CLEERS: Aftertreatment Modeling and Analysis

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Pacific Northwest National Lab

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ACE023

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Overview

- Timeline
  - Status: On-going core R&D
  - DPF activity originated in FY03
  - Now also includes LNT, SCR and DOC technologies
- Budget
  - FY11 funding - $750K
  - FY12 funding allocation $750K
    - SCR task – 60%
    - LNT task – 30%
    - DPF task – 10%

- Barriers
  - Emission controls contribute to durability, cost and fuel penalties
    - Low-temp performance of particular concern
  - Improvements limited by:
    - available modeling tools
    - chemistry fundamentals
    - knowledge of material behavior
  - Effective dissemination of information
- Partners
  - DOE Advanced Engine Crosscut Team
  - CLEERS Focus Group
  - 21CTP partners
  - USCAR/USDRIVE ACEC team
  - Oak Ridge National Lab

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Goal and Relevance

- "CLEERS is a R&D focus project of the Diesel Cross-Cut Team. The overall objective is to promote development of improved computational tools for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems."

CLEERS PNNL Subprogram Goal

Working closely with our National Lab partners, the CLEERS industrial/academic team and in coordination with our CRADA portfolio, PNNL will…

…provide the practical & scientific understanding and analytical base required to enable the development of efficient, commercially viable emissions control solutions and modeling tools for ultra high efficiency vehicles.

- VT program goals are achieved through these project objectives:
  - interact with technical community to indentify relevant technological gaps
  - understand fundamental underlying mechanisms and material behavior
  - develop analytical and modeling tools, methodologies, and best practices
  - apply knowledge and tools to advance technologies leading to reducing vehicle emissions while improving efficiency
- Specific work tasks in support of the objectives are arrived at through:
  - focus group industrial monthly teleconferences, diesel X-cut meetings
  - yearly workshops and surveys
  - submission of SOW to the VT office

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Technical Milestones & Approach

- The overall performance measure of the project is inextricably linked to the interests of industry
  - PNNL CLEERS activities have resulted in the formation of new CRADAs
  - Tremendous success of the annual workshops
  - Strong participation in the monthly teleconferences
- Specific performance measures are developed with the industrial/academic partners and captured in SOW
  - Specific technical targets and major milestones are described in our AOPs and annual reports to VT
- Approach - “Science to Solutions”
  - We build off of our strong base in fundamental sciences and academic collaborations
    - Institute for Integrated Catalysis (IIC)
    - Environmental Molecular Sciences Laboratory (EMSL)
  - With a strong pull towards industrial applications and commercialization
    - OEMs
    - TIER 1 suppliers
  - Working closely with our partners and sponsors
    - ORNL (coordination of website, workshops, etc.)
    - DOE Advanced Engine Cross-Cut Team

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PNNL FY12 Portfolio

CLEERS activity

Integrated Systems – George Muntean

- DPF subtasks* – Mark Stewart
- SCR subtasks* – George Muntean
- LNT subtasks – Chuck Peden

CRADA activities

DPF – DOW Automotive (Stewart)**

Fuel Neutral Particulate study (Stewart)

SCR/DPF – PACCAR (Rappe)

SCR, HC – Ford Motor Company (Peden)

SCR, DOC – General Motors (Peden)**

SCR Dosing Systems – GM & Ford (Autrey)

LNT – Cummins Inc. (Peden)

Oxidation Catalysts

– General Motors (Herling)

– SDC Materials (Herling)

– Caterpillar (Rappe)**

*PNNL-led subteam
**Past activities

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FY2011/2012 Scope Objectives

- Selective Catalytic Reduction (SCR)
  - Develop a model based on single NH_3 storage site for the state-of-the-art Cu SCR catalyst based on CLEERS SCR transient protocol data
  - Extend the model to incorporate two NH_3 storage sites and use it as a benchmark to model performance degradation for various SCR reaction pathways during catalyst aging
  - Initiate detailed kinetic and mechanistic studies for NO reduction over the state-of-the-art small-pore zeolite-based Cu SCR catalysts, including characterization measurements that probe the nature of the active Cu species.
- NO_x Storage-Reduction (NSR) Catalysts
  - Continue fundamental studies of morphology changes and NO_x uptake mechanisms of novel high-temp LNT catalyst materials
  - Investigate the formation and stability of PGM particles (also relevant to DOC, TWC)
- Diesel Particulate Filter (DPF)
  - Investigate particulate oxidation mechanisms for relevant oxidants (O_2, NO_2) through reactor experiments and TEM analysis
  - Seek incremental improvements to 0D and detailed 3D filter modeling tools

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Technical Accomplishments Outline

- SCR
  - Developed and validated a Cu SCR model considering a single NH_3 storage site, based on CLEERS SCR transient protocol data from ORNL.
  - Investigated the nature of Cu species and obtained kinetic parameters for small-pore zeolite-based Cu SCR catalyst.
  - Catalyst characterization has been performed on these catalysts both before and after hydrothermal aging.
- NSR
  - Examined the effects of support materials for Ba-based LNT catalysts, and found magnesium aluminate may improve the NO_x reduction performance at high temperatures.
  - Performed systematic studies of K loading effects on NOx storage performance for both alumina- and magnesium aluminate-supported NSR catalysts.
  - Initiated detailed characterization studies of K-based NSR catalysts including in-situ XRD measurements.
- DPF
  - Kinetics experiments were carried out for medium duty and light duty diesel particulate samples
  - Advanced TEM analysis was used to examine evolution of particulate nano-structure during oxidation

Selective Catalytic Reduction

- modeling studies
  - overall goal is to develop catalyst aging factors, essential for model based control adaptation, using 1D SCR models.
  - transient protocol and TPD data collected on Cu-CHA samples at ORNL were used to develop the SCR model.
- materials characterization
  - characterization data of Cu-zeolite
  - hydrothermal deactivation

Single Site NH_3 Storage Model

- Model parameters tuned using a TPD test without isothermal desorption (top right)
- Validation on a TPD with isothermal desorption (bottom right)
- Storage dependent desorption kinetics is assumed in the model.

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

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

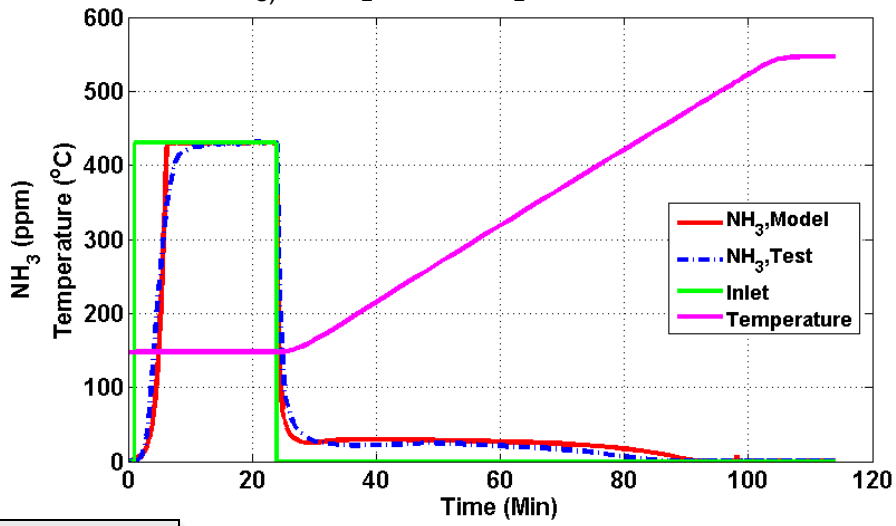
$$r_{ads} = A_{ads} c_{g,NH_3}(1-\theta_{NH_3})$$

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

A_{ads}	$m^3/mol/s$	0.99
A_{des}	1/s	1.01E11
E_{des}	kJ/mol	180.2
γ	-	0.81
Ω	mol/m^3	225

Data used for model parameter tuning

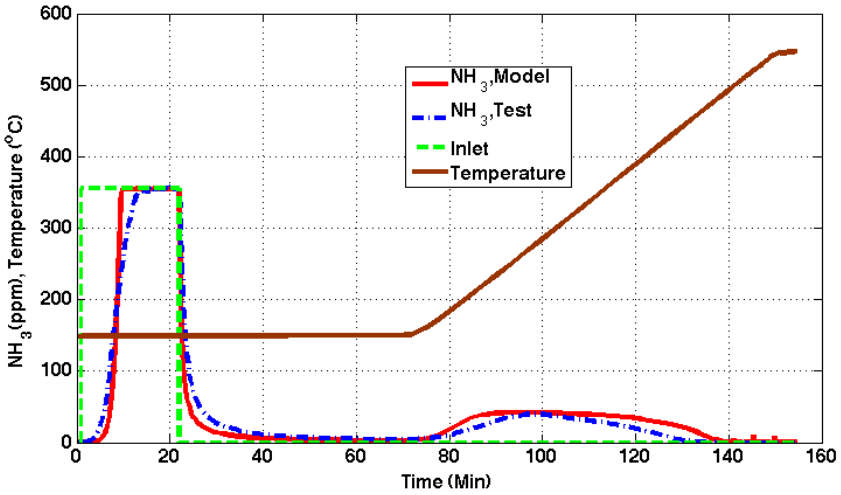
430 ppm NH_3, 5% H_2O, 5% CO_2 at T = 150°C, 30k SV



Test data from ORNL

Data used for model validation

350 ppm NH_3, 5% H_2O, 5% CO_2 at T = 150°C, 60k SV



SCR Reaction Pathways

- In addition to NH_3 adsorption and desorption on SCR catalyst surface, the following reactions have been incorporated in this Cu 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	$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O$

- The following slides show the kinetic model development for each of these reactions

