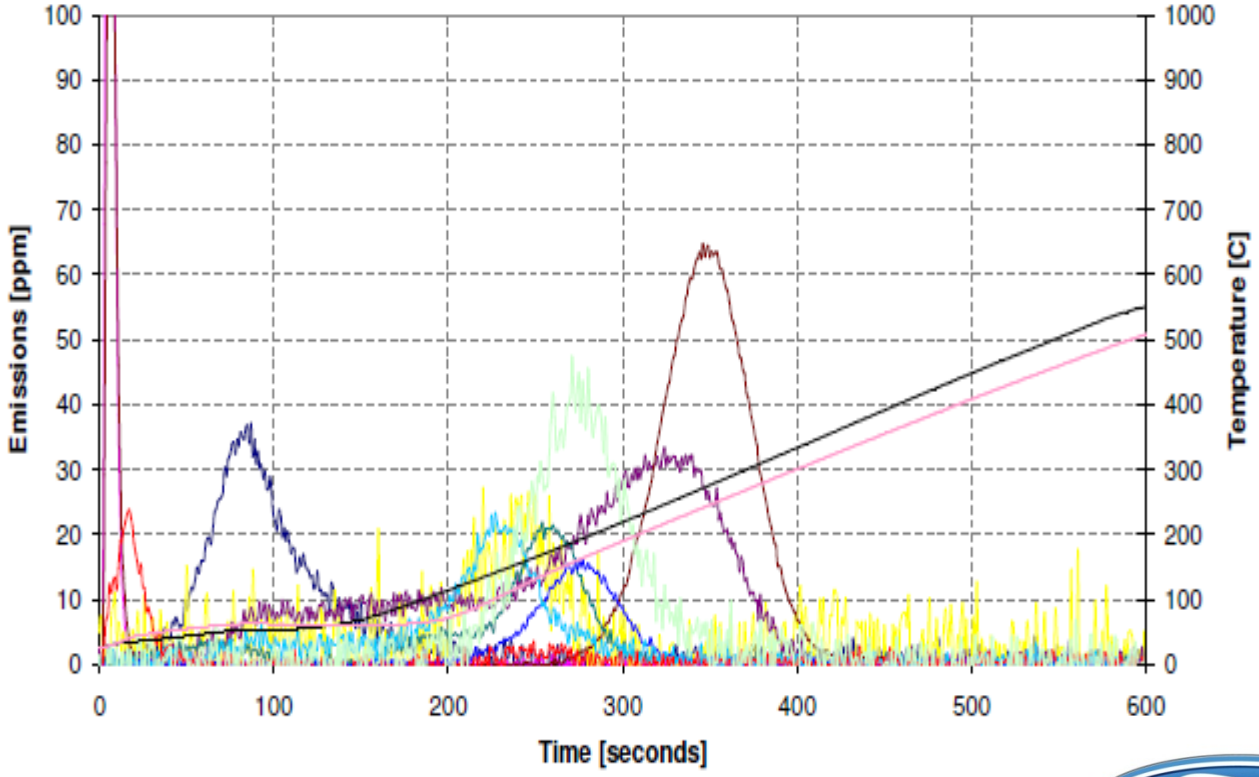
Example of Recent Results from Studies at Ford

Jason Lupescu, 2/13/12 CRADA Conference Call

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



- 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.

