Lean NO_x Trap Chemical Behavior and Deactivation Effects of Temperature and Sulfur

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November 2004

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Objective

- **Determine model catalyst chemical storage behavior between 150 and 400C**
  - **Identify key reaction steps for model**
- **Investigate regeneration behavior**
  - **Determine limitations and key steps**
- **Inspect thermal deactivation effects**
  - **NO_x capacity**
  - **Catalyst regeneration**
  - **Precious metal sintering**

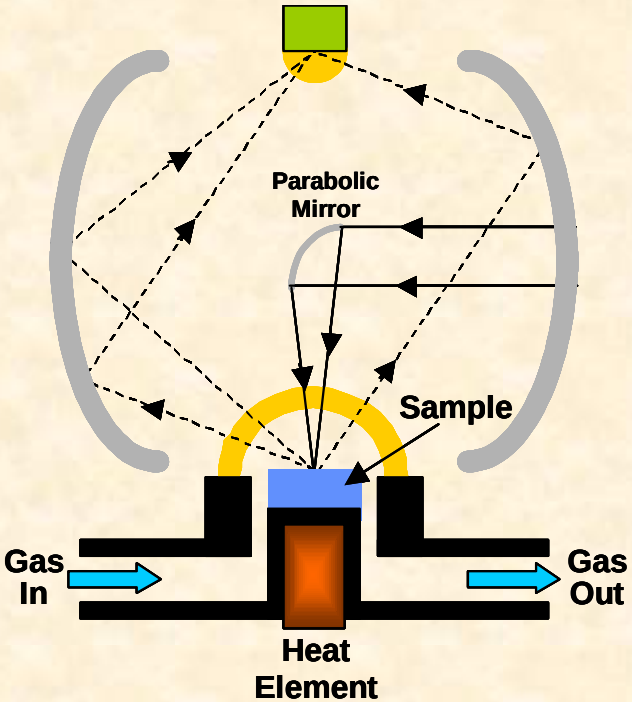
Approach

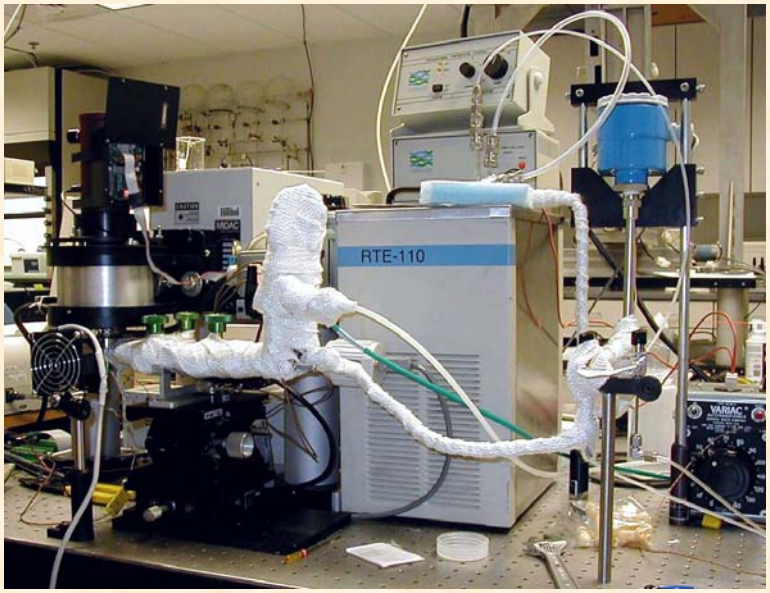
- **Two model powder catalysts studied**
  - **Pt/K/Al_2O_3: 1% Pt, 8% K_2CO_3 on γ-Al_2O_3**
    - **Also studied Al_2O_3, Pt/Al_2O_3, and K/Al_2O_3**
  - **Pt/Ba/Al_2O_3: 1% Pt, 20% BaO on γ-Al_2O_3**
  - **~50-100 g Pt/ft^3 equivalent**
  - **Some data on Englehard's model LNT (LI-10-19)**
    - **150 g PM/ft^3 (14:1 Pt:Rh), Ba/γ-Al_2O_3**
- **Multiple techniques employed**
  - **DRIFTS: surface species investigation**
  - **Physisorption/Chemisorption: Pt size, catalyst surface area, static and flowing LNT capacity**
  - **Mass Spectrometry: effluent speciation**

NO_x Storage Discussion on $Pt/K/Al_2O_3$

DRIFTS with High Sensitivity

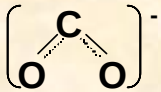
- *In situ* DRIFTS measurements
  - Catalyst temperature up to ~530°C
  - Heated lines for up to 10% H2O
- MIDAC FTIR spectrometer
  - 2 Hz scan rate; 2 cm^{-1} resolution
- Harrick Barrel Ellipse DRIFT accessory
  - Design increases signal and sensitivity
- Chemisorption calibrates DRIFTS
  - Standards obtained to determine DRIFT response factors

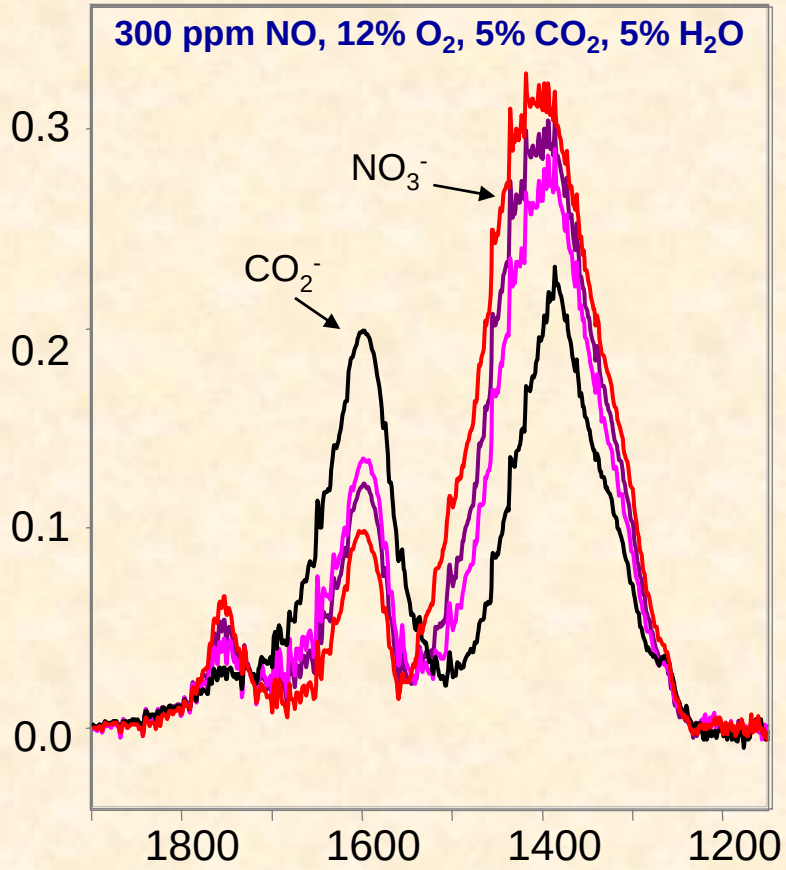




NO_3^- and CO_2^- Dominate $Pt/K/Al_2O_3$

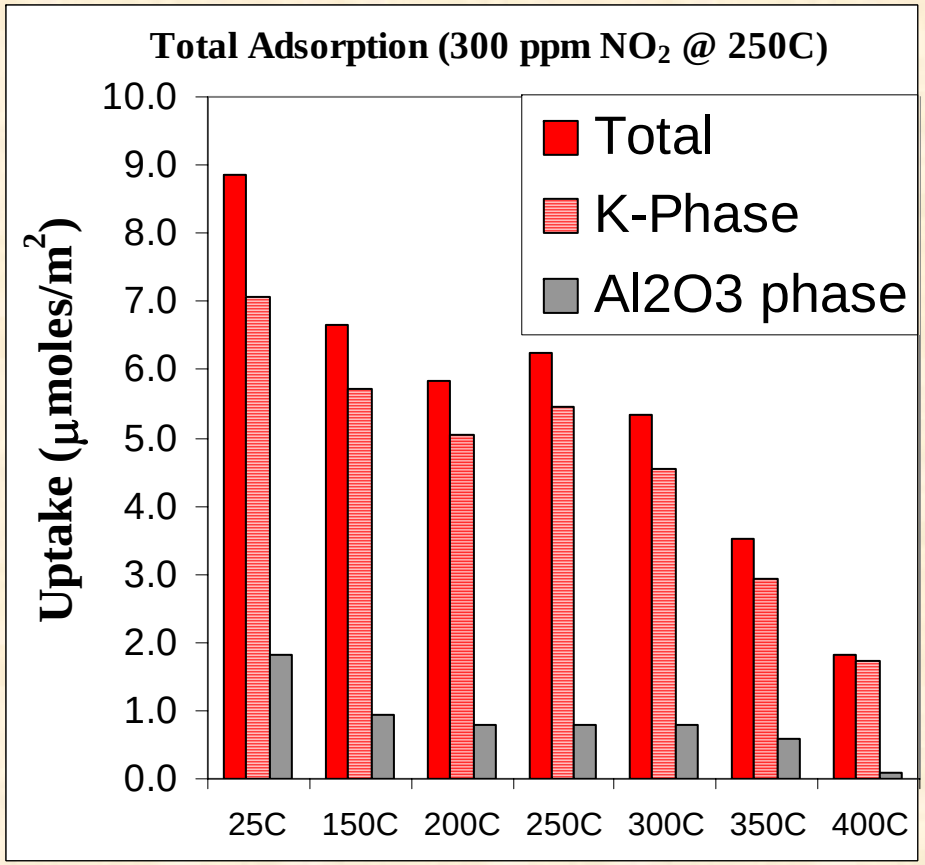
- **Measurements with H_2O and CO_2**
  - **H_2O spectra subtracted**
- **Al_2O_3-based nitrates unstable in H_2O**