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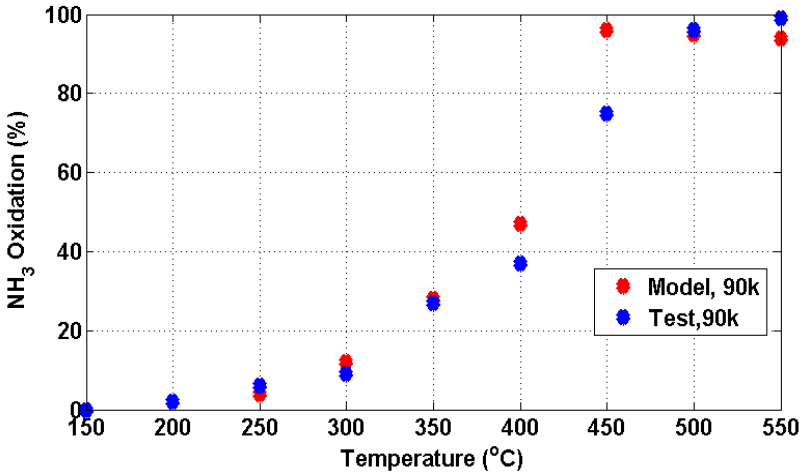
Kinetic Models for NH_3 and NO Oxidation

NH_3 Oxidation

Test data from ORNL

NO Oxidation

430 ppm NH_3, 10% O_2, 5% CO_2, 90k SV



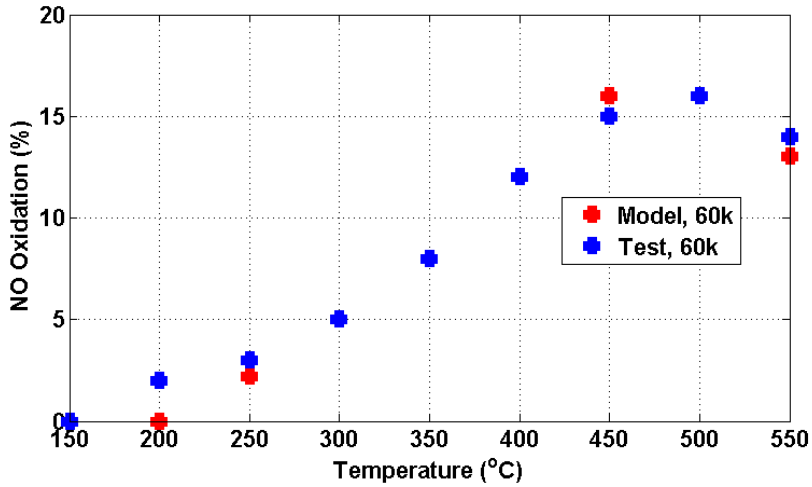
$$\frac{\partial c_{g,NH_3}}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial c_{g,NH_3}}{\partial x} + \frac{\Omega}{\varepsilon}(r_{des} - r_{ads})$$

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

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

$$r_{NH_3,oxi} = k_{NH_3,oxi} c_{g,O_2} \theta_{NH_3}$$

350 ppm NO, 10% O_2, 5% CO_2, 60k SV



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

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

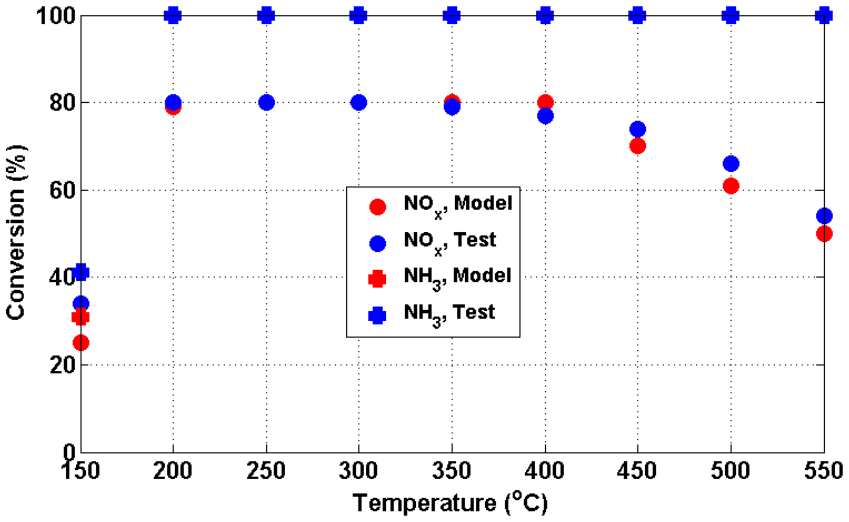
$$r_{NO,oxi} = k_{NO,oxi}(c_{g,NO} c_{g,O_2}^{\frac{1}{2}} - \frac{c_{g,NO_2}}{k_{eq}})$$

$$k_{eq} = A_{eq}\sqrt{T} e^{\frac{E_{eq}}{RT}}$$

Kinetic Models for SCR Reactions

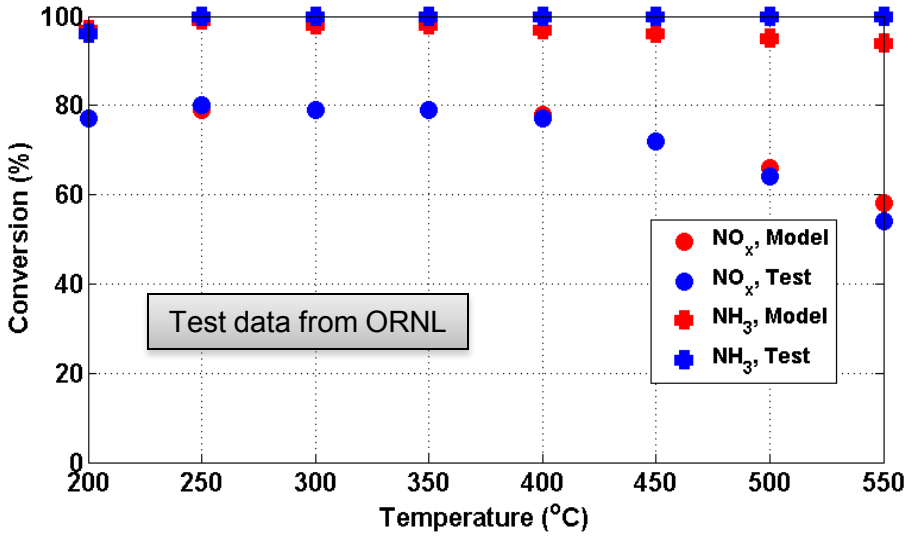
Standard SCR

350 ppm NO, 350 ppm NH_3, 10% O_2, 5% CO_2, 5% H_2O, 60k SV



Fast SCR

175 ppm NO, 175 ppm NO_2, 350 ppm NH_3, 10% O_2, 5% CO_2, 5% H_2O, 90k SV



- Standard SCR pre-exponential was manually adjusted at 150°C, 30k/hr SV and the model was validated at the remaining data points.
- Model (Standard SCR) mismatch in NO_x conversion at T > 450°C was observed at higher space velocities, possibly due to NH_3 oxidation to NO, which is not considered in the model.
- NO_2-SCR kinetic model was included for better match at low temperatures. At high temperatures NO_2-SCR can be neglected.
- No parameter tuning was done for Fast SCR & NO_2-SCR reactions. Parameters from Olsson et al., (2008) on Cu-Z SCR model were used in the model directly.

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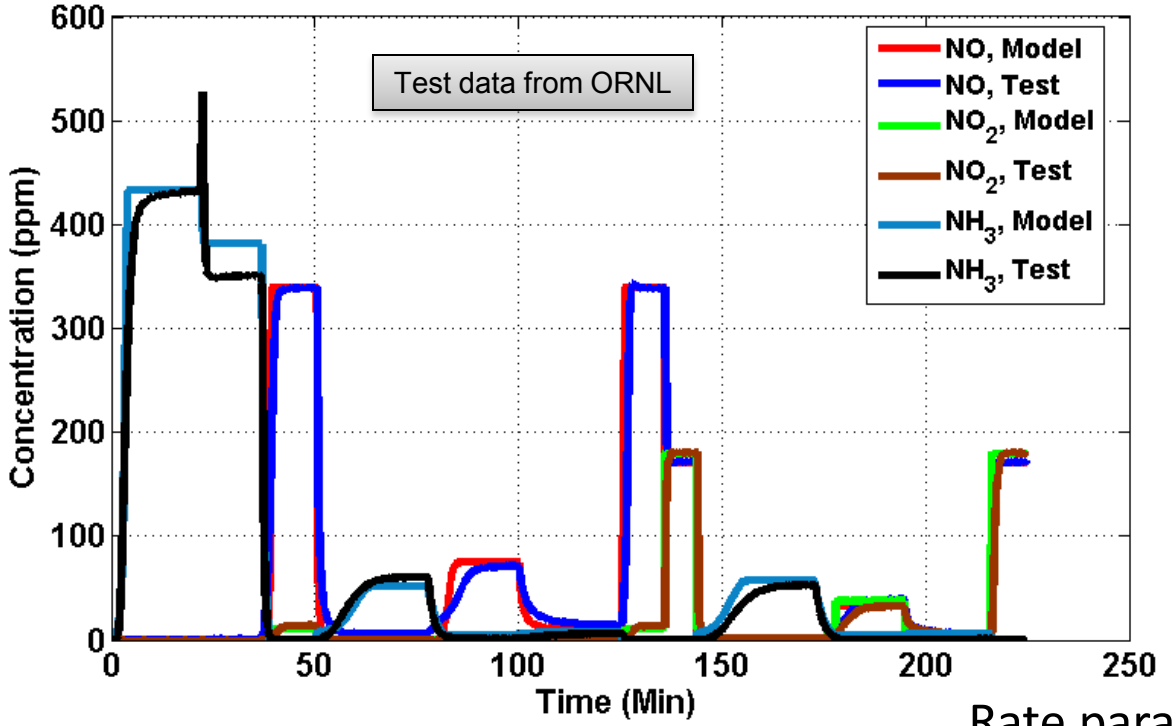
SCR Model Validation Against CLEERS Transient Protocol