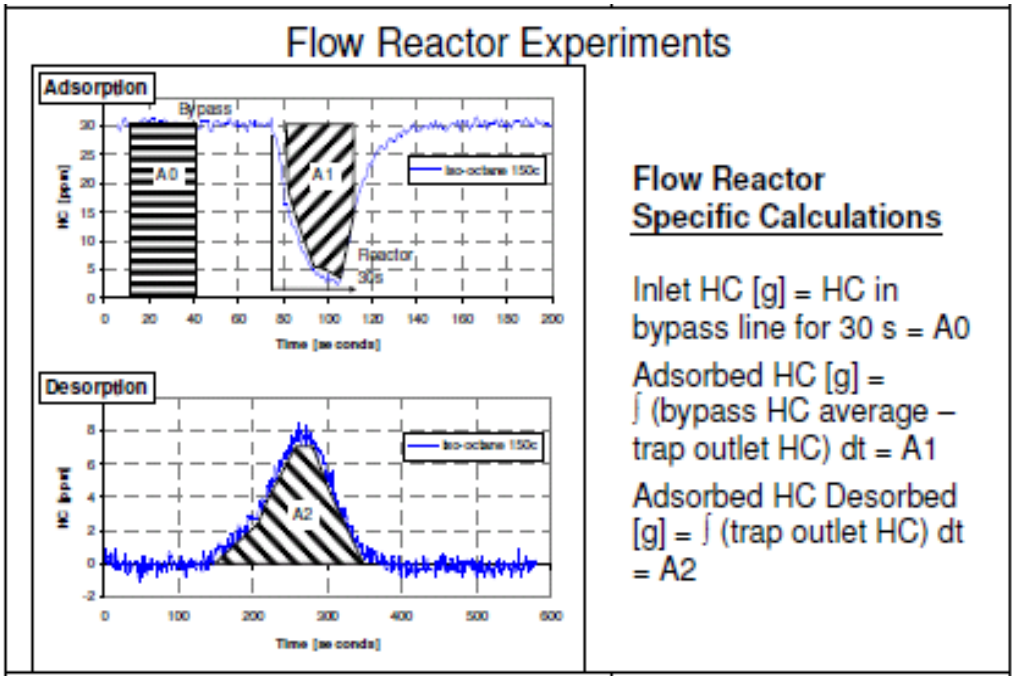
PNNL Progress Since the Last Review

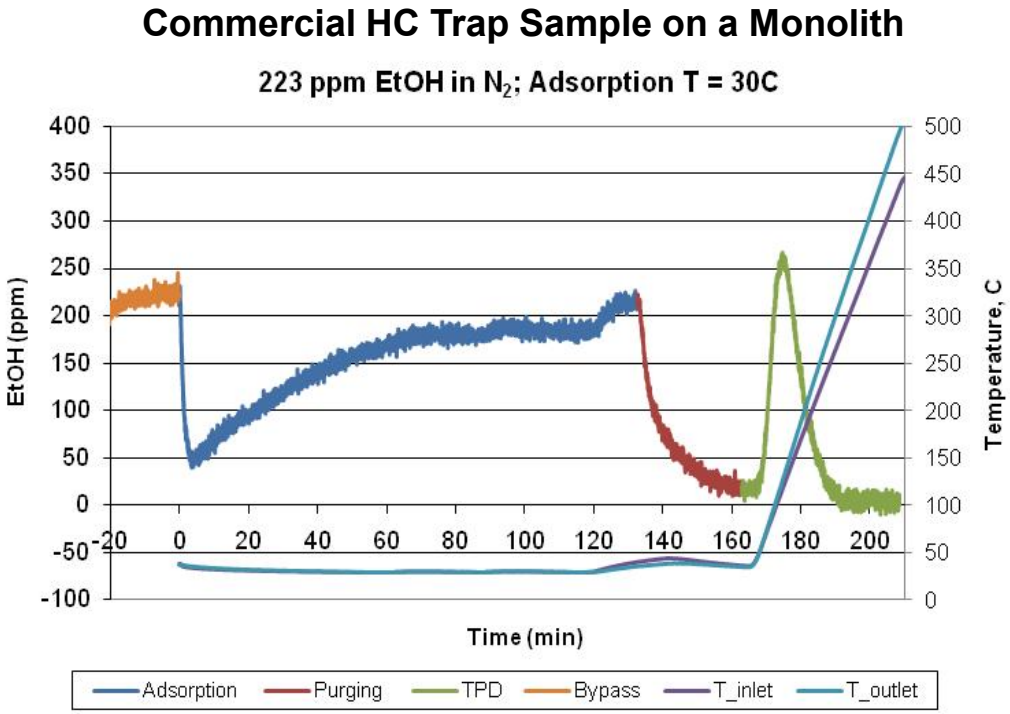
- Obtained model zeolite samples relevant to studies being carried out at Ford and designed to probe the effects of various zeolite properties on HC adsorber performance and durability.
- Examined the effects of HTA of the model zeolites on their physical properties
  - Determined when loss of crystallinity, 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.

