Investigation of Aging Mechanisms in Lean NOx Traps

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Purpose of Work

- Understand main chemical and physical processes occurring during LNT aging
- Correlate washcoat composition with catalyst durability
  $\Rightarrow$ Effect of Pt, Rh, Ba, CeO_2, CeO_2-ZrO_2
- Establish effect of LNT catalyst aging on NOx performance and desulfation behavior
- Provide insights that will assist the design of more durable catalysts and/or allow for optimized catalyst operation as it ages

Barriers

- Aftertreatment needed to meet NOx emission goals
  - Engine conditions that have the highest overall efficiency typically give rise to NOx levels exceeding the 2010 regulations
- Limited durability of LNT catalysts impediment to widespread use
- Deeper understanding of “commercial” catalyst materials required:
  - role of individual components
  - effect on aging characteristics
- Providing insights that optimize catalyst operation over the lifetime of the vehicle
  - Improve catalyst efficiency and therefore minimize fuel penalty

Approach

- Employ well characterized model catalysts which are representative of 2nd generation LNT formulations
  ⇒ use of ceria; also of relevance for lean-burn gasoline LNTs

- Examine effect of washcoat components/loadings on catalyst durability:
  ⇒ systematic variation of component concentrations:
  Pt, Rh, Ba, CeO_2(-ZrO_2)

- Employ realistic aging protocol, with simultaneous measurement of catalyst NOx storage/reduction performance

- Perform detailed physico-chemical characterization of aged catalysts

  ➢ U. of Kentucky, ORNL, Ford and Umicore as partners

Performance Measures

- Prepare model LNTs with sequential variation of component loadings: Pt, Rh, Ba, CeO_2(-ZrO_2)
- Evaluate de-greened catalysts to determine key component effects:
  - NOx performance (conversion, selectivity)
  - intra-catalyst chemistry
  - desulfation behavior
- Age catalysts in realistic and reproducible manner for subsequent studies (bench reactor + physico-chemical analysis)

Accomplishments

- Prepared model monolith and powder catalysts with well defined compositions
- Demonstrated that ceria improves low temperature NOx conversion and improves selectivity to N_2
- Demonstrated that ceria significantly improves storage capacity and regeneration of LNTs, especially at low temperature
- Demonstrated that balanced ceria loading is required to maximize *in situ* H_2 generation via WGS reaction
- Demonstrated that ceria improves catalyst desulfation
- Implemented LNT aging cycle on UK bench reactor

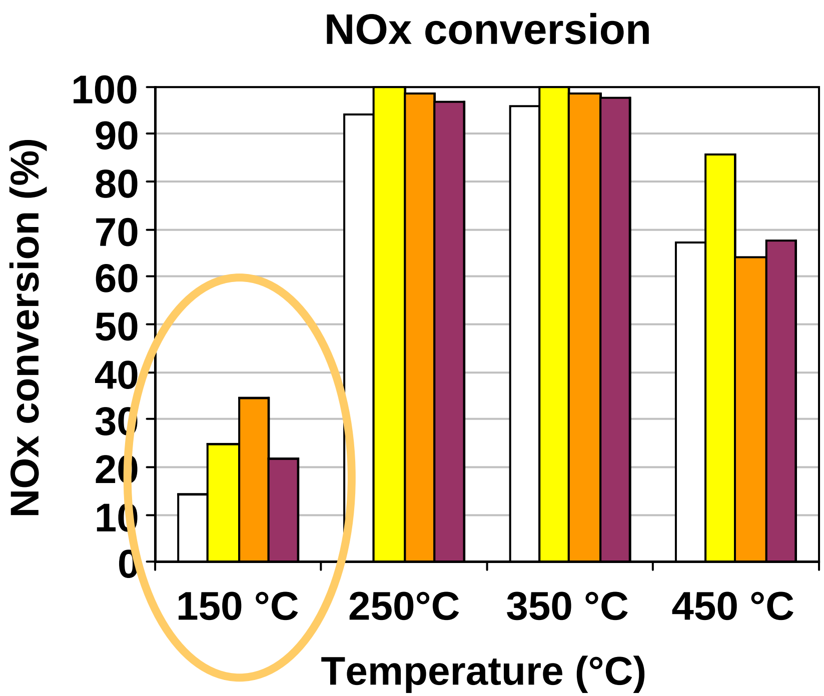
Model Monolith Catalyst Compositions Prepared