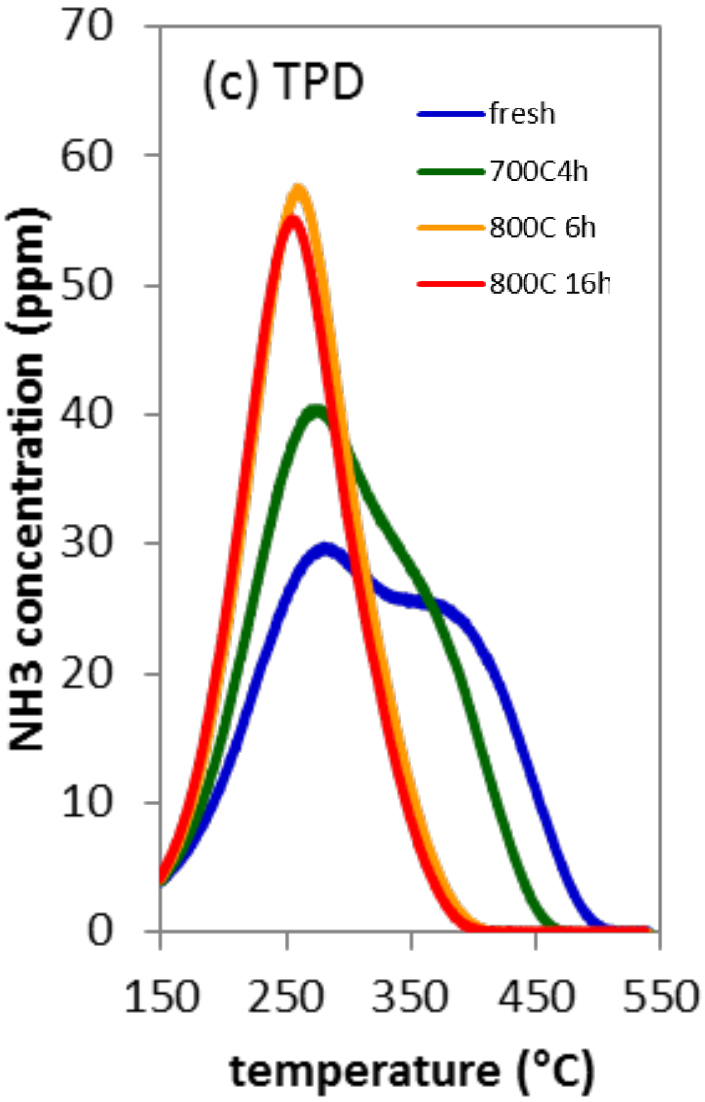


- SCR Model validation shown at 90k SV at T = 300°C
- Model was successfully validated for various cases: $0.8 \leq NH_3/NOx \leq 1.2$ and $30k \leq SV \leq 90k$

Rate parameter comparison

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

Current Work – SCR Model using Two NH_3 Storage Sites



- Recent data on a fresh catalyst sample (NH_3 desorption vs temperature during TPD shown on the left) shows two peaks indicating the possibility of more than one active site with different stabilities in the catalyst.
- The two peaks convolute into one as the sample is degreened and aged as shown in the figure.
- This has motivated us to develop a model with two NH_3 storage sites so that the aging effect on NH_3 storage and other reaction pathways can be accurately predicted.

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State-of-the-art Cu SCR Catalyst Research

- Both Cu-SSZ-13 and Cu-SAPO-34 catalysts synthesized and studied at PNNL – these model catalysts allow for fundamental studies of their catalytic and material properties
  - Both CHA zeolites synthesized by published hydrothermal methods.
  - Cu loaded into SSZ-13 via aqueous ion exchange
  - Cu loading into SAPO-34 is difficult; we added Cu during zeolite synthesis.

- Results to date have included:
  - NO_x SCR performance as a function of Cu loading and hydrothermal treatments (publication on this work has been released)
  - Characterization of the Cu species as a function of Cu loading by temperature-programmed reduction (TPR) and EPR spectroscopy measurements (three slide shown in the back-up section)
  - Characterization of various Cu-zeolite catalysts before and after hydrothermal aging via XRD, ^{27}Al NMR, and TPR.

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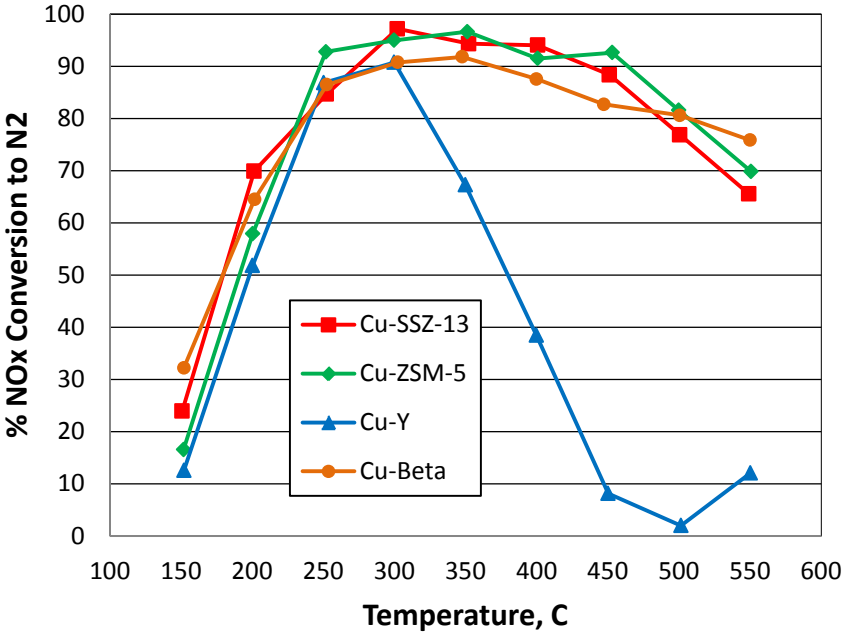
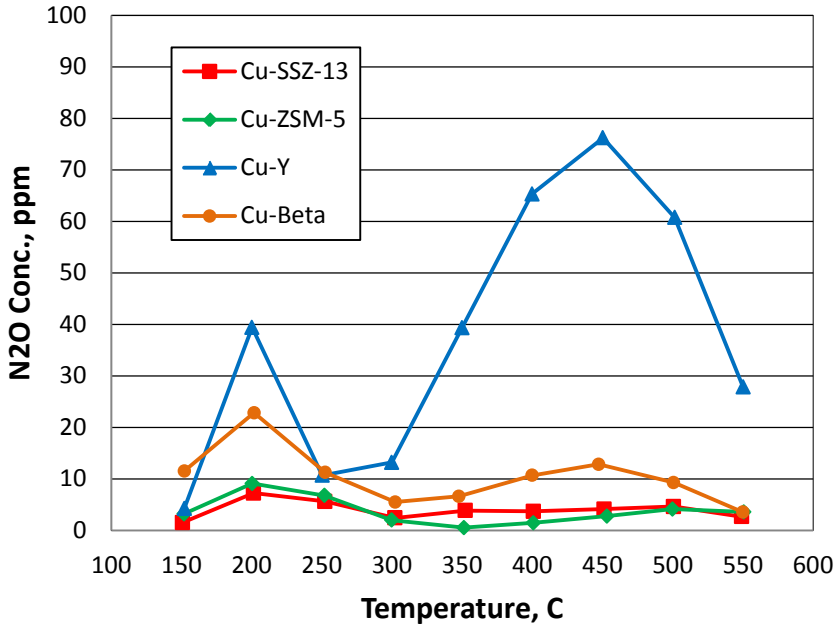
“Standard” SCR Reaction – Fresh Catalysts

NO Reduction to N_2 (estimated)



N_2O Formation

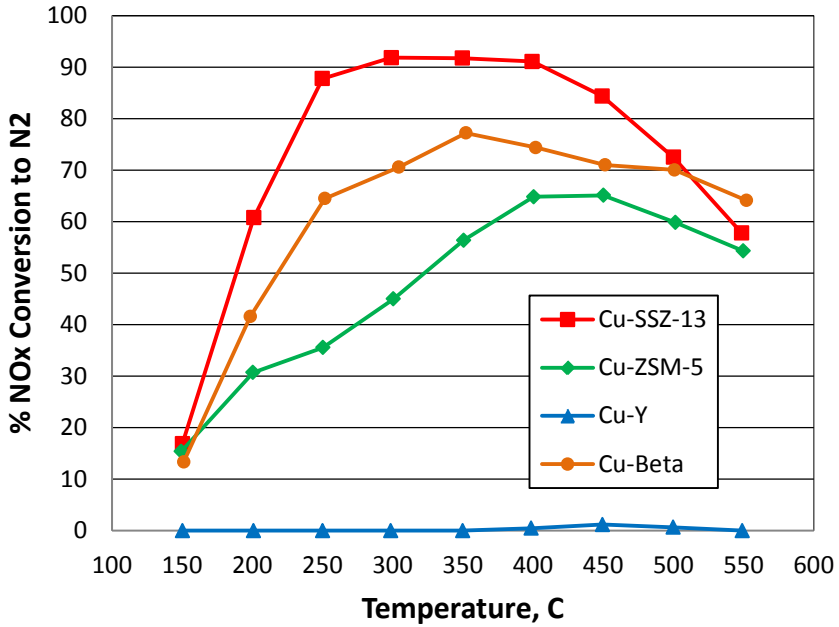


- Cu/ZSM-5, Cu/beta and Cu/SSZ-13 are roughly equivalent in performance.
- Very low N_2O formation over Cu/SSZ-13 and Cu/ZSM-5.
- Cu/Y has low activity at higher temperatures due primarily to N_2O production.
- Effects of hydrothermal aging?

