Enhanced High and Low Temperature Performance of NOx Reduction Materials

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ACE026

Project Overview

Timeline

- Start – March 2009
- 3-Year Renewal Executed – March 2013

Budget

- Matched 50/50 by Cummins as per CRADA agreement
- DOE funding for FY12: $300K; Same expected for FY13 – $60K received through March 2013.

Barriers

- Discussed on next slide

Partners

- Pacific Northwest National Laboratory
- Cummins, Inc.
  - w/Johnson Matthey

Barriers - Relevance

- As noted in a recent USDRIVE-sponsored workshop, low exhaust temperatures of future engines will create major challenges for exhaust aftertreatment technologies.
- In addition NOx reduction systems will also require **improved higher temperature performance** and stability.
  - For example, NOx removal performance during high temperature system maintenance events, including DPF regeneration. NOx treatment for natural gas engines will also require higher temperature performance.
- It is important to reduce system costs by, for example, **minimizing the precious metal content** while maintaining, even improving, performance and long-term stability.

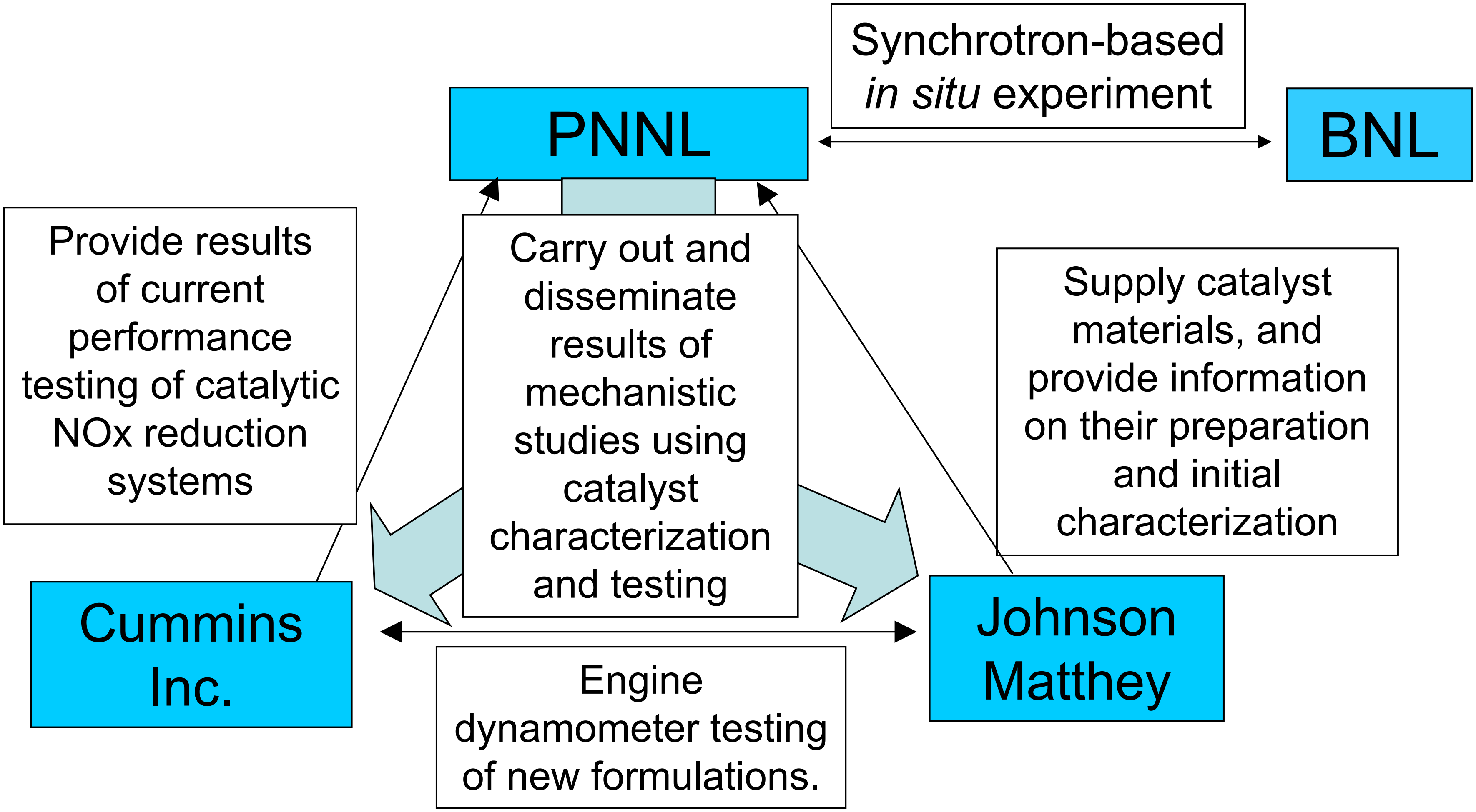
Goals and Objectives

- For NOx after-treatment from lean-burn (including diesel) engines, develop a fundamental understanding of the limitations of candidate next generation materials for operation at lower and higher temperatures.
- Focus on characterizing and understanding the following specific issues:
  - determination of factors that limit low and high temperature performance;
  - mechanisms for deactivation for candidate materials;
    - determination of significant causes of low and high temperature performance loss;
    - characterization of material changes with hydrothermal aging
    - the sulfur adsorption and regeneration mechanisms for modified and/or alternative catalyst materials.

Approach

- **Prepare and Process Catalyst Materials**
  - **Fully formulated (proprietary) catalysts have been provided by Johnson Matthey.**
  - **Based on prior PNNL results and published literature, PNNL is preparing model candidate materials:**
    - **Variations in LNT storage element and support material;**
    - **Identification of optimum synthesis procedures for preparing reproducible SCR catalysts.**
  - **These materials are studied:**
    - **Fresh, as-received (AR) and degreened**
    - **Variably sulfated and/or thermally-aged**
- **Utilize expertise and state-of-the-art catalyst characterization and testing facilities at PNNL's IIC to address mechanisms and structure/function**
    - **XRD, XPS, NMR, TEM/EDX and SEM/EDX**
    - **NO_2 TPD, H_2 TPRX**
    - **Synchrotron based techniques (*in situ* time-resolved XRD)**
    - **Lab reaction system**

Collaborations/Interactions



PNNL

Synchrotron-based *in situ* experiment

BNL

Provide results of current performance testing of catalytic NOx reduction systems

Carry out and disseminate results of mechanistic studies using catalyst characterization and testing

Supply catalyst materials, and provide information on their preparation and initial characterization

Cummins Inc.

Johnson Matthey

Engine dynamometer testing of new formulations.

- Conference calls were held typically once every month or two to discuss the results.
- The next annual face-to-face CRADA Review will be held in Columbus, IN (either April or September, 2013).