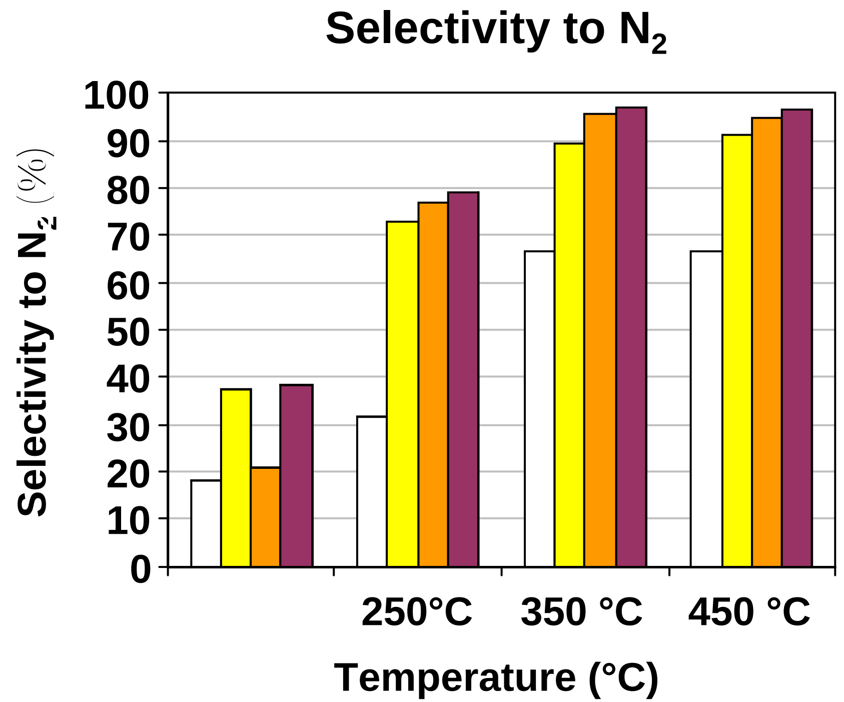
Component	Loading		
	Series 1	**Series 2**	**Series 3**
Pt, g/L (g/cuft)	3.53 (100)	3.53 (100)	3.53 (100), 2.65 (75), 1.77 (50)
Rh, g/L (g/cuft)	0.71 (20)	0.71 (20)	0.35 (10)
BaO, g/L	15, 30, 45	30	30
CeO_2, g/L	0, 50, 100	-	50
CeO_2-ZrO_2, g/L	-	50, 100	-
Al_2O_3, g/L	Balance	Balance	Balance

- Target washcoat loading = 260 g/L
- Actual average loading = 262 g/L, stand. dev. = 16.6 g/L (6.3%)
- Monoliths coated at DCL Int. Inc.

Ceria Addition Improves N_2 Selectivity and Low Temperature Performance

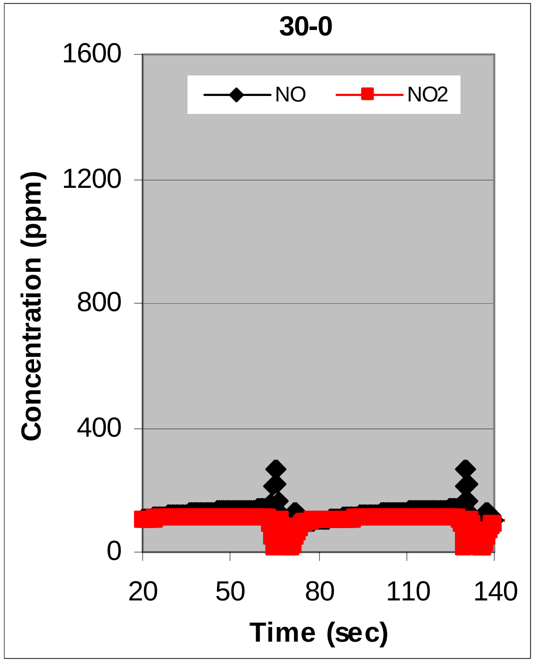
- Ceria improves NOx conversion for T< 350°C
  - most significant at 150°C
- Ceria-addition improves N_2 selectivity
  - increases w/ OSC

