Effect of Thermal Aging on NO oxidation and NOx storage in a Fully-Formulated Lean NOx Trap

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15th DEER

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U.S. DEPARTMENT OF ENERGY

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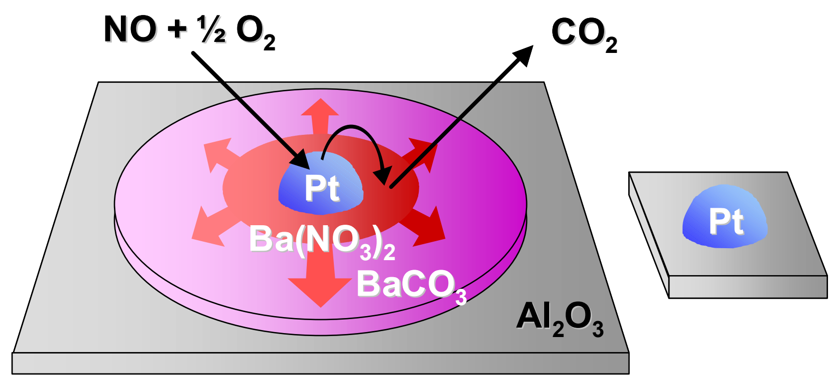
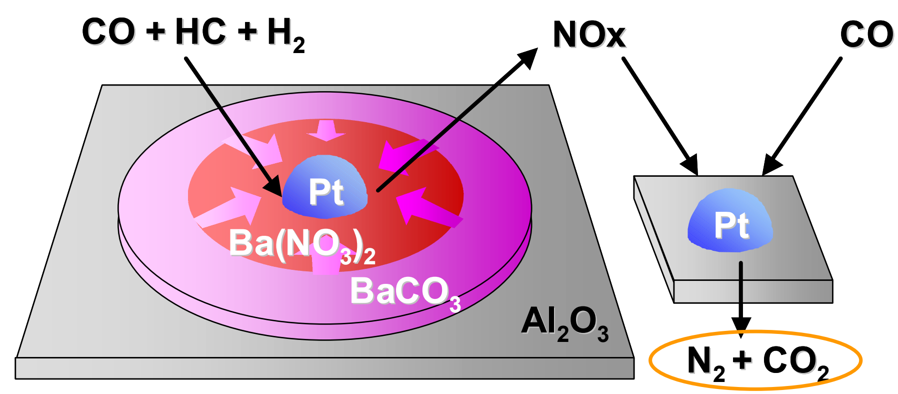
LNT behavior comprised of three main steps: oxidation, storage, and reduction

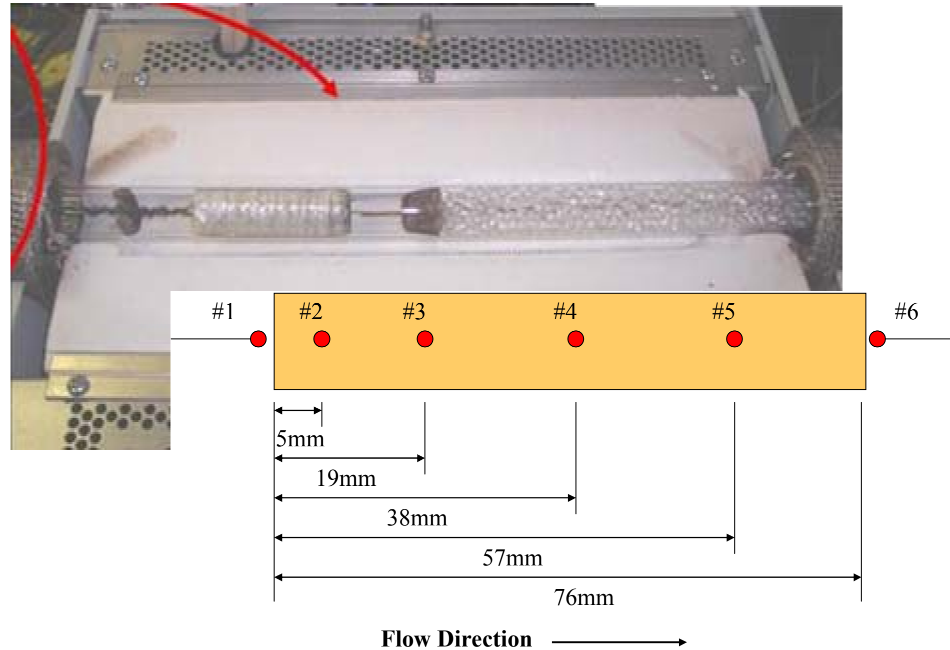
- Modeling efforts must capture the independent reaction steps
- Aging effects these steps…differently
- Optimizing injection strategies relies on understanding the state of LNT as a function of age
  - If LNT optimized for end of life performance near term fuel penalties will be higher than necessary
  - If LNT optimized for fresh performance, will fail emissions during use

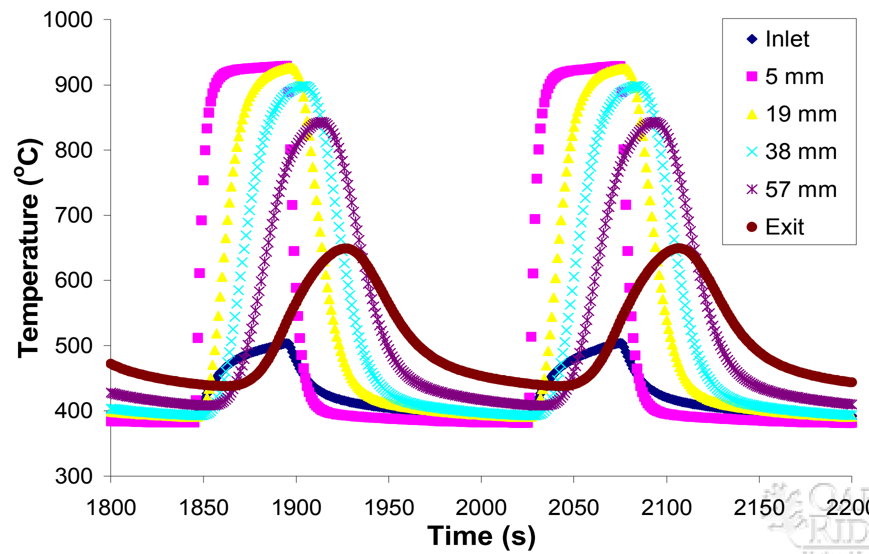




Thermally-aged catalysts generated using bench-generated exotherms

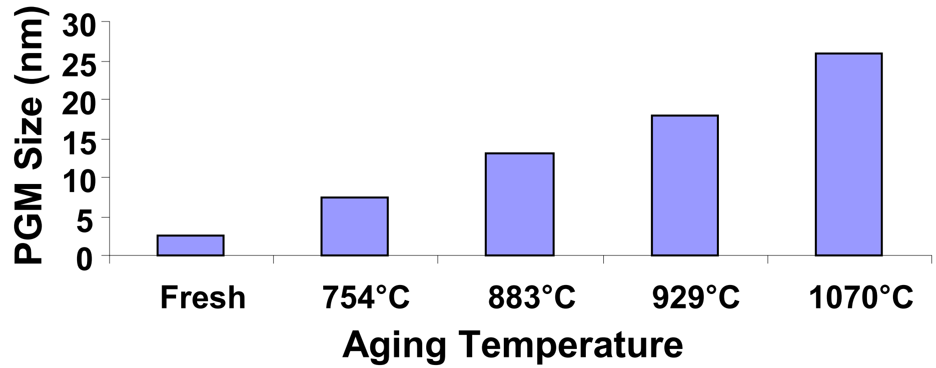
- Effort began as a Rapid Aging Protocol development project
- Temperatures studied
  - 700, 800, 900, 1000°C
  - Up to 350 thermal cycles
- Study generated LNTs with wide range of aging properties
  - Pt-Pd-Rh/Ba/γ-Al_2O_3 plus other additives
  - Umicore samples (formerly Delphi)