Collaborations/Interactions

Synchrotron-based
in situ experiment

BNL

Prov
of
per
testing
NOx
s

on
on

Cu

Results obtained on similar model catalyst formulations in more fundamental CLEERS-funded studies are essential for this program's success.

of new formulations.

- Conference calls were held typically once every month or two to discuss the results.
- The next annual face-to-face CRADA Review will be held in Columbus, IN (either April or September, 2013).

Current Year Studies

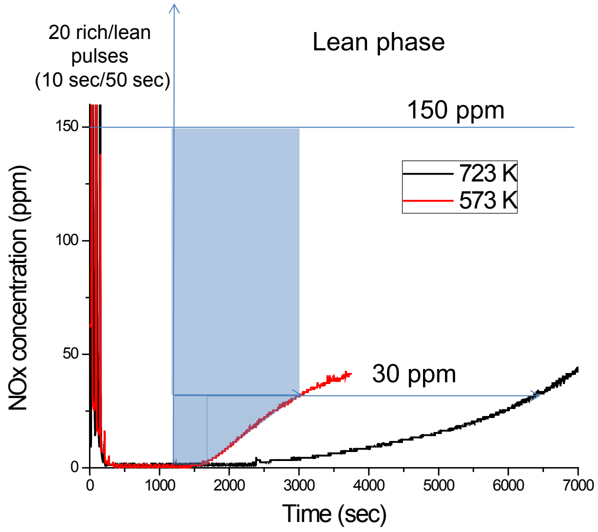
- **High temperature LNT catalysts prepared by PNNL**
  - Studies of the effects of storage elements and various supports on the NOx storage activity, are being carried out as part of PNNL's CLEERS activities.
  - Detailed studies of the deactivation mechanisms in these high temperature NOx storage materials. These studies involve activity testing, thermal treatments, variable desulfation processing, and extensive catalyst characterization.
- **Realistic and model catalyst studies of low and high temperature performance of new SCR catalysts**
  - Optimum preparation of model Cu-SAPO-34 catalysts being carried out in CLEERS activities.
  - Characterization and reactivity of Cu-SAPO-34 as a function of Cu loading – effects on low and high temperature performance.
  - Detailed characterization of vehicle- and laboratory-aged SCR catalysts.

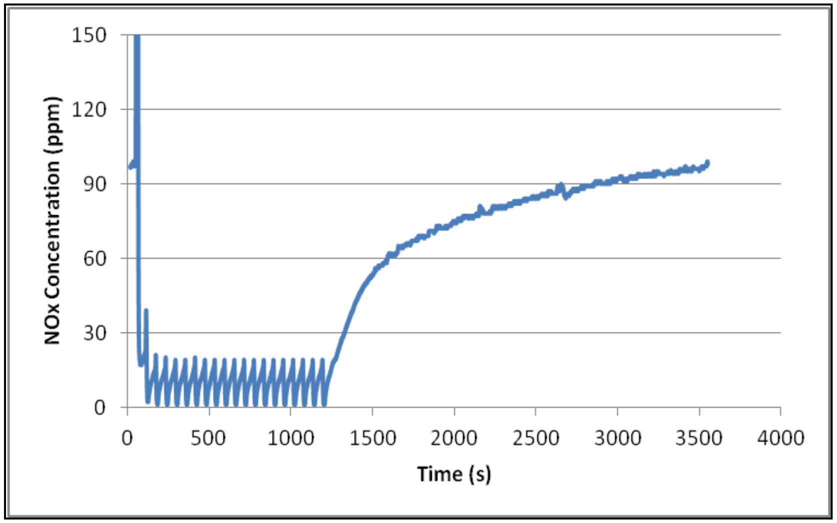
Technical Accomplishments – LNT Studies

- $K/Pt/Al_2O_3$ (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):
  - **$MgAlO_x$ Supports** (Pural® MG30: Mg/Al=0.6; MG50: Mg/Al=1.4; MG70: Mg/Al=3.0): Calcination of MG30, MG50 and MG70 600ºC for 4hrs
  - **K and Pt loading:** as with the alumina-supported catalysts
- $K/Pt/TiO_2$ (2%, 5%, 10%, 15%, 20%, weight):
  - **TiO_2 Supports** (P-25, Hombicat)
  - **K and Pt loading**: as with the alumina-supported catalysts
- Baseline performance and characterization studies – CLEERS program.
- Aging and sulfur tolerance issues are being addressed as part of this CRADA. Two issues currently being addressed:
  - Mobility of K species
  - Reactivity of K with other catalyst components

Brief highlight of recent thermal aging results for TiO_2-supported LNTs.

Reaction Protocol





- 20 cycles first to reach a steady cycle-to-cycle performance.
- **NOx Uptakes:** Total amount of adsorbed NO_x in final long lean cycle until outlet NO_x reached 30 ppm).

Sample: 0.12g sample loaded in fixed bed quartz reactor (I.D.=3/8 in.)

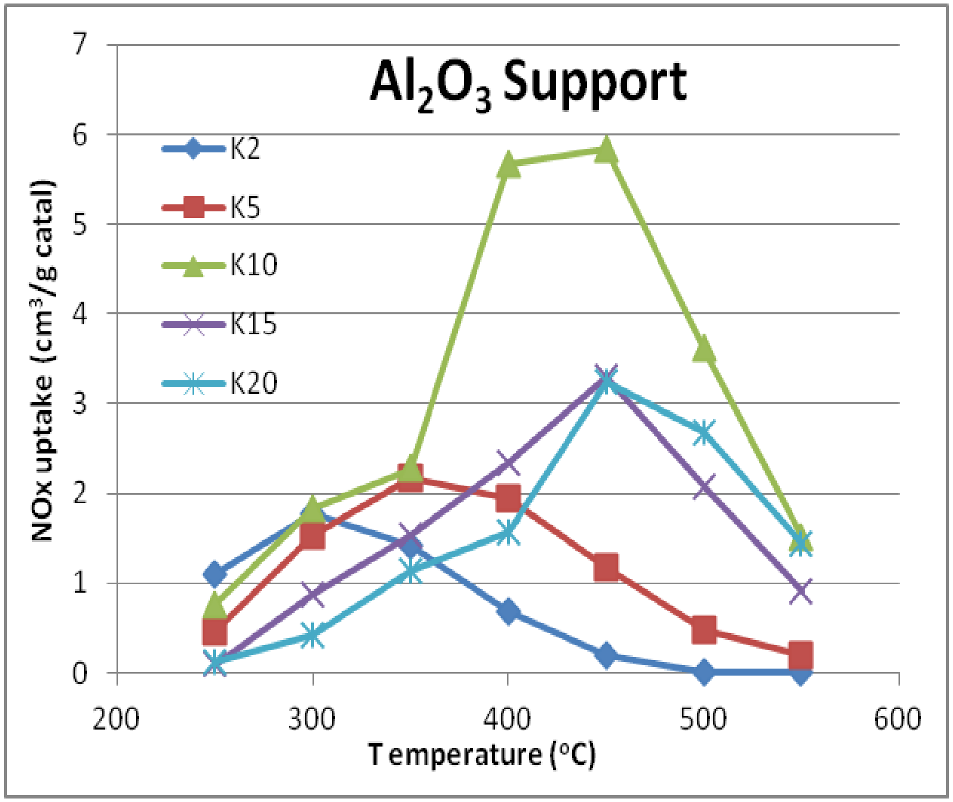
Aging conditions:

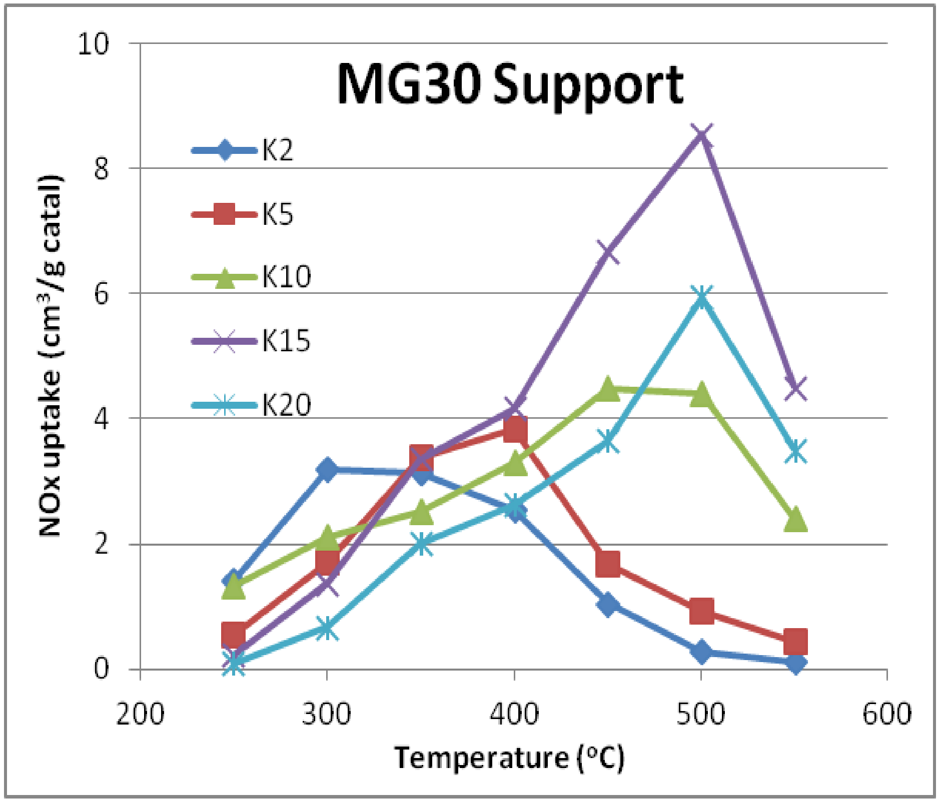
- Calcination in laboratory air ("lean aging") at 800 ^{0}C for 4 hours
- Reduction in 4% H_2/He at 800 ^{0}C for 1 hours

Reactant gas mixtures:

- Total gas flow: 400 sccm (~ 30k h^{-1} G.H.S.V)
- Lean: 10%O_2, 5%CO_2, 5%H_2O, 150 ppm NO, balance He
- Rich: 0%O_2, 5%CO_2, 5%H_2O, 5%H_2, balance He

