Effect of High Temperature Lean/Rich Thermal Aging on NO_x Storage and Reduction over a Fully-Formulated LNT

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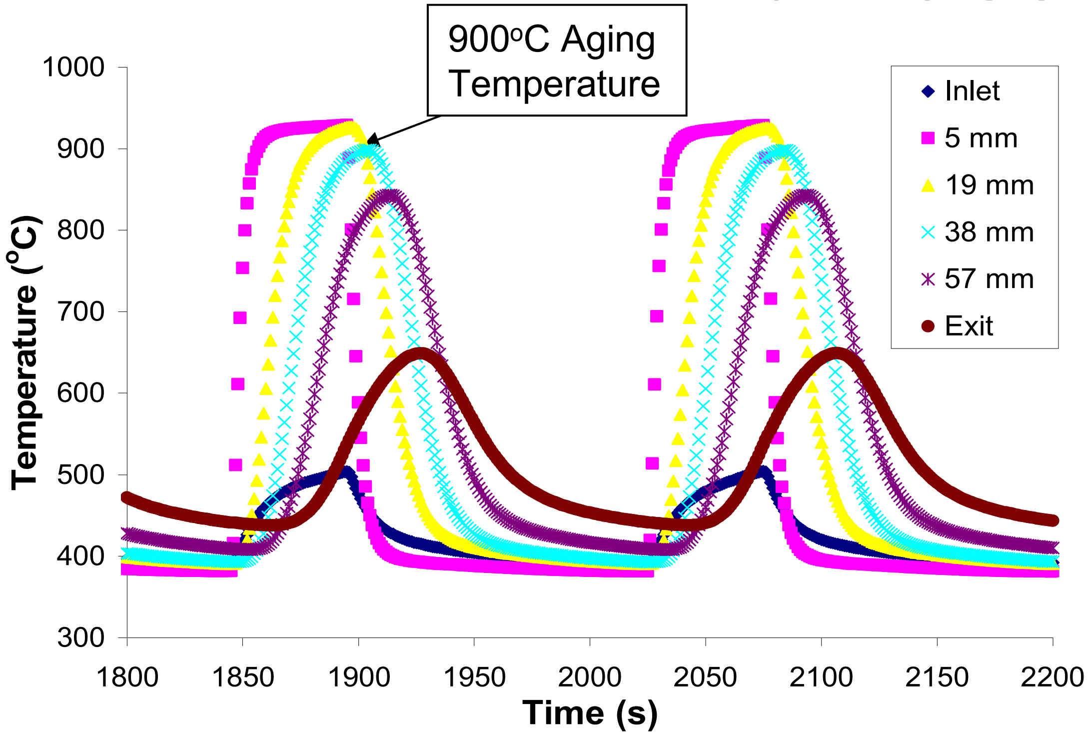
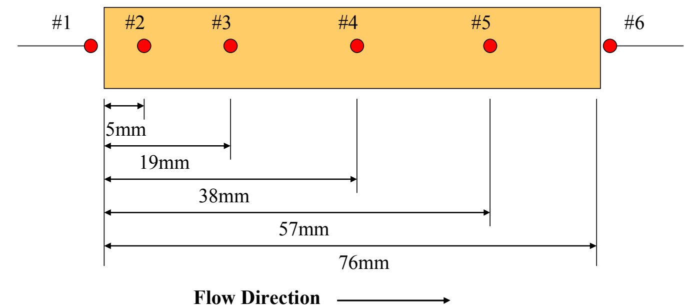
Objective

- Determine the effect of thermal aging on LNT's components during NO_x storage and reduction
  - How is NO_x storage capacity affected by aging?
  - How does PGM dispersion affect NO oxidation and NO_x reduction?

Thermal-Aging with Exotherm in a Furnace





	Lean (130s)		Rich (50s)
NO_x	**300 ppm**		**300 ppm**
CO_2	**5%**		**5.00%**
CO	**0**		**5.10%**
H_2	**0**		**3.25%**
O_2	**11%**		**4.00%**
H_20	**4.2%**		**4.20%**
N_2	**balance**		**balance**

- Low Temperature Ba-only LNT (fully-formulated)
- The center of the catalyst reaches a nominal aging temperature of ~900°C
- The front section of the catalyst experiences higher aging temperature

Experimental Apparatus

Micro-Reactor

- NO_x Storage
- NO Oxidation
- BET Surface Area

at FEERC

Bench-Reactor

- NO_x Conversion

at UT Knoxville

DRIFTS

- NO_x Storage
- NO_x TPDs

at FEERC

STEM/EDS

- PGM Particle Size

at HTML

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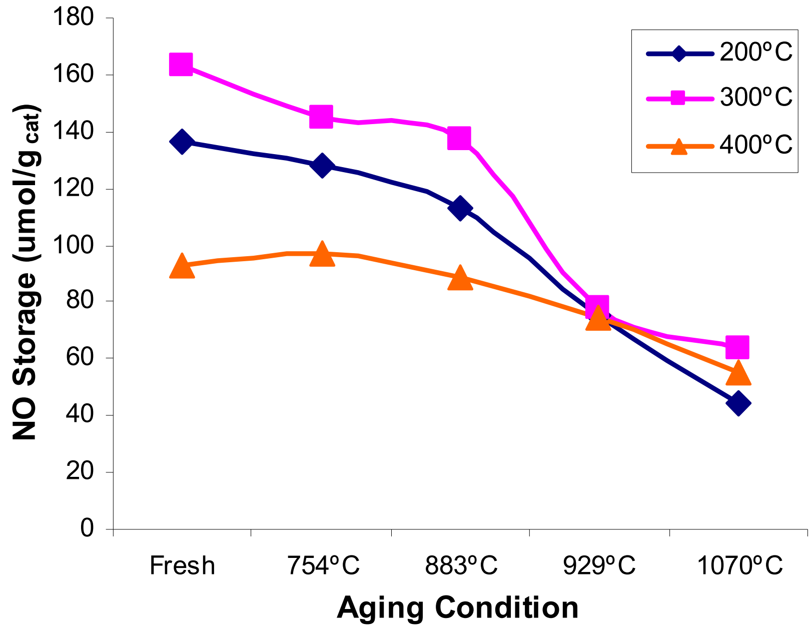
Results:

Effect of Aging on NO_x Storage, NO Oxidation, and PGM Activity

Micro-reactor, Bench-Reactor, and STEM

Impact of Thermal Aging on NO_x Storage Capacity is Function of Evaluation Temp.