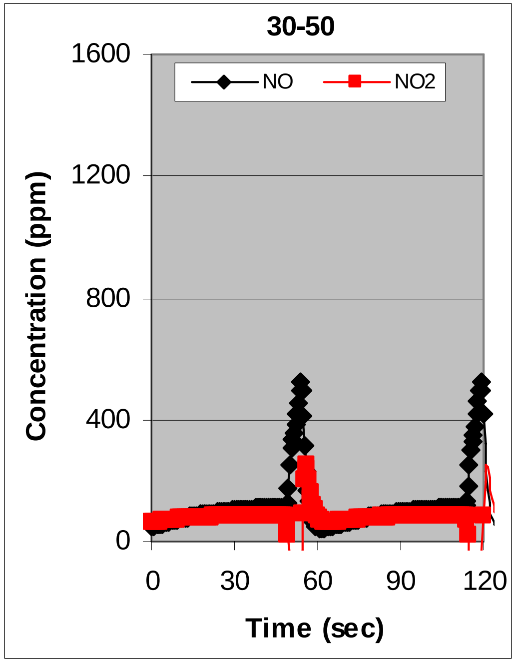


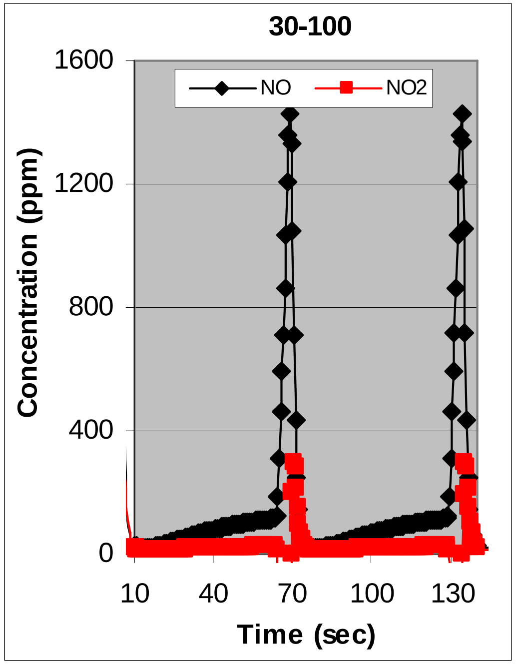


Ceria Improves Effective NOx Storage Capacity at 150 °C

- NOx storage capacity improves with increasing ceria loading
  - NO_2 in effluent shows NO to NO_2 oxidation not limiting for 30-0 and 30-50
- Rich phase NOx release also increases with ceria loading
  - More NOx released with ceria-based LNTs ⇒ reduction kinetics are too slow