Comparison of Al_2O_3- and $MgAl_2O_4$-Supported LNTs

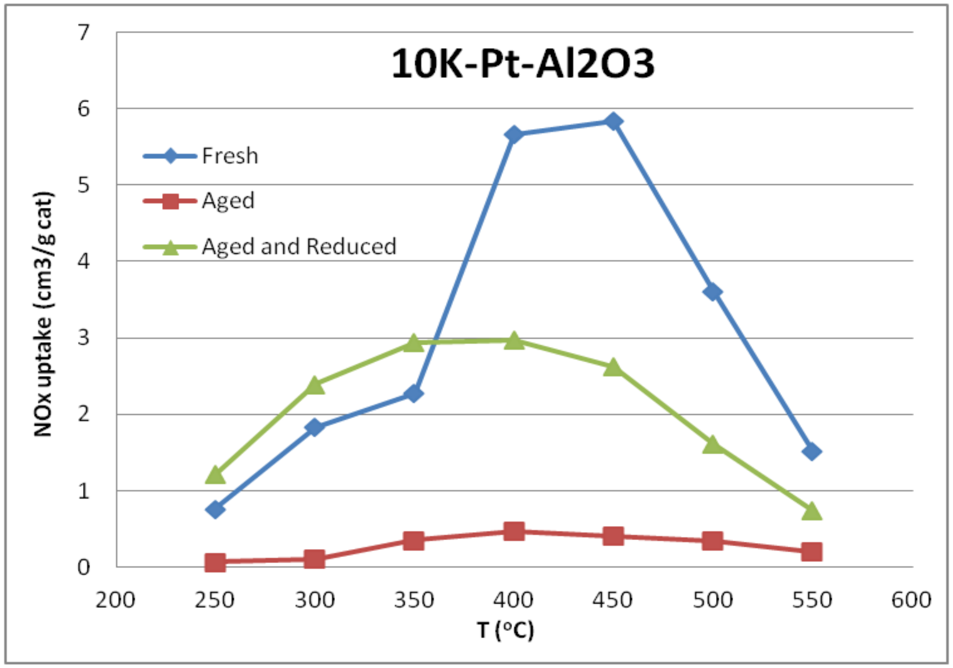


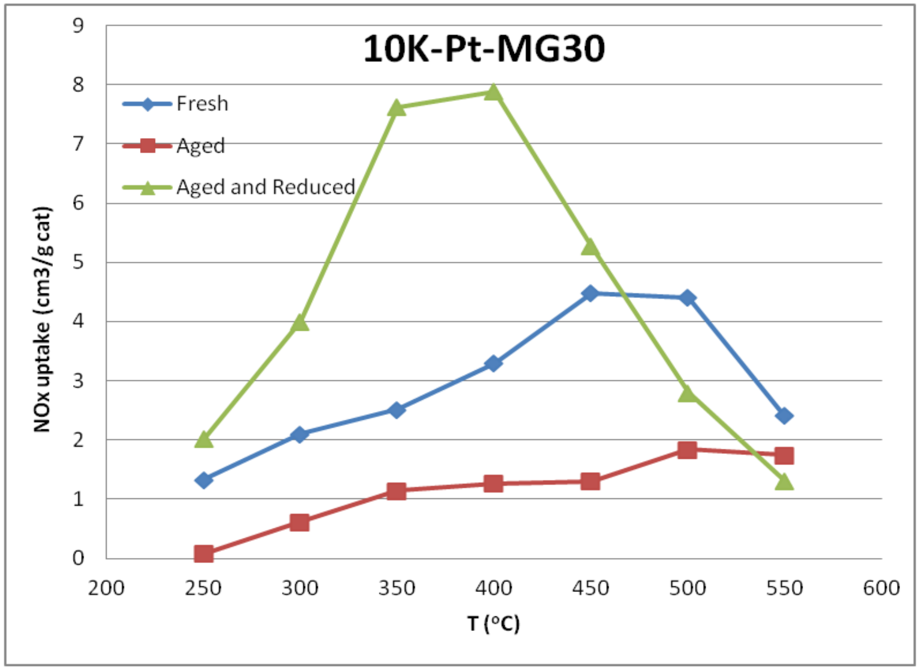


- ☐ Unlike Ba-based LNTs, the temperature for optimum performance of Al_2O_3-supported K LNT catalysts show a large and unexpected dependence on loading
- ☐ $MgAl_2O_4$ support materials provide for even higher temperature performance of K-based LNTs, and also show the unusual dependence on K loading.

J Luo, F Gao, DH Kim, and CHF Peden,
Applied Catalysis B (2013) submitted.

While deactivation is severe after aging, some restoration of performance is possible





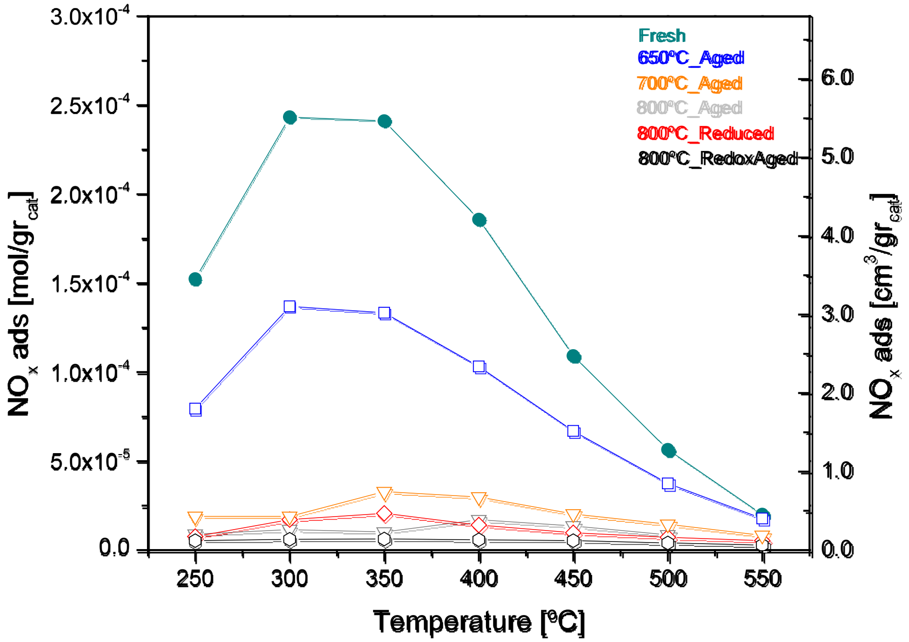
K Loading was 10% in all of these samples

- ☐ Facile K migration is clearly an issue for K-based LNTs, in part explaining the above results.
- ☐ Postulated that titania-based supports might reduce K migration and also provide reduced sensitivity to sulfur.
- ☐ Despite favorable literature reports, we find considerable K reaction with titania during typical lean-rich cycling and laboratory aging.

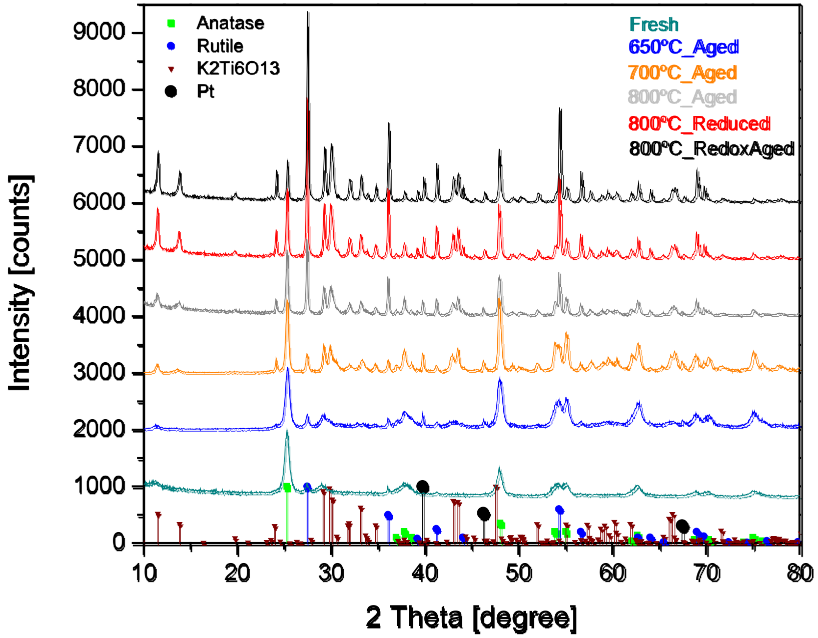
J Luo, F Gao, DH Kim, and CHF Peden, Applied Catalysis B (2013) submitted.

Unlike Al_2O_3- and $MgAl_2O_4$-Supported LNTs, TiO_2-supported K catalysts can't be regenerated

Pt-K(10%)/TiO_2



Pt-K(10%)/TiO_2



- ☐ Modest amount of Pt sintering observed during various aging treatments.
- ☐ Deactivation almost certainly related to formation of $K_2Ti_6O_{13}$ phase via solid-state reaction of K with the TiO_2 support material, resulting also in significant loss of surface area.
- ☐ Current studies are exploring the use of K-titanates ($K_2Ti_6O_{13}$) as supports for K, as well as addition of TiO_2 to Al_2O_3 and $MgAl_2O_4$ supports.