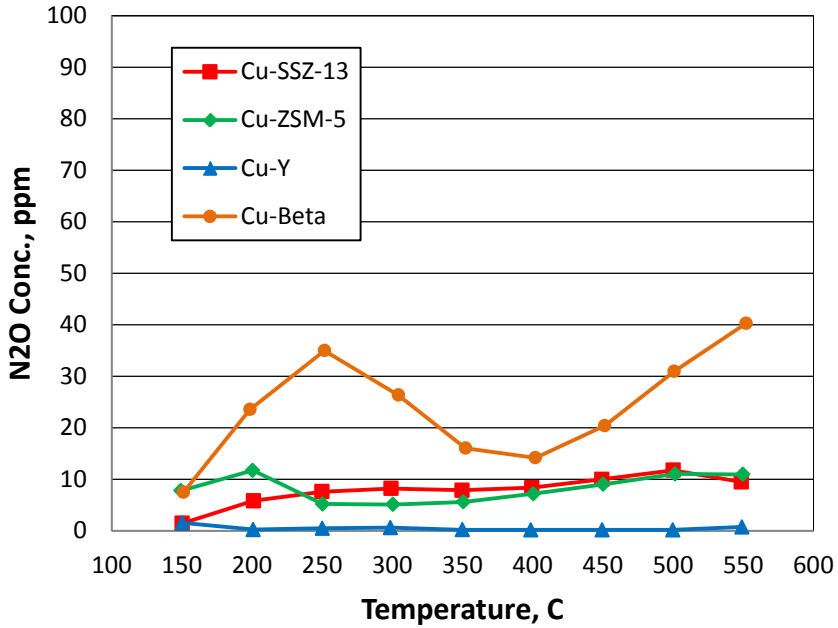
JH Kwak, D Tran, SD Burton, J Szanyi, JH Lee, CHF Peden, Journal of Catalysis 287 (2011) 203.

“Standard” SCR Reaction – Hydrothermally Aged (HTA)

NO Reduction to N_2 (estimated)



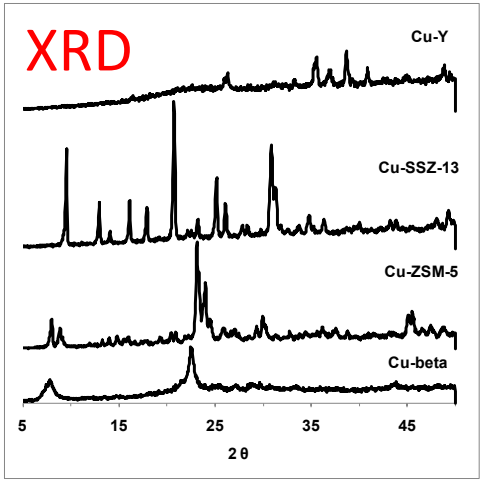
N_2O Formation



- Cu/SSZ-13 catalyst is quite stable to HTA
- Further reduction of performance for the other Cu catalysts due, in part, to increased N_2O formation after HTA
- Essentially complete loss of Cu/Y activity after HTA

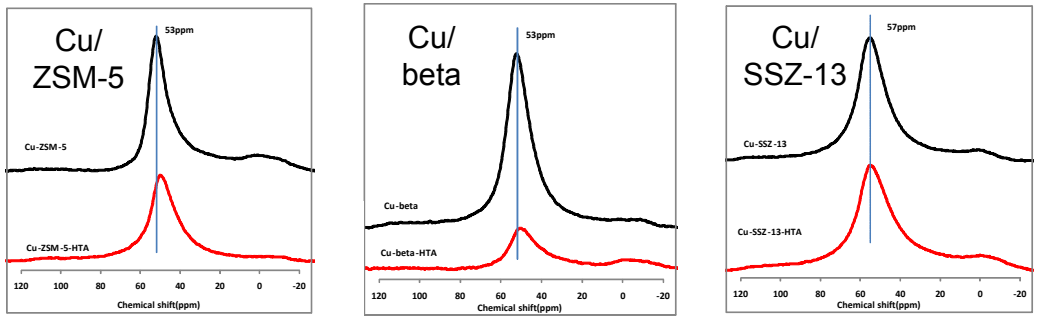
JH Kwak, D Tran, SD Burton, J Szanyi, JH Lee, CHF Peden, Journal of Catalysis 287 (2011) 203.

XRD and ^{27}Al NMR after Hydrothermal aging



- Cu/Y: peaks for CuO + broad background
- At most, small changes in the XRD patterns for the other zeolites.
- However, ^{27}Al spectra indicate partial loss of zeolite structure for Cu/ZSM-5 and Cu/beta

^{27}Al NMR



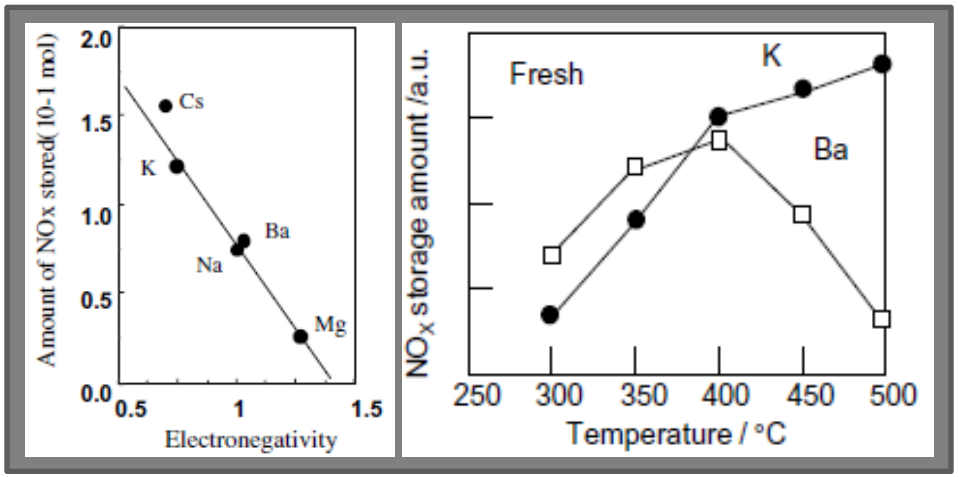
As prepared (black curves); After hydrothermal treatment (red curves)

- Cu/ZSM-5 and Cu/beta both show a significant drop in the ^{27}Al peak due to tetrahedral aluminum (zeolite structure loss)
- No change in the spectrum for Cu/SSZ-13 after HTA

JH Kwak, D Tran, SD Burton, J Szanyi, JH Lee, CHF Peden, Journal of Catalysis 287 (2011) 203.

NO_x Storage-Reduction (NSR) Catalysts {aka. LNT}

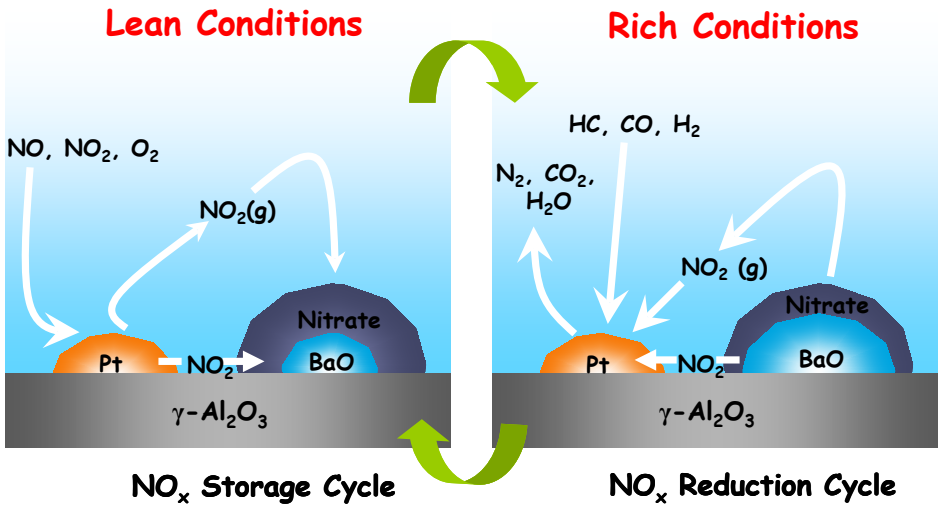
Conventional Ba-based NSRs operate best between 350 and 400°C; K-based NSRs show potentially much better performance at higher temperatures



Toyota: Top Catal. 28(2004)151

Approach

- Higher temperature NO_x reduction performance required for:
  - Difficult to meet "not to exceed" regulations during desulfations
  - Possible use of NSRs for lean-gasoline applications



- PNNL/Cummins/JM CRADA focusing on degradation of possible materials for next-generation high temperature NSRs.
- CLEERS studies are addressing more fundamental issues of these potential new NSR materials related to composition, morphology, and chemical reaction kinetics and mechanisms.
- For these studies, PNNL has prepared a range of materials based on literature and prior CLEERS work at PNNL.