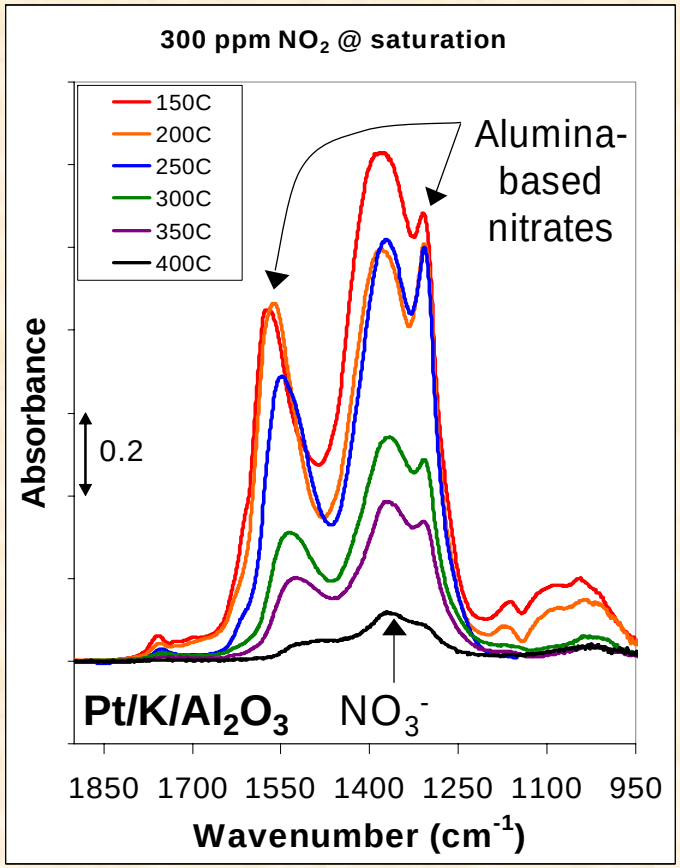
Peak Position	Infrared Stretch	Structure
1750	combination bands	n/a
1600	COO^- asymmetric	
1310	COO^- symmetric	
1510	N=O & NO_2 asymmetric	Al_2O_3 nitrates
1260	NO_2(a)symmetric	
1380	free nitrate ion	NO_3^-
1250	free nitrite ion	NO_2^-



NO_x stored as NO_3^- at All Temperatures

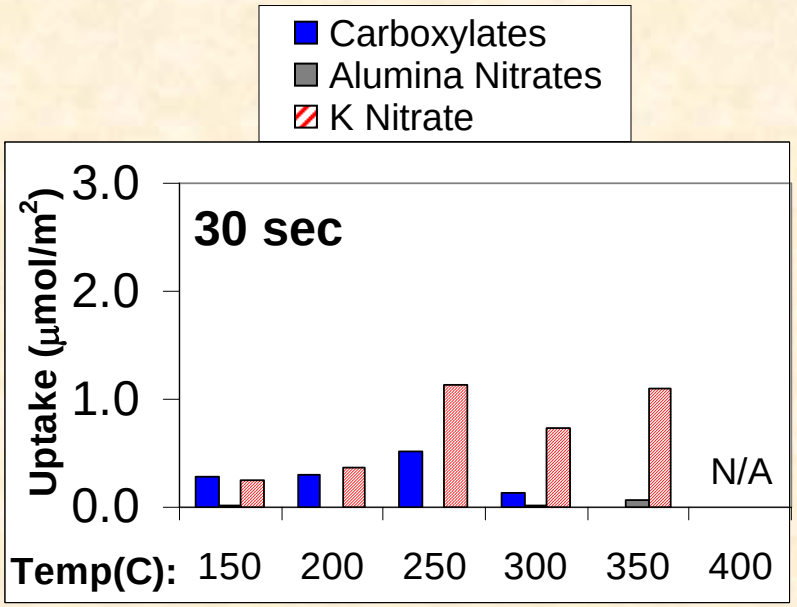
- **Potential Storage Decreases above 150C for K-based**
  - **Relatively Stable for Ba-based**
- **Temperature does not effect nature of trapped NO_x**

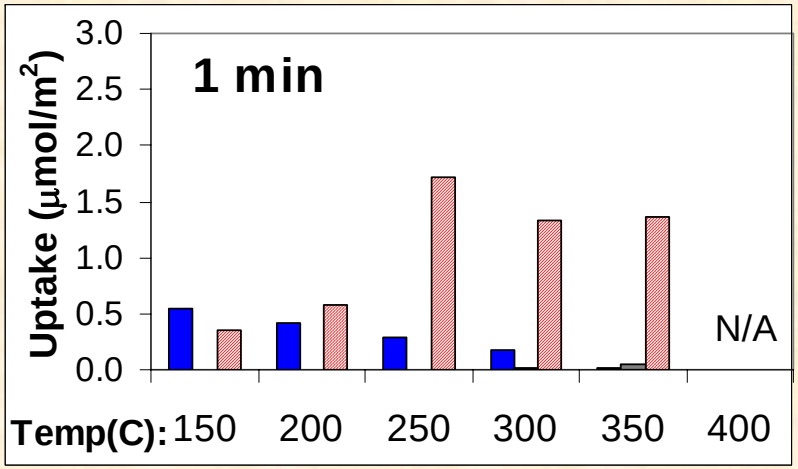


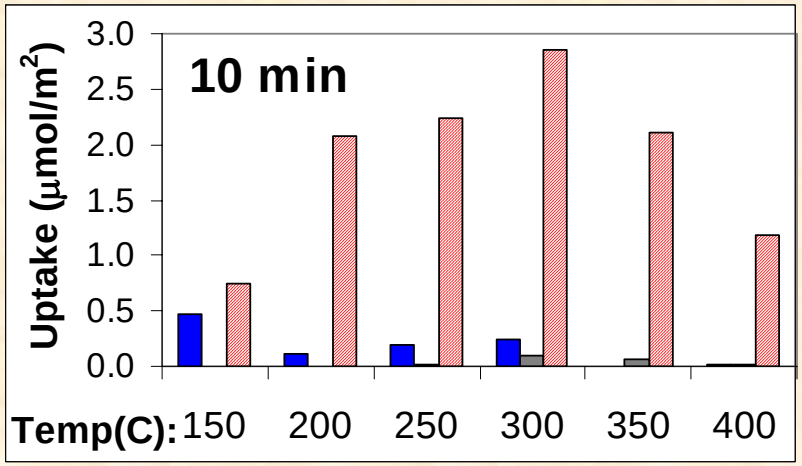


Kinetics Control Adsorption

- **Results for 300ppm NO, 12%O_2, 5% CO_2, and 5% H_2O**
- **Potential is not realized at lower temps due to kinetic limitations**
- **At higher temps adsorption is within 70% of saturation after 10 minutes**

