# Investigation of Aging Mechanisms in Lean NOx Traps

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# Overview

### Timeline

- Start – Oct. 2005
- Finish – Sept. 2009
- *Ca*. 90% complete

### Budget

- Total project funding:
  - DOE: $882k
  - Cost-share: $217k
- Sub-contracts:
  - ORNL: $210k

### Barriers

- A. Cost
- C. Emission control (NOx)
- E. Durability (120,00 miles)

### Partners

- ORNL – studies using SpaciMS, *in situ* DRIFTS
- Ford – sulfation/desulfation studies using CI-MS
- Umicore Autocat – prepn. of selected catalysts

# Objectives (Phase 2/3)

- Sulfation-desulfation studies on degreened model catalysts in order to examine role of ceria
- Aging of model monolithic LNT catalysts according to realistic protocol
- Characterization of NOx storage-reduction properties of aged catalysts on bench reactor, with use of SpaciMS:
  → assessment of which catalyst functions are (most) affected
- Physico-chemical characterization of aged catalysts
- Correlation of physico-chemical properties with NOx storage-reduction characteristics

# Milestones

Phase 1:

Model monolith and powder catalysts were prepared (with systematic variation of the main washcoat components), characterized and their NOx storage-reduction characteristics evaluated

Phases 2 & 3:

*In situ* DRIFTS studies

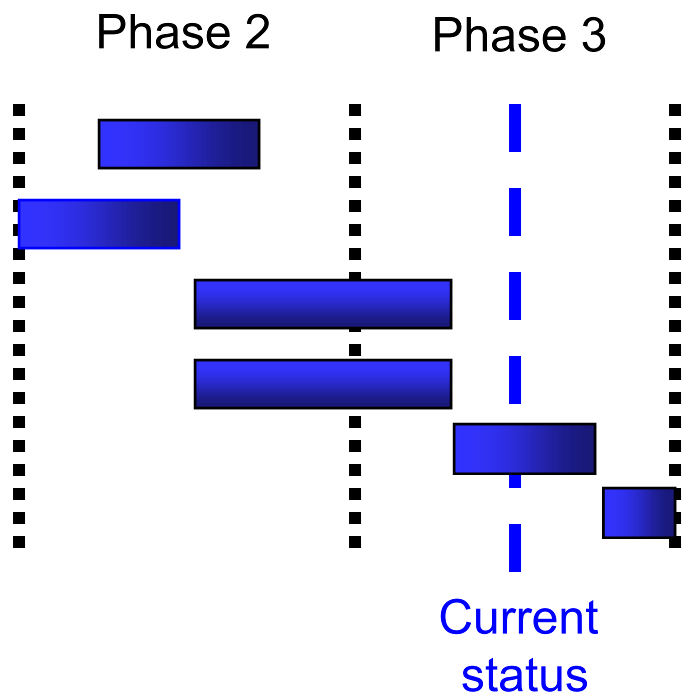
Catalyst aging

Aged catalyst evaluation

Aged catalyst characterization

Modeling of LNT deactivation

Reporting



# 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 ($N_2$ physisorption, CO/$H_2$ chemisorption, ELAN, XRD, SEM/EDS, TEM/EDS)

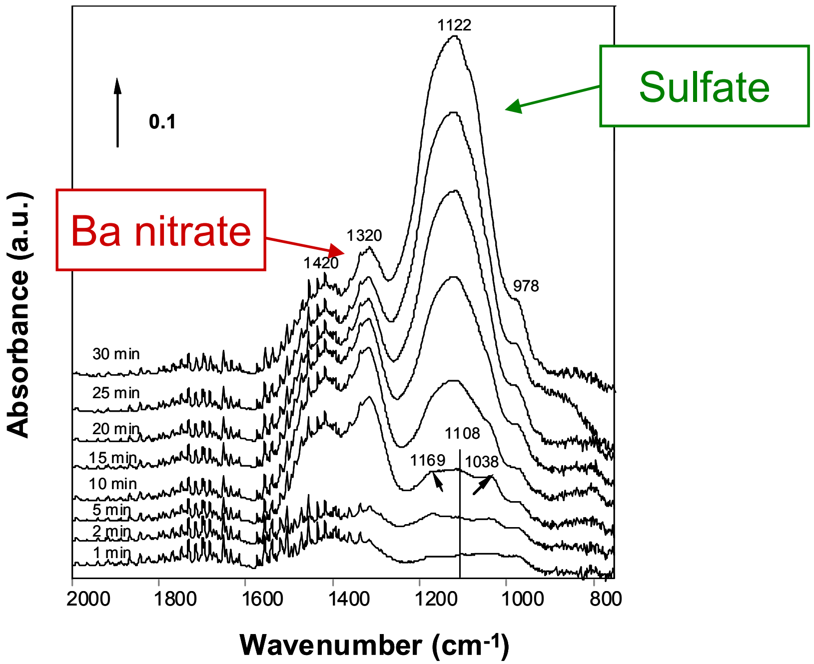
# Technical Accomplishments

- Studies on powder model catalysts provided further insights into effect of ceria and Pt/Ba interaction on LNT sulfation-desulfation behavior
- Model monolith catalysts aged according to Ford protocol for simulated road aging
- Characterized performance of aged catalysts w.r.t. OSC, NOx storage efficiency, NOx conversion and NOx reduction selectivity
- Characterized aged catalysts using $N_2$ physisorption, $H_2$ chemisorption, ELAN, XRD
- Identified correlations between LNT composition and properties of aged catalysts, e.g.:
  - washcoat surface area/OSC
  - NOx conversion/Pt dispersion