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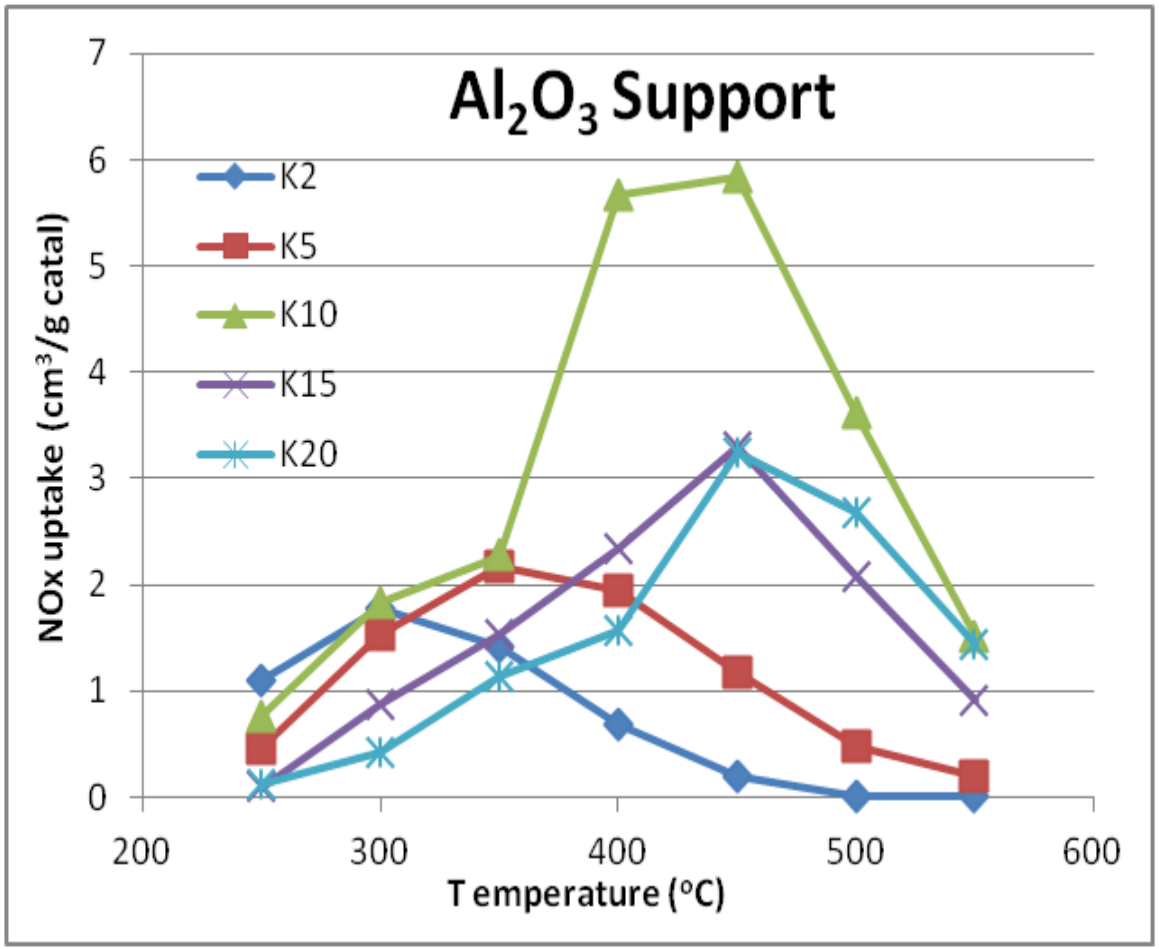
High Temperature NSR Catalyst Materials

- $K/Pt/Al_2O_3$ (2%, 5%, 10%, 15%, 20%, weight):
  - **Pt/Al_2O_3** (1%): Impregnation of Al_2O_3 (150 m^2/g) with $Pt(NH_3)_4(NO_3)_2$, 500ºC calcination for 4hrs
  - **K loading**: Impregnation of Pt/Al_2O_3 with K_2CO_3 of different K loadings, 600ºC calcination for 4hrs
- $K/Pt/MgAlO_x$ (2%, 5%, 10%, 15%, 20%, weight):
  - **$MgAlO_x$ Support** (Pural MG30: Mg/Al=0.6): Calcination at 600ºC for 4hrs
  - **K and Pt loading**: as with the alumina-supported catalysts
- NO_x storage performance testing and catalyst characterization by KNO_3-TPD (decomposition), NO_x TPD (after NO_2 adsorption), XRD and TEM
- Aging and sulfur tolerance being studied as part of Cummins CRADA.
- Will emphasize recent performance data today.

Effect of K loading on Al_2O_3-Supported NSRs



- Optimum operating T increases with K loading until 10%, then stays at 450ºC with K loading higher than 10%.
- 10% $K/Pt/Al_2O_3$ exhibits best overall performance in the whole temperature range, especially between 400 and 450ºC.

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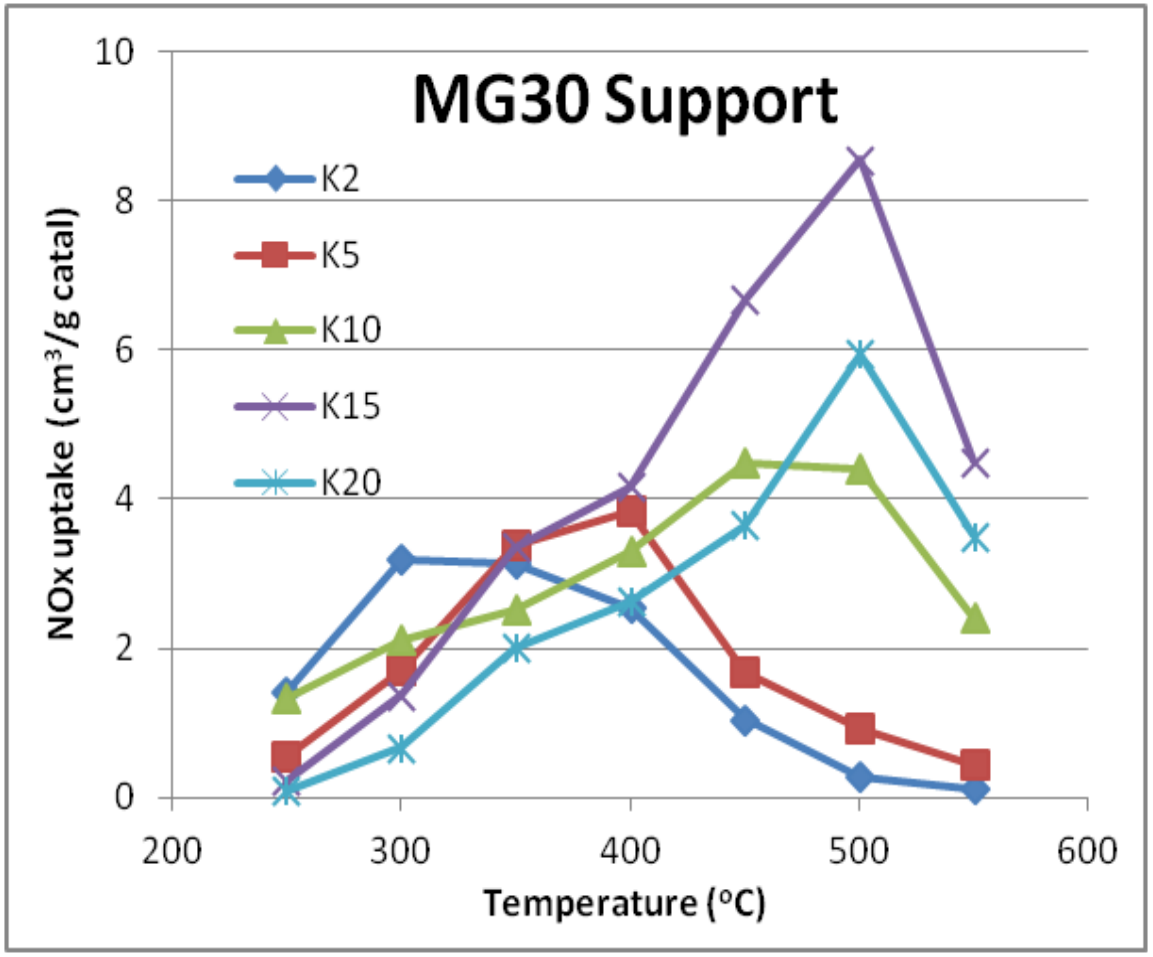
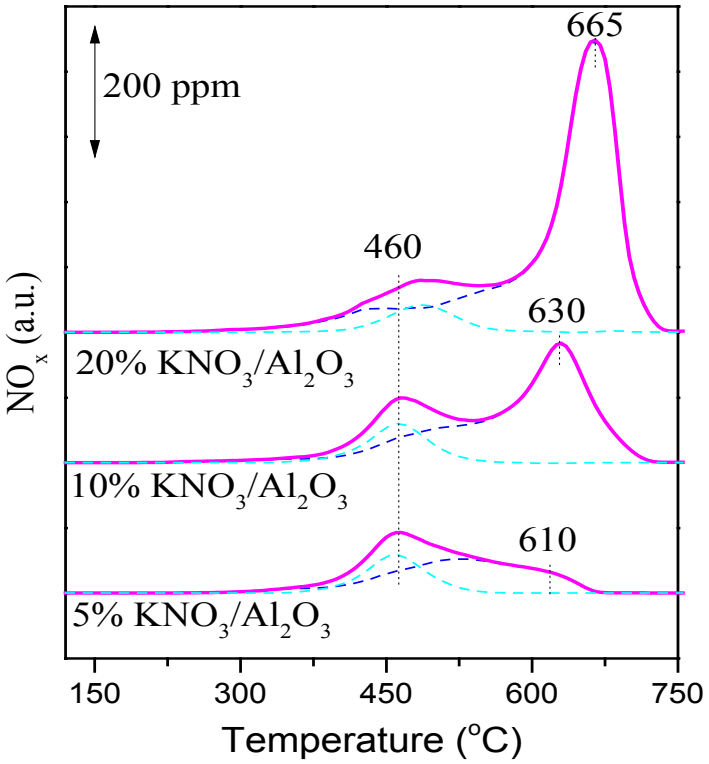
Effect of K loading on MG30 ($MgAlO_x$)- Supported NSRs