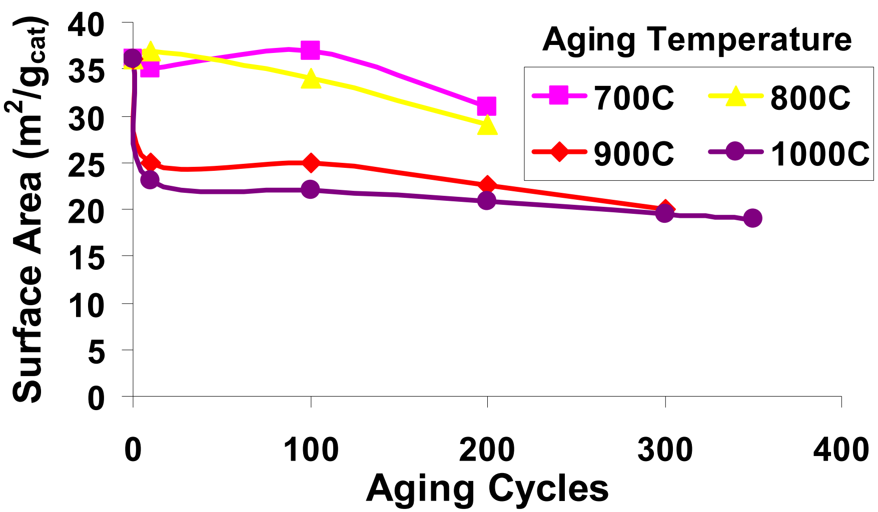


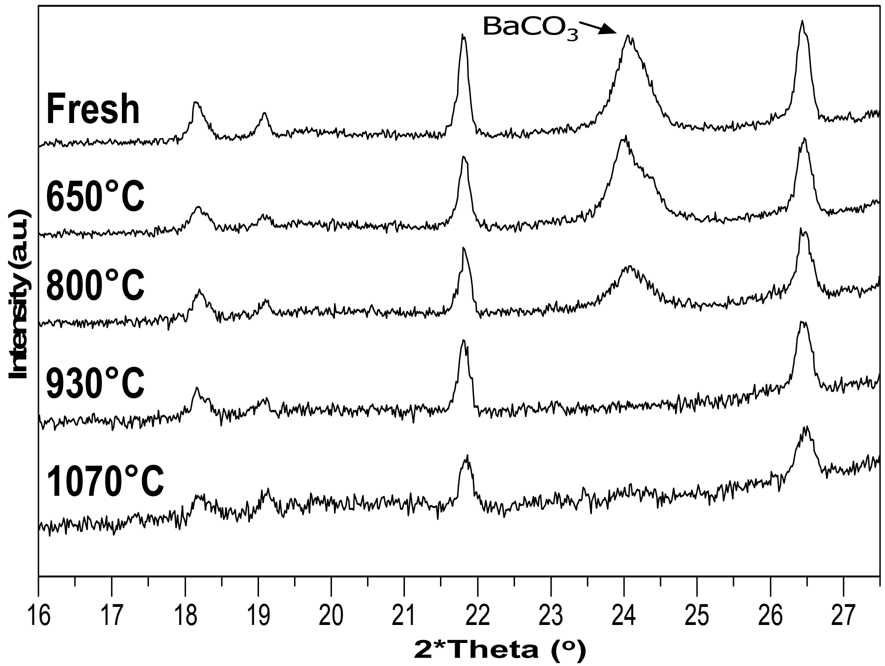


Thermal aging has clear effect on material properties

- Pt group metals (PGM) increase in size
  - therefore, surface metal decreases
- Phase changes as depicted by XRD
  - Ba-phase appears to be dispersing
- Total surface area of support + storage material decreases



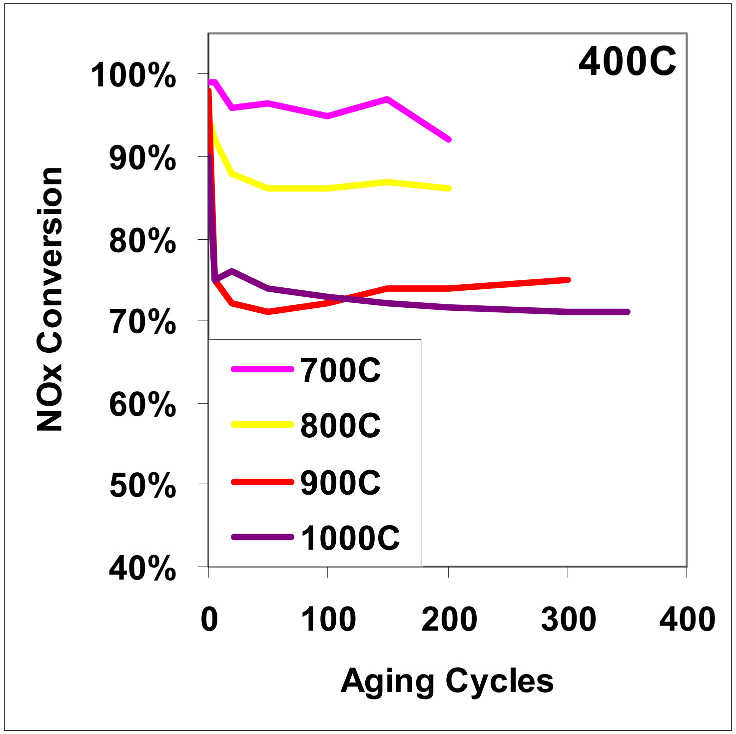


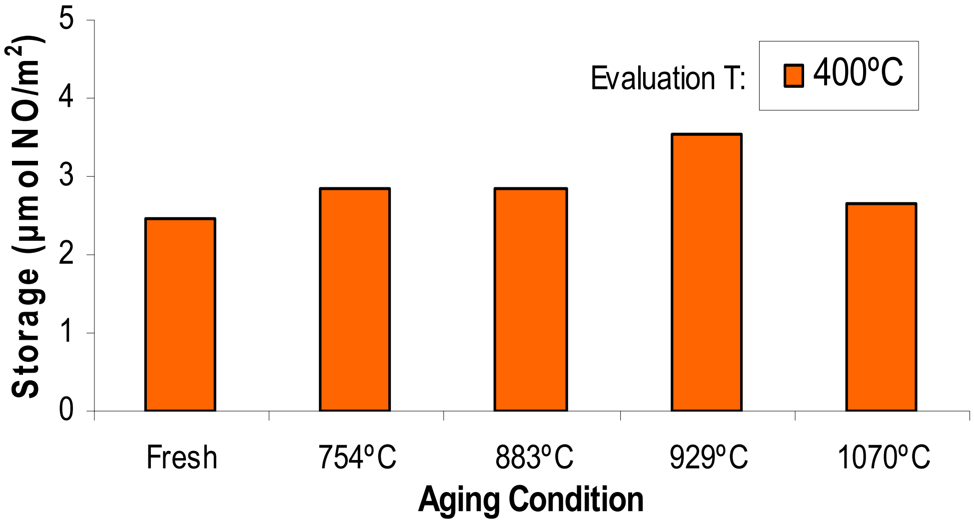


XRD Spectra of samples aged at indicated temperature

Thermal aging affects the chemical reactions of an LNT differently

- Overall performance decreases with aging
- However, not all LNT functionality decreases
- What materials effects change the functionality?





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Effects of Aging on LNT functionality:

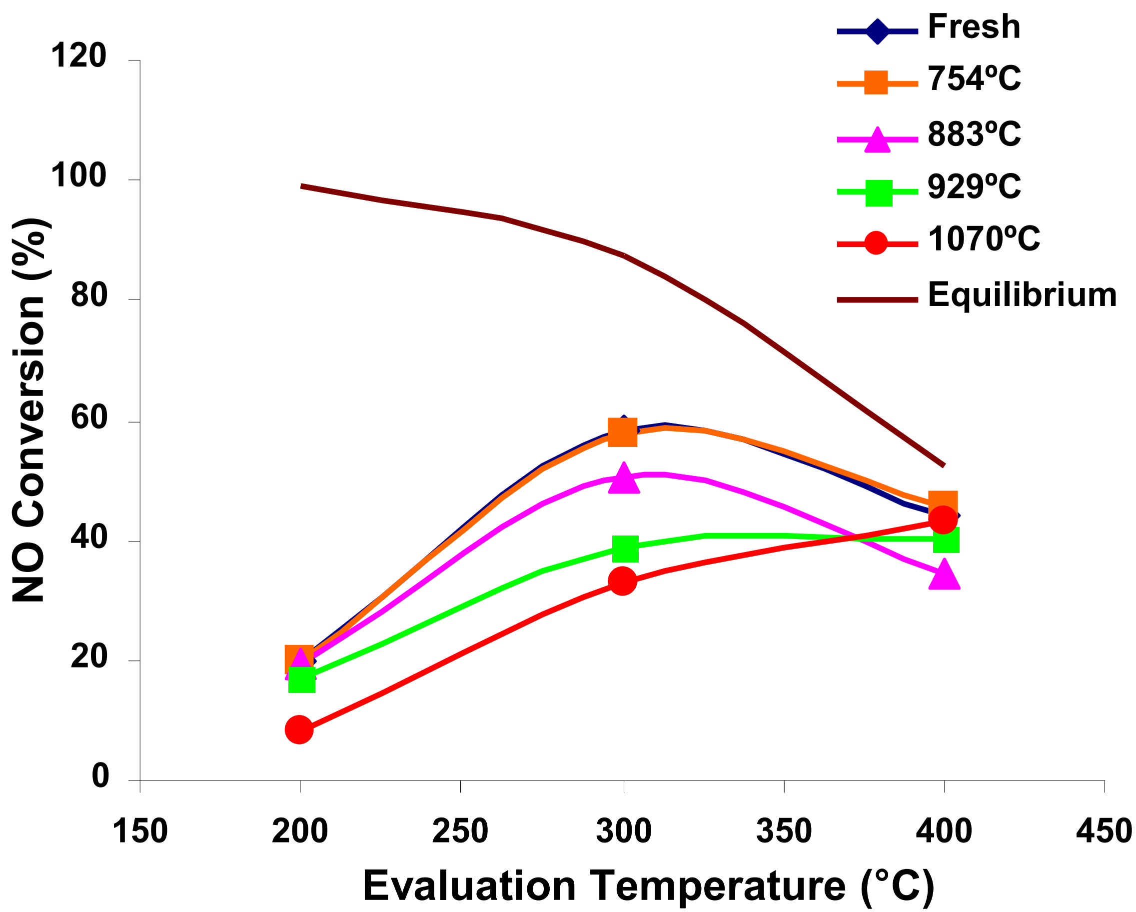
NO Oxidation

NO_x Storage

NO_x Reduction

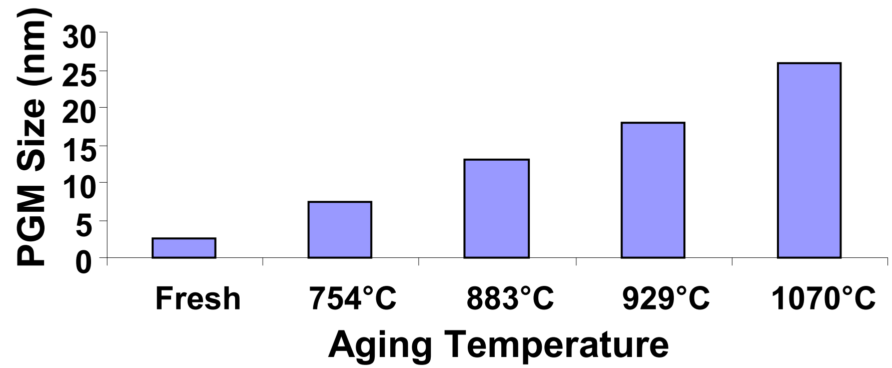
Overall NO oxidation rate decreases

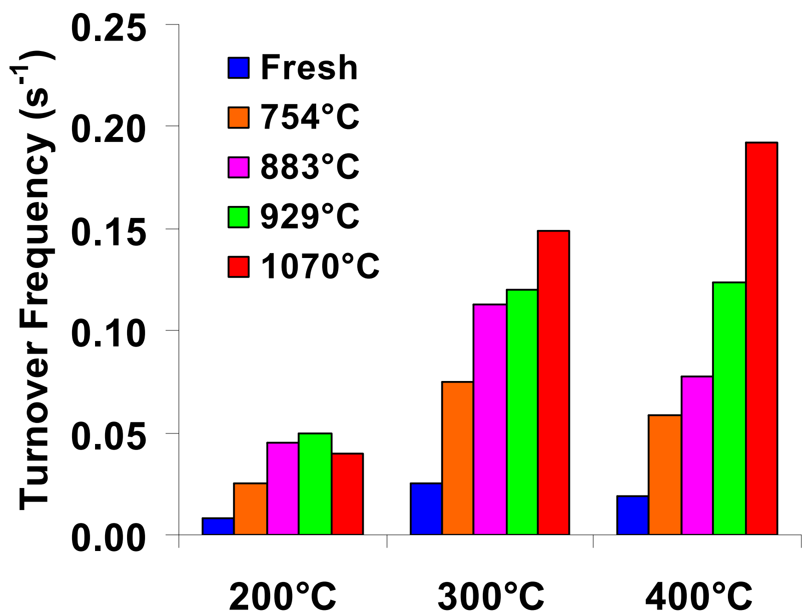
- NO oxidation measured after measuring total NOx storage capacity
- NO oxidation at 200 and 300°C decreases with aging temperature
- Approximately constant at 400°C
  - Equilibrium limited



Although NO oxidation decreases, the effectiveness of the PGM increases

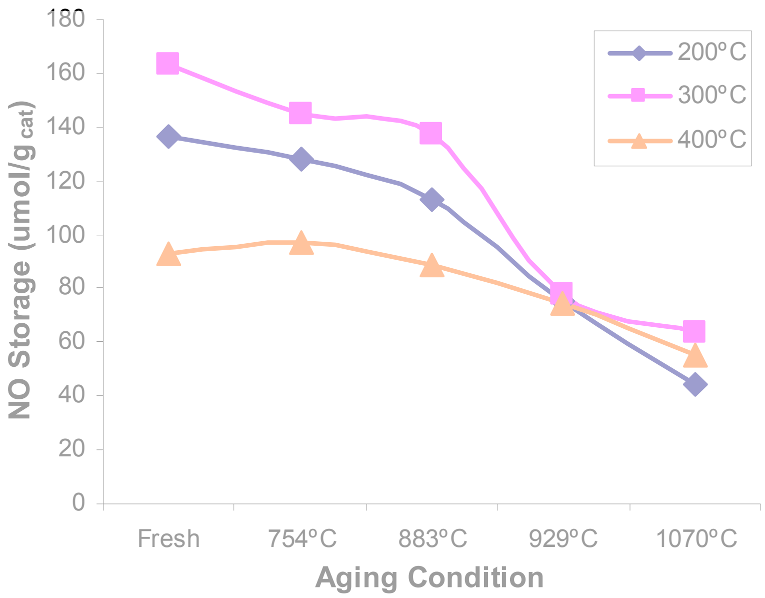
- Ten-fold increase in average PGM size after aging at 1000°C
- NO conversion *per PGM$_s$* increases at all evaluation temperatures
  - 0.02 to 0.2 s^{-1} at 400°C
  - mol NO/mol PGM$_s$/s → s^{-1} (TOF)
  - TOF : turnover frequency
- Qualitatively illustrated by Olsson et al.
  - *L. Olsson, E. Fridell, Journal of Catalysis 210 (2002) 340.*





NOx storage capacity effects

- Maximum NO_x storage capacity at 300°C
- Storage decreases per gram of catalyst at higher aging temperatures



Nitrates adsorb on Al_2O_3- and Ba-phases; Fewer Al_2O_3 nitrates after aging at 900°C

- Fresh sample: Significant fraction of nitrates stored on Al_2O_3; ~25% by peak area
- Aging to 900°C reduces Al_2O_3 peak height/area
  - corresponds to reduction in exposed Al_2O_3 surface
- Ba nitrates not as affected by aging
  - Ba could be re-dispersing and covering γ-Al_2O_3