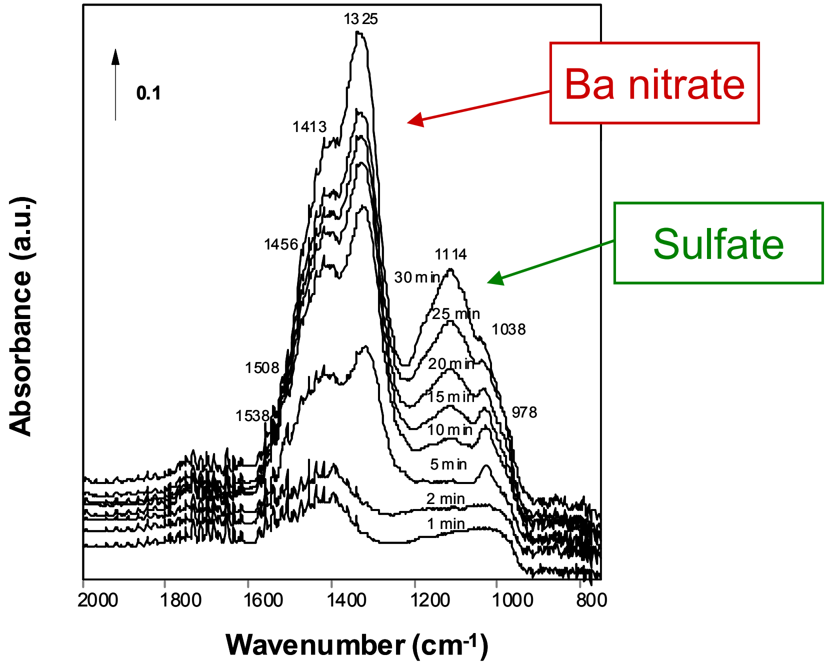
# LNT Sulfation-Desulfation: Role of Ceria