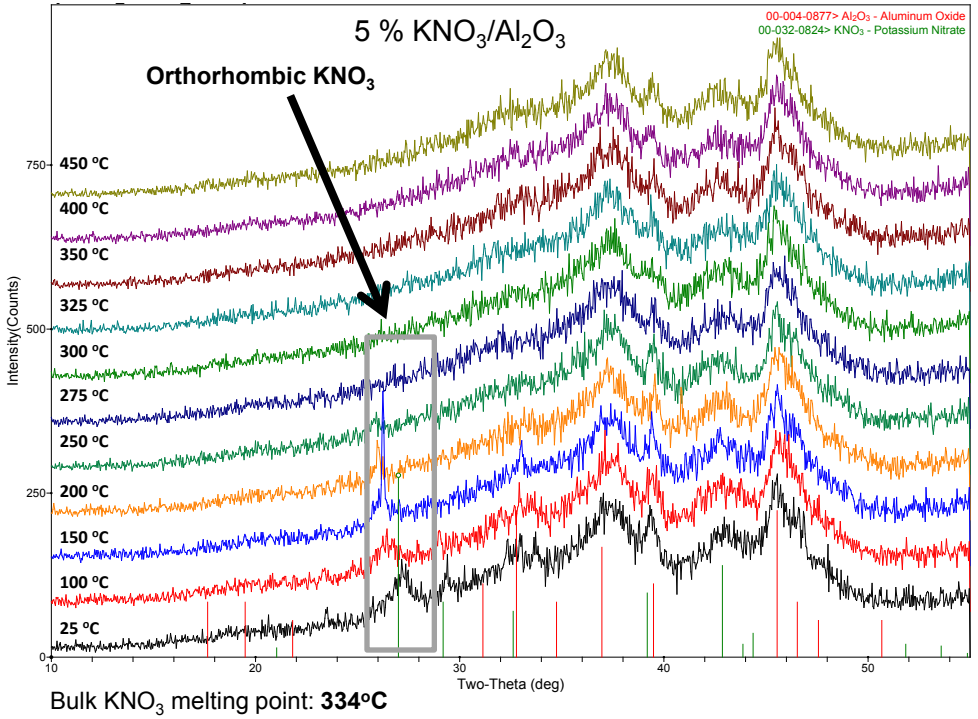
- Similar to Al_2O_3-supported catalysts, optimum operating T increases with K loading to 15%, then stays at 500ºC with higher K loading.
- 15% K/Pt/Mg30 exhibits best overall performance above temperatures of 400ºC.
- Maximum uptake is higher for 15% K/Pt/Mg30 than for 10% K/Pt/Al_2O_3

Unlike Ba, nitrates of K 'melt' at temperatures significantly below their decomposition.

Temperature-programmed decomposition of K-nitrates on Al_2O_3



In-site XRD during the decomposition of K-nitrates on Al_2O_3



Bulk KNO_3 melting point: **334°C**

- Decomposition of K-nitrates occur above 400 °C.
- XRD features due to K-nitrates disappear at temperatures below 300 °C.

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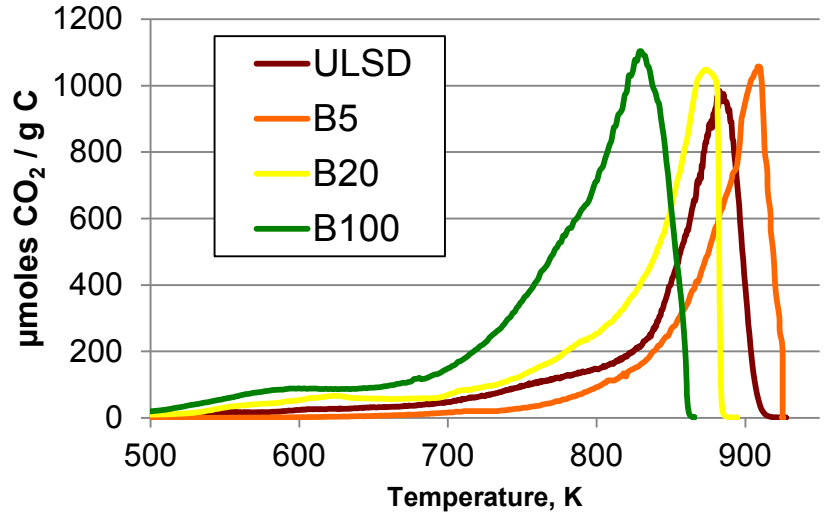
Diesel Particulate Filter

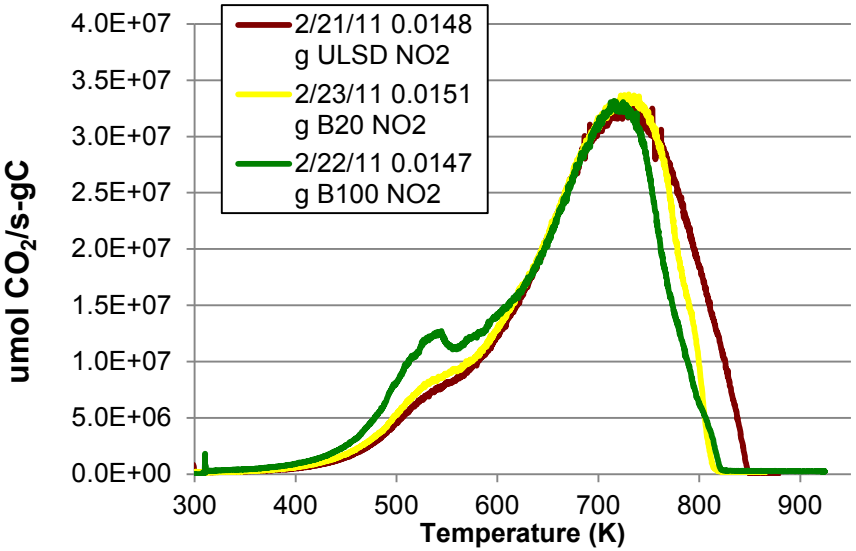
O_2 versus NO_2 TPO experiments

Soot collected and experiments performed at Oak Ridge National Laboratory

Oxygen TPO



1% NO_2 TPO



- Temperature Programmed Oxidation experiments conducted with LD particulate from various biodiesel blends
- O_2 oxidation is dramatically affected by biodiesel content (which changes the primary particle structure)
- NO_2 oxidation is not sensitive to fuel blend
- Differences in low temperature peak correspond to increasing VOF content

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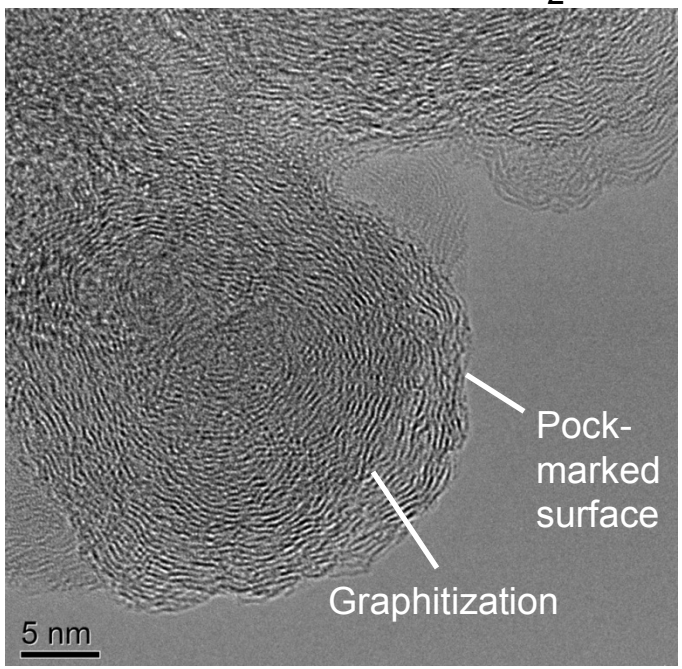
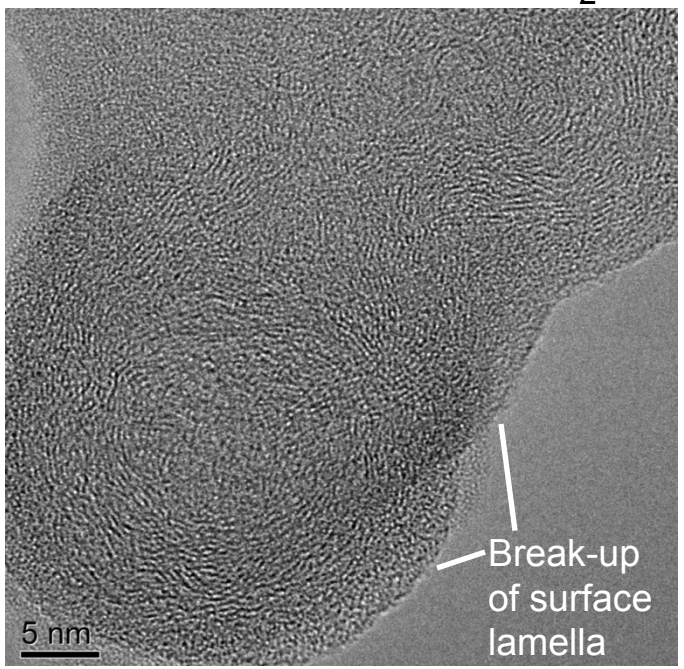
HR-TEM examination of partially oxidized MD-particulate