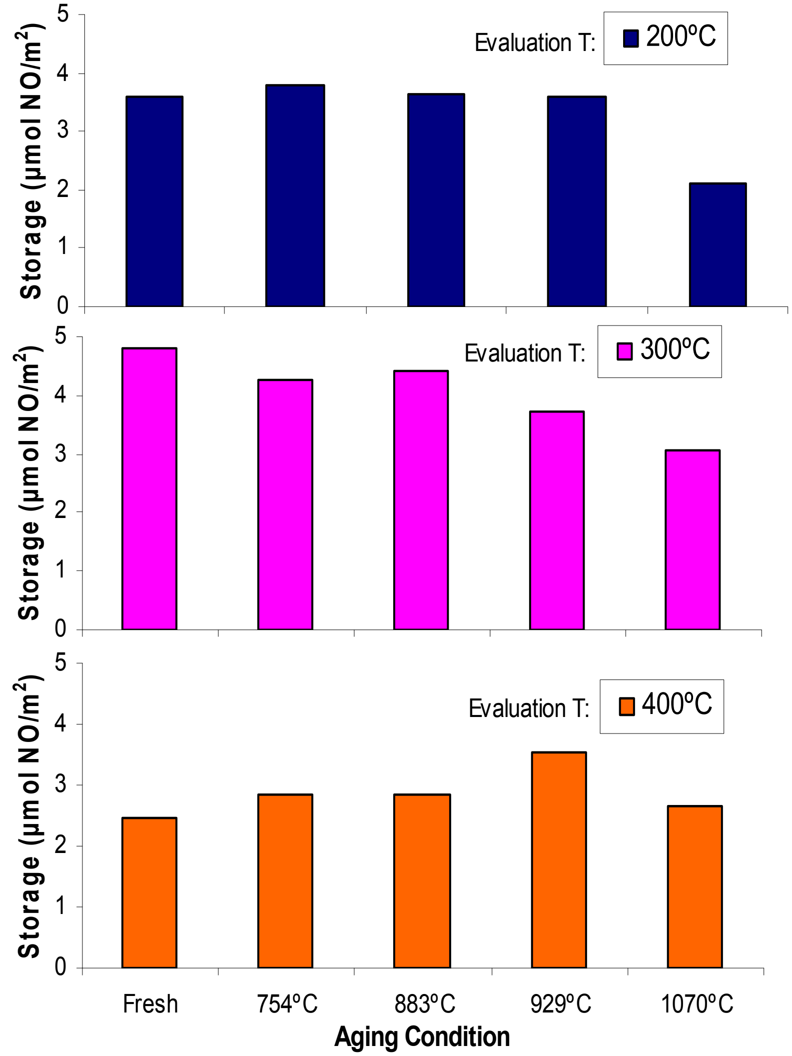
- Maximum NO_x storage capacity at 300°C
  - Capacity at 400°C is only half of 300°C in fresh LNT
- NO_x capacity decreases at all aging temperatures
  - Largest reduction at highest aging temperature
- Capacities are similar after aging at 900 and 1000°C
  - Storage at 400°C is less affected by aging



Flow Conditions: 1000 ppm NO, 10% O_2, and Ar balance

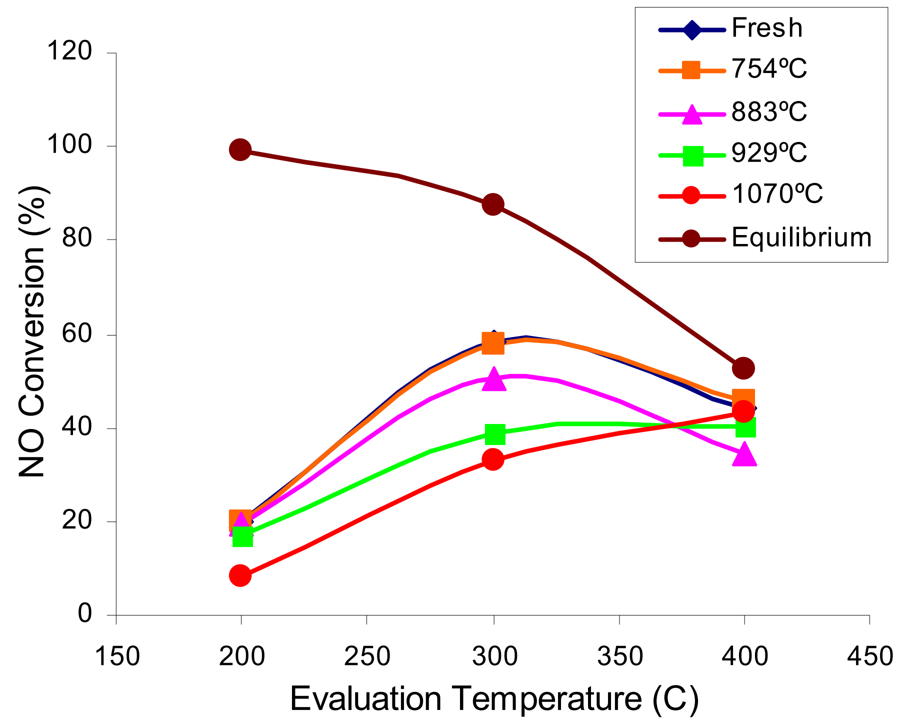
Normalizing NO_x Storage Capacity to Surface Area Reveals Three Relationships

- 200°C
  - Capacity constant on surface area basis until 1000°C
- 300°C
  - Capacity decreases 36% from 4.8 to 3 μmol NO/m^2
- 400°C
  - Capacity increases 31% after 929°C
  - Ba dispersion is either constant or increasing with SA loss



NO Oxidation is Most Affected at 300°C by Aging

- Max of 58% at 300°C and 20% at 200°C in fresh LNT
- NO oxidation at 200 and 300°C decreases with aging temperature
- Approximately constant at 400°C
  - Equilibrium limited