Feed: 300 ppm NO, 27 ppm $SO_2$, 5% $H_2O$, 10% $O_2$, bal. Ar, T = 300 °C

## $Pt/BaO/Al_2O_3$




## $Pt/BaO/Al_2O_3$ + $Pt/CeO_2$



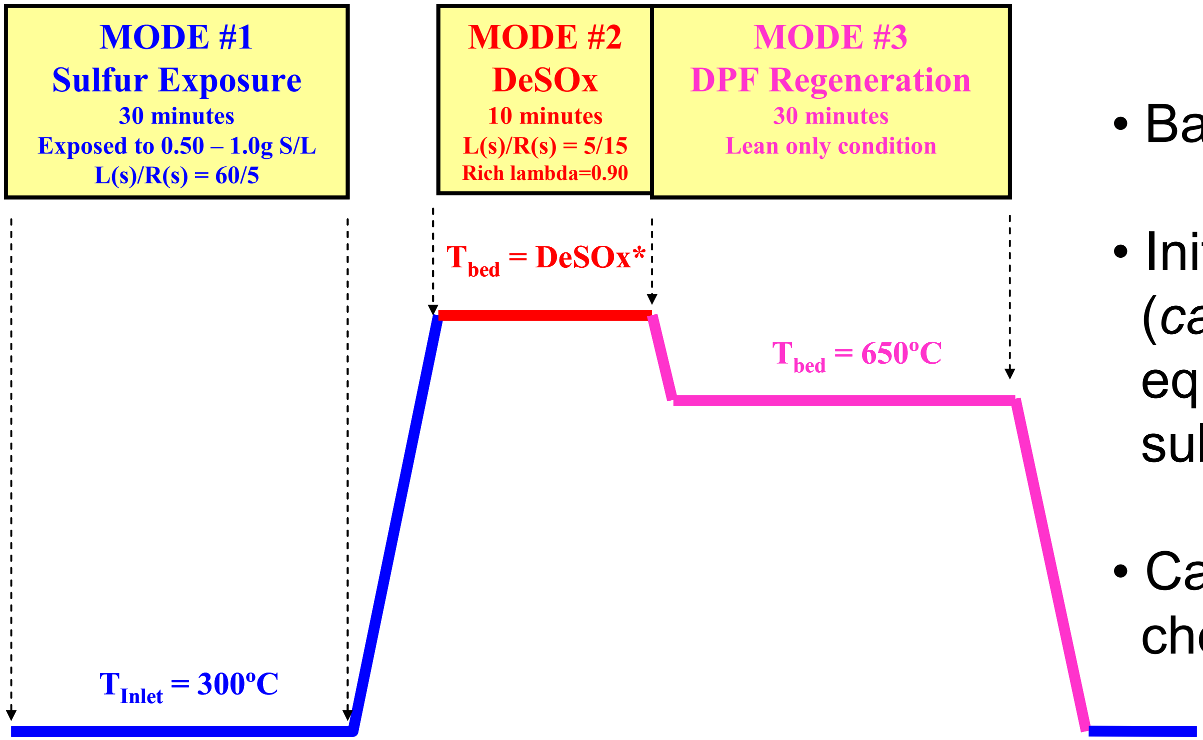

- For ceria-containing LNT, DRIFTS shows that extensive NOx storage occurs on BaO in presence of $SO_2$ (unlike ceria-free LNT)
- Temp. programmed desulfation confirms that relatively less sulfur is stored on Ba phase in ceria LNT than in ceria-free analog, and that sulfur is released at a lower temperature from Ce than from Ba

# 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.

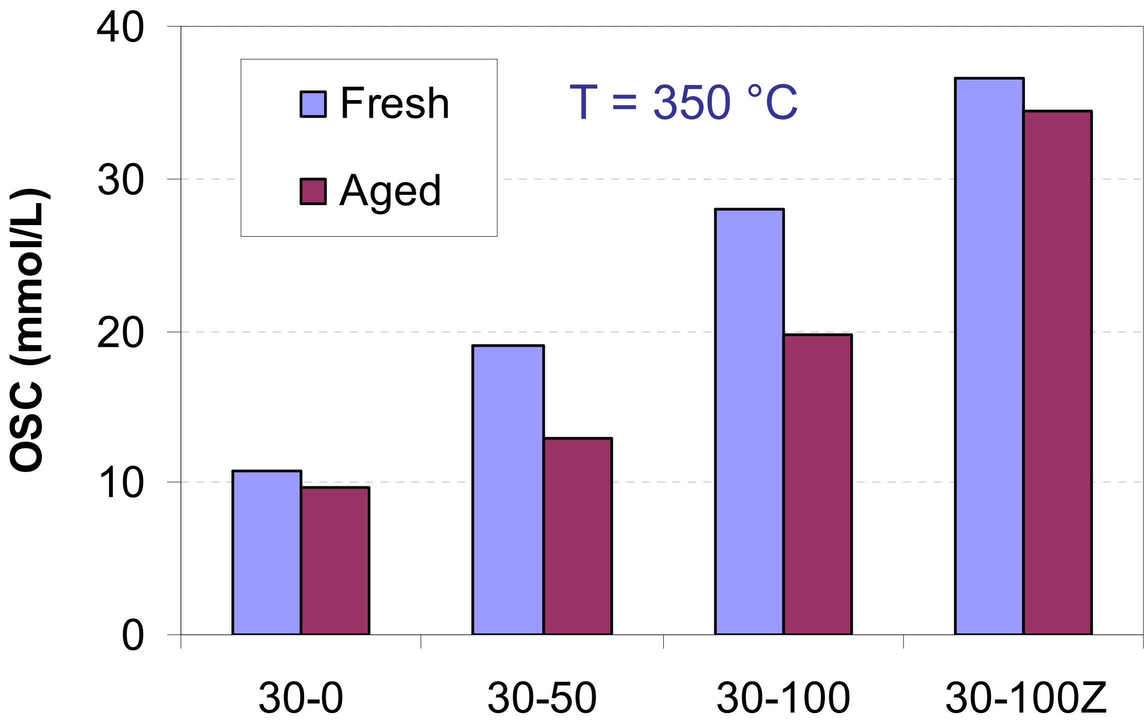
# LNT Aging




- Based on Ford protocol
- Initial aging to 50 cycles (*ca*. 50-75 k miles road equivalent based on fuel sulfur content)
- Catalyst performance check every 10 cycles

- Optimized desulfation temperature balances desulfation with thermal deactivation (→ 700 °C)
- At end of run, final desulfation performed with 2% $H_2$ (5% $H_2O$, 5% $CO_2$) at 750 °C for 10 min to remove as much residual sulfur as possible

# Comparison of OSC for Fresh and Aged Catalysts




<u>Key to catalyst codes</u>:

**30-0**: 0 g $CeO_2$/L

**30-50**: 50 g $CeO_2$/L

**30-100**: 100 g $CeO_2$/L

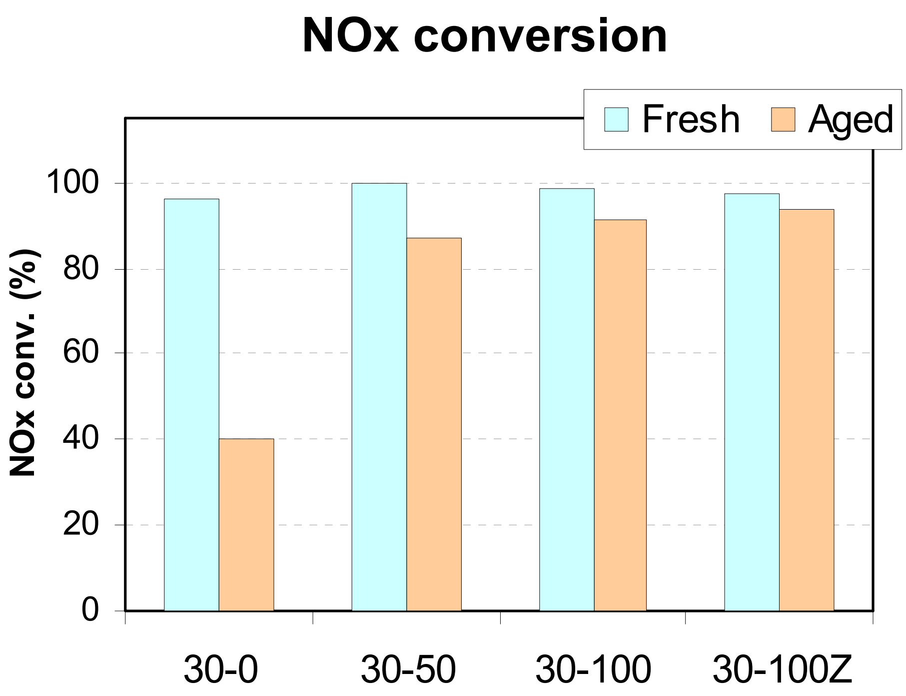
**30-100Z**: 100 g $CeO_2$-$ZrO_2$/L

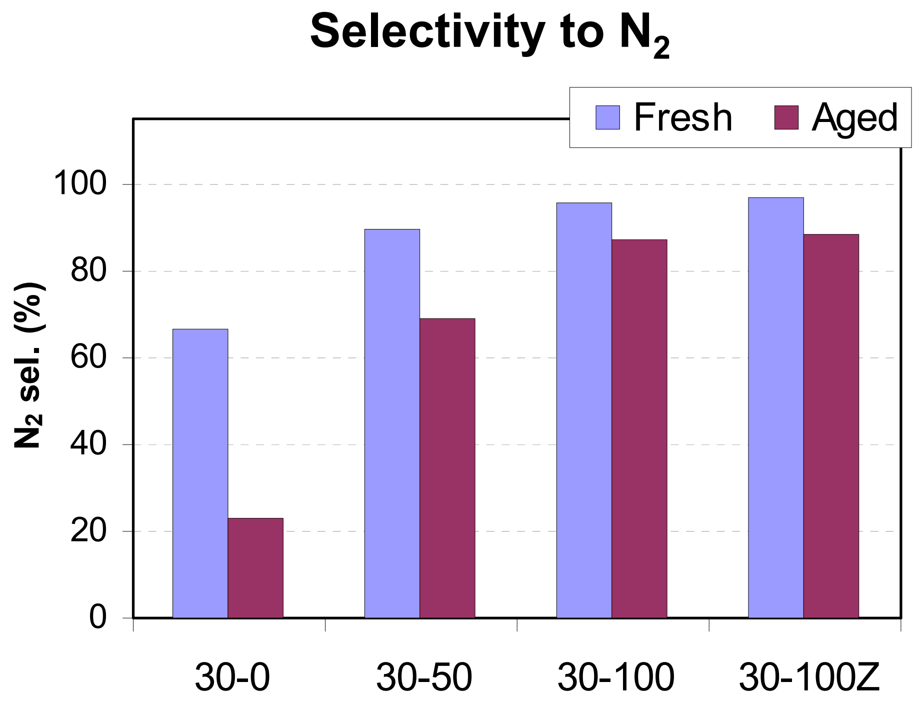
- All catalysts contain 30 g BaO/L

- Sintering of La-stabilized $CeO_2$ reflected in lower OSC values after aging
- OSC of $CeO_2$-$ZrO_2$ containing catalyst (30-100Z) hardly affected