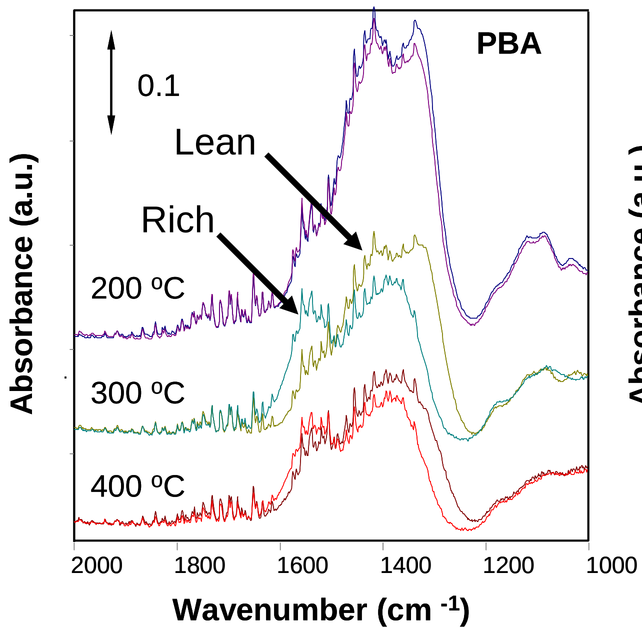


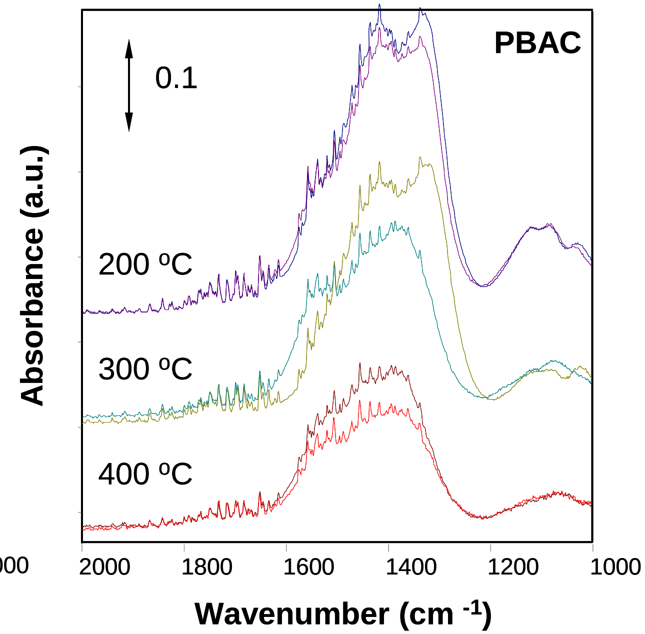
Key: 30-0 = 30 g BaO/$L_{cat.}$ + 0 g CeO_2/$L_{cat.}$, etc.

Studies with Model Powder Catalysts Provide Basis for Explaining Monolithic Catalyst Results

- In situ DRIFTS studies performed on two model powder catalysts:
  - **- PBA:** 1 wt% Pt/BaO/Al_2O_3 (equivalent to monolith catalyst 30-0)
  - **- PBAC:** PBA (74 wt%) + 1 wt% Pt/CeO_2 (26 wt%), physical mixture (equivalent to monolith catalyst 30-50)

In situ DRIFTS spectra during lean-rich cycling:



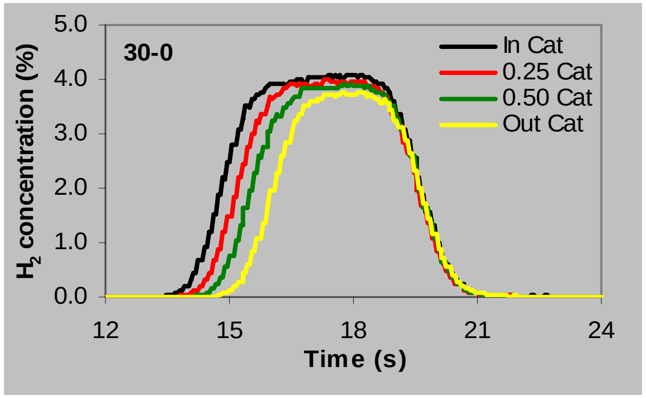


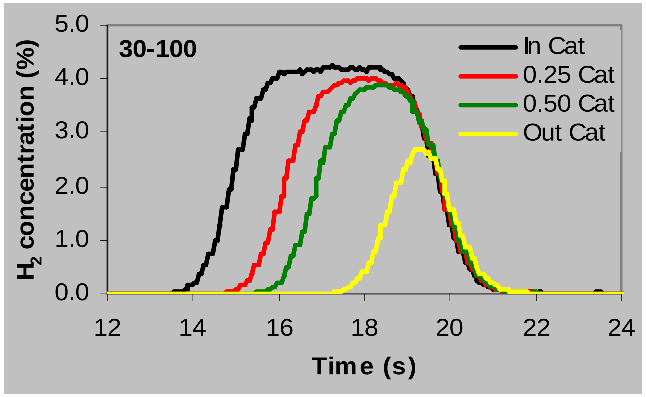
Conditions: lean phase (6 min): 300 ppm NO and 8% O_2; rich phase (0.5 min): 5625 ppm CO, 3375 ppm H_2, with 5% H_2O and 5% CO_2 added in both phases.

- In situ DRIFTS:
  - only a fraction of stored NOx is purged during L/R cycling
  - PBAC shows superior rich phase regeneration
- Microreactor results consistent
  - PBAC shows superior dynamic NOx storage capacity while cycling between lean and rich

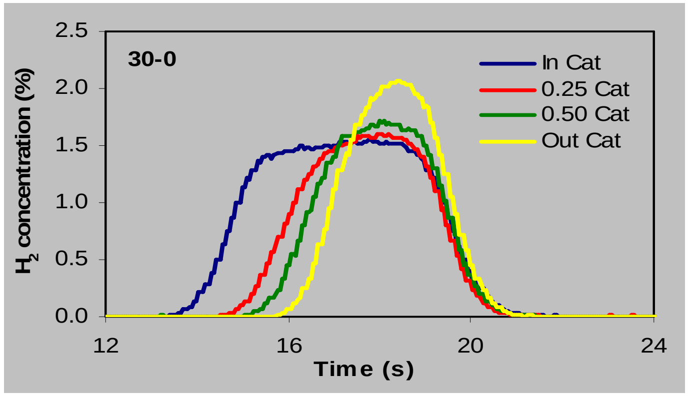
Intra-Catalyst Chemistry: H_2 Concentration Profile from SpaciMS (T = 350 °C)