Work has been carried out by Laura Righini, visiting graduate student from Politechnico Milano

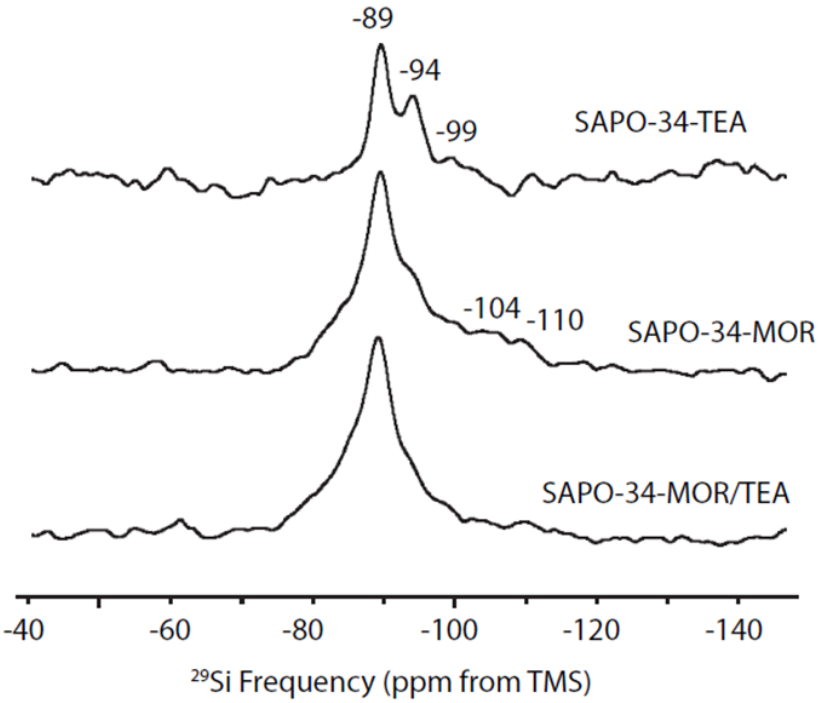
Technical Accomplishments – SCR Studies

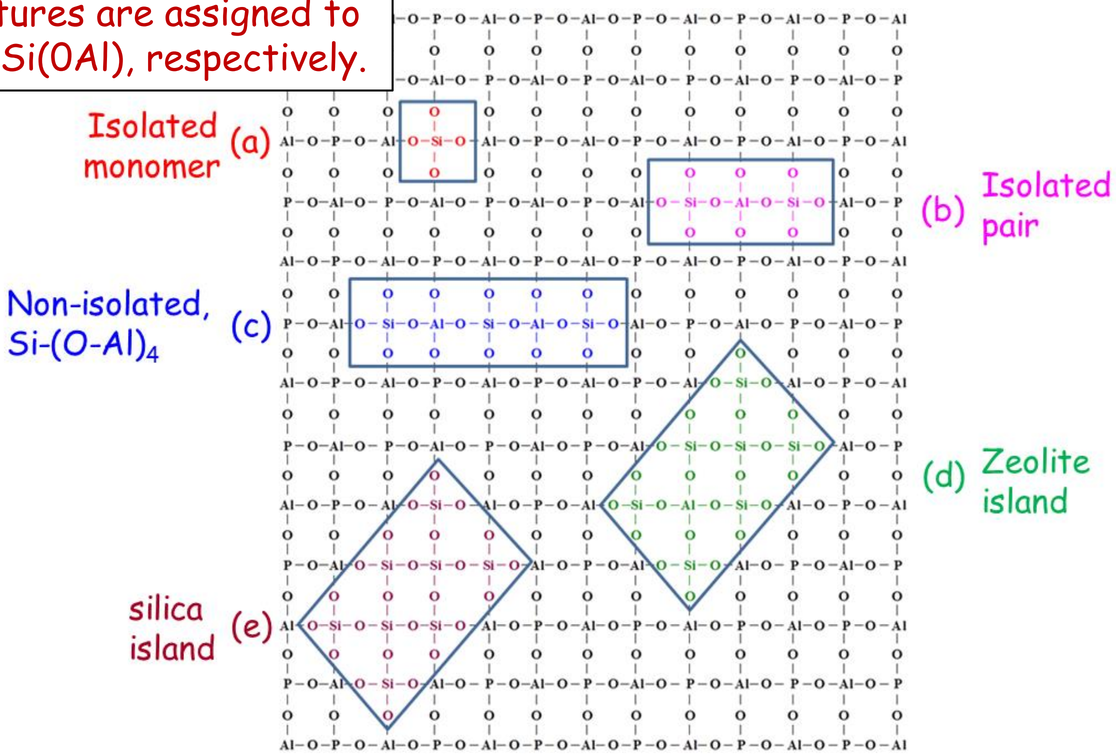
- Significant CLEERS-funded effort to synthesize Cu-SAPO-34 model catalysts
  - Solution ion-exchange of Cu into SAPO-34 CHA zeolites:
    - **SAPO-34 synthesis:** multiple structure-directing agents (SDAs) used for hydrothermal synthesis, followed by conversion to ammonium-ion form. The dependence of stability on silicon content also explored.
    - **Cu loading:** Exchange with $Cu(OAc)_2$ solutions at 50-80ºC for 1 hour followed by drying overnight and calcination at 800ºC for 16hrs.
  - ‘One-pot synthesis’ of Cu-loaded SAPO-34 CHA zeolites:
    - **Cu incorporated during SAPO-34 synthesis:** Modification of procedures proposed by Corma and coworkers, Applied Catalysis B **127** (2012) 273.
  - Solid-state ion exchance of Cu into SAPO-34 CHA zeolites:
    - **SAPO-34 synthesis:** multiple structure-directing agents (SDAs) used for hydrothermal synthesis of proton form of SAPO-34.
    - **Cu loading:** varying amounts of nanosized CuO; calcine at 800ºC for up to 16hrs.
- Origins of low and high temperature performance limits, and loss due to hydrothermal aging are current focus of this CRADA. Issues currently being addressed:
  - Cu loading effects
  - Nature of active Cu species by EPR spectroscopy and TPR
  - Mechanisms of performance changes due to laboratory and vehicle aging

Focus here will be on recent studies of Cu loading and thermal aging.

2D Model of SAPO-34

^{29}Si -89, -94, -99, -104 and -110 ppm features are assigned to Si(4Al), Si(3Al), Si(2Al), Si(1Al) and Si(0Al), respectively.