  For today, will describe some of our recent work with ethanol:
  - 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

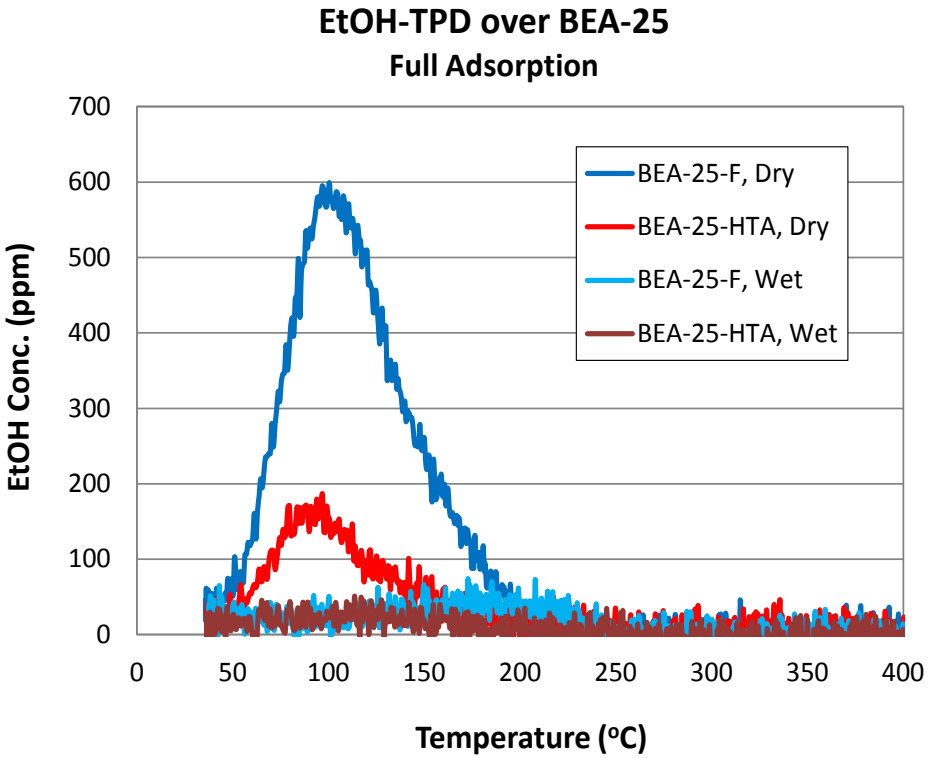
HC Adsorption/Desorption Testing

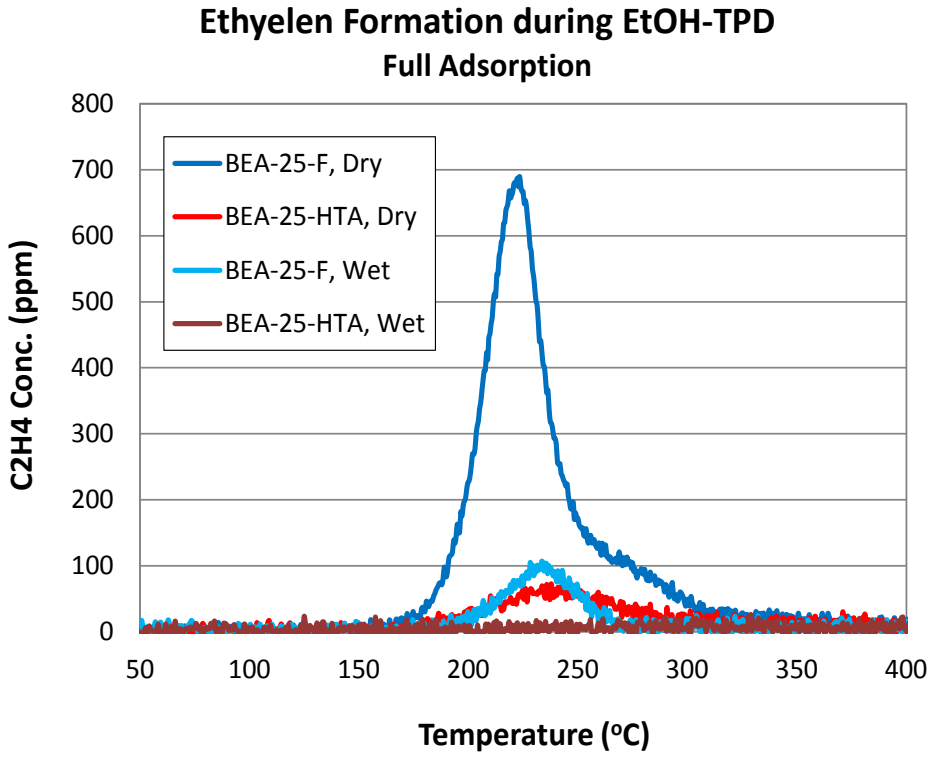
- Reactor setup and test procedures established with a commercial sample
  - Reactor system to handle both monolith and powder samples
- For ethanol adsorption/desorption studies to be described today:
  - Temporal exposure to ethanol at room temperature, followed by TPD
  - Effects of H_2O, aging, Si/Al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