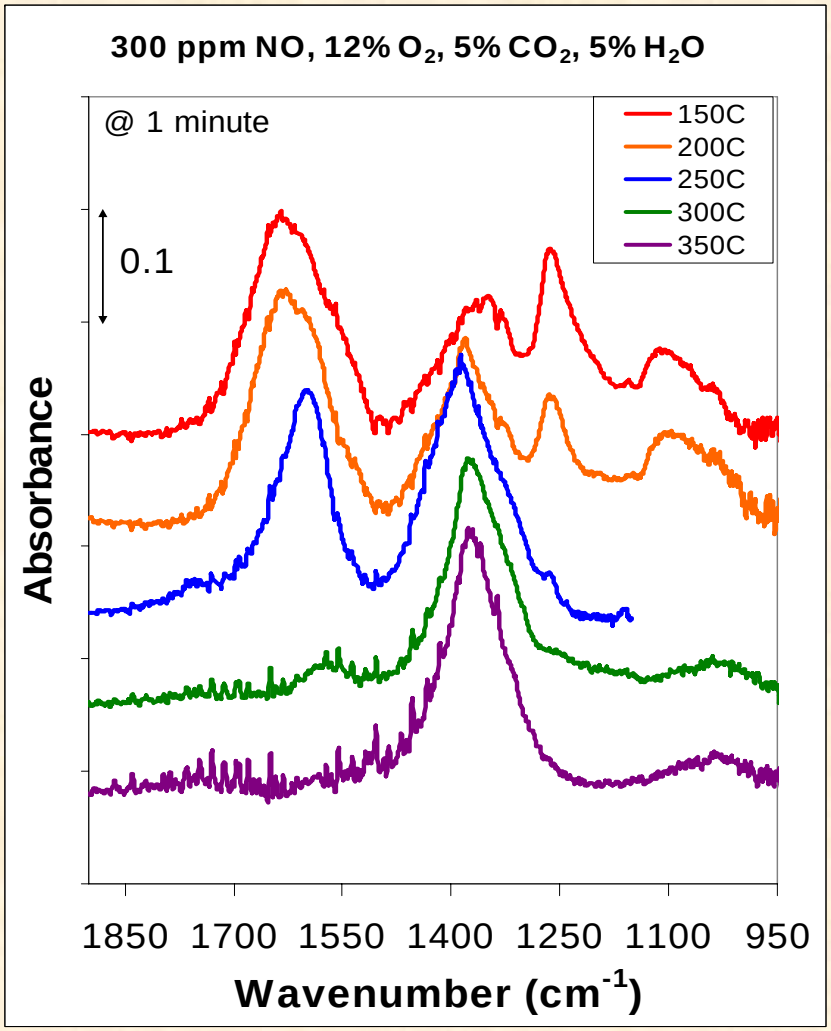






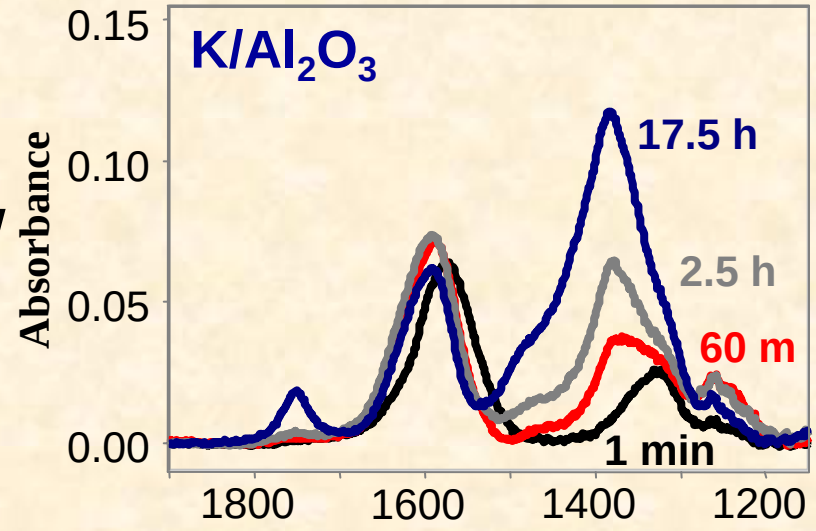
NO Adsorbs on Sites near Pt

- **NO adsorption not observed on K/Al_2O_3**
- **Nitrites observed when Pt is poor oxidizer of NO**
  - **NO surface presence high**
  - **Eventually converted to nitrates since saturated form is same for all T**
- **<u>Conclusion</u>: NO only adsorbs on sites near Pt**
  - **Unoxidized NO forms nitrite**
  - **Nitrites oxidized to nitrates**
  - **Not significant above 200C**

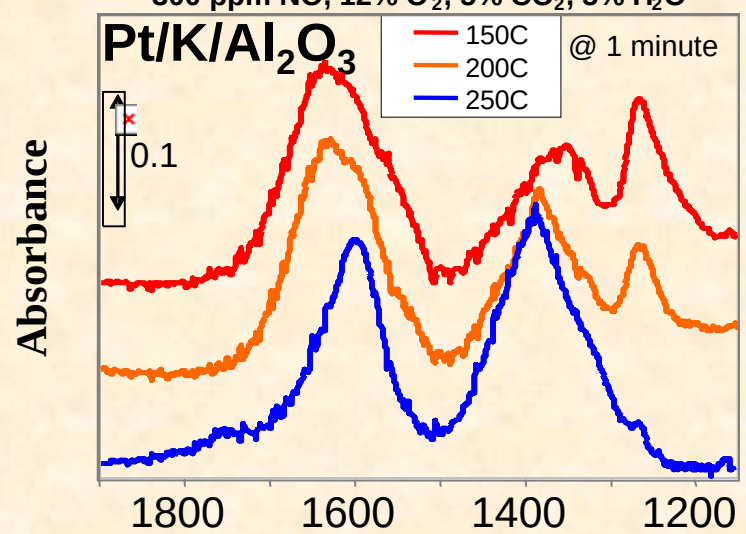


NO_2 Stored Through Two Routes

- **Nitrites not observed on K/Al_2O_3 with NO + O_2**
  - **Even when adsorption is slow**
  - **NO_2 does not adsorb as a Nitrite**
- **NO_2 is stored near Pt sites as an ionic nitrate through "spill over" route**
- **NO_2 also stored on isolated Potassium sites through disproportionation reaction**
  - **Simulations support conclusion**
  - **Not yet verified with DRIFTS reactor**



300 ppm NO, 12% O_2, 5% CO_2, 5% H_2O



Key Steps in $Pt/K/Al_2O_3$ Storage

- **NO only adsorbs on sites near Pt**
- **NO_2 does <u>not</u> adsorb as a nitrite**
- **NO_2 "spills-over" from Pt**

  $$K_2O + 2NO_2 + Pt\text{-}O \leftrightarrow 2KNO_3 + Pt$$

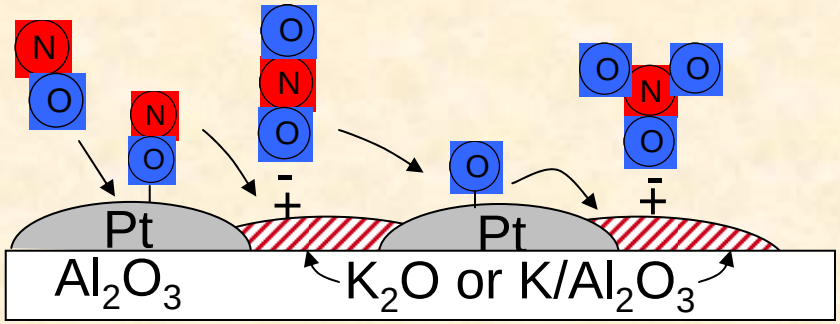
- **Without Pt, as a nitrate through disproportionation**

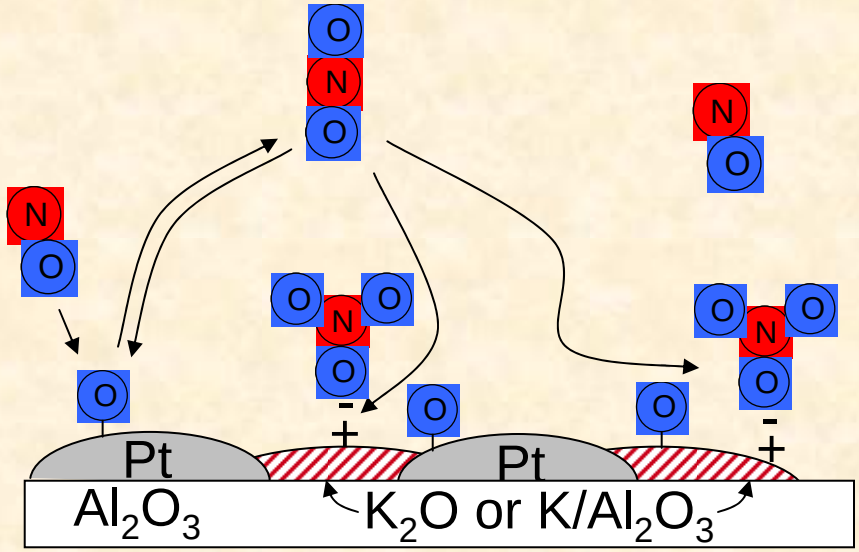
  $$NO_2 + K_2O \leftrightarrow K_2O\text{-}NO_2$$