# Effect of Aging on Cycled Averaged NOx Conversion and Selectivity

T = 350 °C, 60/5 s lean/rich cycles, CLEERS protocol gas composition

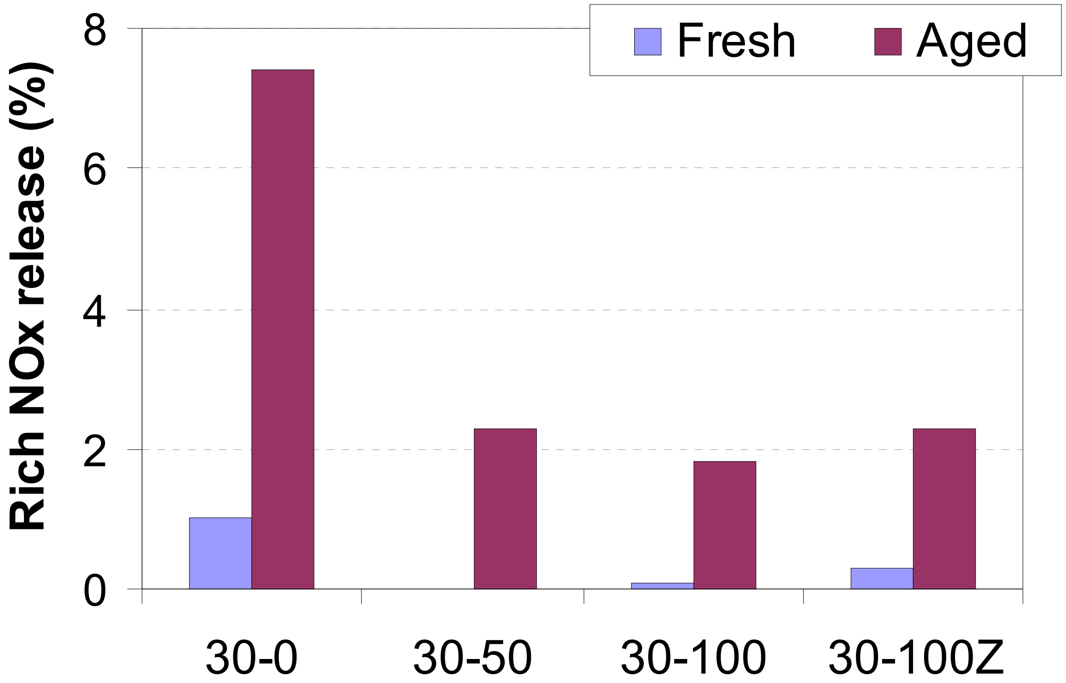



- Remarkable enhancement in performance of aged catalysts evident when $CeO_2$ or $CeO_2$-$ZrO_2$ is incorporated
- Aged catalysts show increased $NH_3$ make; may be due in part to lower OSC

# Effect of Aging on Rich Phase NOx Release

T = 350 °C, 60/5 s lean/rich cycles, CLEERS gas composition




% Rich phase NOx release =

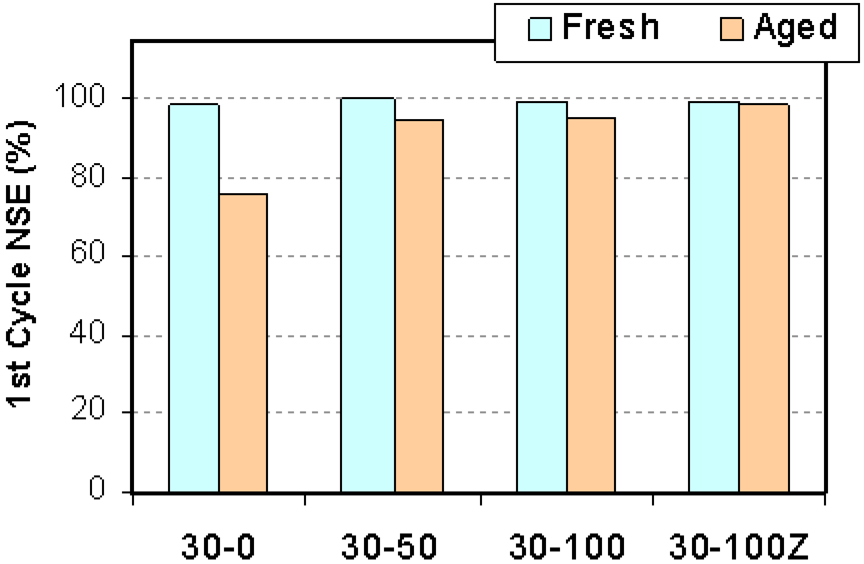
$$\frac{\text{rich phase NOx slip}}{\text{NOx stored in lean phase}} \times 100$$