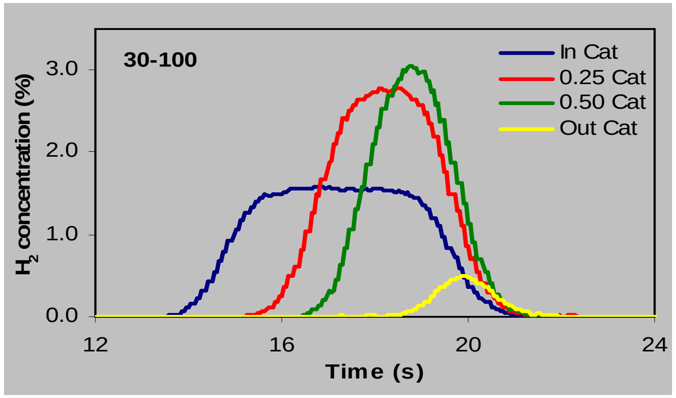
During OSC test





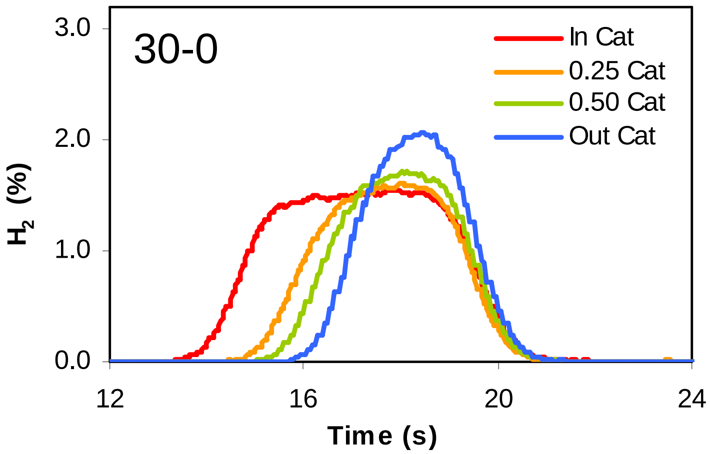
During testing w/ NOx (rich phase)