HR-TEM conducted at Penn State University

50% Oxidized – O_2



50% Oxidized – NO_2



- Particulate (collected at MTU) was partially oxidized (50% mass remaining) in a flow through reactor
- Fundamentally different evolution of nano-structure with the two oxidants
- Less reactive O_2 preferentially oxidizes locations if higher reactivity, highly reactive NO_2 seems to react indiscriminately on contact

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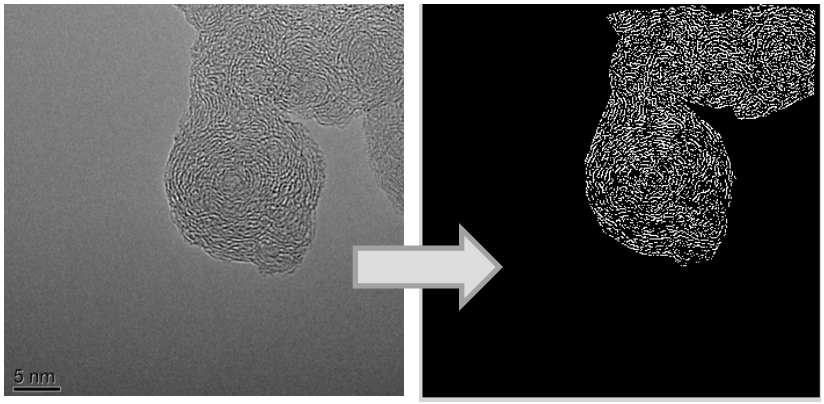
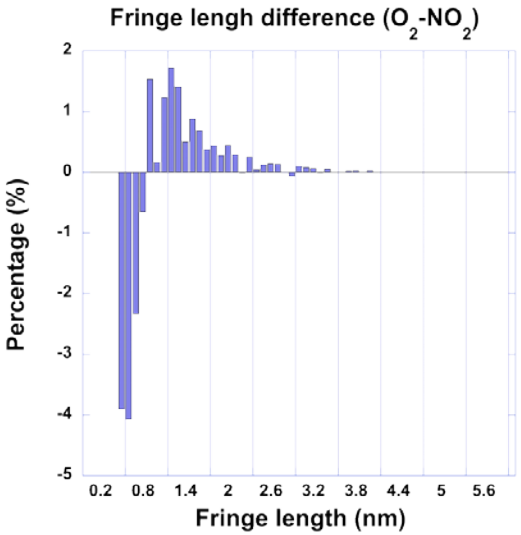
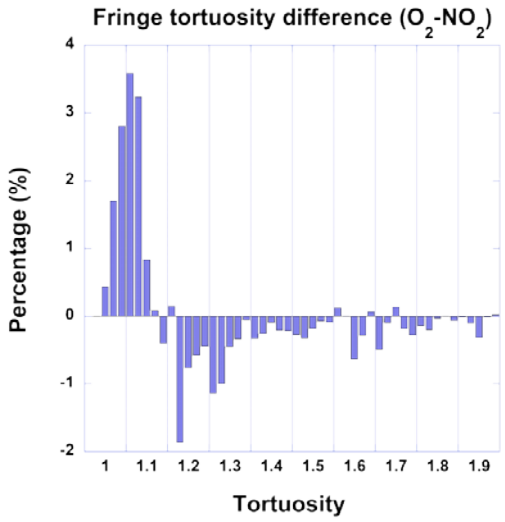
Quantitative image analysis



- Advanced image analysis allows qauntificaiton of nano-structural metrics
- Fringe length is a measure of the extent of graphene sheets
- Tortuosity measures sheet curvature





- Particulate oxidized by O_2 has fewer short and highly curved lamella
- O_2 appears to attack areas of higher reactivity
- NO_2 is indiscriminate and tends to break up graphene layers on contact (diffusion limited)

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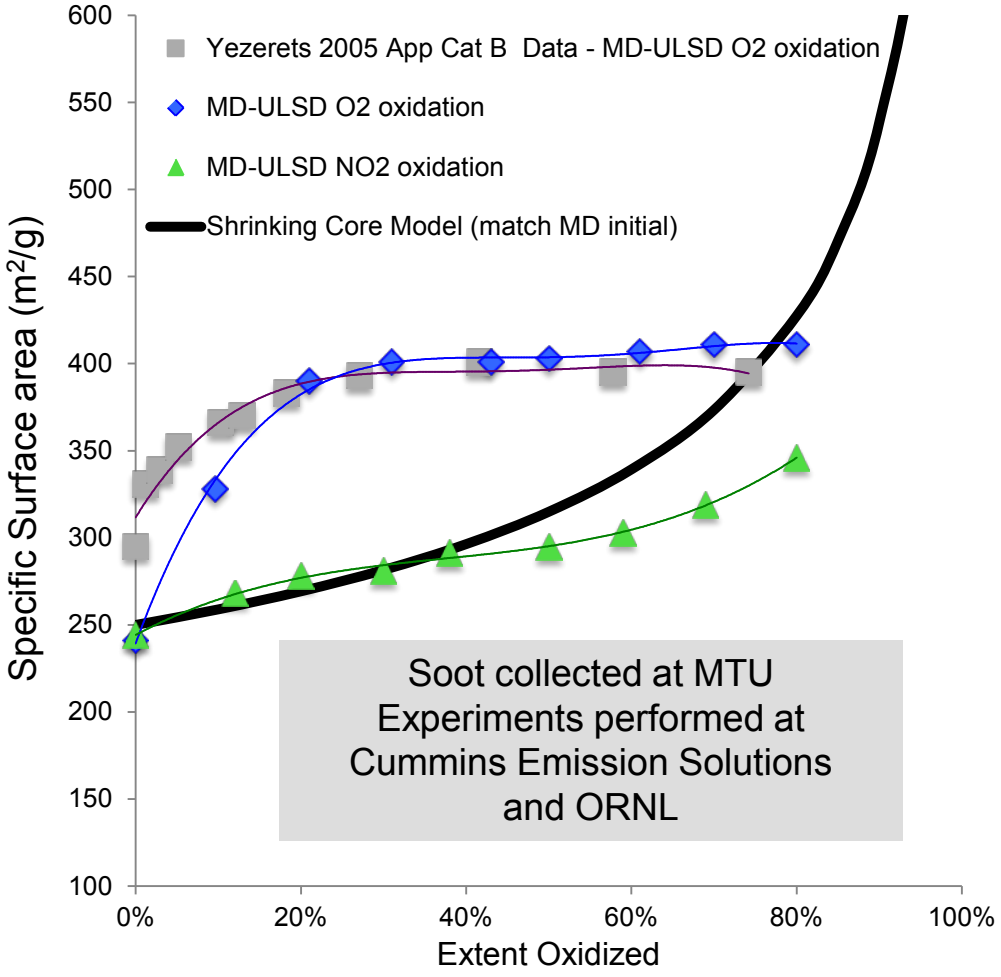
Evolution of surface area during oxidation



- Surface area measured by BET at points in the particulate burnout
- Previous work has shown that surface area evolution during O_2 oxidation depends on engine and fuel and does not follow the shrinking core model
- Very different surface area development during NO_2 oxidation, consistent with the shrinking core prediction, also shown in the HR-TEM images

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Conclusion & Future Work

Conclusions

- SCR
  - Developed and validated a Cu SCR model considering a single NH_3 storage site, based on CLEERS SCR transient protocol data from ORNL.
  - Currently extending the SCR model to two NH_3 storage sites for future studies involving performance degradation due to catalyst aging.
  - Cu-CHA zeolites display a number of enhanced properties compared to other zeolite-based catalysts, including improved selectivity (low N_2O production) and significantly better hydrothermal stability.
  - Our recent TPR, FTIR and EPR studies give strong evidence for the presence of multiple Cu species in CHA-based catalysts. Their various roles for optimum performance are being explored.
- NSR
  - Unlike Ba-based NSRs, the temperature for optimum performance of Al_2O_3-supported K NSR catalysts show a large and unexpected dependence on loading.
  - $MgAl_2O_4$ support materials provide for even higher temperature performance of K-based NSRs, and also show the unusual dependence on K loading.
  - Characterization of these potential high-temperature NSR catalysts has been initiated to understand their interesting properties; also important for determining mechanisms of failure.
- DPF
  - Due to the highly reactive and indiscriminate nature of NO_2, particulate reactivity for NO_2 oxidation seem to independent of fuel type. This is unlike O_2 oxidation, which depends on the exposed reaction surface area, which has been shown to depend on biodiesel blend level.
  - Fundamentally different oxidation modes appear to be involved in oxidation of diesel particulate by NO_2 and O_2

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Future Work

- SCR
  - Develop and validate SCR aging models based on CLEERS transient protocol data.
  - Identify critical rate/model parameters that need to be adapted for catalyst aging/deactivation and develop maps/math expressions to support model-based controls.
  - Publish the modeling methodology and results in a peer-reviewed scientific publication.
  - Continue studies of the active Cu species in the CHA-based catalysts, including new studies of SAPO-34 zeolite catalysts.
  - Initiate studies of the reaction mechanism for these catalysts; low NO oxidation activities for these catalysts suggest a fundamentally different chemical process.

- NSR
  - Continue catalyst characterization to determine origins of optimum high temperature performance of K-based NSRs.
  - Initiate studies of ways to control the mobility of K in this class of NSR catalysts which is a significant concern for their practical application.