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

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

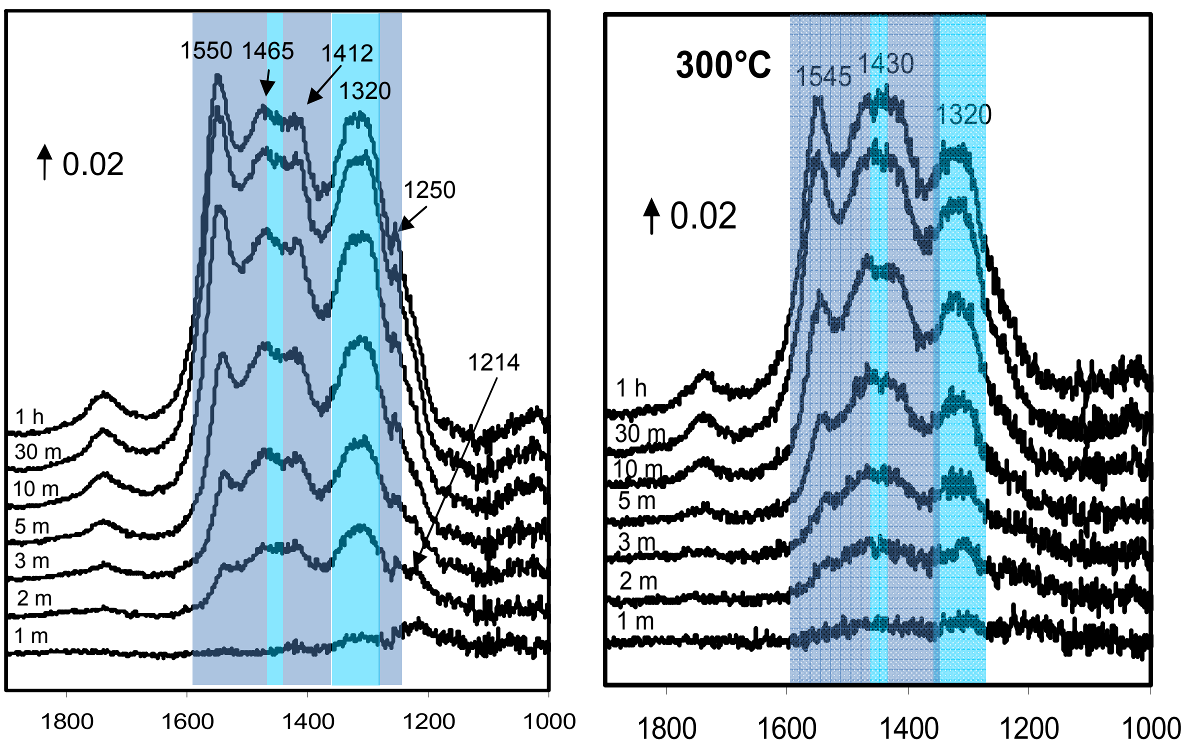
$Ba(NO_3)_2$
• 1320 and 1430

$Ba(NO_2)_2$
• 1215

<u>Flow Conditions</u>

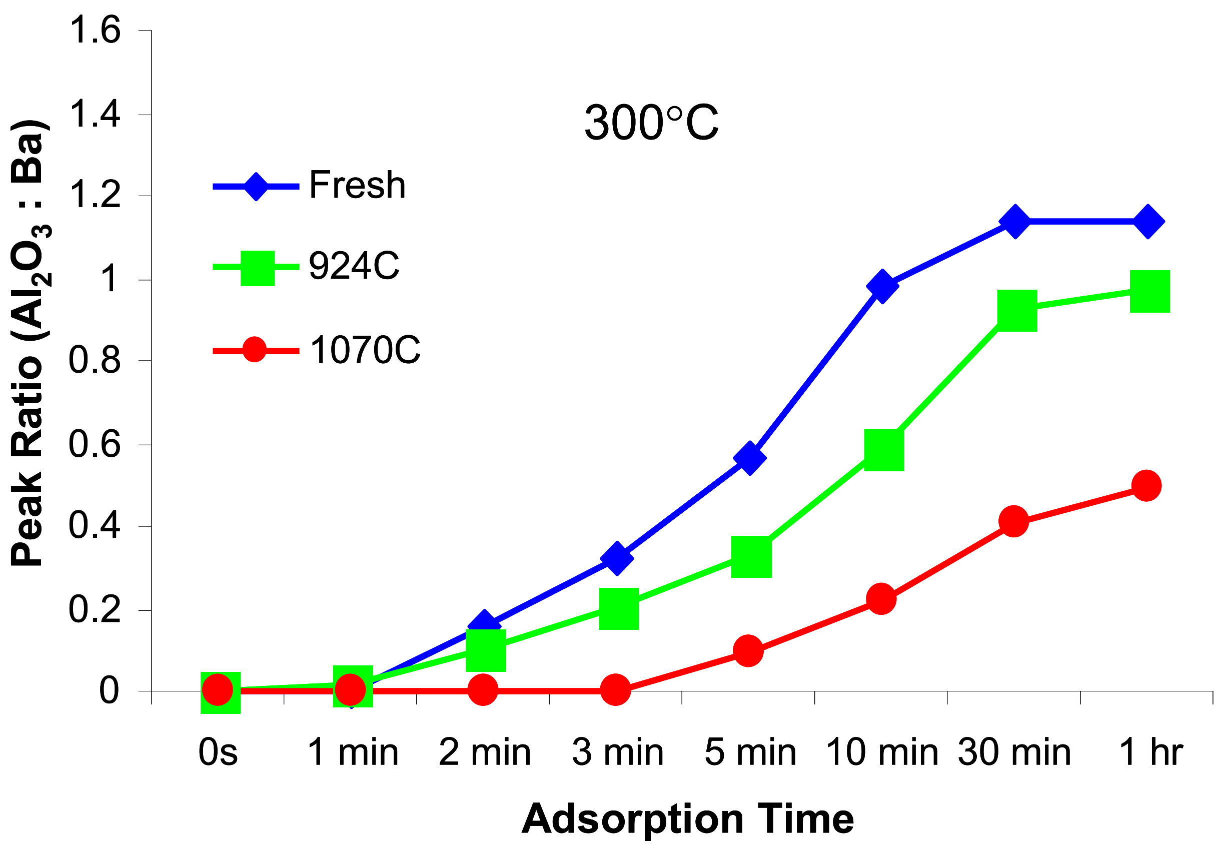
• 300 ppm NO, 10% O_2, and Ar bal.

Fresh   Aged at 900° C



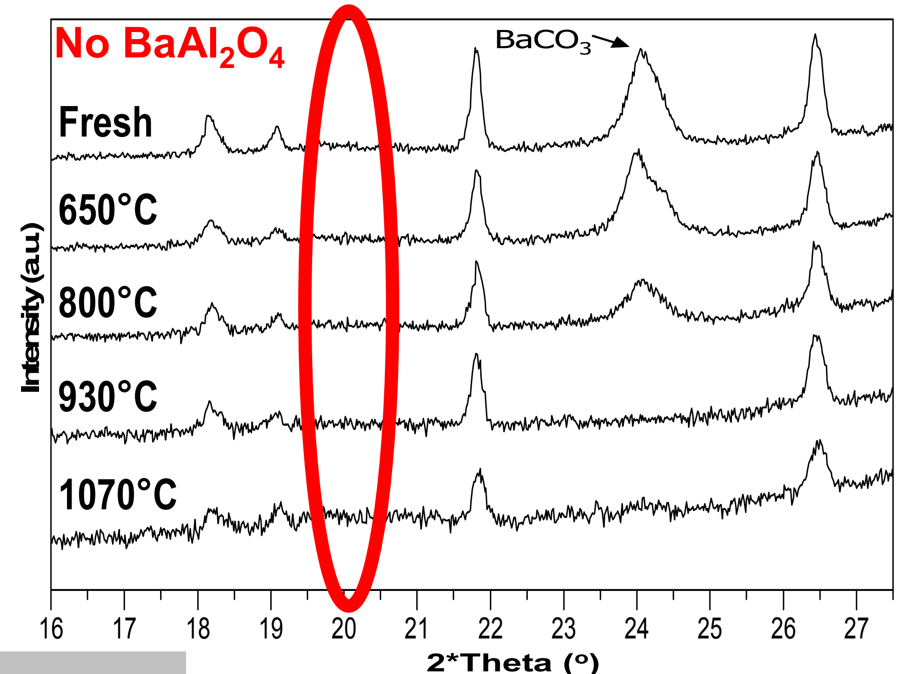
Ratio of peak heights illustrates decrease in Al_2O_3 nitrates

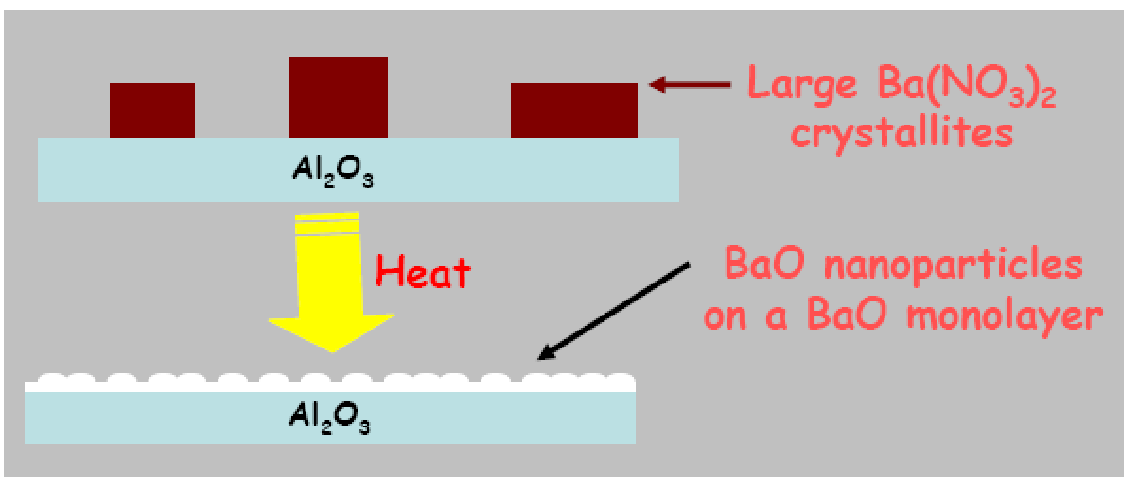
- Peak height ratios of Al_2O_3 nitrate and $Ba(NO_3)_2$ peaks
  - 1550 and 1430 cm^{-1}, respectively
- Decrease in peak ratio above 900°C



XRD and DRIFTS results suggest Ba dispersion occurring on aged samples

- 200 and 300°C
  - Reductions in NO_x storage when aging at T > 900°C largely due to loss of Al_2O_3 nitrates
    - Possible Ba dispersion
  - Ba-nitrates much less affected by aging





- Evidence of this previously reported on model catalyst systems
  - *Peden et al. CLEERS Workshop #9, 2005*

Al_2O_3 nitrates not stable at 400°C

- No formation of nitrates on Al_2O_3
- LNT is saturated after 30 min of NO exposure
- 400°C
  - Storage affected only by Ba sites

Peak Assignments (cm^{-1})

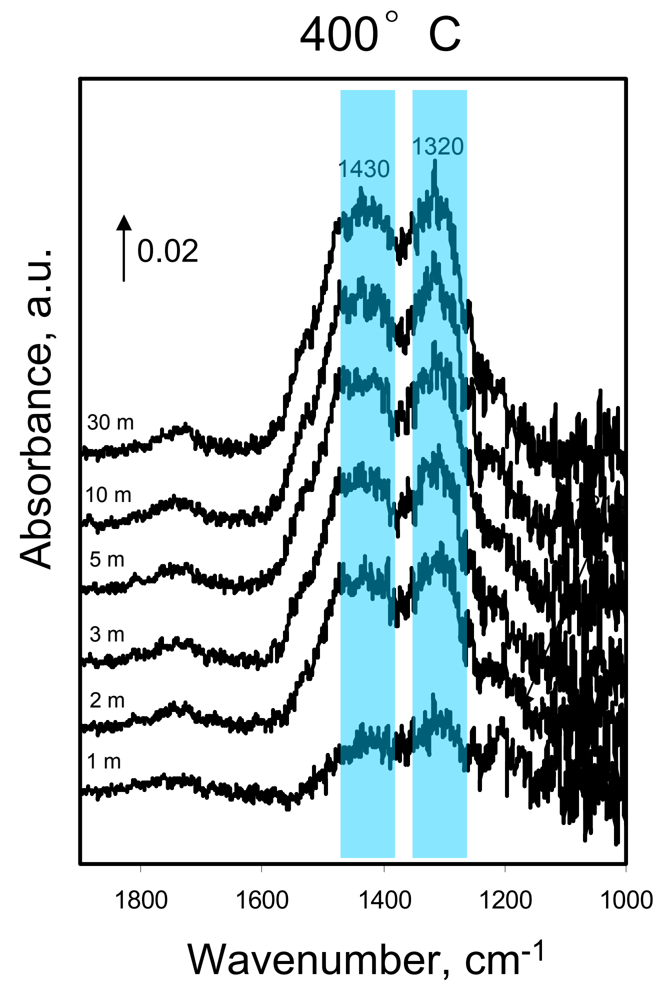
γ-Al_2O_3-NO_3
• 1250, 1412, 1465, and 1550