  $$K_2O\text{-}NO_2 \leftrightarrow K_2O\text{-}O + NO$$

  $$K_2O\text{-}O + 2NO_2 \leftrightarrow 2KNO_3$$

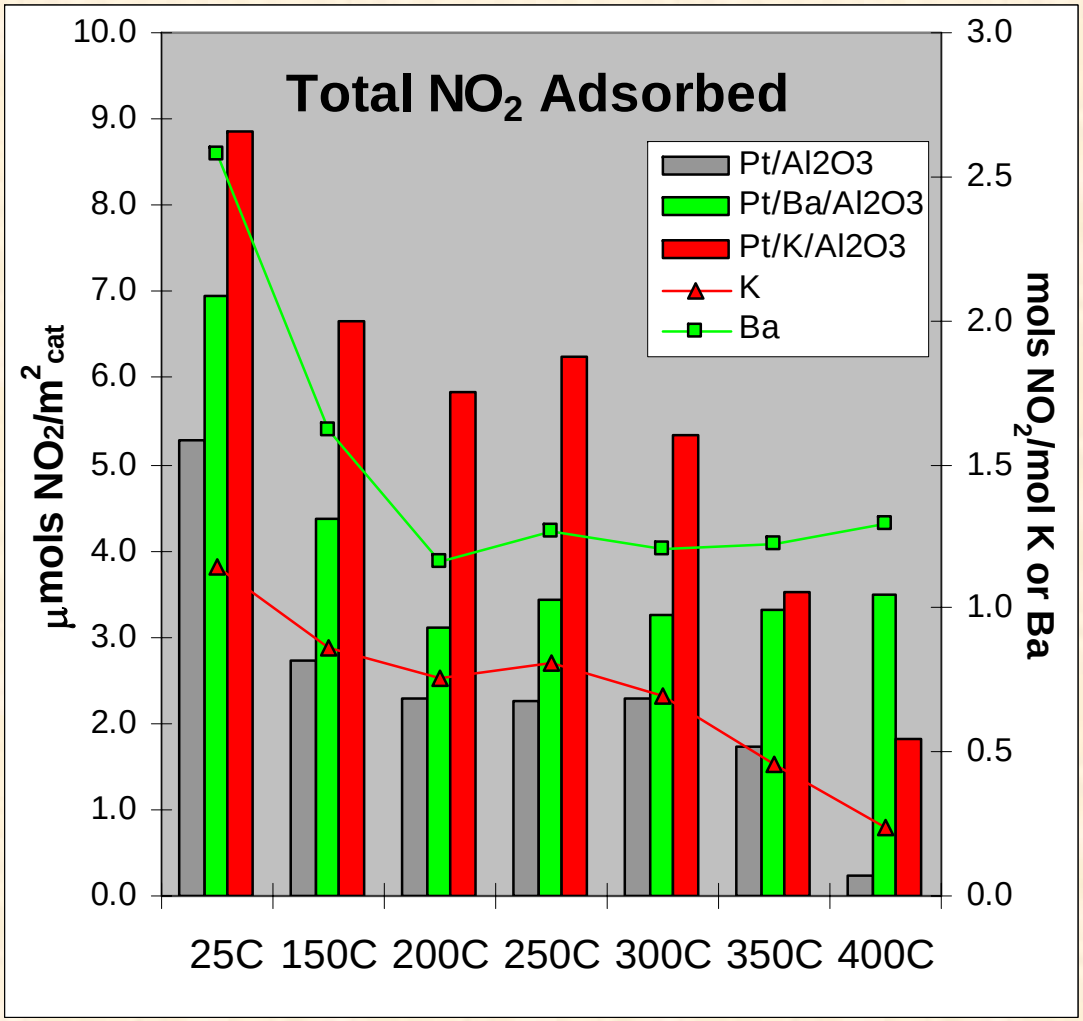
- **Basis for ORNL's Global model**





NO_2 Capacity Comparison to Ba

- **Potential Storage Decreases above 150C for K-based LNT**
- **Relatively Flat for Ba-based LNT**
- **Theoretical max uptake**
  - **Ba:N = 2**
  - **K:N = 1**



Regeneration on $Pt/K/Al_2O_3$

H_2O Important for Regeneration

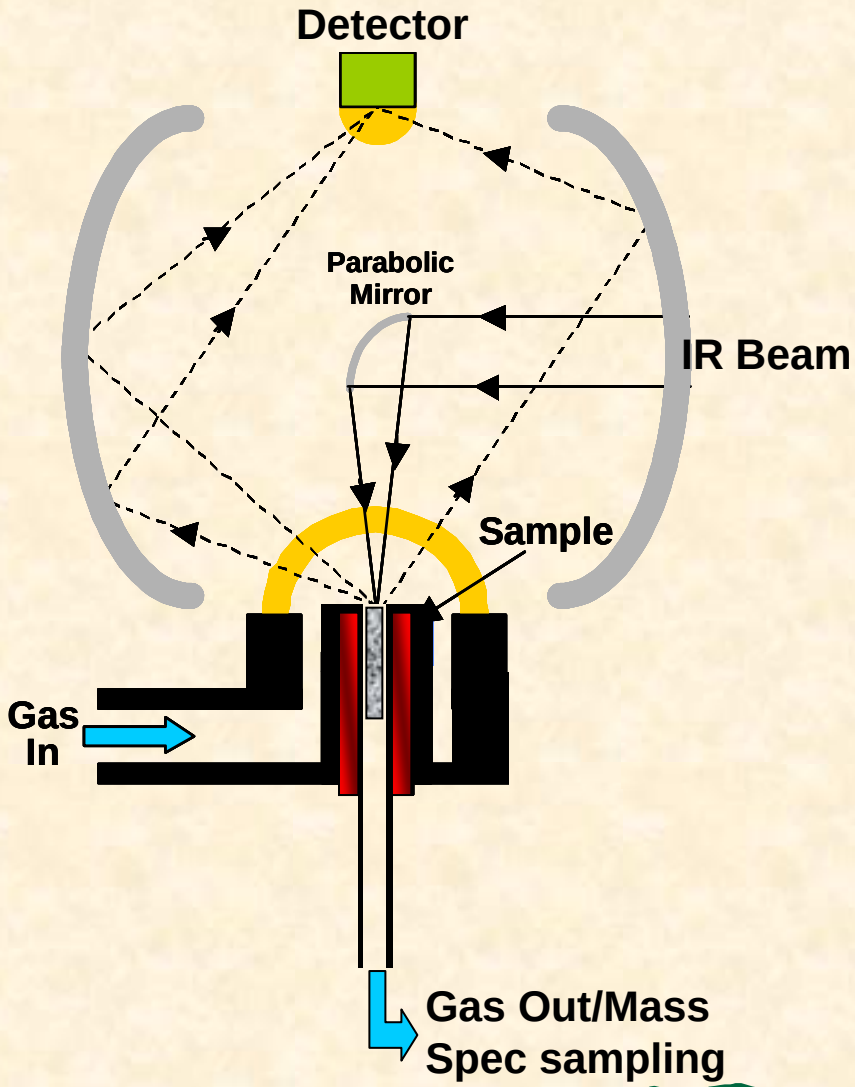
- **Saturated Pt/K/Al_2O_3 catalyst**
- **Pt critical for regeneration**
  - **K/Al_2O_3 only regenerates thermally**
- **Regeneration very slow below 200C**
- **H_2O inhibits nitrate reduction**
  - **H_2O stabilizes nitrate on K**

Regeneration Extent and Times of Saturated Catalyst

	0.4% H_2	0.4% H_2 + 5% CO_2 +5% H_2O
150C	21% after 15 min	<5% after 15 min
200C	62% after 15 min	12% after 15 min
250C	90% after 3.5 min	n/a
300C	90+% < 20s	11% after 15 min
350C	90+% < 20s	n/a
400C	90+% < 20s	72% after 15 min