- DPF
  - Characterize current production and advanced DPF substrates through advanced image and statistical analysis of high resolution Computed Tomography (CT) data
  - Investigate the use of micro-scale simulation to improve the commonly used unit collector models for DPF substrates

Acknowledgements

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- Industry

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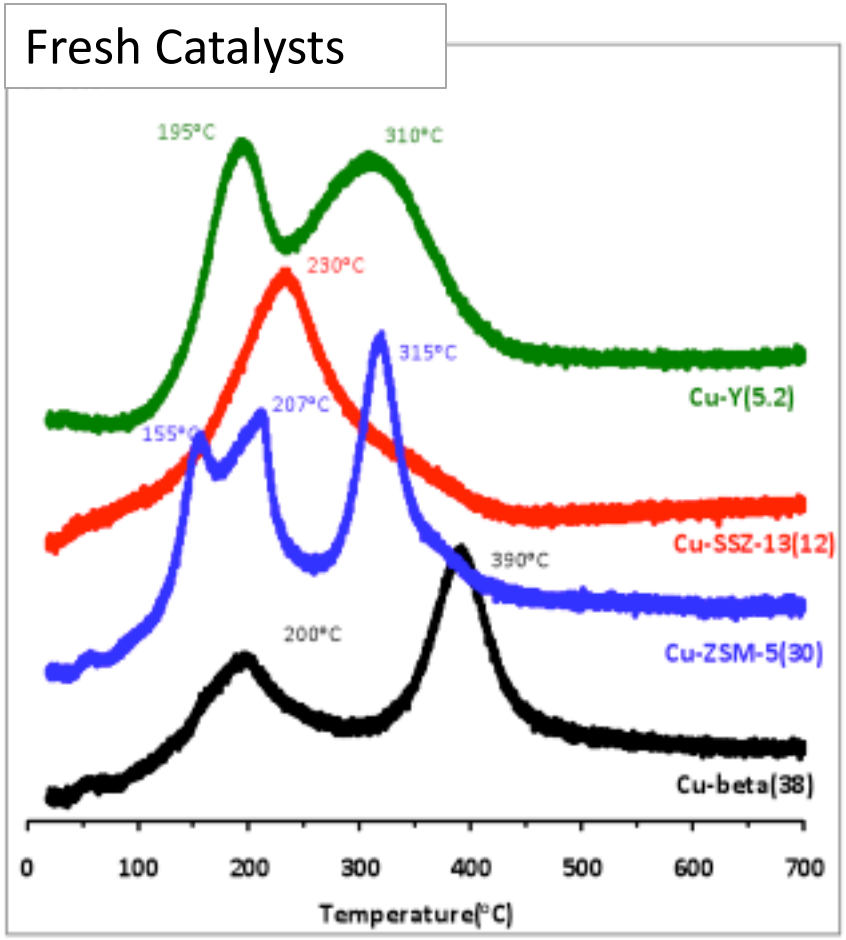
Technical Back-up Slides

Reduction of Cu Species Varies Considerably with Zeolite Type

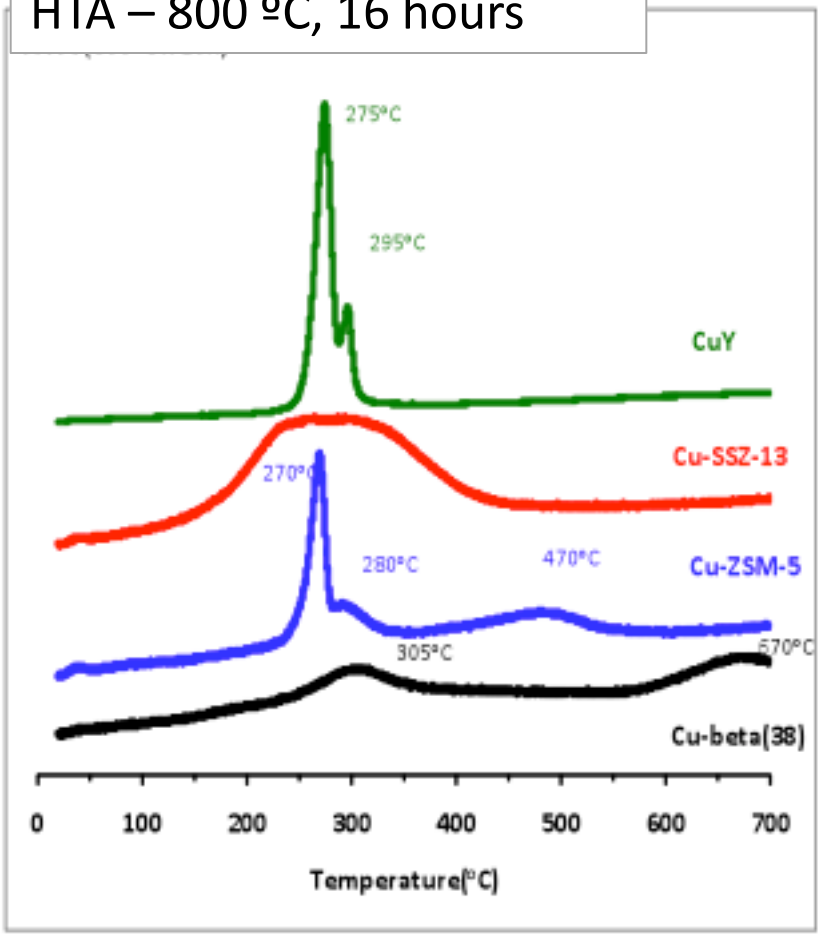


- Cu/beta and Cu/ZSM-5 fully reduced to Cu^0 by 500 ºC; according to Iglesia and coworkers, the two main features are due $Cu^{+2} \rightarrow Cu^{+1}$ and $Cu^{+1} \rightarrow Cu^0$. Catalyst powders were colored after reduction.
- Cu in Cu/Y and Cu/SSZ-13 remained as Cu^{+1} even after TPR to 700 ºC.
- Two peaks for Cu/Y due to two Cu species (in super- and sodalite-cages)
- Cu/SSZ-13 also has two peaks which may be two sites; *however, recent studies by Lobo and coworkers suggest a single Cu site*.

JH Kwak, D Tran, SD Burton, J Szanyi, JH Lee, CHF Peden, Journal of Catalysis 287 (2011) 203.

Effect of Hydrothermal Aging on the Reduction of Cu Species in the various Zeolites Studied Here

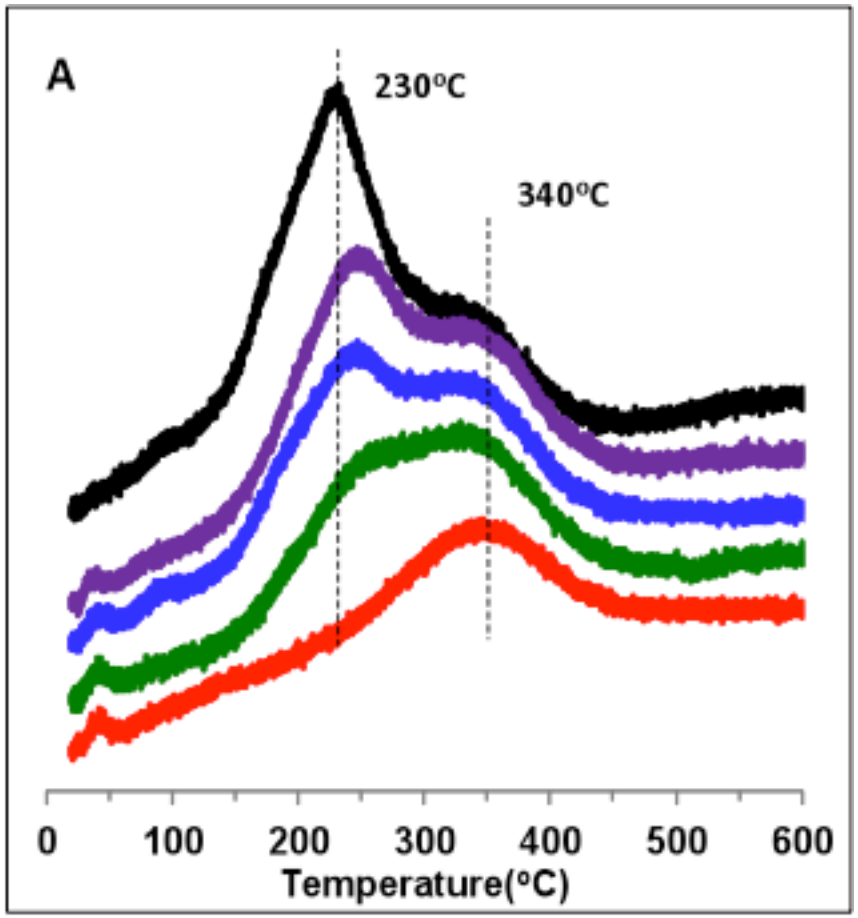
HTA – 800 ºC, 16 hours



- CuY only shows features due to reduction of bulk-like CuO.
- TPR of Cu/SSZ-13 remains essentially unchanged after hydrothermal aging, and powders are still white after reduction during TPR to 700 ºC.
- Cu/ZSM-5 also shows evidence for bulk-like CuO along with other peaks likely associated with Cu still near ion-exchange sites in the zeolite.
- Changes in TPR for Cu/beta are particularly significant.

JH Kwak, D Tran, SD Burton, J Szanyi, JH Lee, CHF Peden, Journal of Catalysis 287 (2011) 203.

Effect of Cu Loading on the Reduction of Cu Species in Cu-SSZ-13 Zeolites Catalysts



- At low loading, only a single H_2 TPR reduction peak at ~340 ºC.
- At higher loadings, a second TPR peak appears at ~230 ºC, which monotonically increases in size with increasing Cu loading.
- However, recent literature from Lobo and coworkers has suggested a single Cu site in SSZ-13 CHA zeolite.
- Our TPR results are consistent with our recent FTIR and EPR spectroscopic measurements (not shown here).

JH Kwak, H Zhu, JH Lee, CHF Peden, J Szanyi, Chemical Communications, submitted (2011).