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?

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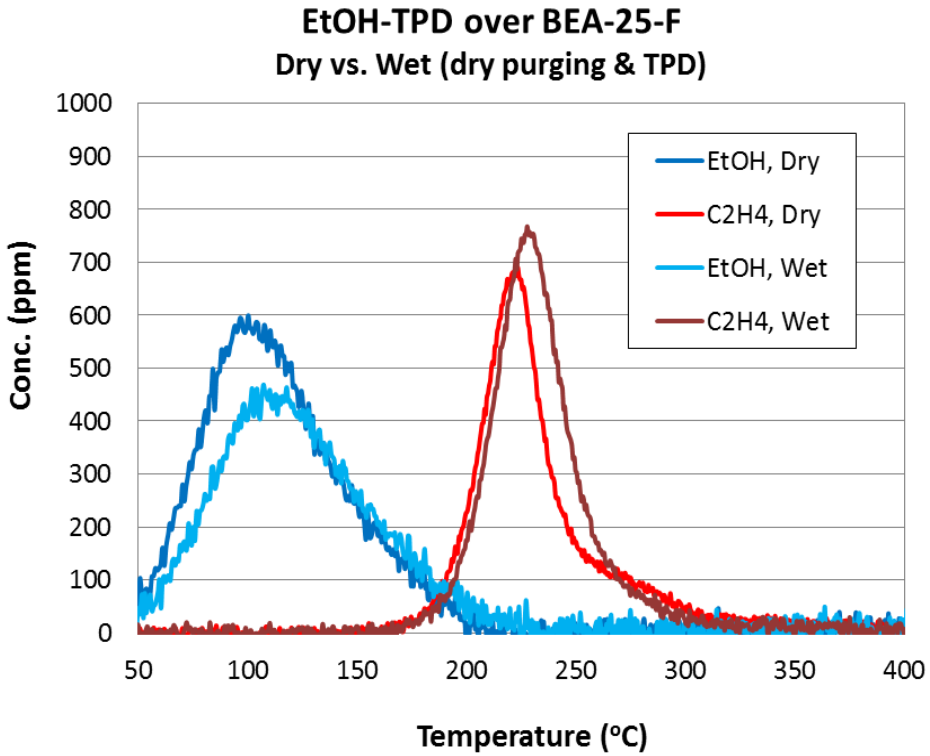
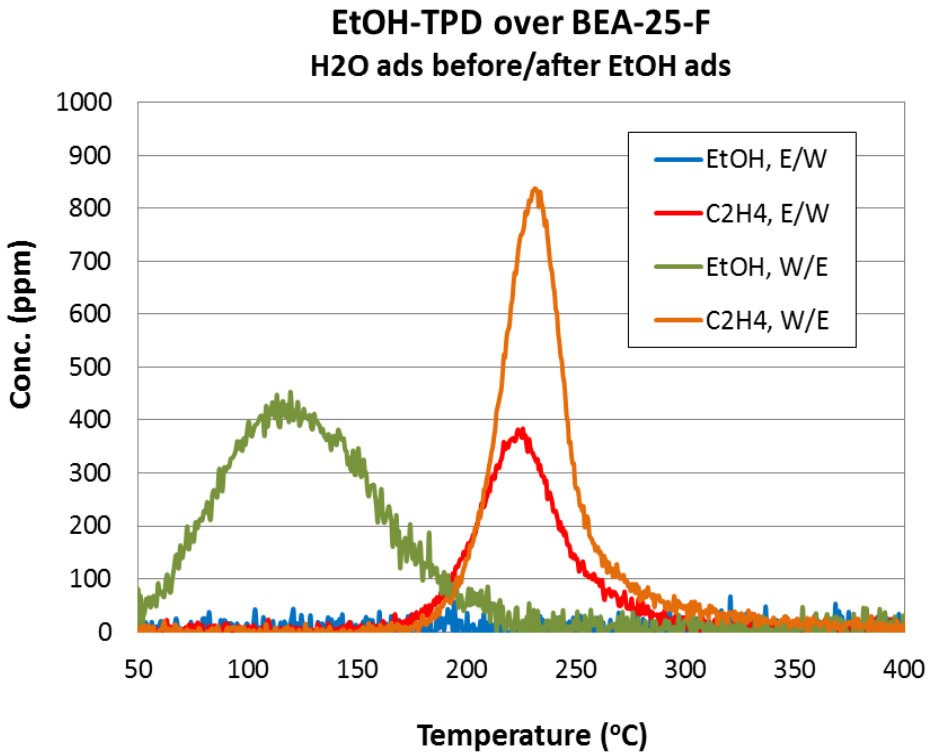
Interaction between Ethanol and Water