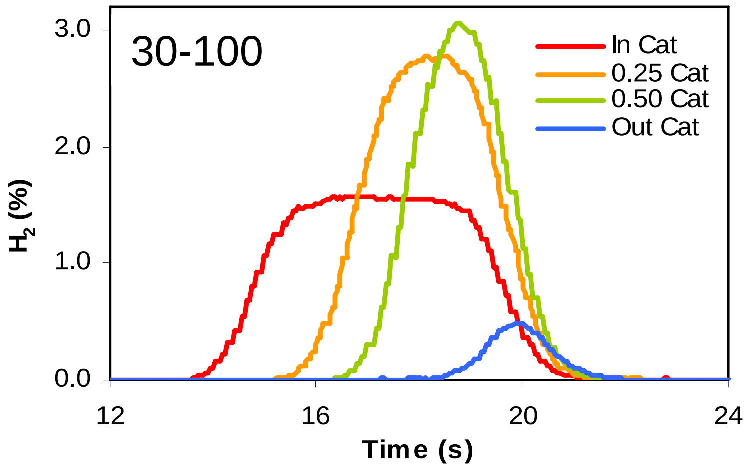


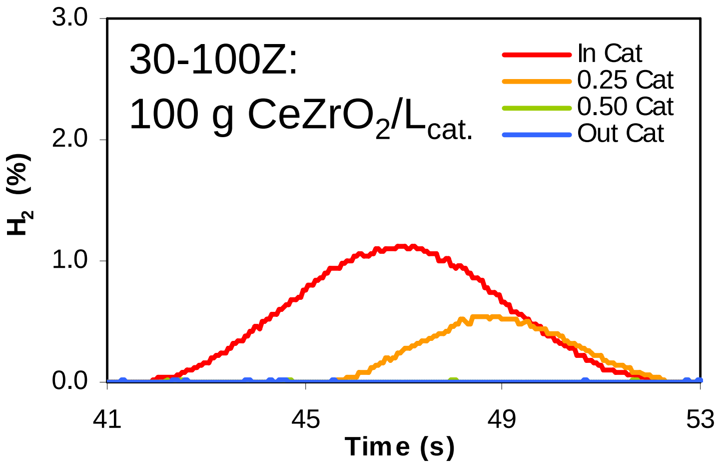


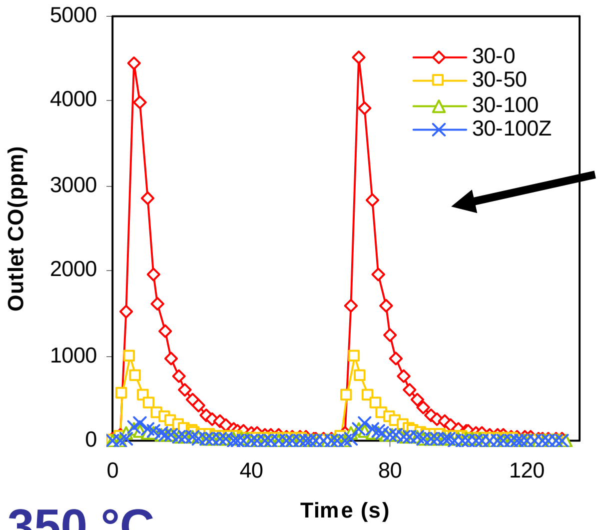
- High water-gas shift activity of 30-100 results in greatly increased H_2 production compared to 30-0. However, H_2 was largely consumed at the end of the bed for 30-100

Balanced Ceria/OSC Loading Required for Optimum Water-Gas Shift Activity





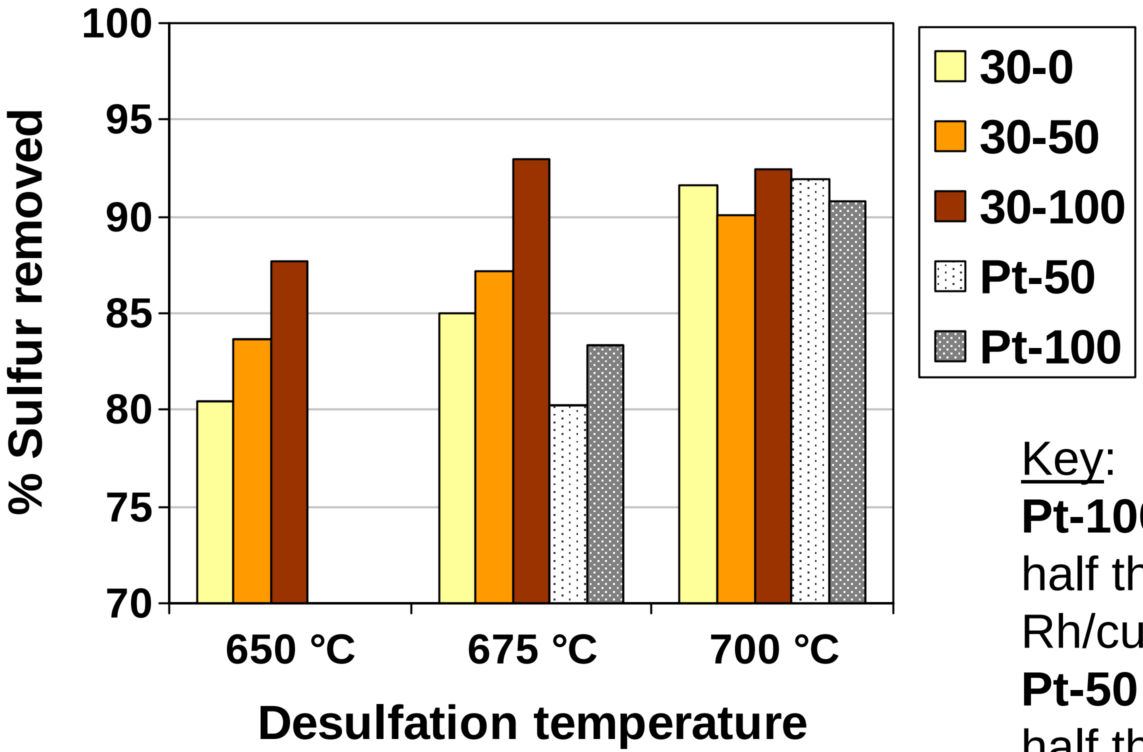




Outlet CO concn. during rich purge: low CO ⇒ consumption by WGS reaction and by stored oxygen

T = 350 °C

Desulfation Studies: Effect of Catalyst Composition on Efficiency of Sulfur Removal