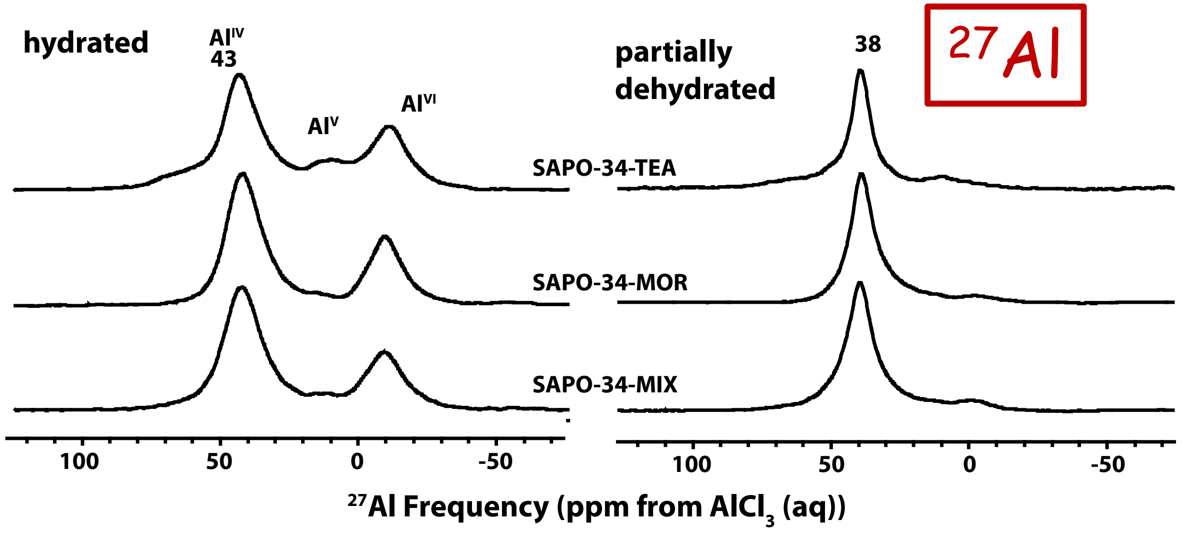


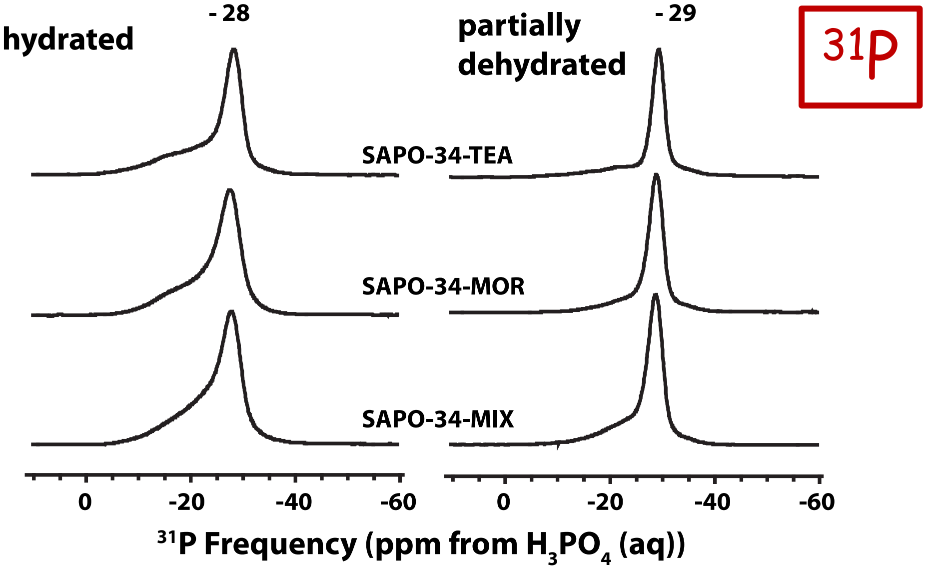
Bao and coworkers, Microporous and Mesoporous Materials 53 (2002) 97–108

- ^{29}Si NMR found to be particularly useful for characterizing SAPO-34 catalysts
- Incorporation of Si in SAPO-34 is highly dependent on the synthesis which can effect the number of ion exchange sites as well as hydrothermal stability

F Gao, ED Walter, NM Washton, RG Tonkyn, J Szanyi, and CHF Peden, J. Catal. (2013) submitted.