- Decreased NOx reduction efficiency evident after aging, especially for 30-0

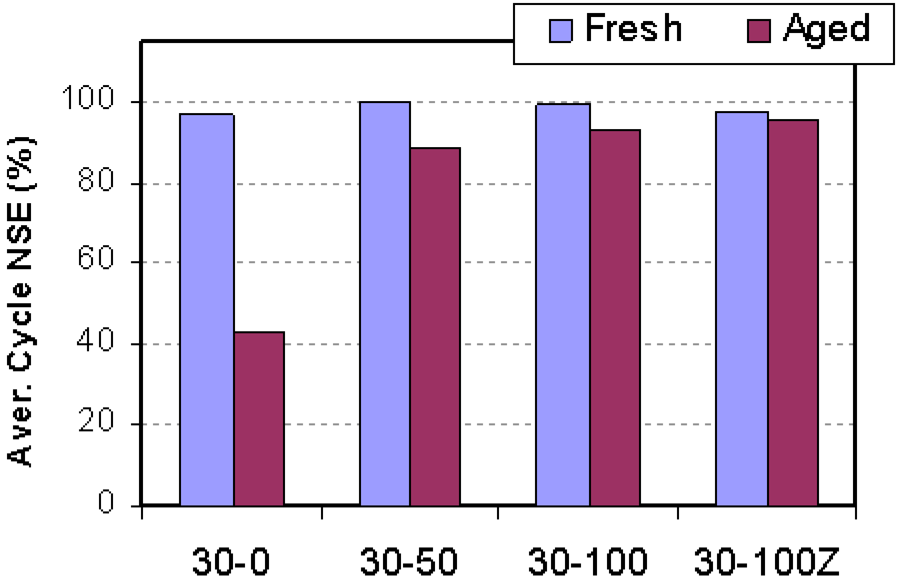
# Comparison of Cycle Averaged and First Cycle NOx Storage Efficiencies Before and After Aging

T = 350 °C, 60/5 s lean/rich cycles, CLEERS gas composition

**1st cycle NOx storage efficiencies ("clean catalyst")**



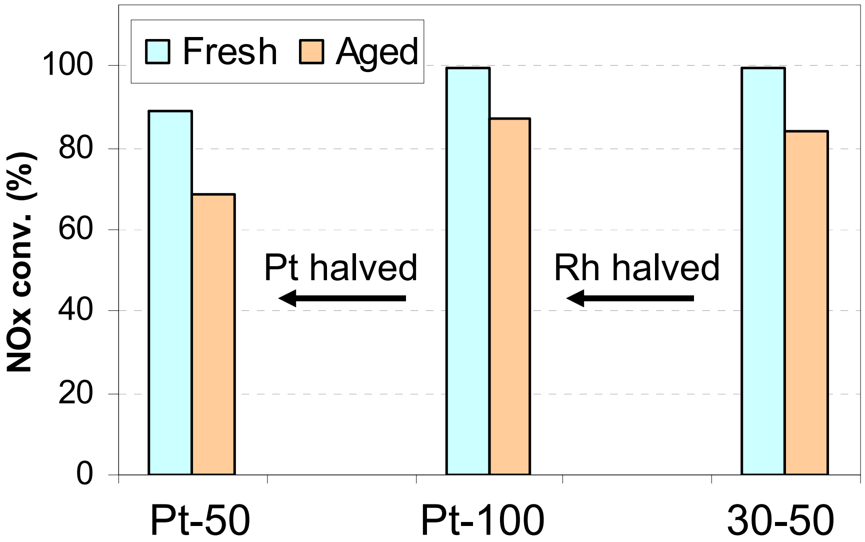

**Cycle averaged NOx storage efficiencies**




- Clear decrease in intrinsic NSE for 30-0 after aging

- Deterioration in cycle av. NSE reflects combination of reduced intrinsic NSE and lowered extent of rich phase LNT regeneration:
  → both effects important

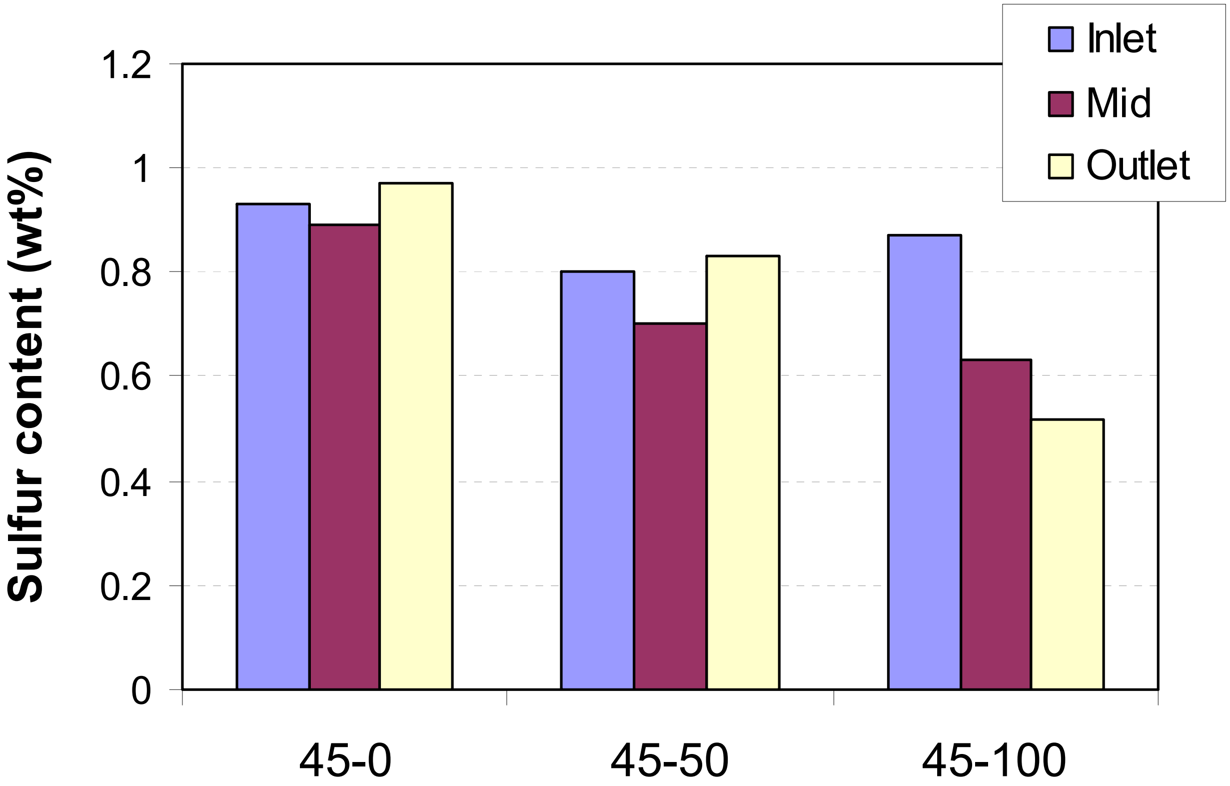
# Effect of Reduced Precious Metal Loading on Catalyst Performance (T = 250 °C)