Conditions:
Sulfation: 350 °C, 100 ppm SO_2, 10% O_2, 5% CO_2, 5% H_2O, bal. N_2; *ca.* 2 g S/L cat.;
Desulfation: 1% H_2, 10 min, bal. N_2

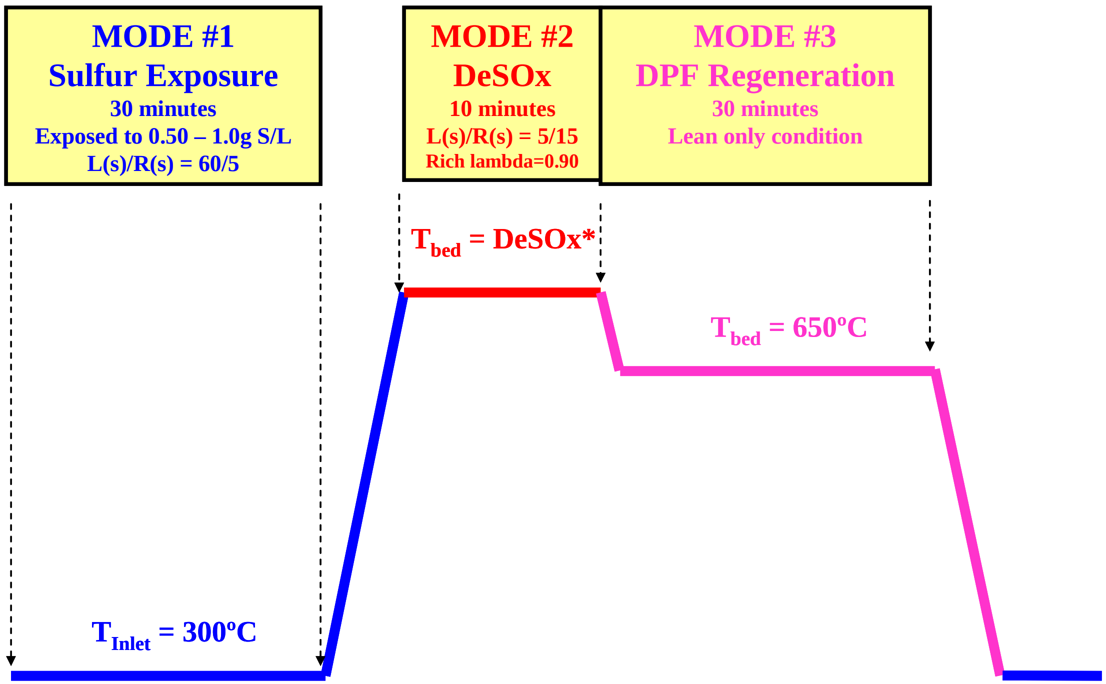
Key:
Pt-100 = same as 30-50 but with half the Rh loading (10 *vs.* 20 g Rh/cuft)
Pt-50 = same as Pt-100 but with half the Pt loading (50 *vs.* 100 g Pt/cuft)

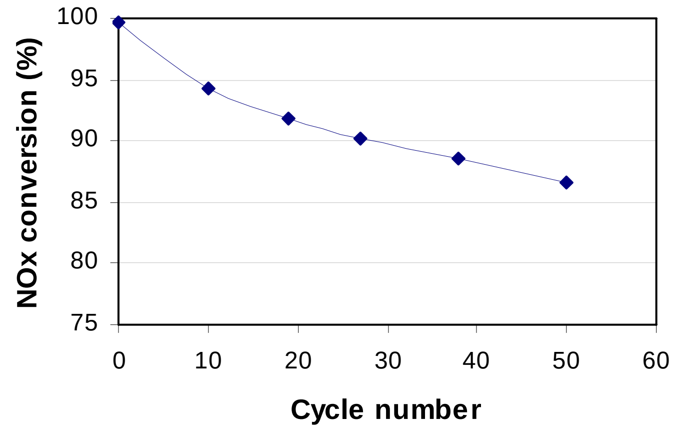
- Beneficial effect of ceria confirmed
- Reduction of precious metal content has adverse effect

Catalyst Aging

- Goal is to subject model monolith catalysts to realistic accelerated aging for subsequent reactor studies and physico-chemical characterization
- Catalyst aging on automated bench reactor
- Initial aging to 50 cycles: *ca*. 50-75 k miles road equivalent based on fuel sulfur content
- Catalyst performance check every ~10 cycles