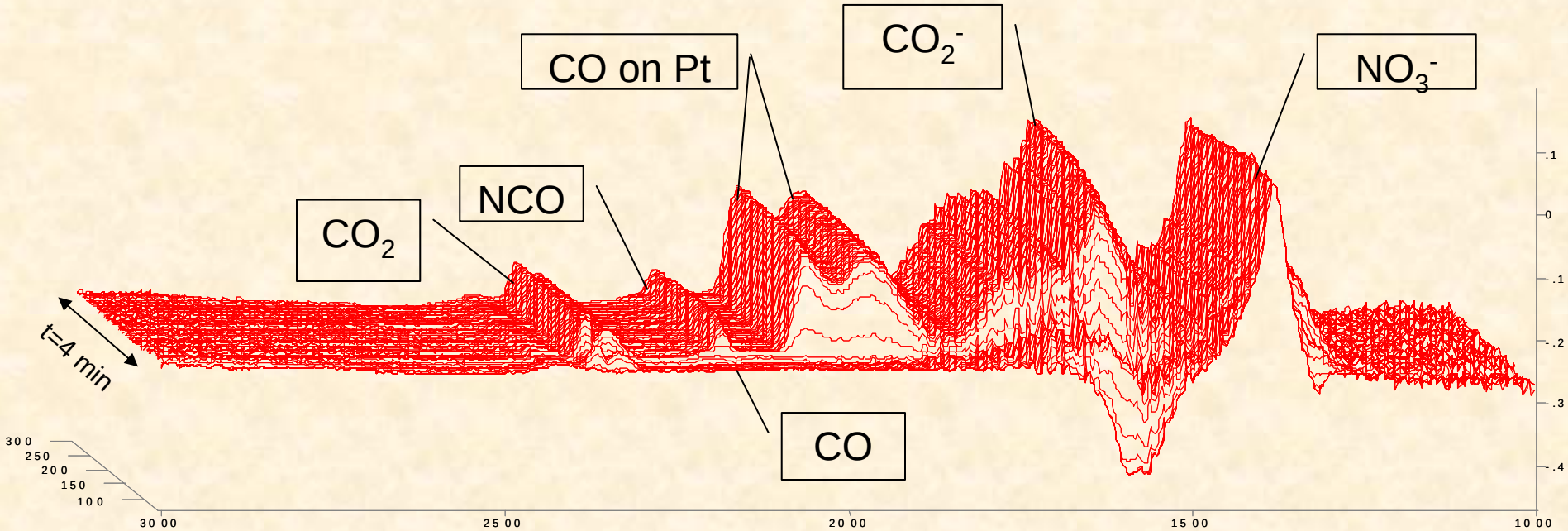
Flow-Through PF/DRIFTS Reactor

- *In situ* DRIFTS measurements
  - Catalyst T up to ~500°C
  - Heated lines for up to 10% H_2O
- MIDAC FTIR spectrometer
  - 2 Hz scan rate; 1 cm^{-1} resolution
- Harrick Barrel Ellipse DRIFT
  - Increased signal and sensitivity
    - Nearly 360^0 of reflected IR; compared to <90^0 typically
  - LN_2 cooled MCT detector
- Demonstrated temperature gradients <3°C
- DRIFTS results replicated from initial storage study



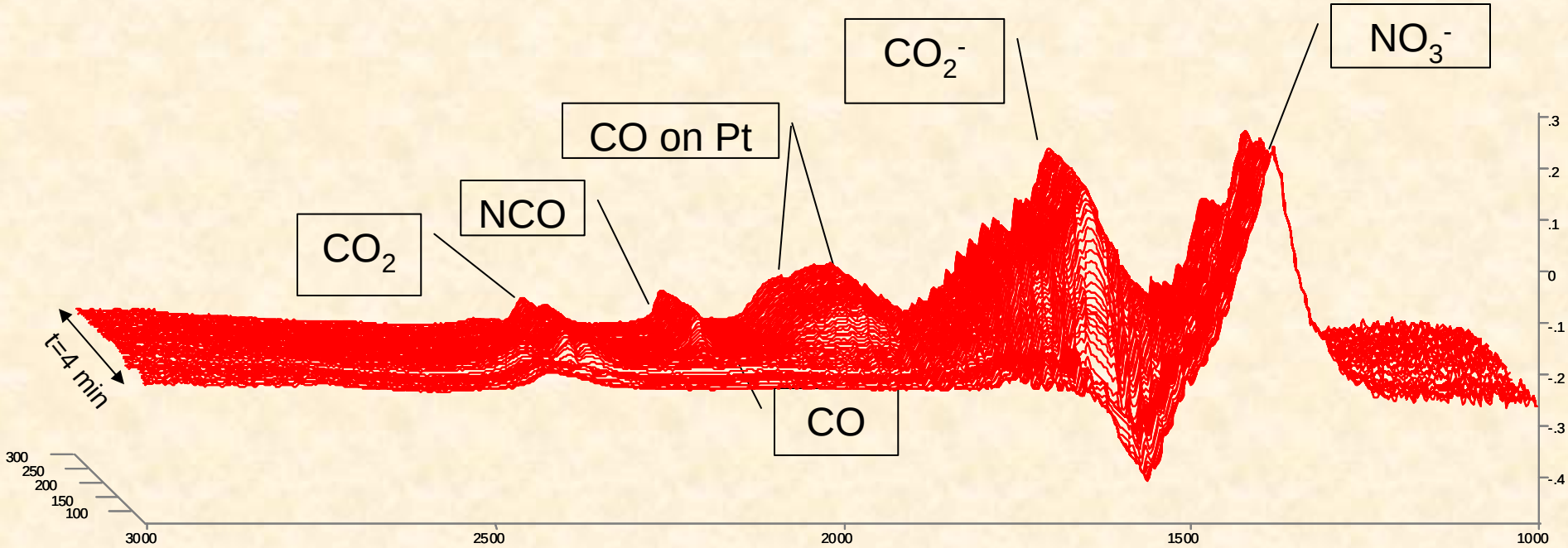
Regeneration Limited Using CO-only

- **Regeneration with 4% CO + 1% O_2 + 5% H_2O**
  - **Pt/K/Al_2O_3; 30k h^{-1} for total reactor bed; DRIFTS of inlet**
  - **Preceded by a 5 minute NO_x storage cycle at 300˚C.**
- **20% Nitrate reduction after 3 minutes (area basis)**
  - **CO needs finite reactor length to become active reductant**
- **MS measurements unavailable (capillary clogging)**



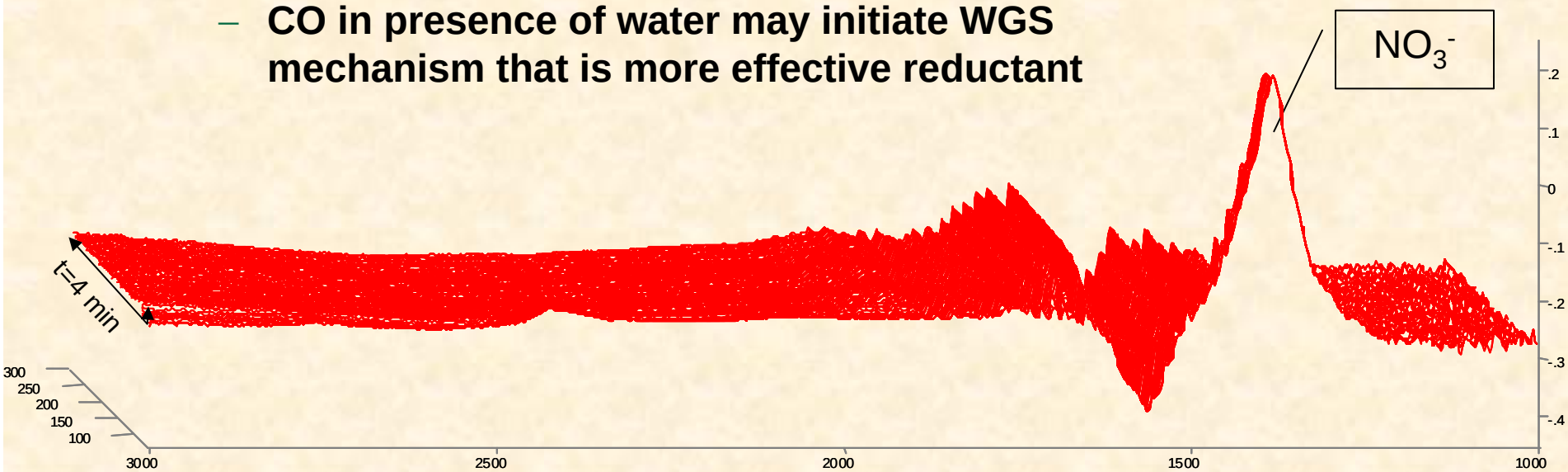
Regeneration Incomplete w/ $CO+H_2$

- **Regeneration with 2% CO + 2% H_2 + 1% O_2 + 5% H_2O**
  - **$Pt/K/Al_2O_3$; 30k h^{-1} for total reactor bed; DRIFTS of inlet**
  - **Preceded by a 5 minute NO_x storage cycle at 300˚C.**
- **69% Nitrate reduction after 3 minutes (area basis)**
  - **CO also blocks Pt, limiting H_2 activity**