SAPO-34: ^{27}Al and ^{31}P NMR

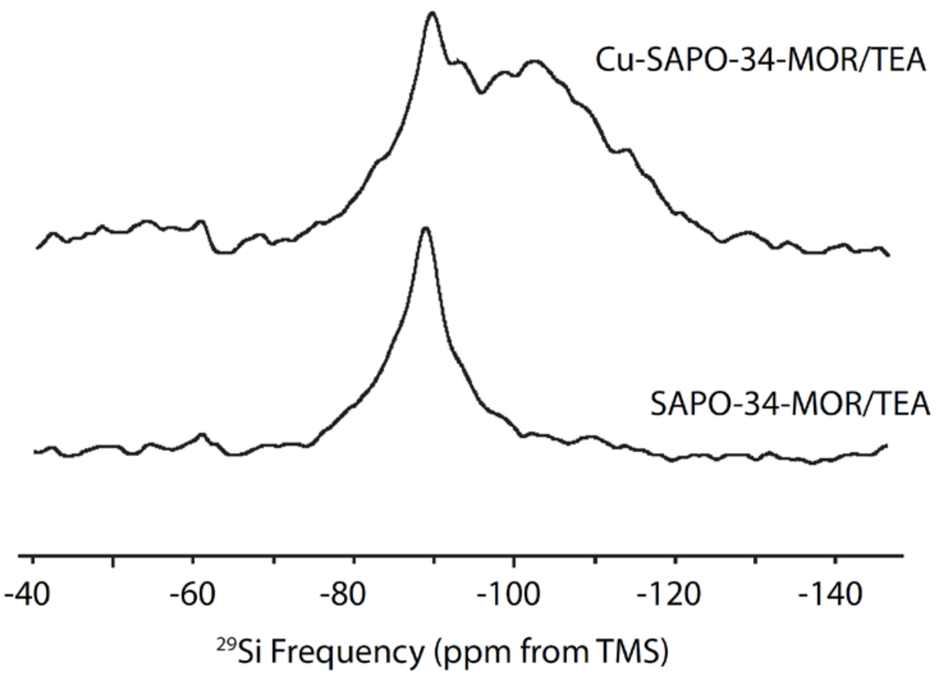


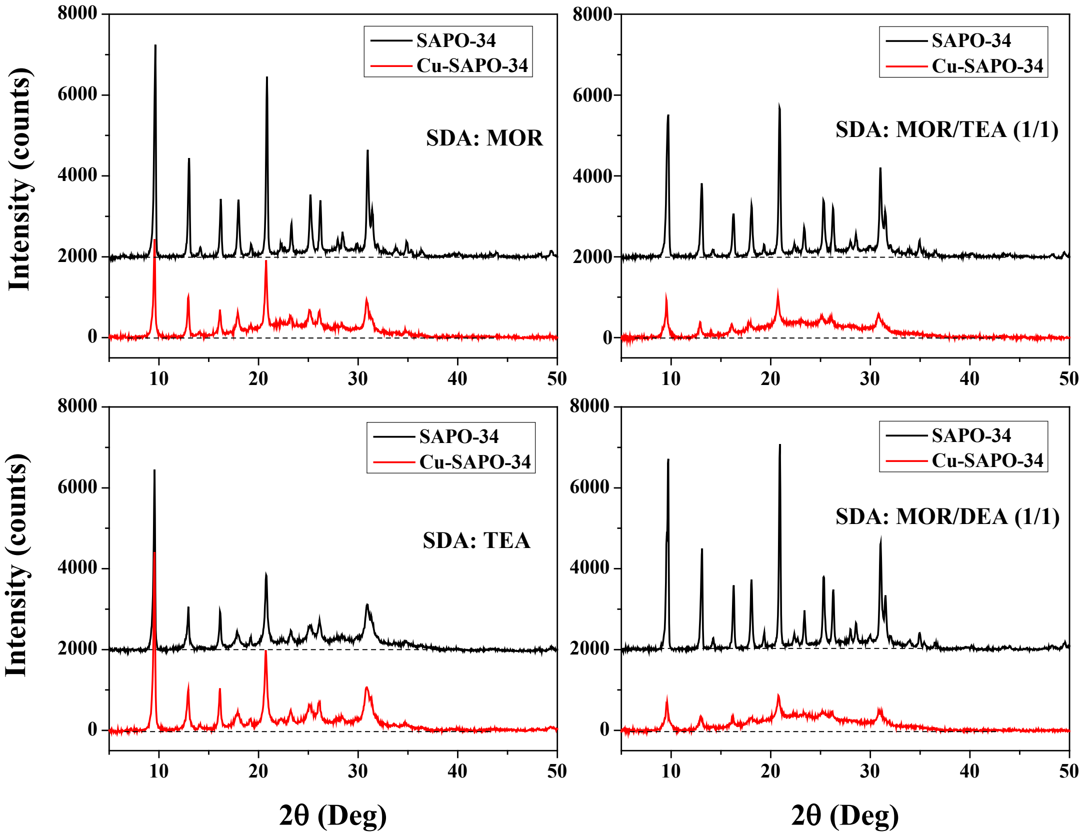


- ^{27}Al and ^{31}P NMR both show significant changes during mild dehydration of SAPO-34 catalysts
- These results indicate some sensitivity of Al-O-P bonds in SAPO-34 to water.
- The template used can have an impact on the potential changes observed to the stability to hydration / dehydration.

F Gao, ED Walter, NM Washton, RG Tonkyn, J Szanyi, and CHF Peden, J. Catal. (2013) submitted.

Considerable loss of zeolite crystallinity during Cu ion exchange

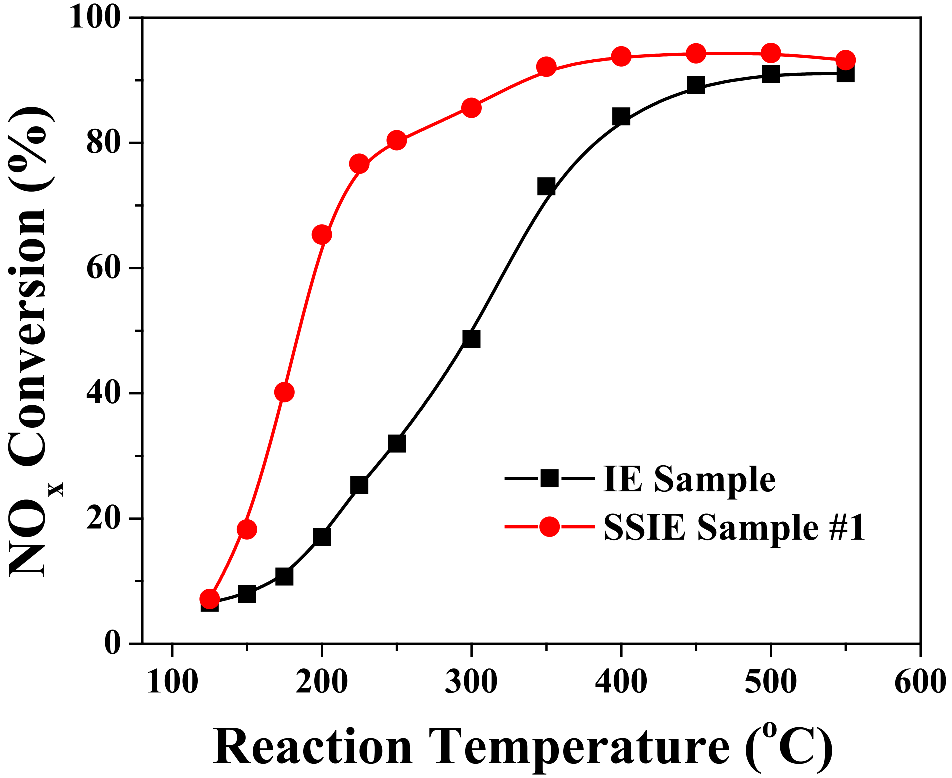


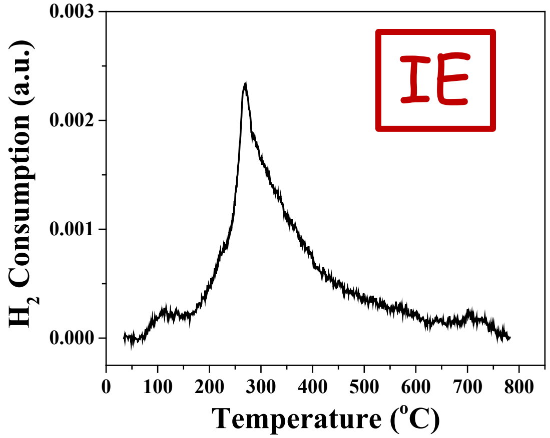


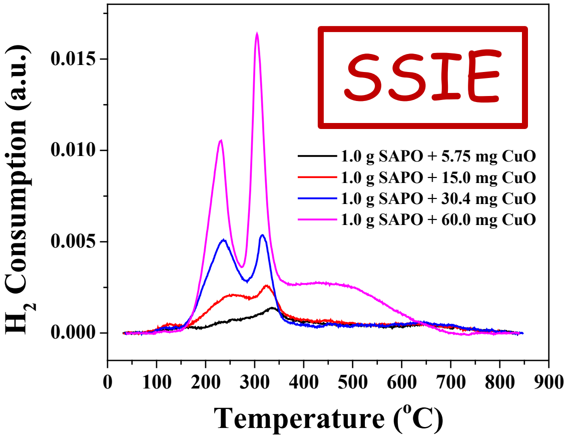
- We also find some loss of zeolite crystallinity during solution ion exchange of Cu, depending on the SAPO-34 synthesis.
- Nature of ion-exchanged Cu also dependent on SAPO-34 synthesis (TPR).
- ***Tentative conclusion*** – solution ion exchange may not be optimum method for incorporating Cu (*opinion of PNNL* after considerable number of experiments).