LNT Aging Protocol





Aging profile for catalyst 30-100 (T = 300 °C)

- Based on Ford protocol
- Optimized desulfation temperature balances desulfation with thermal deactivation (→ 700 °C)

Technology Transfer

- Technology transfer via Ford Motor Co. (project partner)

- Model monolith catalysts prepared in this project currently being utilized in Ford R&D (Bob McCabe):

  - fundamental studies pertaining to catalyst sulfation and desulfation

  - effect of catalyst composition on selectivity to different N-species

- Joint U. of Kentucky/Ford project planned as follow up to current DOE-sponsored project (Ford University Research Program)

- Results of the project presented at conferences and in the literature:

  - 3 publications, 7 presentations to date

Publications, etc.

<u>Publications</u>:

- Y. Ji, J.-S. Choi, T. J. Toops, M. Crocker, M. Naseri, Influence of Ceria on the NO*x* Storage/Reduction Behavior of Lean NO*x* Trap Catalysts, *Catal. Today*, in press.
- Y. Ji, T.J. Toops, M. Crocker, "Effect of Ceria on the Storage and Regeneration Behavior of a Model Lean NO*x* Trap Catalyst", *Catal. Lett*. **119** (2007) 257.
- Y. Ji, T.J. Toops, U.M. Graham, G. Jacobs and M. Crocker, "A kinetic and DRIFTS study of supported Pt catalysts for NO oxidation", *Catal. Lett*. **110** (2006) 29.

<u>Presentations</u>:

- Y. Ji, T.J. Toops and M. Crocker, "Effect of Ceria Addition on the Regeneration of a Model LNT Catalyst", Tri-State Catalysis Society Fall Symposium, Lexington, KY, November 19, 2007.
- Y. Ji, T.J. Toops, J.-S. Choi, M. Crocker, "Composition-Activity Relationships in Lean NO*x* Trap Catalysts", Europacat VIII, Turku, Finland, August 26-30, 2007, paper P14-9.
- Y. Ji, T.J. Toops, J.-S. Choi, M. Crocker, "Investigation of Aging Mechanisms in Lean NO*x* Trap Catalysts", 1st Annual DOE Semi-Mega Merit Review Meeting, Crystal City, VA, June 18-19, 2007.
- Y. Ji, T.J. Toops, J.-S. Choi, M. Crocker, "Effect of CeO_2 on the Storage and Regeneration Behavior of Lean NOx Traps", 20th North American Catalysis Society Meeting, Houston, TX, June 17-22, 2007, paper O-S4-41.
- Y. Ji, T.J. Toops, J.-S. Choi, M. Crocker, "The Effect of CeO_2 on the Performance of Lean NOx Trap Catalysts", 10th Cross-Cut Lean Exhaust Emissions Reduction Simulation (CLEERS) Workshop, Dearborn, MI, May 1-3, 2007.
- Y. Ji, T.J. Toops and M. Crocker, "Effect of Ceria Addition on the Regeneration of a Model LNT Catalyst", Southeastern Catalysis Society Fall Symposium, Asheville, NC, September 18, 2006.
- Y. Ji, T.J. Toops, U.M. Graham, G. Jacobs and M. Crocker, "A kinetic and DRIFTS study of supported Pt catalysts for NO oxidation", 9th Cross-Cut Lean Exhaust Emissions Reduction Simulation (CLEERS) Workshop, Dearborn, MI, May 3-4, 2006.

Plans for Next Fiscal Year

- Complete accelerated aging of monolith catalysts according to Ford protocol

- Characterize NOx storage and reduction properties of aged model monolith catalysts:

  → ORNL bench reactor, with use of spaci-MS

- Performed detailed physico-chemical characterization of aged catalysts:

  → SEM, TEM, N_2 physisorption, H_2 chemisorption, XRD

- Derivation of LNT deactivation model:

  → spatial resolution possible?

Summary

- Model LNT catalysts have been prepared & characterized with systematic variation of Pt, Rh, Ba and CeO_2(-ZrO_2) loadings
- Correlations have been identified between catalyst performance and CeO_2, Ba and Pt loading
- SpaciMS studies have revealed a strong dependency of intra-catalyst H_2 concentration profiles on the ceria/oxygen storage content in model LNT catalysts

  $\Rightarrow$ need for balanced OSC
- The model catalysts are currently being aged (accelerated LNT aging cycle)
- In the next phase, the aged catalysts will be characterized (NOx storage and reduction, physico-chemical analysis)