$Ba(NO_3)_2$
• 1320 and 1430

$Ba(NO_2)_2$
• 1215

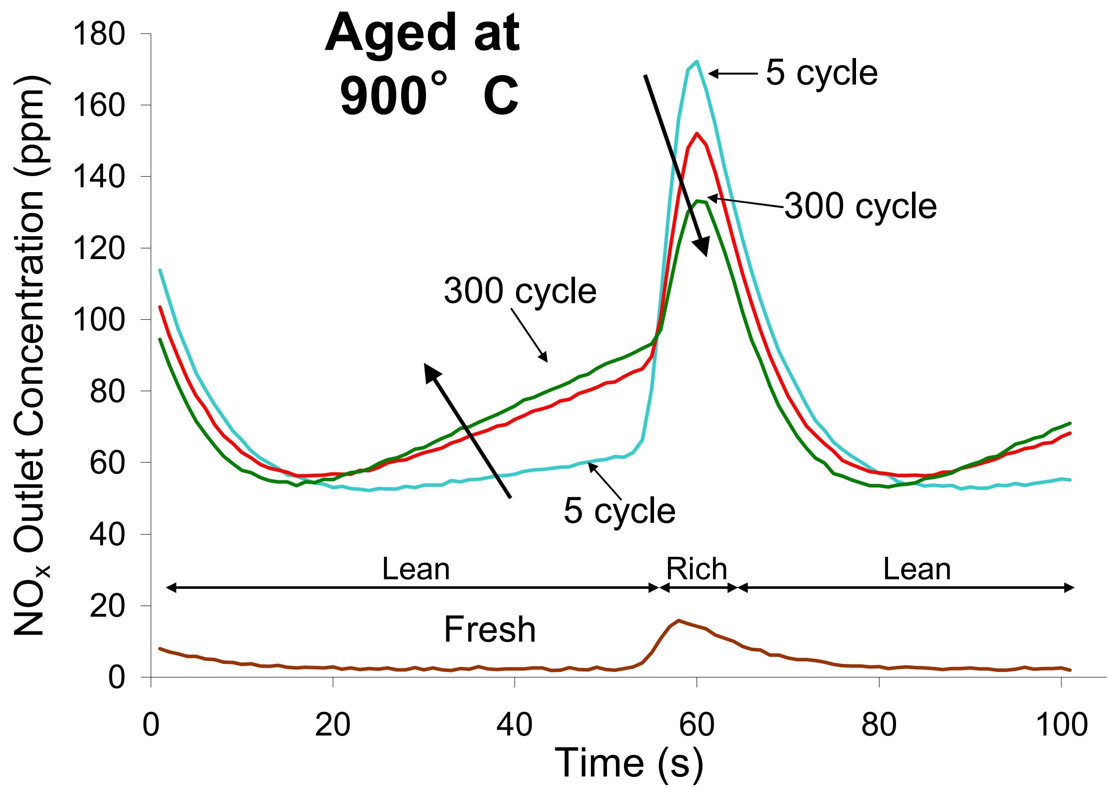
Flow Conditions

• 300 ppm NO, 10% O2, and Ar bal



Rich phase NO_x release (puff) decreases with aging when evaluating at 400°C

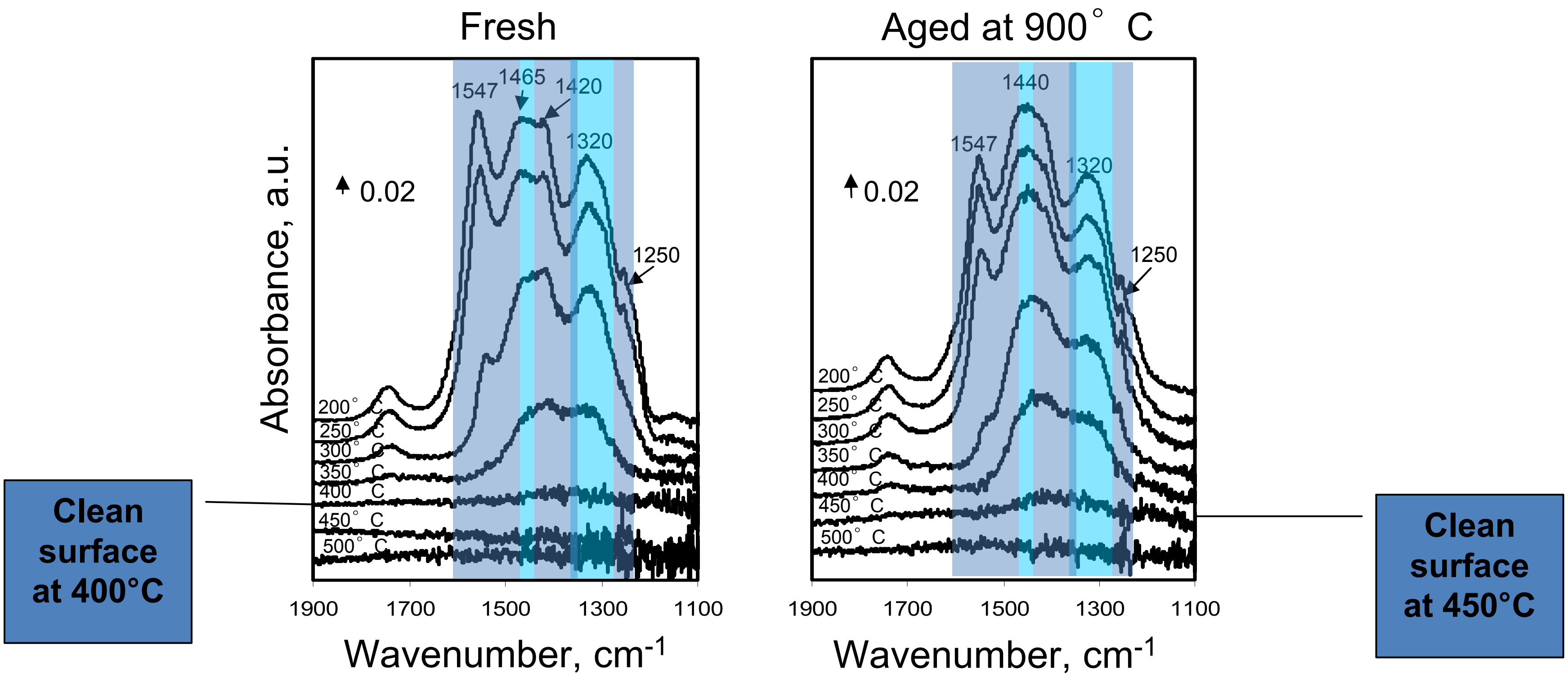
- **Storage Phase (60 seconds)**
  - NO_x slip increases with aging temperature and number of aging cycles
    - Capacity decreases
- **Reduction Phase (5 seconds)**
  - NO_x "puff" decreases with increasing # of aging cycles



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

Nitrates more stable after aging

- Fresh sample desorbs nitrates below 400°C
- Aging increases stability of nitrates by ~ 50°C
  - Suggests Ba redispersion influences Ba-nitrate stability
  - Possible Ba-support interaction

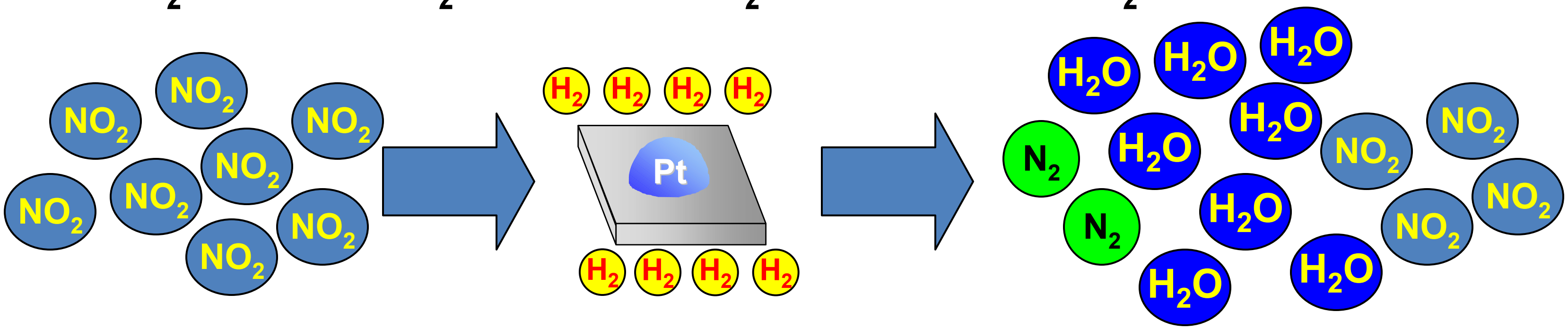


Storage: 300ppm NO, 10% O_2, Ar bal., 200° C
TPD: 100% Ar

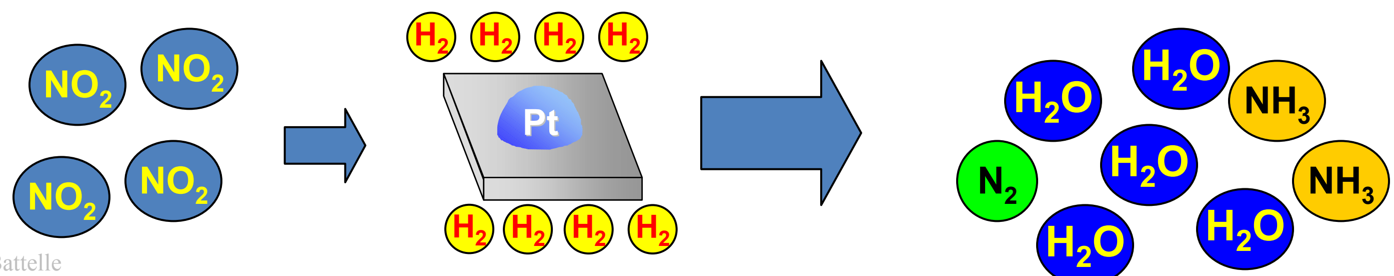
Stable nitrates would also release slower under rich conditions

- The higher the nitrate stability the slower the release of NOx and the more likely that it will react with reductants
  - Leading to smaller NO_x puff
- Depiction of release scenarios and their impact on selectivity:

Fast NO_2 release…NO_2 overwhelms H_2 at Pt surface…NO_2 released in exhaust



Slow NO_2 release…H_2 overwhelms NO_2 at Pt surface…NH_3 formation possible



Conclusions

- Thermal aging of LNT has numerous material and chemical effects
  - Generally, all reaction rates decrease on a mass basis
  - Efficiency of catalysts improve for some steps
- Aging results in improved nitrate stability
  - Effects performance and NH_3 formation
- Evidence of Ba re-dispersion observed after thermal aging
  - Al_2O_3 contribution to NOx storage and reduction minimized

Acknowledgements

- Funding provided by U.S. Department of Energy (DOE) Vehicle Technologies Program – Kevin Stork
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- STEM/EDS performed as a user center proposal at ORNL's High Temperature Materials Laboratory (HTML)

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ADDITIONAL SLIDES

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

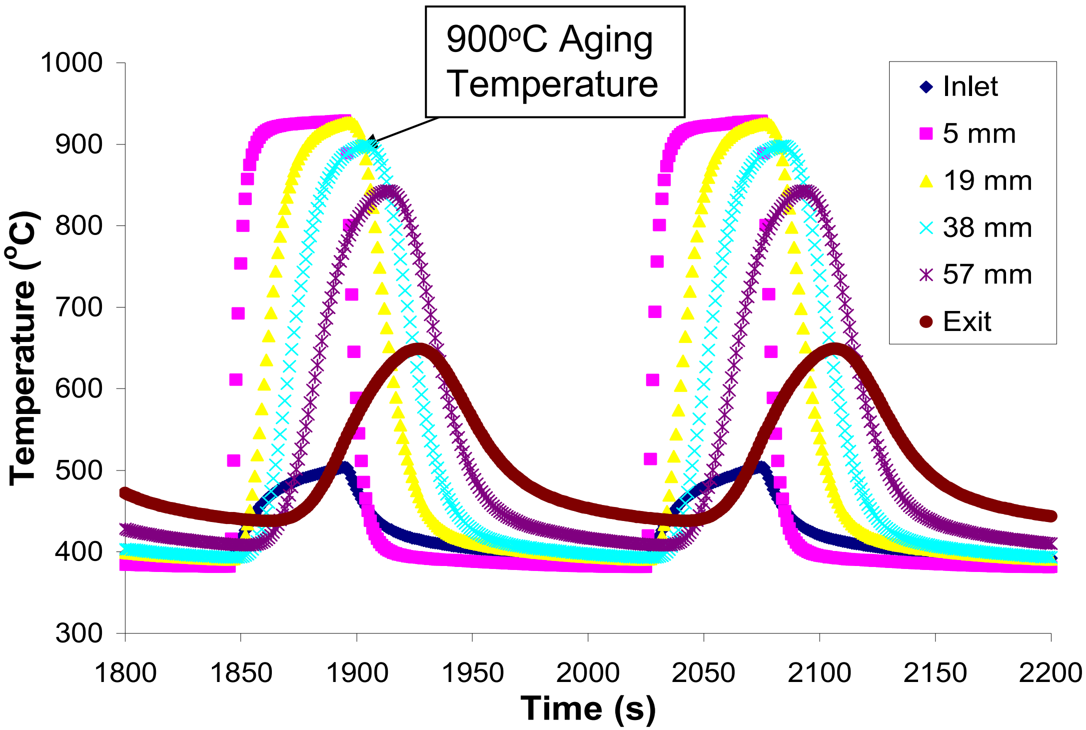
at FEERC

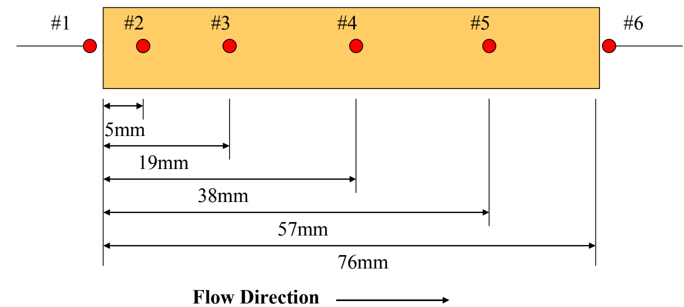
STEM/EDS

- PGM Particle Size

at HTML

Thermal-Aging with Exotherm in a Furnace





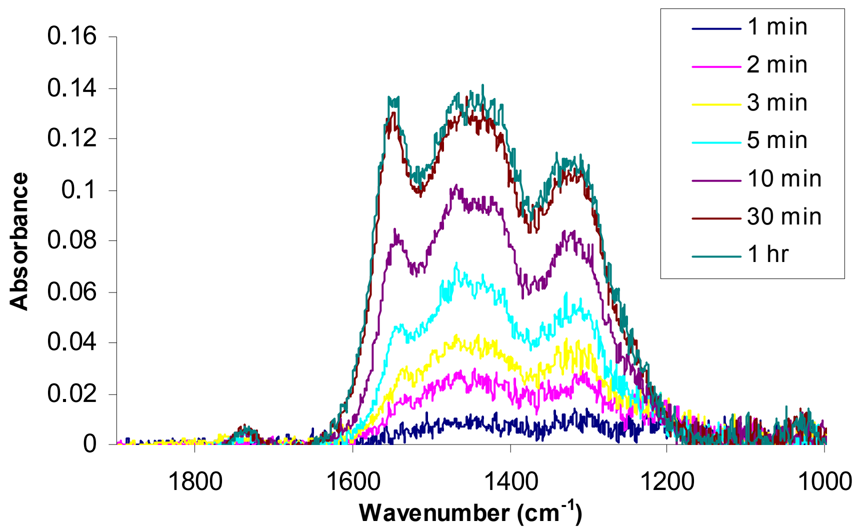
	Lean (130s)	Rich (50s)
NO_x	**300 ppm**	**300 ppm**
CO_2	**5%**	**5.00%**
CO	**0**	**5.10%**
H_2	**0**	**3.25%**
O_2	**11%**	**4.00%**
H_20	**4.2%**	**4.20%**
N_2	**balance**	**balance**

- **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**

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**

Peak Assignments (cm^{-1})

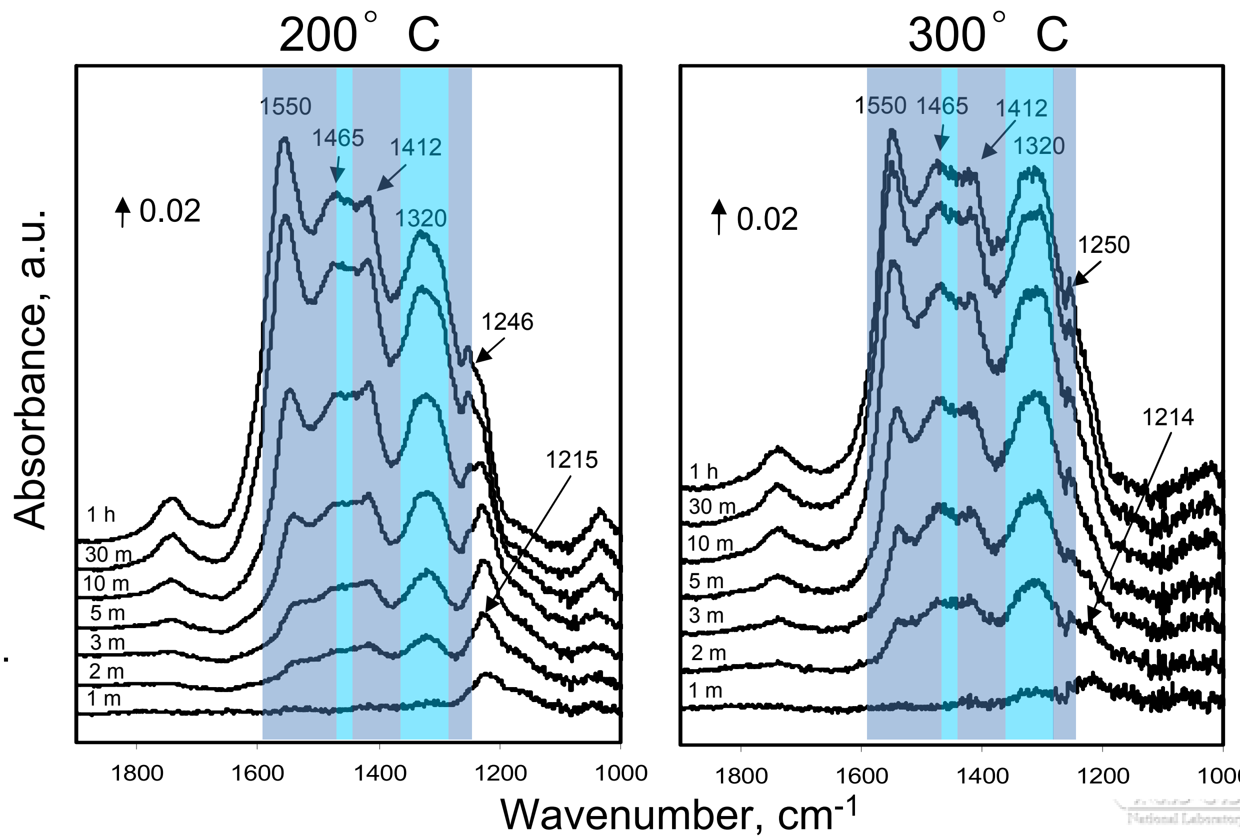
γ-Al_2O_3-NO_3
- 1250, 1412, 1465, and 1550

$Ba(NO_3)_2$
- 1320 and 1430

$Ba(NO_2)_2$
- 1215

Flow Conditions

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



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

Peak Assignments (cm^{-1})