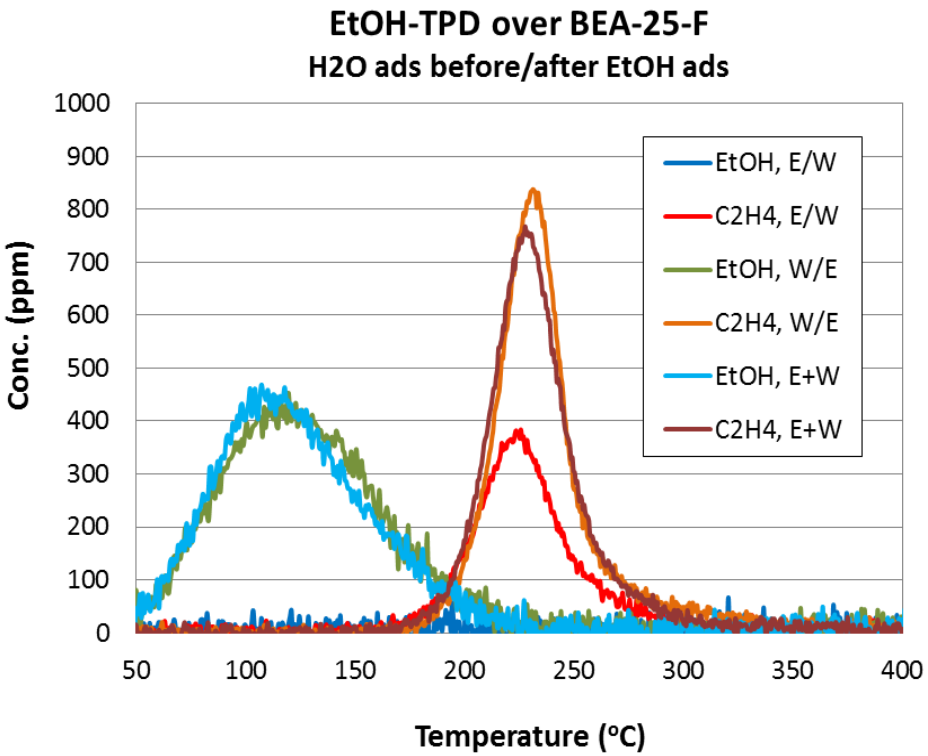
- Ethanol adsorption with/without H_2O, followed by TPD without H_2O (previously TPD with H_2O/N_2)
- Slight reduction in C_2H_5OH ads, but no effect on C_2H_4 formation
- No evidence of pore blocking during co-adsorption of ethanol & water