- Pt-50 = 50 g/ft$^3$ Pt, 10 g/ft$^3$ Rh (PGM = $72/L)
- Pt-100 = 100 g/ft$^3$ Pt, 10 g/ft$^3$ Rh (PGM = $132/L)
- 30-50 = 100 g/ft$^3$ Pt, 20 g/ft$^3$ Rh (PGM = $143/L)
- Other washcoat loadings the same

- Halving Rh loading (30-50 vs. Pt-100) has no effect on performance of fresh or aged catalysts
- Halving Pt loading (Pt-100 vs. Pt-50) decreases NOx conversion for both fresh and aged catalysts (effect more significant at 250 $^o$C relative to 350 $^o$C).

# Sulfur Content of Aged Catalysts




- Residual sulfur present that cannot be removed at 750 °C
- Tendency for lower residual sulfur loading as catalyst ceria content increases

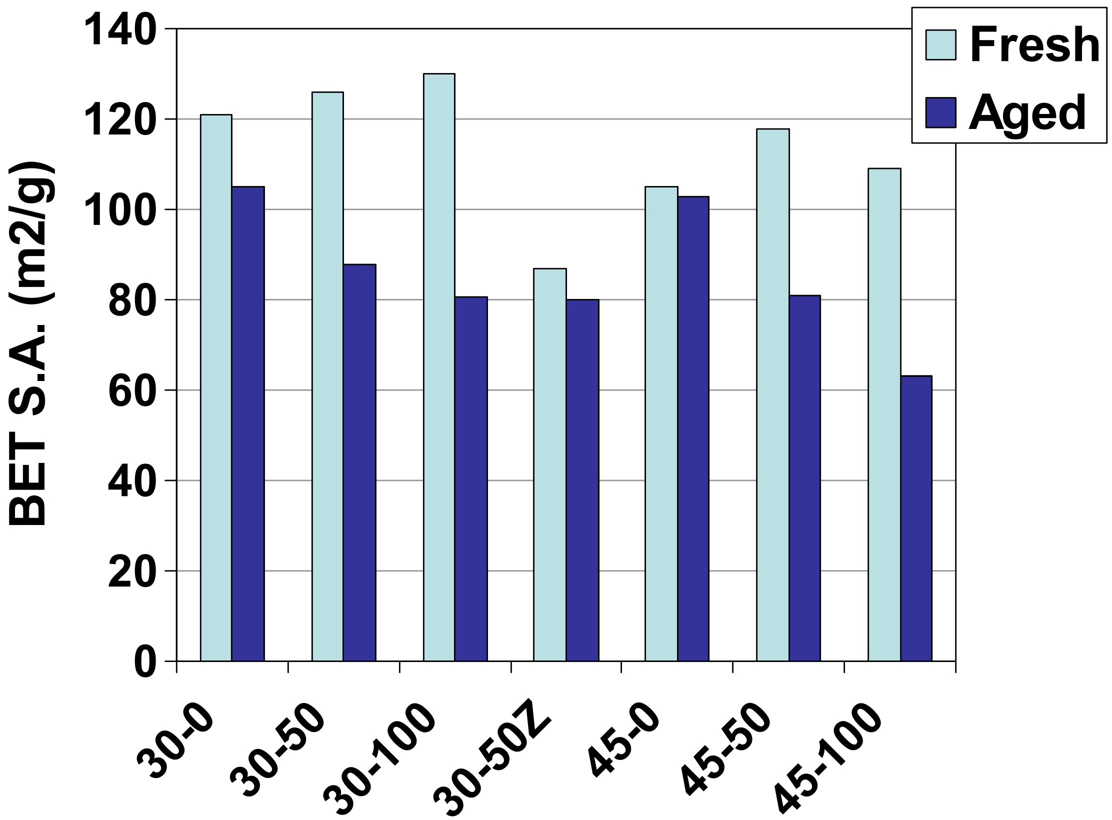
# Effect of Aging on Washcoat Surface Area