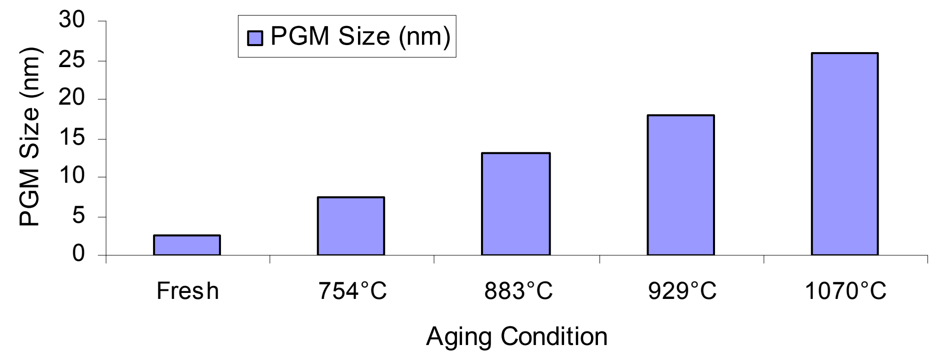


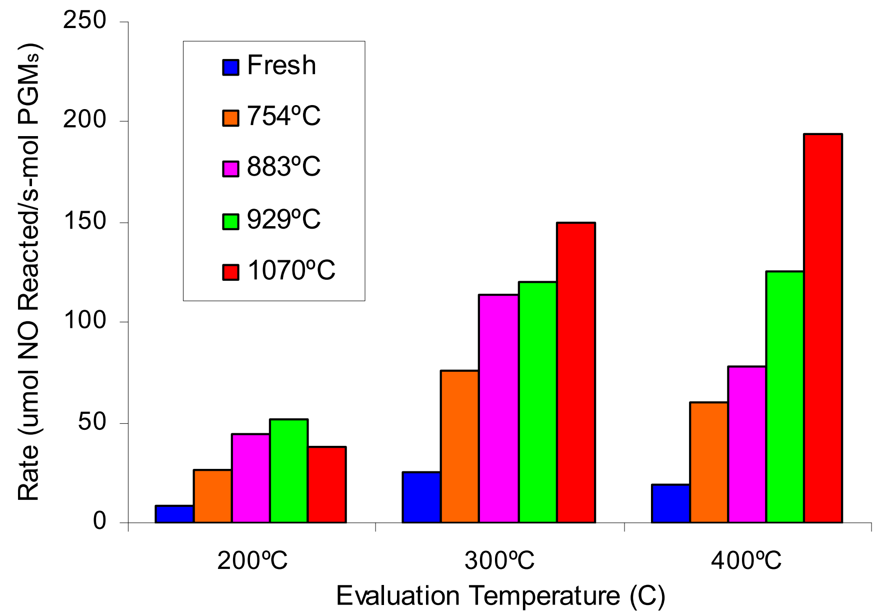
kinetics are too fast to effect

Experiments performed with 1000 ppm NO, 10% O_2, and Ar balance

NO Oxidation Per mol Surface PGM Increases with Aging

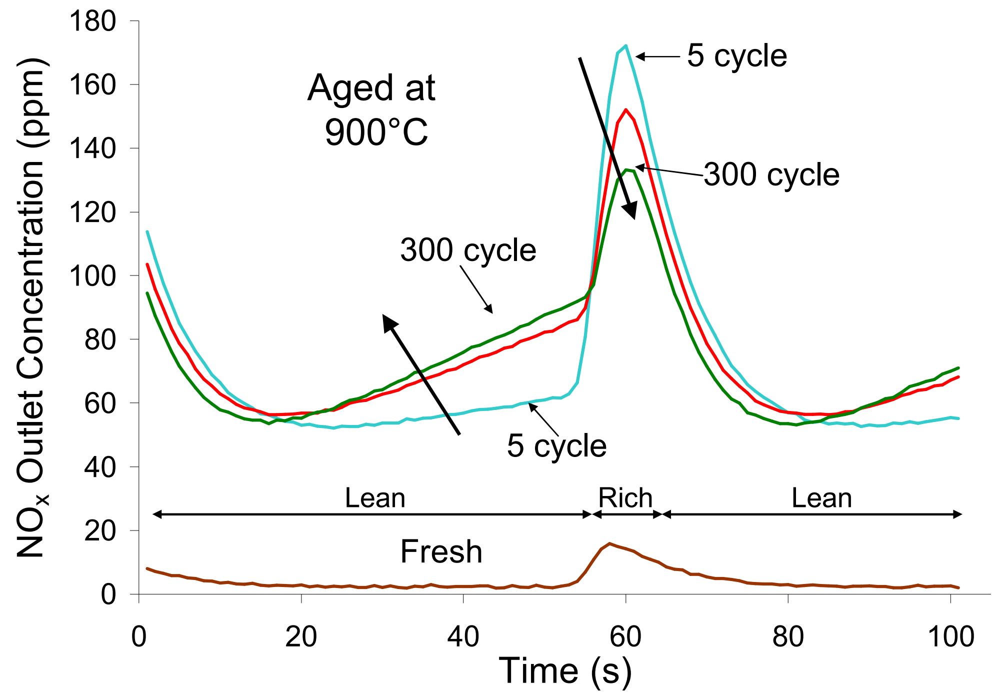
- Ten-fold increase in average PGM size after aging at 1000°C
- NO conversion *per mol PGM_s* increases at all evaluation temperatures
  - 19 to 195 μmol NO/s·mol PGM_s at 400°C
- Qualitatively illustrated by Olsson et al.
  - *L. Olsson, E. Fridell, Journal of Catalysis 210 (2002) 340.*





Rich Phase NO_x Release Reduced After Aging at Evaluation Temp. of 400°C

- Storage Phase
  - NO_x slip increases with aging temperature and number of aging cycles
    - Capacity decreases with aging
- Reduction Phase
  - NO_x excursion decreases with increasing number of aging cycles
    - PGM surface area decreases with aging

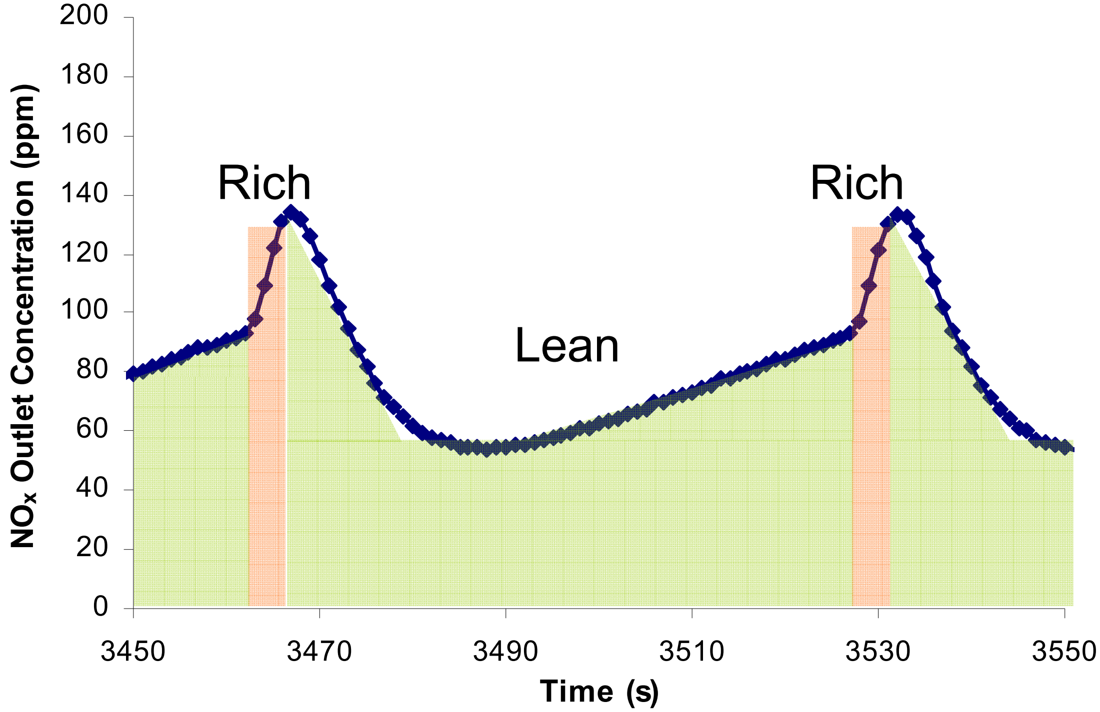


GHSV: 30,000 hr^{-1}
Lean (60s): 300ppm NO, 5% CO_2, 5% H_2O, 10% O_2, N_2 bal
Rich (5s): 300ppm NO, 5% CO_2, 5% H_2O, 1.13% CO, .68% H_2, N_2 bal

Calculating an Unbiased Turnover Frequency is Complicated by Cycling

- Normalized to NO_x stored in previous lean cycle to account for dependence on surface coverage of rich NO_x release

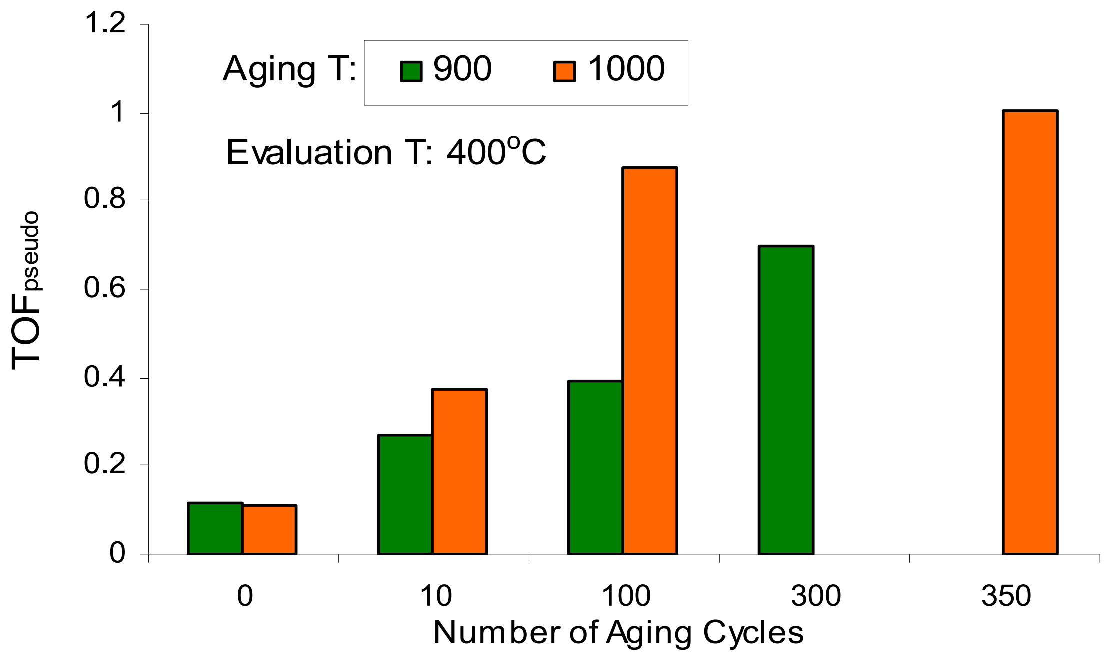
$$TOF_{pseudo} = \frac{NO_x \, Released_{rich\_cycle}}{NO_x Stored_{lean\_cycle} * molPGM_s}$$