F Gao, ED Walter, NM Washton, RG Tonkyn, J Szanyi, and CHF Peden, J. Catal. (2013) submitted.

Solid-state ion exchange generates more active catalysts





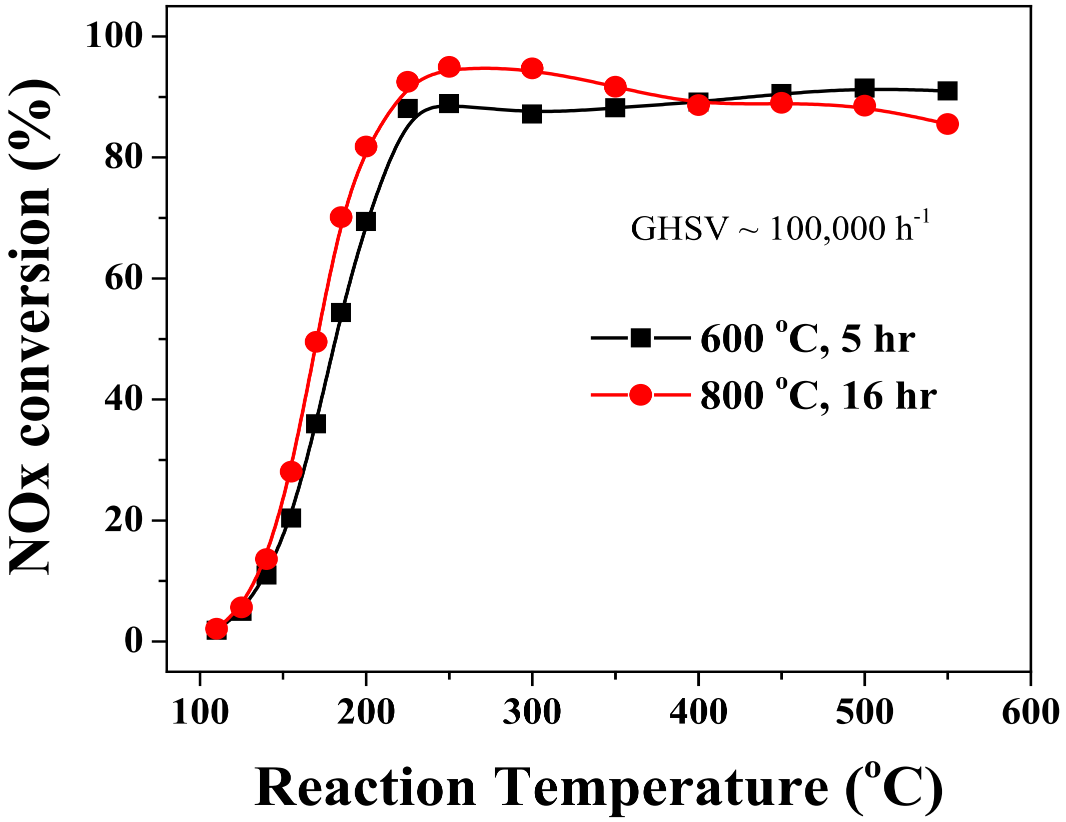


- TPR for solution ion exchange suggests presence of bulk-like CuO.
- Reduction of isolated Cu^{+2} ions predominate in TPR of SSIE samples

- Both TPR and reactivity measurements demonstrate enhanced formation of active Cu^{+2} monomers by solid-state ion exchange (SSIE) methods.
- SSIE also provides better control of Cu loading, enabling current studies of the effects of Cu concentration on catalyst performance and stability.

F Gao and CHF Peden, in preparation.

Some initial thermal aging results



- ‘Standard’ SCR:
  - NO (350 ppm), NH_3 (350 ppm), O_2 (14%), H_2O (2.5%), N_2 (balance)
- GHSV = 100,000 hr^{-1}
- Product analysis with FTIR
- N_2O is considered to be NOx and, thus, does not contribute to NOx conversions; however, at most, a minor product.

- As observed by others, low temperature performance of SAPO-34-based catalysts is actually improved following hydrothermal aging.
- However, the undesirable effects of bulk-like CuO, if present (as in solution IE samples) are exacerbated following hydrothermal aging.

F Gao, ED Walter, NM Washton, RG Tonkyn, J Szanyi, and CHF Peden, J. Catal. (2013) submitted.

Planned Future Work

1. **Model K-based catalysts:**
   - Studies of the stability of the K-storage phase:
     - Explore use of K-titanates as supports for K, and the addition of titania to Al_2O_3 and $MgAl_2O_4$ supports.
     - Microdiffraction and aberration-corrected TEM measurements.
     - At the suggestion of one of last year's reviewer, will explore mixed K-Ba NSR materials as possible route to stabilize K.
2. **SAPO-34-based SCR catalysts:**
   - Detailed characterization (EPR, TPR, x-ray absorption, etc.) of Cu species as a function of loading – in collaboration with Purdue, Notre Dame and Washington State University.
   - Limitations on low and high temperature performance, and effects of 'dopants' to SAPO-34.
   - Initiate mechanistic studies and effects of sulfur.

Summary

- A critical need for future NOx emission control technologies will be significantly **improved lower and higher temperature performance** and stability.
- PNNL and Cummins are carrying out collaborative research aimed at addressing these critical performance issues in LNT and SCR catalysts. This CRADA is also focused on catalyst deactivation due to sulfur poisoning and/or thermal degradation.
- Additional leverage will be provided by studies of SCR catalysts to be carried out at Purdue, Notre Dame and Washington State University as part of a newly NSF/DOE-funded project (Alex Yezerets, Cummins, and Chuck Peden, PNNL, are co-PIs).
- Technical highlights from this project included:
    - K migration and reaction with some catalyst supports continues to be a major challenge for LNT catalysts that perform at higher temperatures.
    - Characterization (particularly NMR) of SAPO-34-based SCR catalysts have identified a number of important aspects of this interesting material.
    - Use of solid-state ion exchange for addition of Cu into SAPO-34 enables reproducible catalysts with variable Cu loading and minimal undesirable CuO.
- Primary focus of future work for this next year will be on limitations of low- and high-temperature performance of SAPO-34-based SCR catalysts. A small and focused effort on LNT catalysts will continue.