Fresh catalysts:

- Surface area decreases with increasing Ba loading

Aged catalysts:

- Sintering of La-stabilized $CeO_2$ apparent
- $CeO_2$-$ZrO_2$ appears fairly stable to sintering under aging conditions used

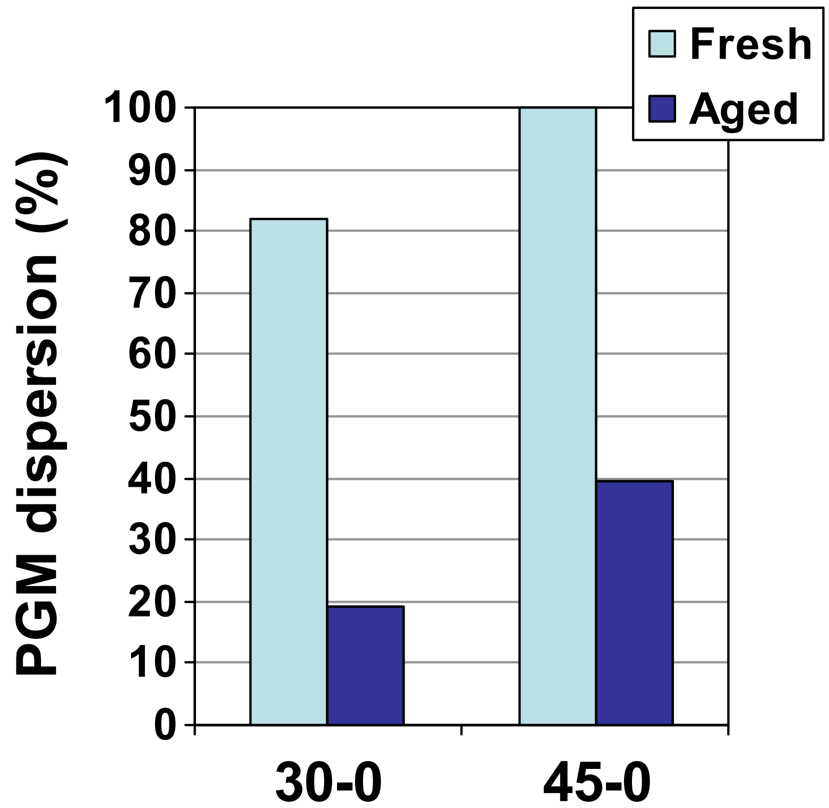


# Effect of Aging on PGM Dispersion

- $H_2$ chemisorption:
Severe sintering of Pt particles evident for 30-0 and 45-0 after aging

- Hypothesis:

1) Pt sintering and concomitant Pt/Ba phase segregation results in:
- less efficient $NO_2$ capture
- less efficient LNT regeneration (reductant spillover)
- less efficient NOx reduction
- however, NO oxidation not significantly affected (literature: rate of NO oxidation increases with Pt particle size)




2) Accumulation of sulfur in washcoat leads to lower intrinsic NOx storage efficiency

➢ Results from steady state measurements should help to confirm these ideas

# Future Work

- Complete characterization of aged catalysts using CO chemisorption and SEM/EDS (element mapping)

- Derivation of LNT deactivation model; two approaches being followed in parallel:

  - fitting of data to Sandia/ORNL model, using L/R cycling and steady state data (Stuart Daw and Kalyan Chakravarthy)

  - Monte Carlo simulation of LNT aging (UK)

- Acquisition of steady state data for aged catalysts for: (i) fitting at ORNL, (ii) further insights into mechanism(s) of LNT aging

- Final report

# Summary

- DRIFTS and NOx storage capacity measurements show that ceria is able to store sulfur and mitigate sulfation of the Ba NOx storage phase

- For aged catalysts, degradation of performance is manifested by:

  - lower lean phase storage efficiency; this is attributed to the inability of the catalyst to be regenerated sufficiently during rich purging, as well as some loss of intrinsic NSE

  - lower rich phase NOx reduction efficiency

- Spectacular improvement in catalyst durability via the incorporation of $CeO_2$-$ZrO_2$ and La-stabilized $CeO_2$ has been demonstrated

- The benefits arising from $CeO_2$-$ZrO_2$ and La-stabilized $CeO_2$ incorporation are attributed in large part to their ability to stabilize Pt w.r.t. sintering