Regeneration Expeditious w/ H_2

- **Regeneration with 4% H_2 + 1% O_2 + 5% H_2O**
  - **Pt/K/Al_2O_3; 30k h^{-1} for total reactor bed; DRIFTS of inlet**
  - **Preceded by a 5 minute NO_x storage cycle at 300˚C.**
- **100% Nitrate reduction after 3 min (85% in 12s)**
- **Suggests H_2 is optimum reductant; However, benchflow experiments have optimum NO_x reduction with CO**
  - **H_2 may drive off more NO than can be reduced**
  - **CO in presence of water may initiate WGS mechanism that is more effective reductant**



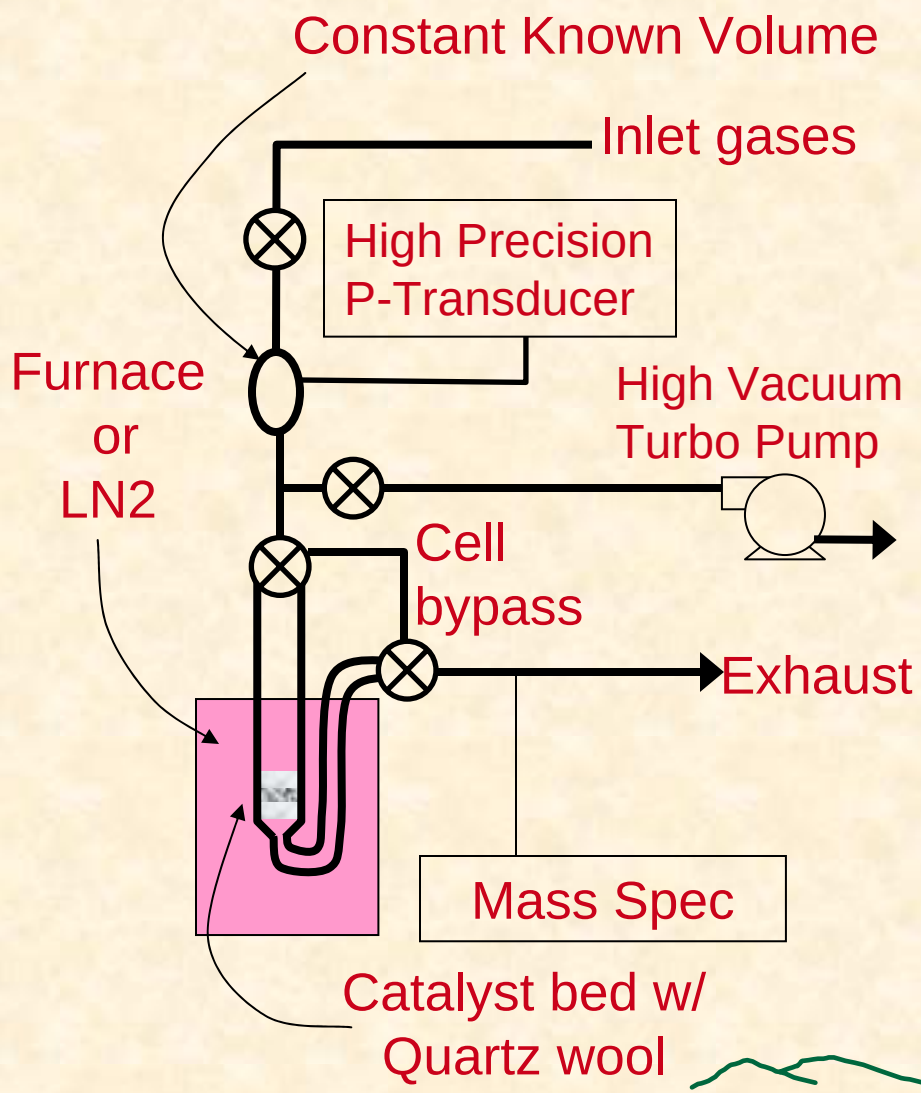
Thermal Deactivation of $Pt/Ba/Al_2O_3$ and $Pt/K/Al_2O_3$

LNT Thermal Deactivation

- **Key mechanisms of concern for LNTs**
  - **Sintering**
    - **Effects on total surface area, adsorber surface area, and Pt size**
  - **Noble metal masking**
    - **Migration of metal oxide to Pt surface**
- **Engine based desulfation at ORNL led to LNT temperatures of 760-780C**

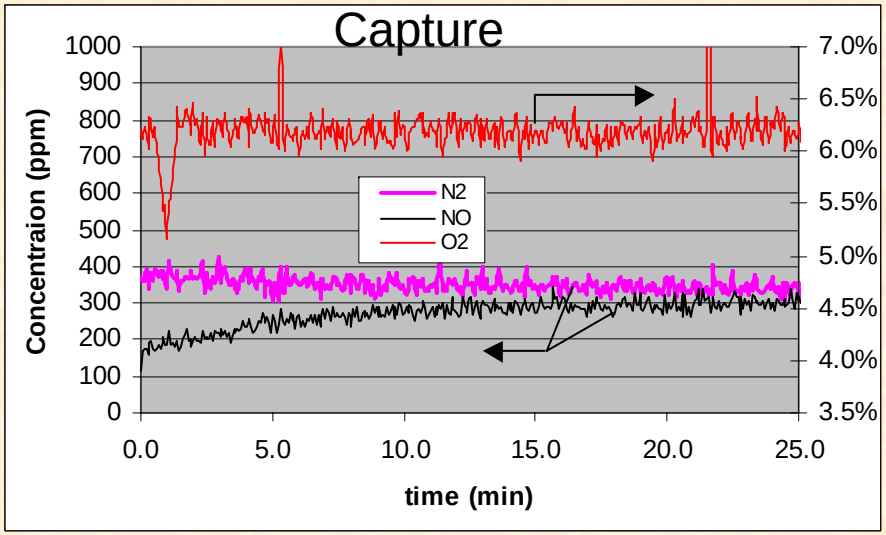
Thermal Deactivation Setup Enables Lean/Rich Cycling and H_2O

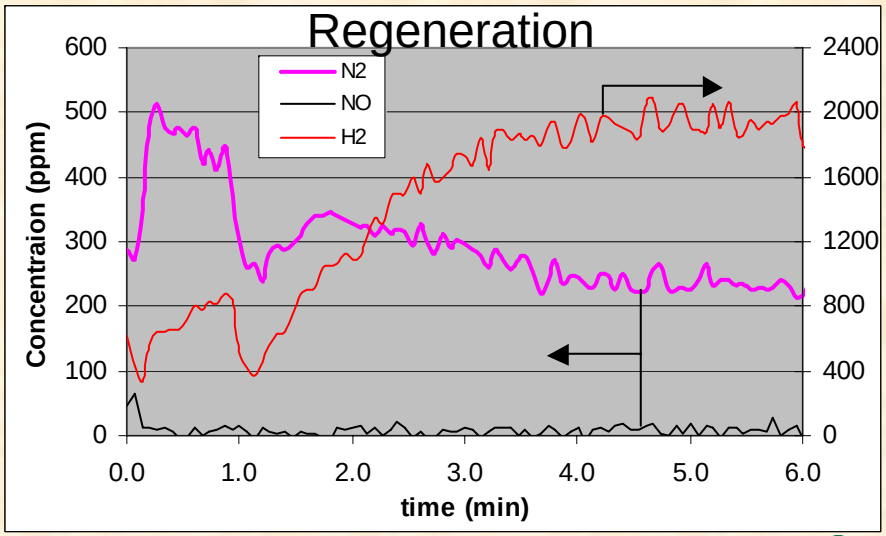
- **Chemisorption and Plug-Flow Reactor with MS capability**
  - **Pt-size effects**
  - **Specific surface area**
  - **NO_x Storage**
  - **Regeneration**
- **Programmable mass flow controllers for lean rich cycling**
- **Focus on catalyst constituent effects**



Thermal Deactivation Procedure

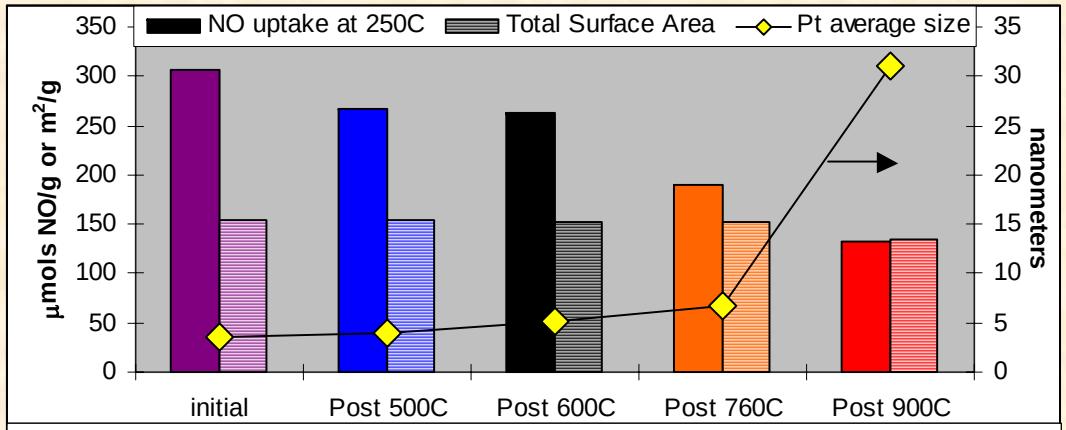
- **Argon Balance**
- **Temperatures Studied**
  - **500C, 600C, 760C, 900C**
- **Flow for 15h at Deactivation Temperature**
  - **9m lean: 300ppm NO, 8%O_2, 5%CO_2, 1.8%H_2O, 120-150K h^{-1}**
  - **1m rich: 0.2% H_2, 2% H_2O, 7%CO_2, 95-120K h^{-1}**
- **Measured NO_x storage at 250C**
- **H_2-O_2 titration at 25C**
- **BET at -196C**