Aging Results in Improved Reduction Efficiency

- NO_x that is released is reduced more efficiently after aging

$$TOF_{pseudo} = \frac{NO_x\,Released_{rich\_cycle}}{NO_x\,Stored_{lean\_cycle} * molPGM_s}$$



GHSV: 30,000 hr^{-1}
Lean (60s): 300 ppm NO, 5% CO_2, 5% H_2O, 10% O_2, N_2 bal
Rich (5s): 300 ppm NO, 5% CO_2, 5% H_2O, 1.13% CO, .68% H_2, N_2 bal

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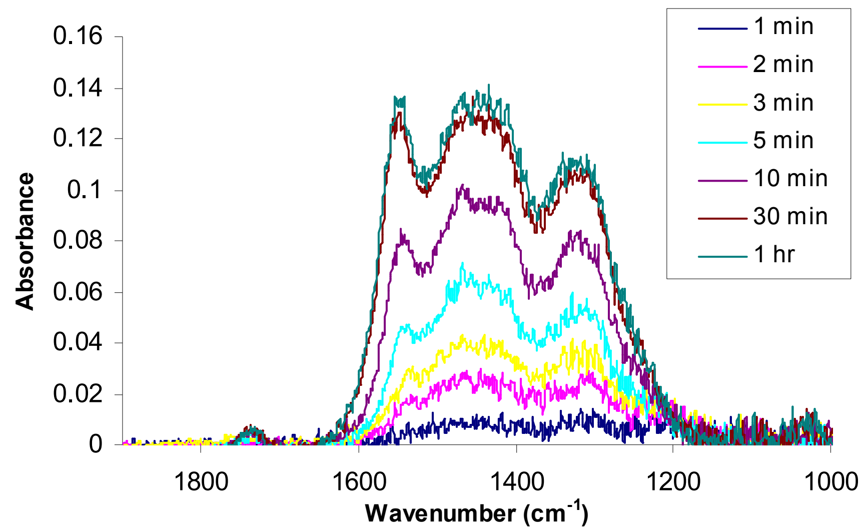
Results:

Effect of Aging on Distribution and Stability of NO_x Storage Sites

DRIFTS

DRIFTS Experimental Setup

- NO_x Storage
  - Pretreatment at 500°C in 1% H_2, Ar bal. for 30 min
  - Take background scan in 10% O_2, and Ar bal. at storage temperature
  - Store NO_x with 300 ppm NO, 10% O_2, Ar bal.



- NO_x TPDs
  - Pretreatment at 500°C in 1% H_2, Ar bal. for 30 min
  - Take background scans while cooling from 500 to 200°C in 10% O_2, Ar bal.
  - Exposure to 300 ppm NO, 10% O_2, Ar bal. at 200°C for 1 hr
  - TPD in Ar

DRIFTS Peak Assignments

- 1220 cm^{-1} – $Ba(NO_2)_2$
  - D. H. Kim, J. H. Kwak, J. Szanyi, S. D. Burton, C. H.F. Peden, Appl. Catal. B: Environ. 72 (2007) 233.
  - J. Yaying, T. J. Toops, J. A. Pihl, M. Crocker, *Submitted to Applied Catal. B*.

- 1430 and 1320 cm^{-1} – $Ba(NO_3)_2$
  - Z. Liu, J. A. Anderson, J. Catal. 224 (2004) 18.
  - F. Prinetto, G. Ghiotti, I. Nova, L. Lietti, E. Tronconi, P. Forzatti, J. Phys. Chem. 105 (2001) 12732.
  - J. Yaying, T. J. Toops, J. A. Pihl, M. Crocker, *Submitted to Applied Catal. B*.
  - Ch. Sedlmair, K. Seshan, A. Jentys, J. A. Lercher, J. Catal. 214 (2003) 308.

- 1550, 1465, 1412, and 1250 cm^{-1} – γ-Al_2O_3 - NO_3
  - Z. Liu, J. A. Anderson, J. Catal. 224 (2004) 18.
  - T. J. Toops, D. B. Smith, W. P. Partridge, Appl. Catal. B: Environ. 58 (2005) 245.
  - J. Yaying, T. J. Toops, J. A. Pihl, M. Crocker, *Submitted to Applied Catal. B*.
  - A. L. Goodman, T. M. Miller, V. H. Grassian, J. Vac. Sci. Technol. A 16 (1998) 2585.

NO_x Storage DRIFTS Spectra from Fresh LNTs

- Spectra at 200 and 300°C are similar
  - Large portion of nitrates stored on γ-Al_2O_3; approximately 25% by peak area
  - Ba nitrites form first, but peak is less intense at 300°C

<u>Peak Assignments (cm^{-1})</u>

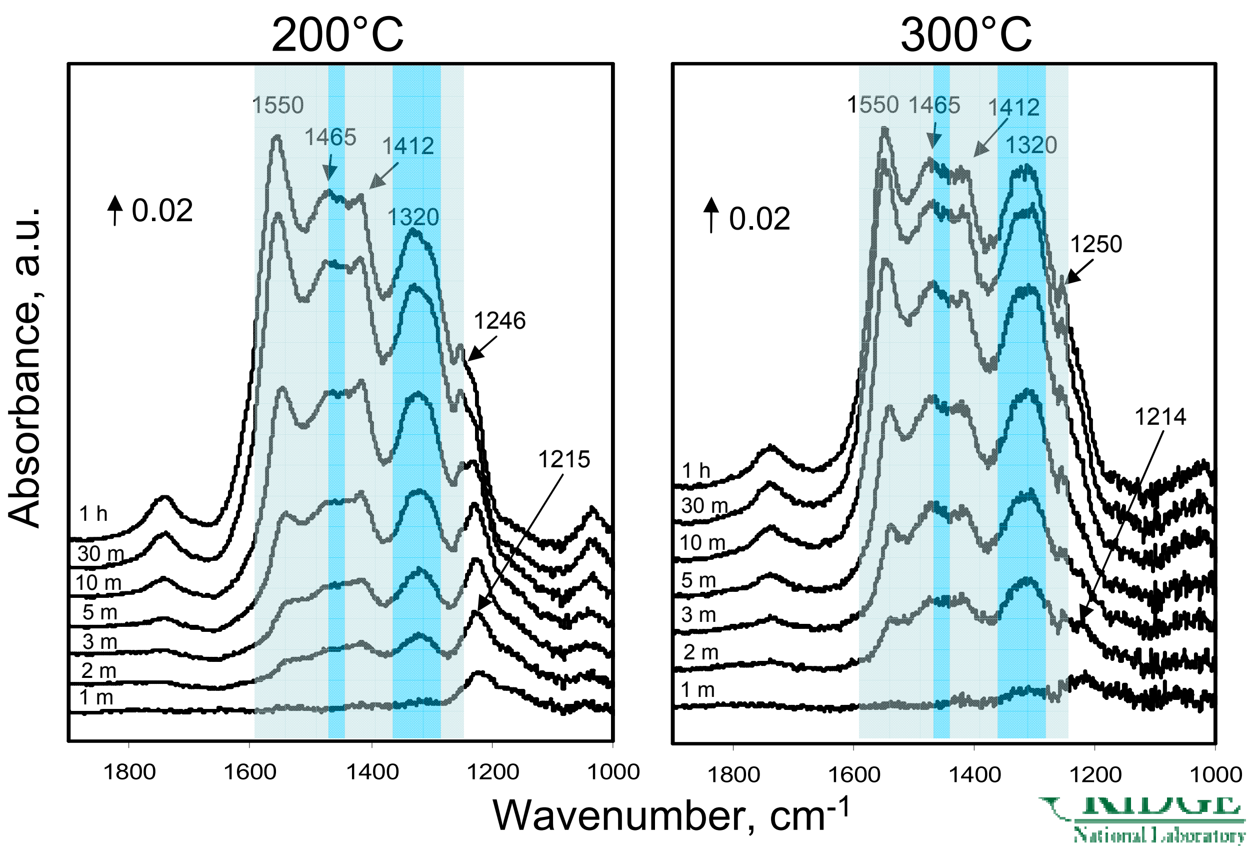
γ-Al_2O_3-NO_3
- 1250, 1412, 1465, and 1550