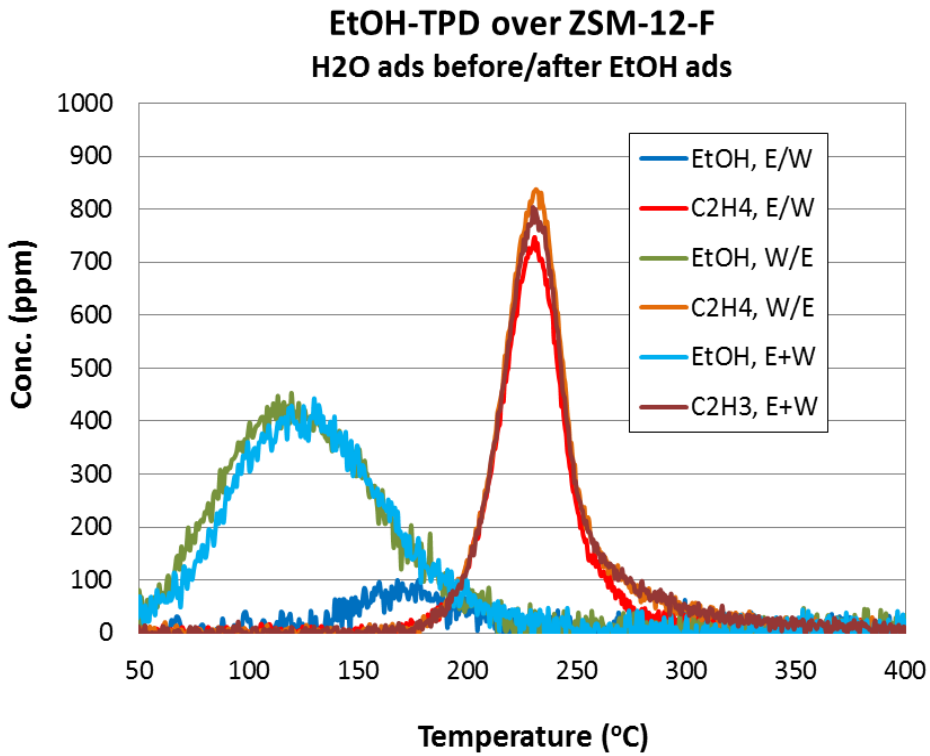
Interaction between Ethanol and Water



- 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?

Technical Summary

Studies of zeolite-based SCR catalysts; a range of studies have been completed including:

- Comparative poisoning by SO_2 and SO_3 (Catal. Today **151** (2010) 266).
- Mechanism of poisoning by phosphorus species.
- Nature of a high-temperature active phase formed upon HTA of zeolite-based SCR catalysts (Catal. Today (2012) in press).
- Detailed studies of laboratory and realistically (engine and vehicle) aged SCR catalysts; establishment of rapid aging protocols (Catal. Today **136** (2008) 34).
  - Results shown today observed and explained the dependence of deactivation on location in a catalyst monolith

Recently initiated studies aimed at providing fundamental insights into complex measurements used to screen relative performance of zeolite-based HC Trap materials:

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

Future Work

Studies of zeolite-based SCR catalysts:

- This portion of the project is nearly complete but will include the following experiments on some important remaining issues.
- Further characterization of laboratory-aged (Ford protocol) model.and commercial Cu-SSZ-13 catalysts. Of particular interest are to understand temperature-programmed reduction (TPR) and electron spin resonance (ESR) data for these hydrothermally-aged zeolite catalysts.
- Correlation of performance and catalyst characterization of cycled lean-rich hydrothermal aging using Ford rapid aging protocols.

Studies of zeolite-based HC Trap materials:

- There are still many areas that are planned for follow-on studies but a short time remaining (possibly for a new CRADA proposal), but specific focus over the next several months will be in the following areas:
- Studies aimed at identifying ways to improve ethanol retention, including:
  - Potential roles for metals and/or other exchangeable cations as pore modifiers and/or production of more stable adsorbed hydrocarbon species.
  - Zeolite pore structure and connectivity.