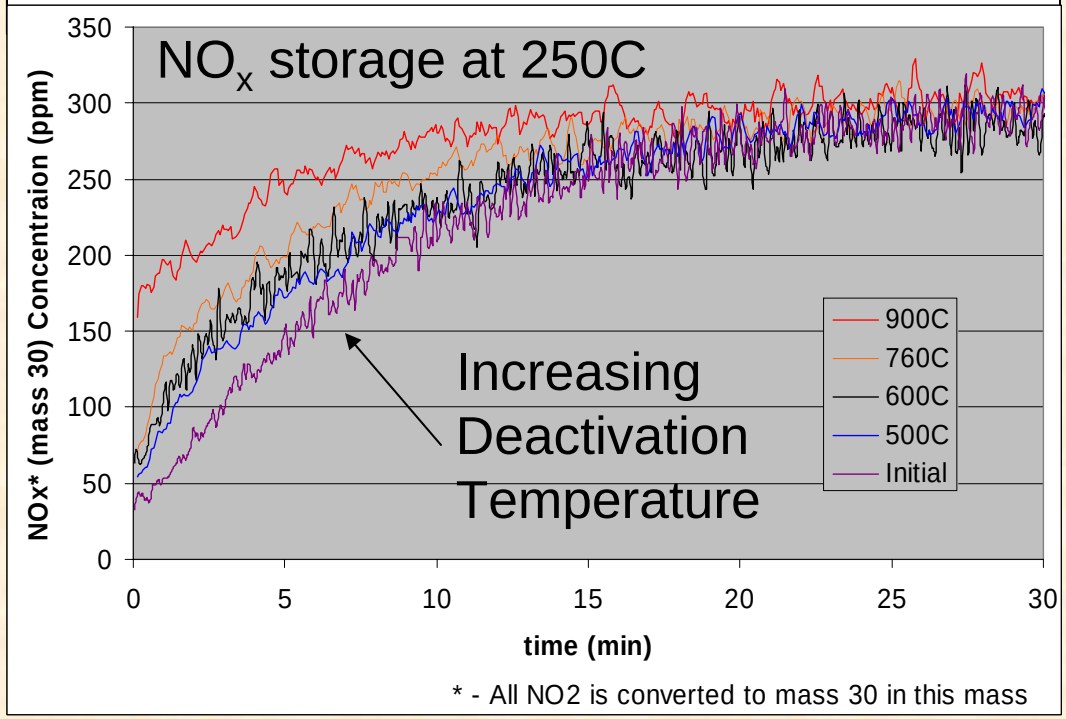




Results on Pt/(8% K_2CO_3)/Al_2O_3

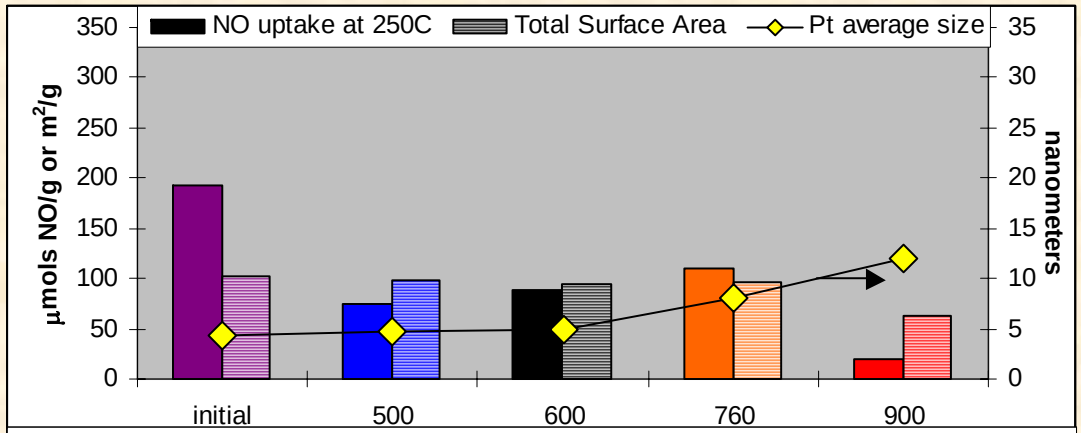
- **SA unaffected until Alumina transition at 850C**
  - $\gamma \rightarrow \delta$
- **Pt size steadily increases with a leap at 900C**
  - **XRD necessary to measure Pt size Post 900C**
- **Effective NO_x capacity decreases steadily**
  - **Not directly linked to Pt size or SA**