$Ba(NO_3)_2$
- 1320 and 1430

$Ba(NO_2)_2$
- 1215

<u>Flow Conditions</u>

- 300 ppm NO, 10% O_2, and Ar bal.



Al_2O_3 Nitrates Not Stable at 400°C

- No formation of nitrates on γ-Al_2O_3
- LNT is saturated after 30 min of NO exposure

<u>Peak Assignments (cm^{-1})</u>

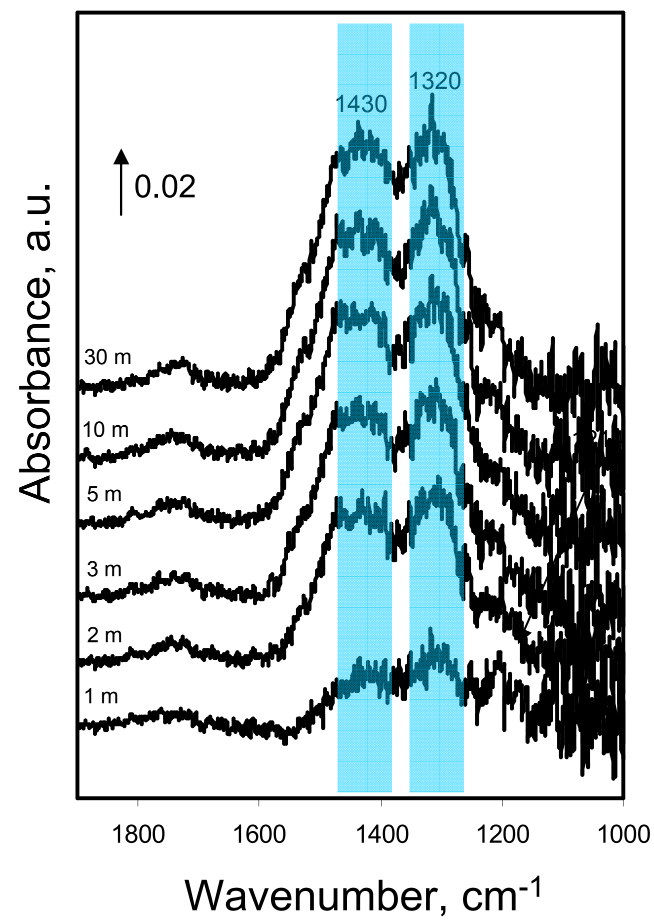
γ-Al_2O_3-NO_3
- 1250, 1412, 1465, and 1550

$Ba(NO_3)_2$
- 1320 and 1430

$Ba(NO_2)_2$
- 1215

<u>Flow Conditions</u>
- 300 ppm NO, 10% O2, and Ar bal.

400°C



Fewer Al_2O_3 Nitrates After Aging at 900°C

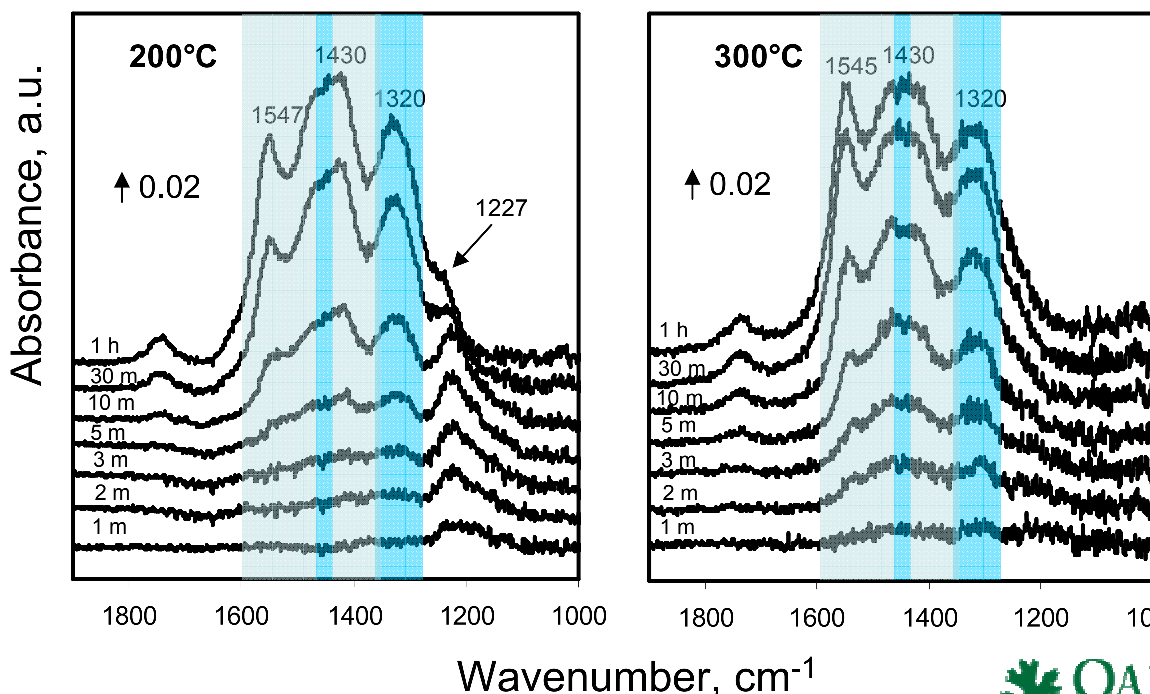
- Reduction in γ-Al_2O_3 peak height/area corresponds to reduction in γ-Al_2O_3 surface area or Ba redispersion over γ-Al_2O_3
- Ba sites appear not to be as affected by aging
  - Consistent with 200°C NO_x storage
  - Ba could be redispersing and covering γ-Al_2O_3