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

$Ba(NO_3)_2$
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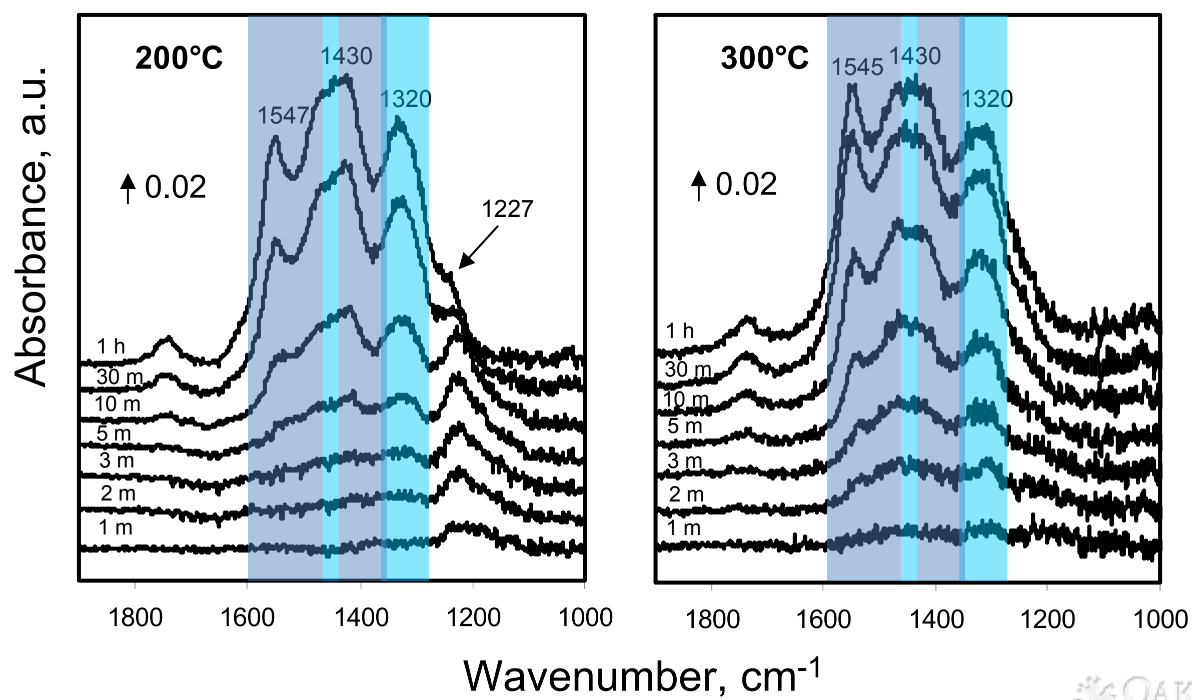

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Further Reduction in Al_2O_3 Nitrates After 1000°C Aging

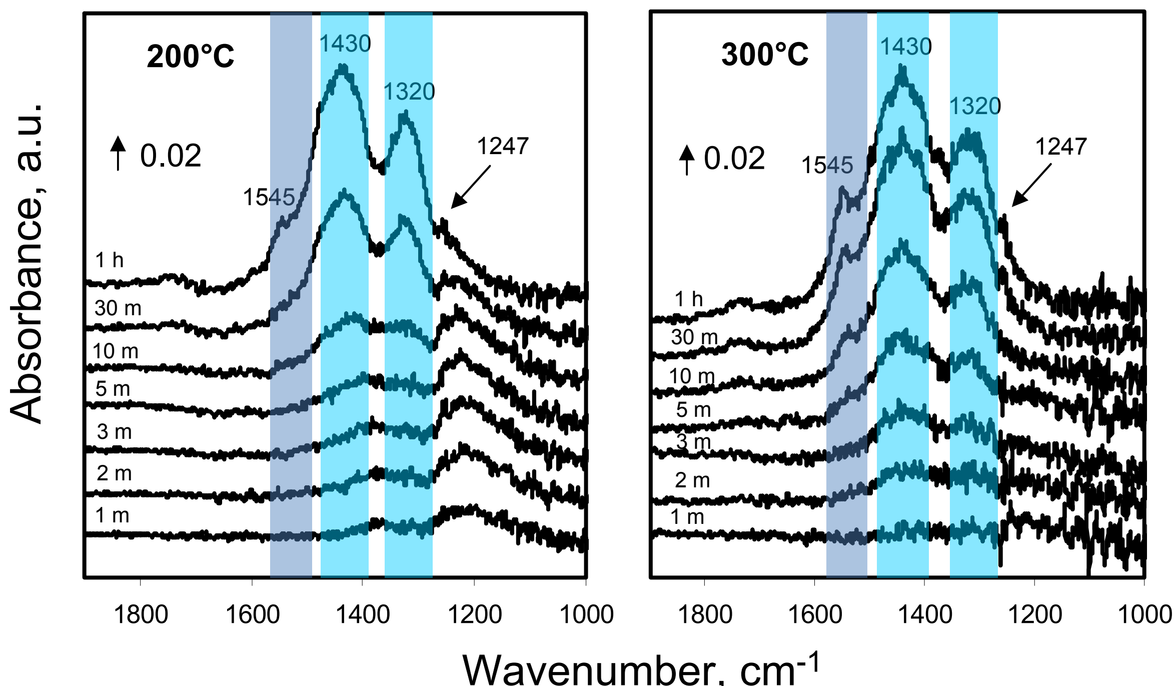
- Almost complete loss of γ-Al_2O_3 NO_x storage sites
- Ba sites appear not to be as affected by aging
  - $Ba(NO_3)_2$ peak at 1430 cm^{-1} is now clearly visible

Peak Assignments (cm^{-1})

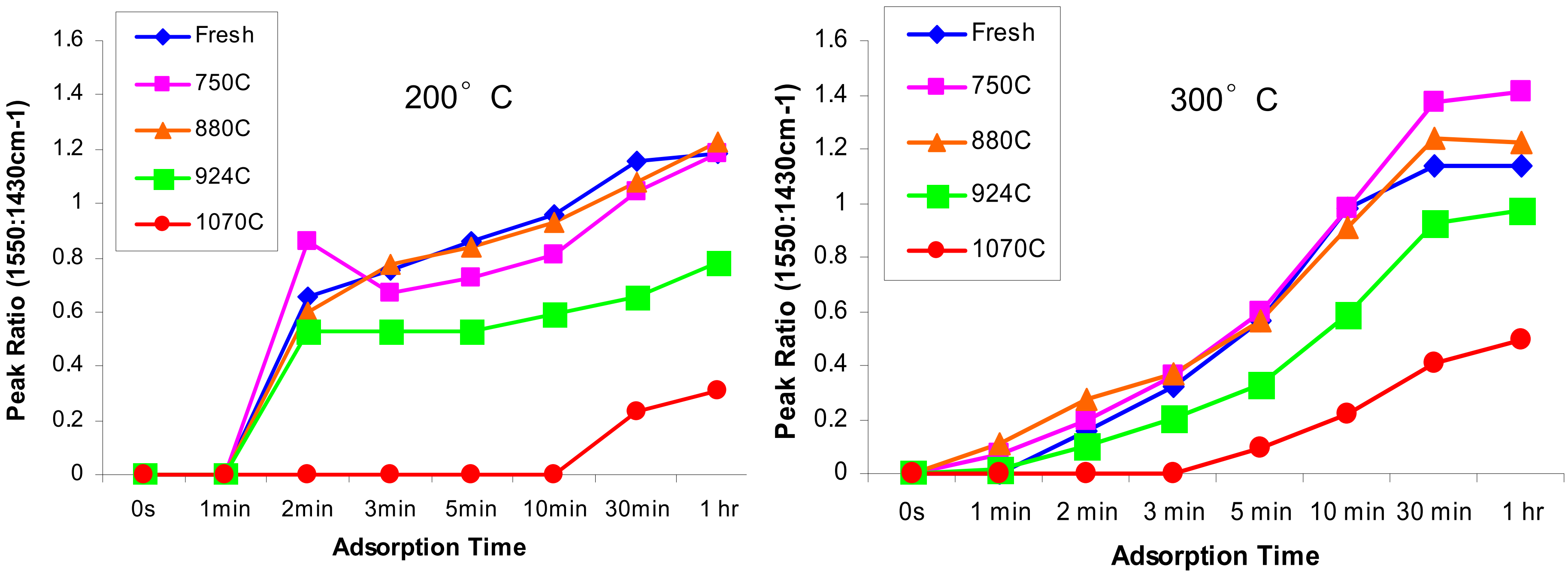
γ-Al_2O_3-NO_3
- 1250, 1412, 1465, and 1550