<u>Peak Assignments (cm^{-1})</u>

γ-Al_2O_3-NO_3
- 1250, 1412, 1465, and 1550

$Ba(NO_3)_2$
- 1320 and 1430

$Ba(NO_2)_2$
- 1215



Further Reduction in Al_2O_3 Nitrates After 1000°C Aging

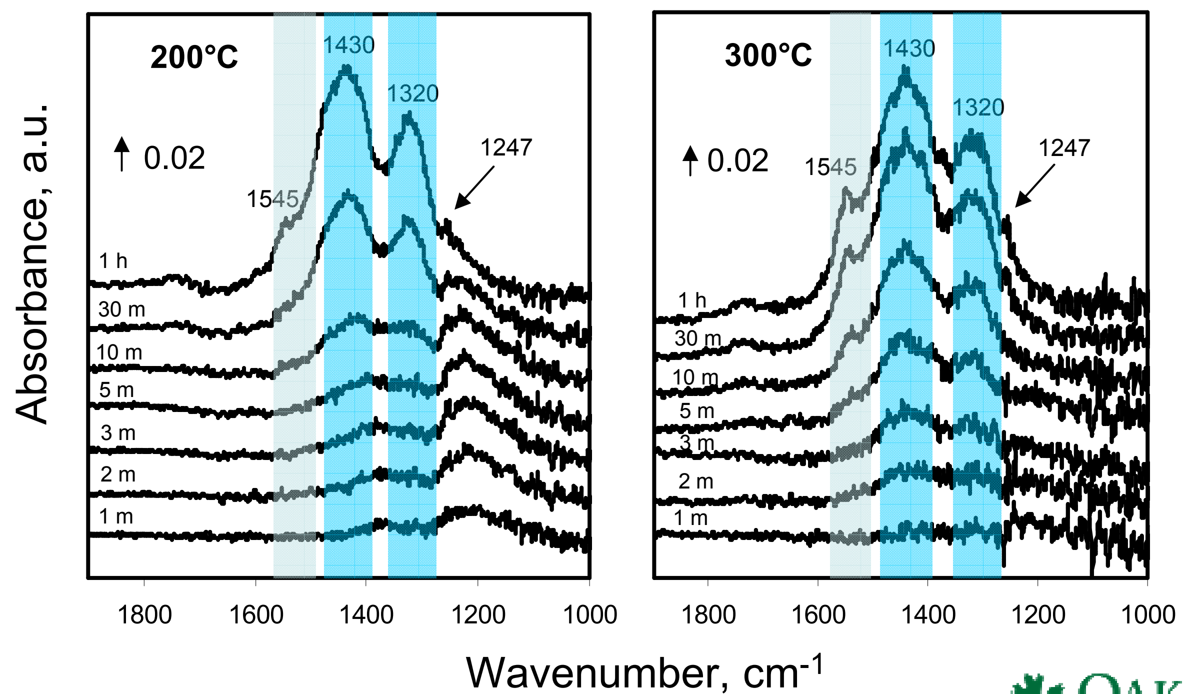
- Almost complete loss of γ-Al_2O_3 NO_x storage sites
- Ba sites appear not to be as affected by aging
  - $Ba(NO_3)_2$ peak at 1430 cm^{-1} is now clearly visible

Peak Assignments (cm^{-1})

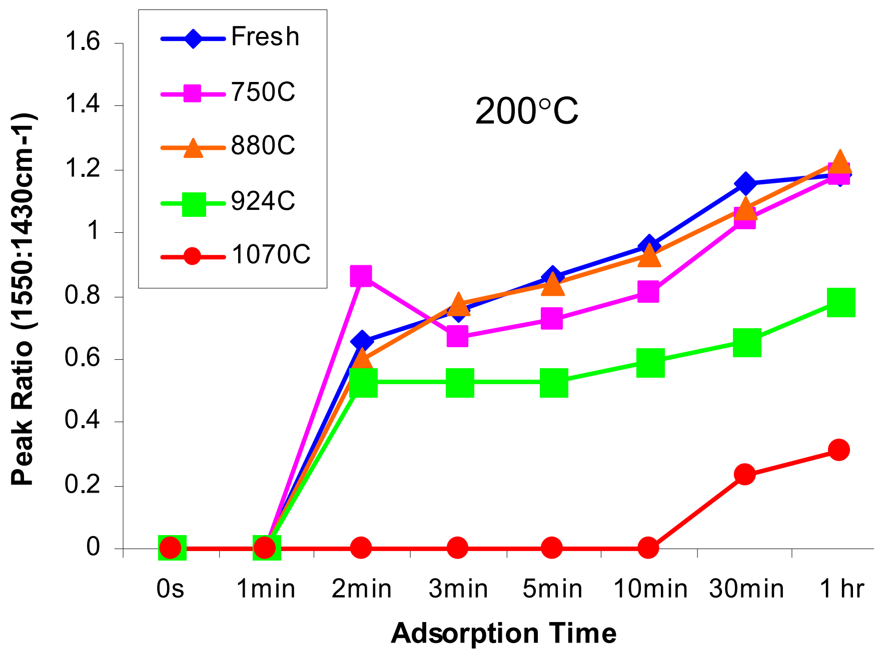
γ-Al_2O_3-NO_3
- 1250, 1412, 1465, and 1550

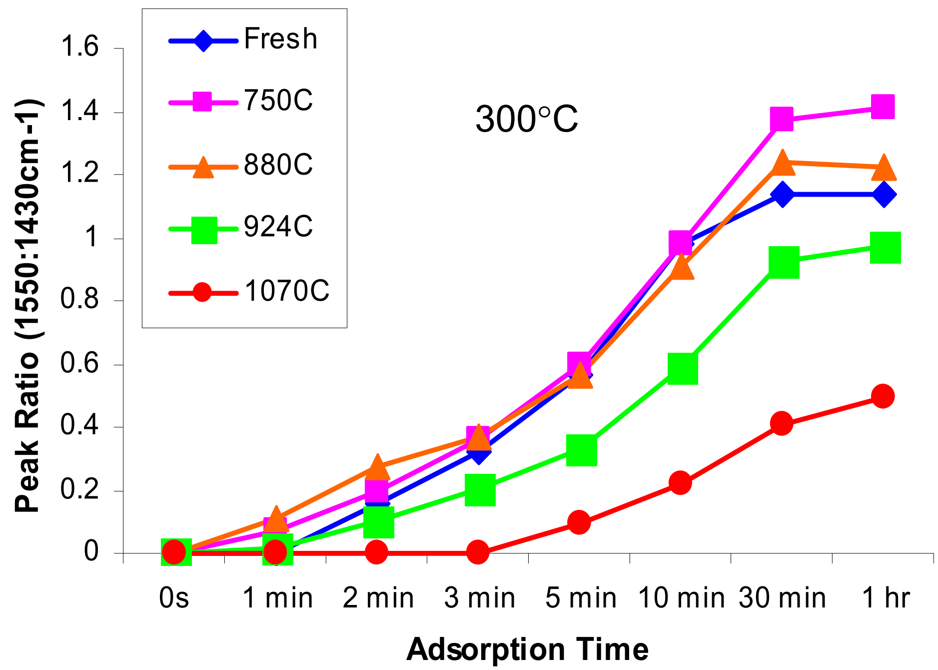
$Ba(NO_3)_2$
- 1320 and 1430

$Ba(NO_2)_2$
- 1215



Effect of Aging on Al_2O_3 Nitrates Not Seen at 700 or 800°C

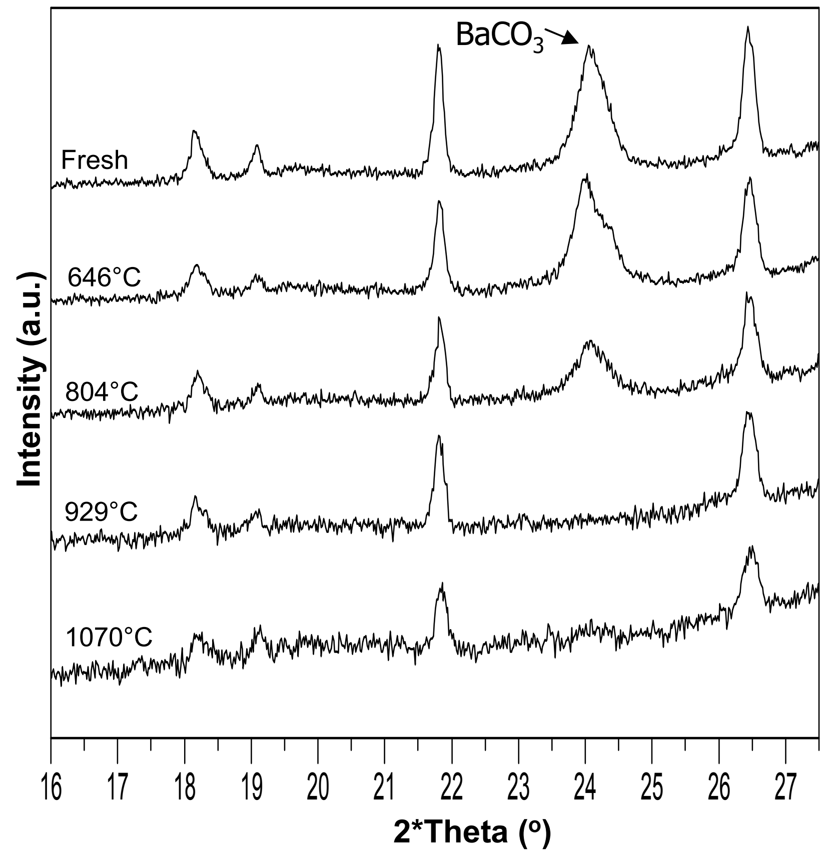




- Maximum peak height ratios of Al_2O_3 nitrate and $Ba(NO_3)_2$ peaks at 1550 and 1430 cm^{-1}, respectively
- Decrease in peak ratio begins when aging above 880°C

XRD Provides Further Evidence of Ba Redispersion

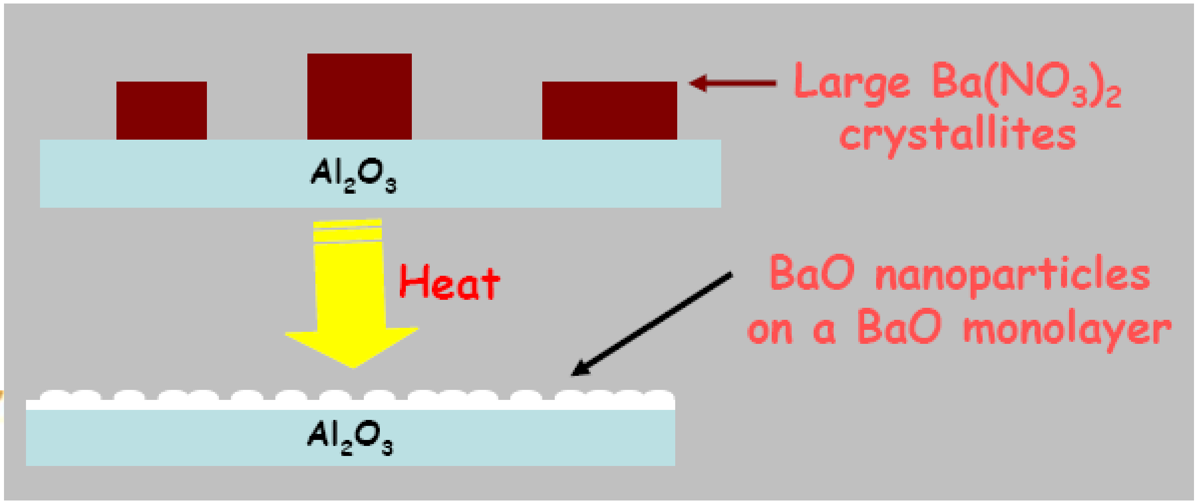
- Disappearance of $BaCO_3$ peaks at 929°C
  - No evidence of formation of other Ba phases, e.g., $BaAl_2O_4$
- Elemental Ba still present in unidentified phase (EPMA)
- $BaCO_3$ transition minimally affects NO_x conversion



XRD Spectra of samples aged at indicated temperature

DRIFTS Elucidates Mechanisms of Reduction in NO_x Storage

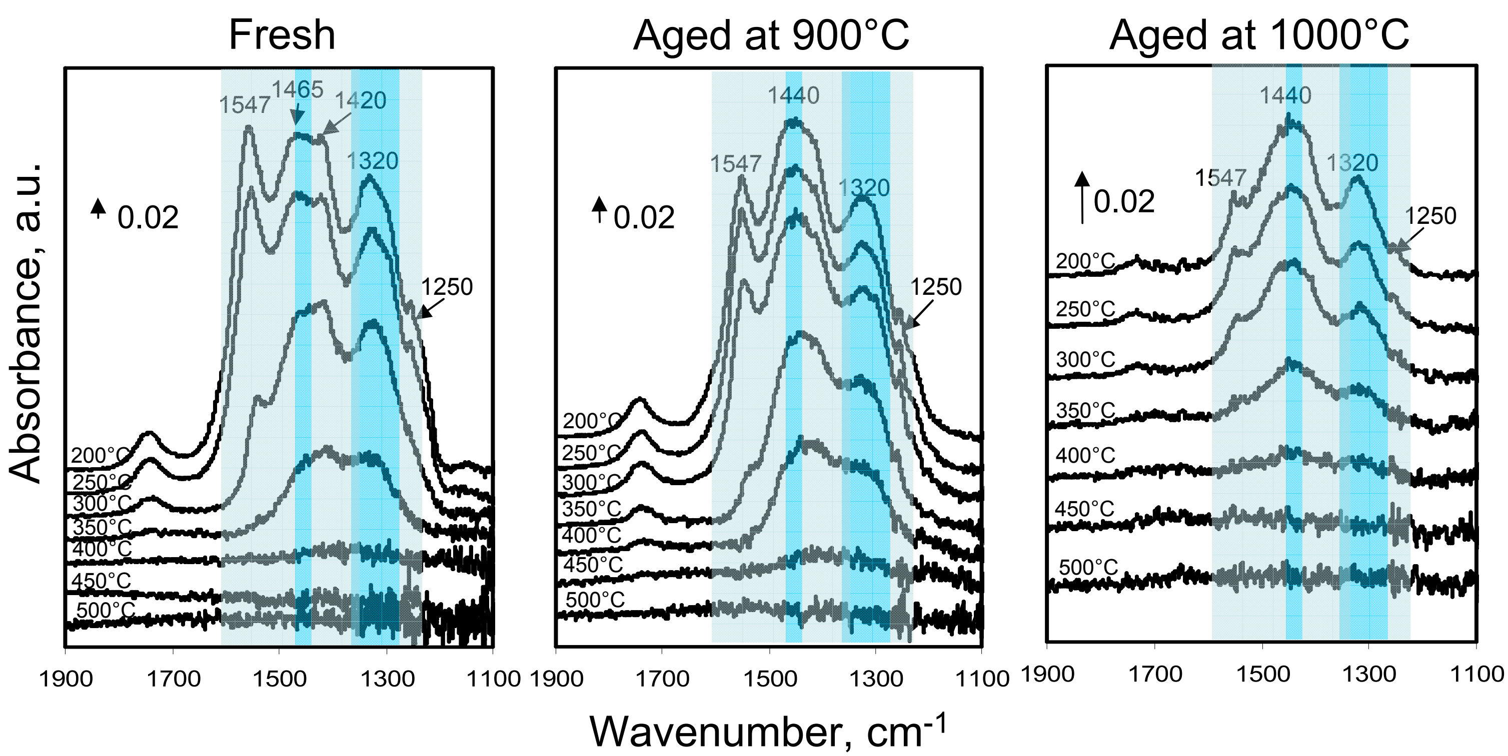
- 200 and 300°C
  - Reductions in NO_x storage at > 900°C are largely a result of loss of Al_2O_3 nitrate sites
    - Possible Ba redispersion
  - $Ba(NO_3)_2$ is much less affected by aging
- 400°C
  - Storage can only be affected by change in Ba sites since Al_2O_3 does not store NO_3's at this T