$Ba(NO_3)_2$
- 1320 and 1430

$Ba(NO_2)_2$
- 1215



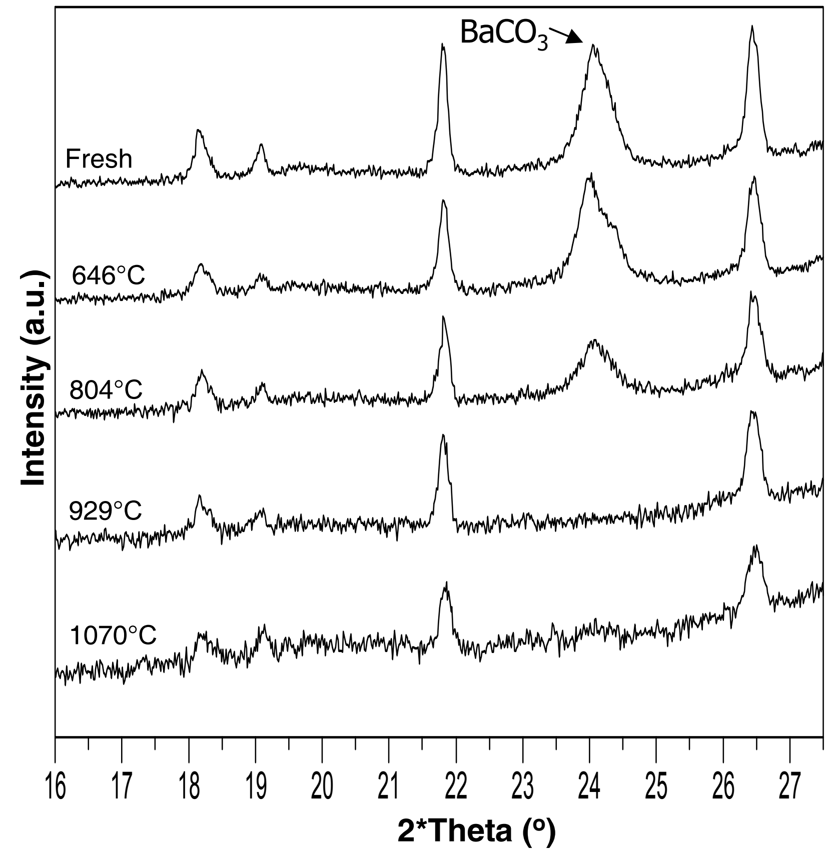
Effect of Aging on Al_2O_3 Nitrates Not Seen at 700 or 800°C



- 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

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

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

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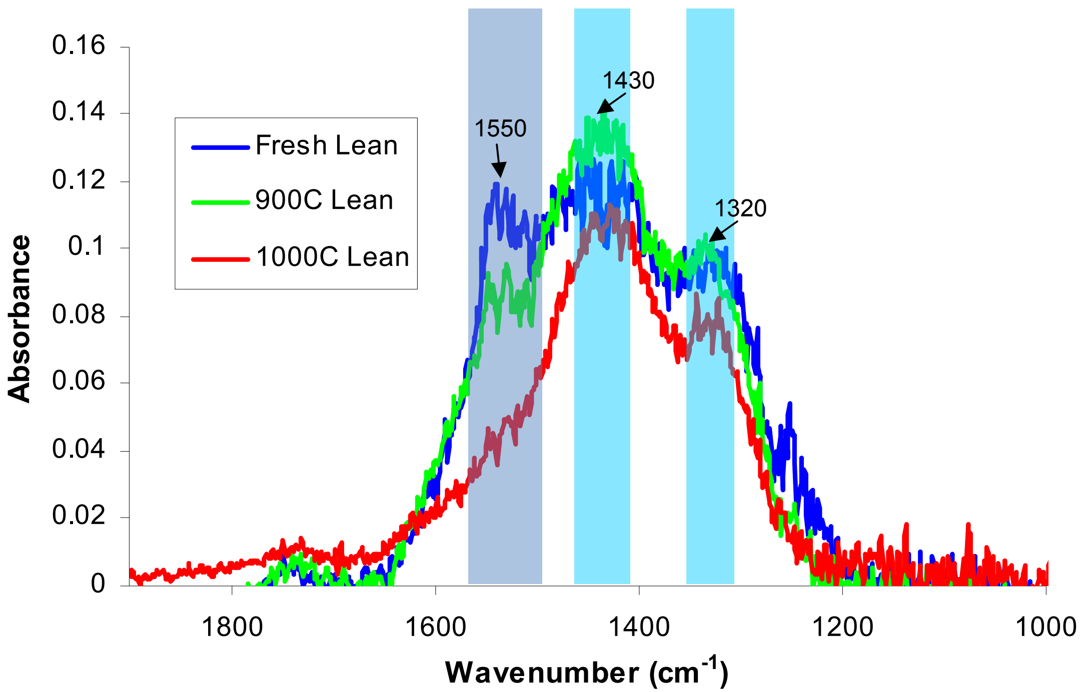

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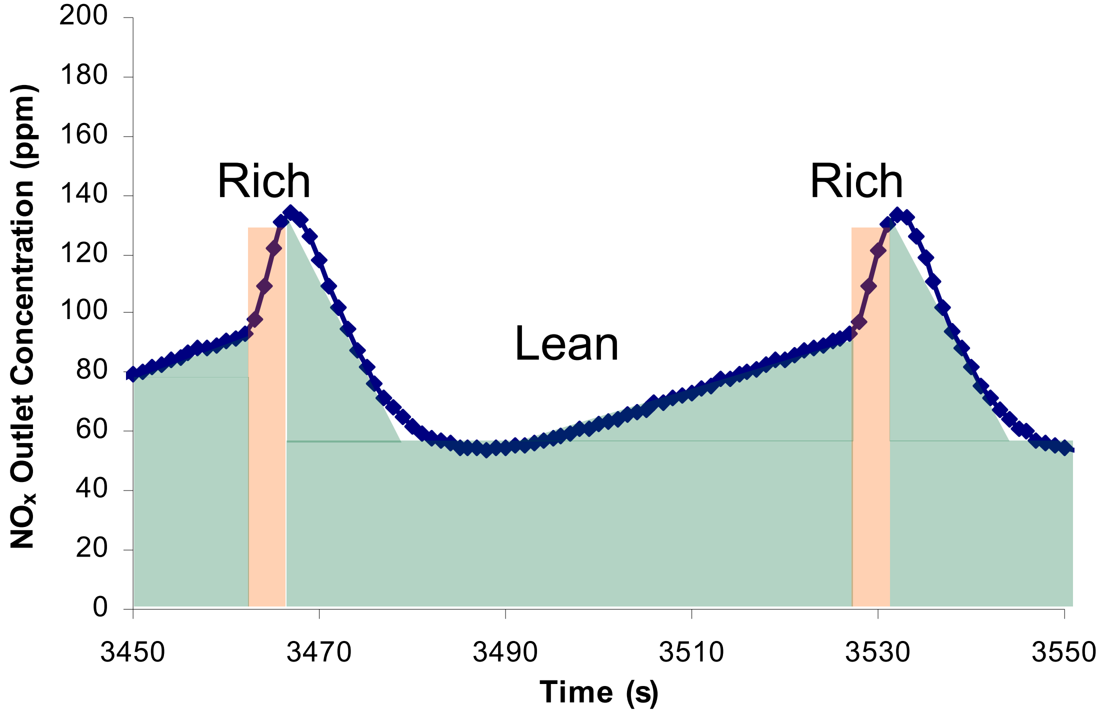
Rich (30s): 300 ppm NO, 5% CO_2, 5% H_2O, 1.13% CO, .68% H_2, N_2 bal

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

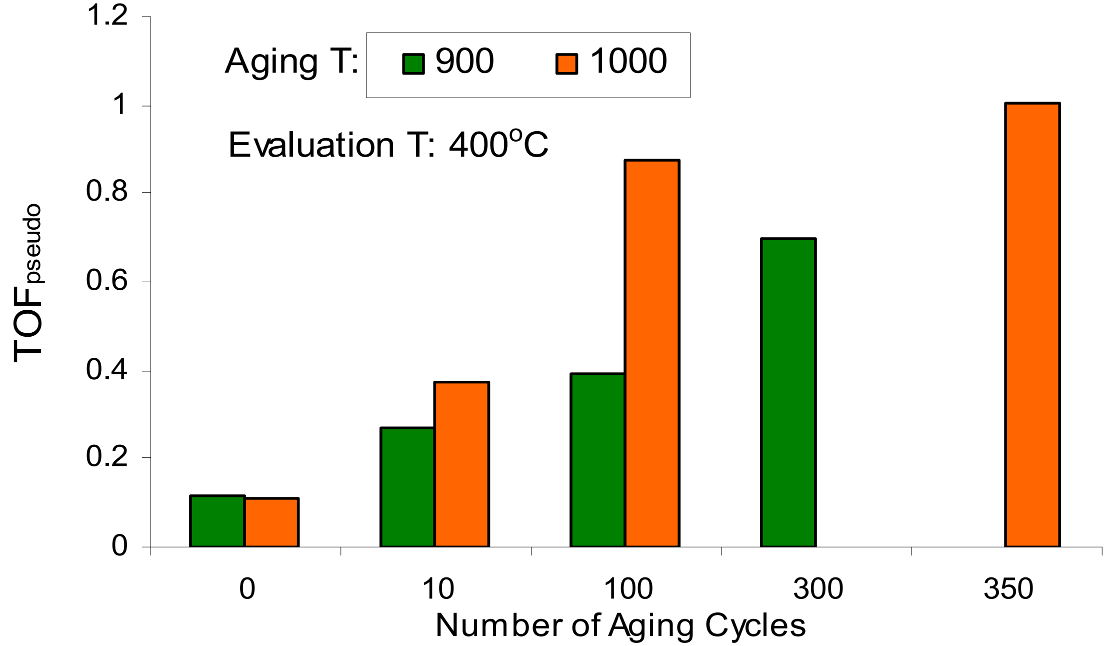
$$TOF_{pseudo} = \frac{NO_x \, \mathrm{Re}\, leased_{rich\_cycle}}{NO_x Stored_{lean\_cycle} * molPGM_s}$$



Aging improves reduction efficiency

- NO_x that is released is reduced more efficiently after aging
- This is observed even though the PGM surface is decreasing
- A pseudo turnover frequency (TOF) illustrates this relationship

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



GHSV: 30,000 hr^{-1}
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Rich (5s): 300 ppm NO, 5% CO_2, 5% H_2O, 1.13% CO, 0.68% H_2