Peden et al. CLEERS Workshop #9, 2005

Ba and Al_2O_3 Nitrates more Stable After Aging

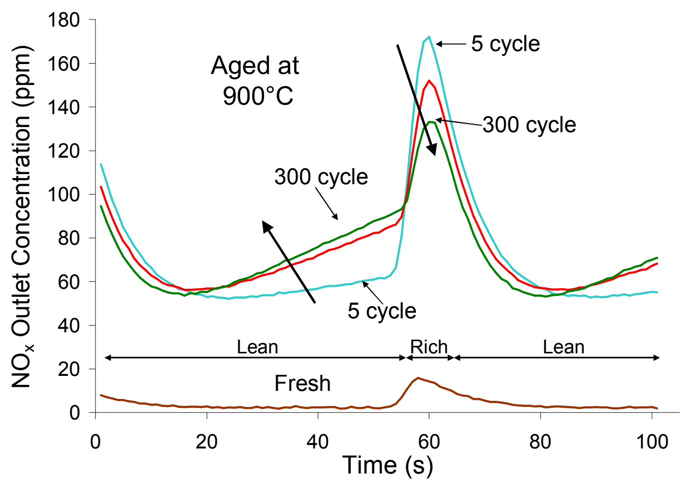
- γ-Al_2O_3 nitrates decompose first below 400°C
- Aging increases stability of both γ-Al_2O_3 and Ba nitrate bonds by ~ 50°C
  - Possible Ba redispersion and effect of Ba-support interaction

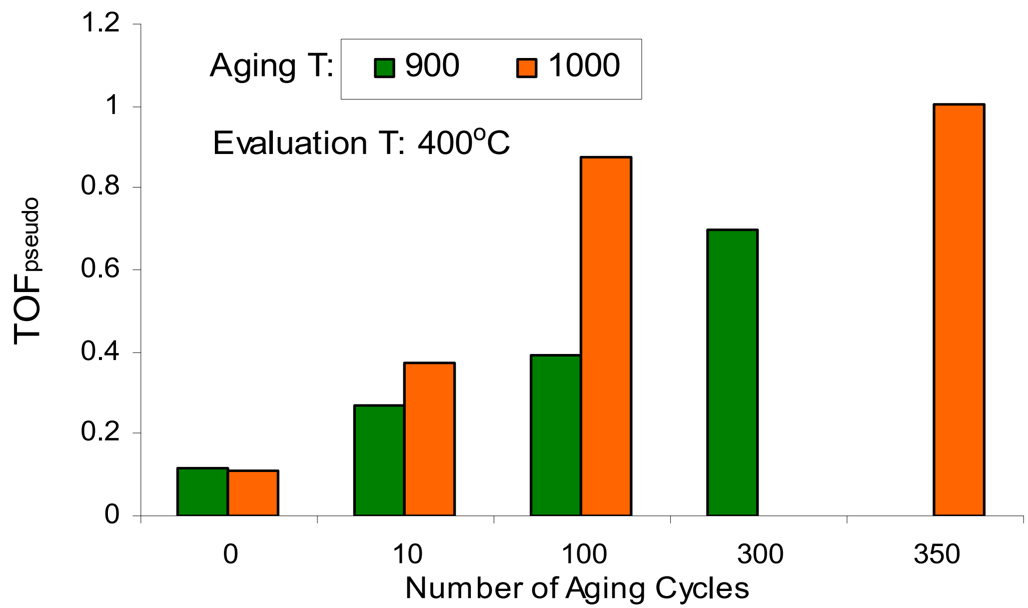


Storage: 300ppm NO, 10% O_2, Ar bal.
TPD: 100% Ar

Higher Stability Nitrates Possible Explanation for More Efficient Reduction

- Higher stability nitrates would release slower and be more effectively reduced
  - Smaller NO_x puff





Conclusions

- NO oxidation seems to be improved by increasing PGM particle size
- Improvement in NO_x reduction efficiency is explained by increasing nitrate stability with aging
- γ-Al_2O_3 stores a significant amount of NO_x before high-temperature aging
- Large reductions in NO_x storage capacity at 200 and 300°C are consistent with alumina surface area reduction

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- Funding provided by U.S. Department of Energy (DOE) Office of Vehicle Technologies

U.S. Department of Energy
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umicore
materials for a better life

- STEM/EDS performed at ORNL High Temperature Materials Laboratory (HTML)

html

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Thank you for your attention

Questions?

Introduction of H_2O and CO_2 Marginally Reduces Al_2O_3 NO_3 Formation

- Switching exp's with H_2O and CO_2 show similar trends to SS NO_x adsorption
  - Al_2O_3 nitrates are most affected by aging

Peak Assignments (cm^{-1})

γ-Al_2O_3-NO_3
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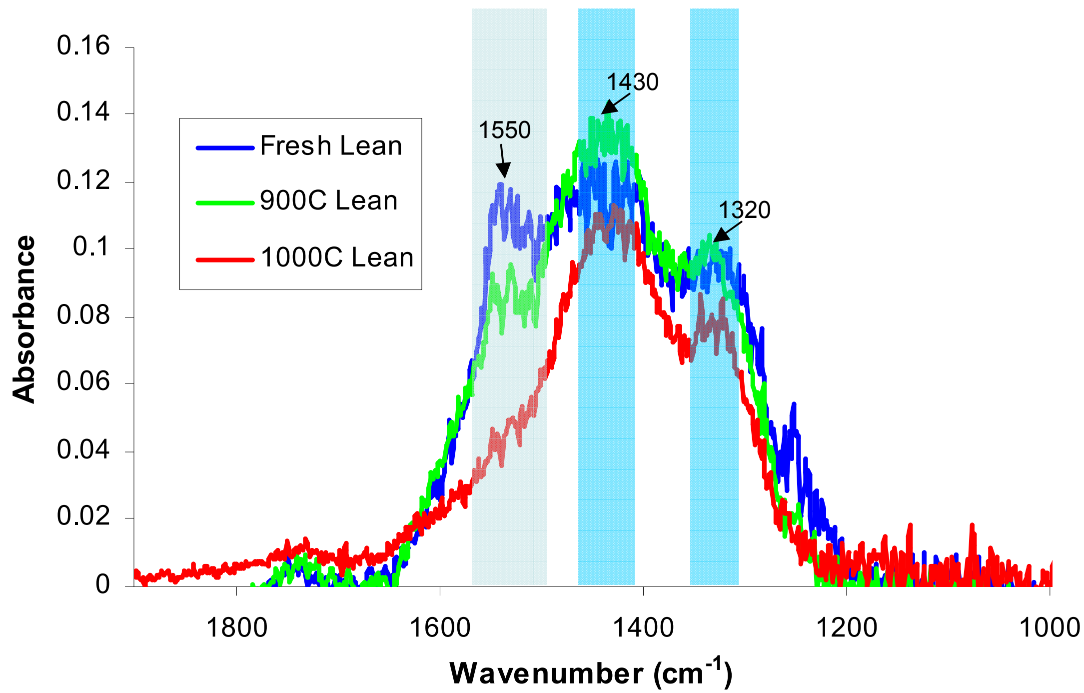

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Rich (30s): 300 ppm NO, 5% CO_2, 5% H_2O, 1.13% CO, .68% H_2, N_2 bal

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