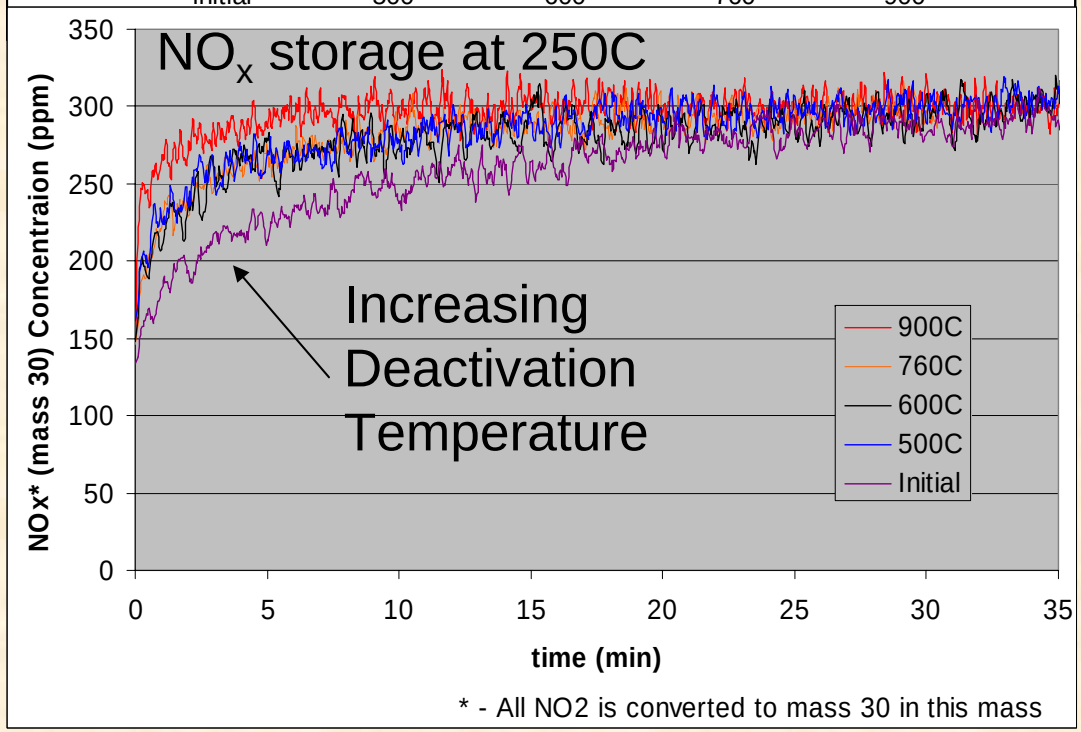




Results On Pt/(20% BaO)/Al_2O_3

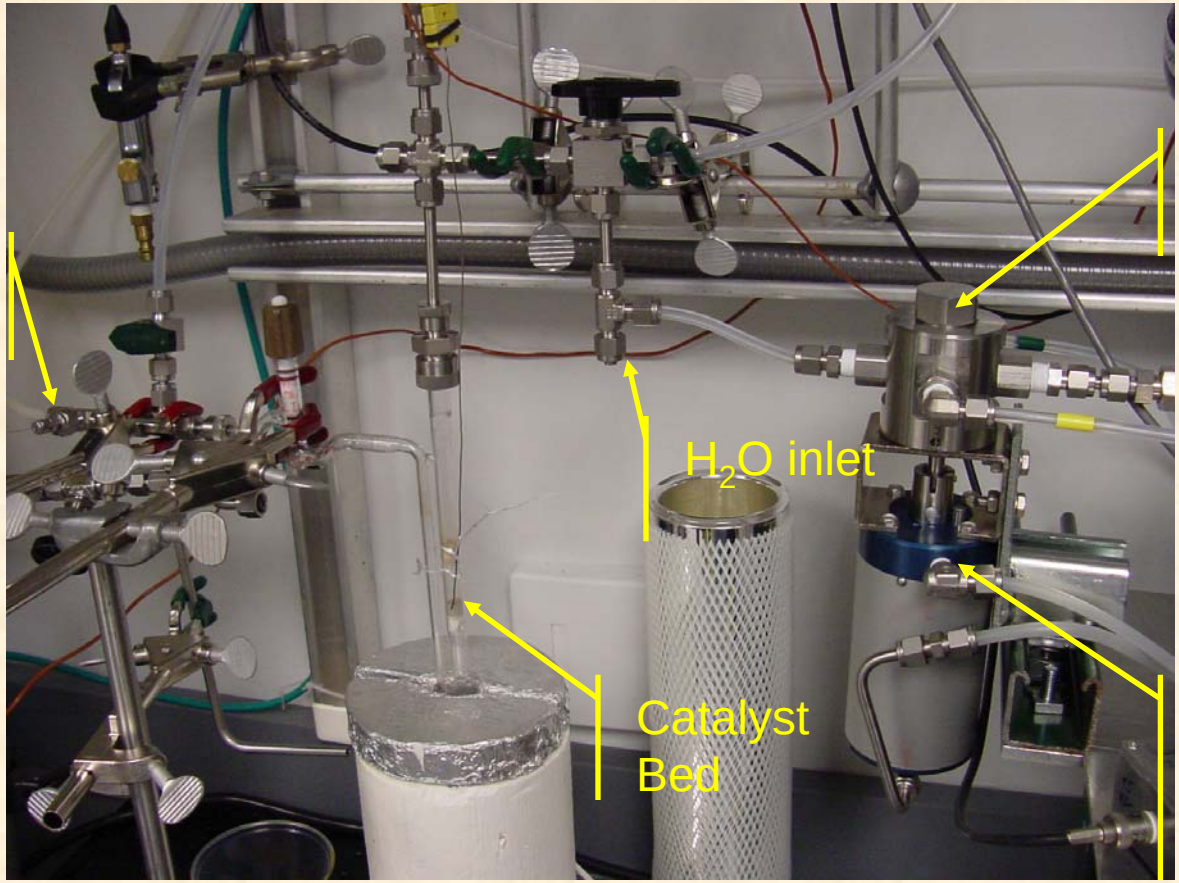
- **SA still unaffected until $\gamma \rightarrow \delta$ transition**
  - **Larger drop off**
- **Pt size relatively steady with only a minor increase between 760 and 900C**
  - **Chemisorption proved unreliable after 760C**
  - **XRD shows size to be reasonable**
  - **suggests Ba is covering Pt**
- **Below 900C NO_x capacity ~constant after initial decrease**
  - **Large decrease after heating to 900C**
  - **Suggests Ba phase also significantly affected**





Modification of Chemisorption/Plug Flow Reactor for Fast Switching

Capillary to Mass Spec



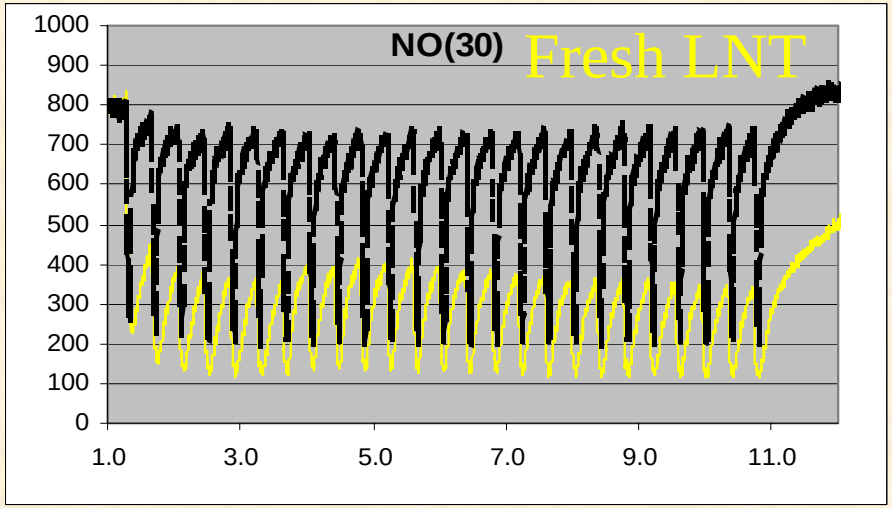
4-way valve

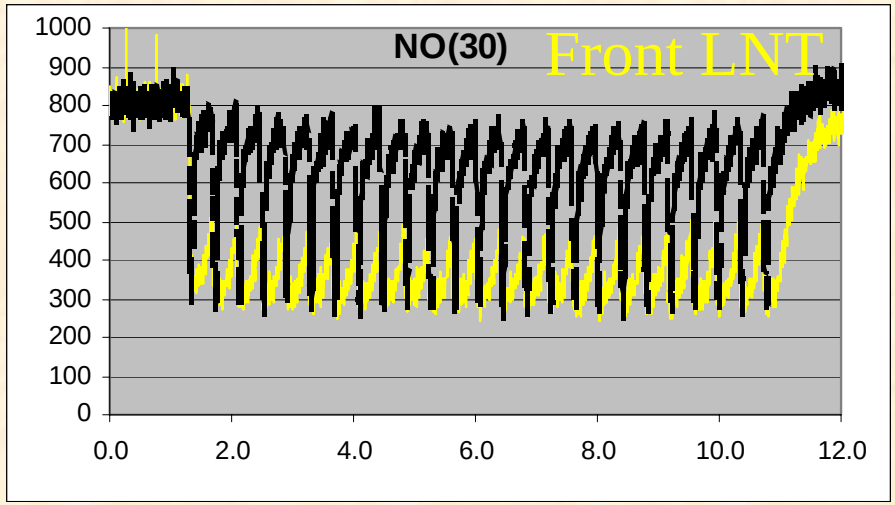
Pneumatic switching valve

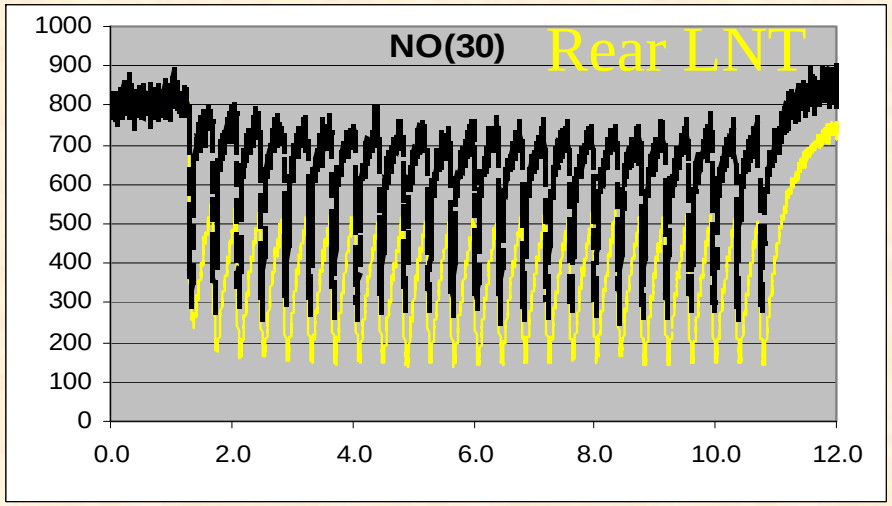
Englehard LNT: Aged at 800-920C

	Fresh	Front	Rear
Space Velocity (h^{-1})	58k	54k	61k
Surface Area (m^2/g)	28	16	17
Avg. PM Size (nm)	~1.0	8	8
NO_x Storage Capacity @ 400C			
μmoles/g_{cat}	126	82	73
μmoles/m^2	4.5	5.2	4.3
SS NO_x Conv. (400C)	95%	95%	98%
Cycling Conv. At 400C (20s lean, 4s rich)			
0-10 min	56%	43%	44%
8-10 min	60%	41%	43%
Lean: 10% O_2, 800 ppm NO, 5%H2O, 5% CO2			
Rich(A/F=13): 1%H2, 0.44%CO, 5%H2O, 5% CO2			

- **Aged by engine**
- **Ground washcoat**







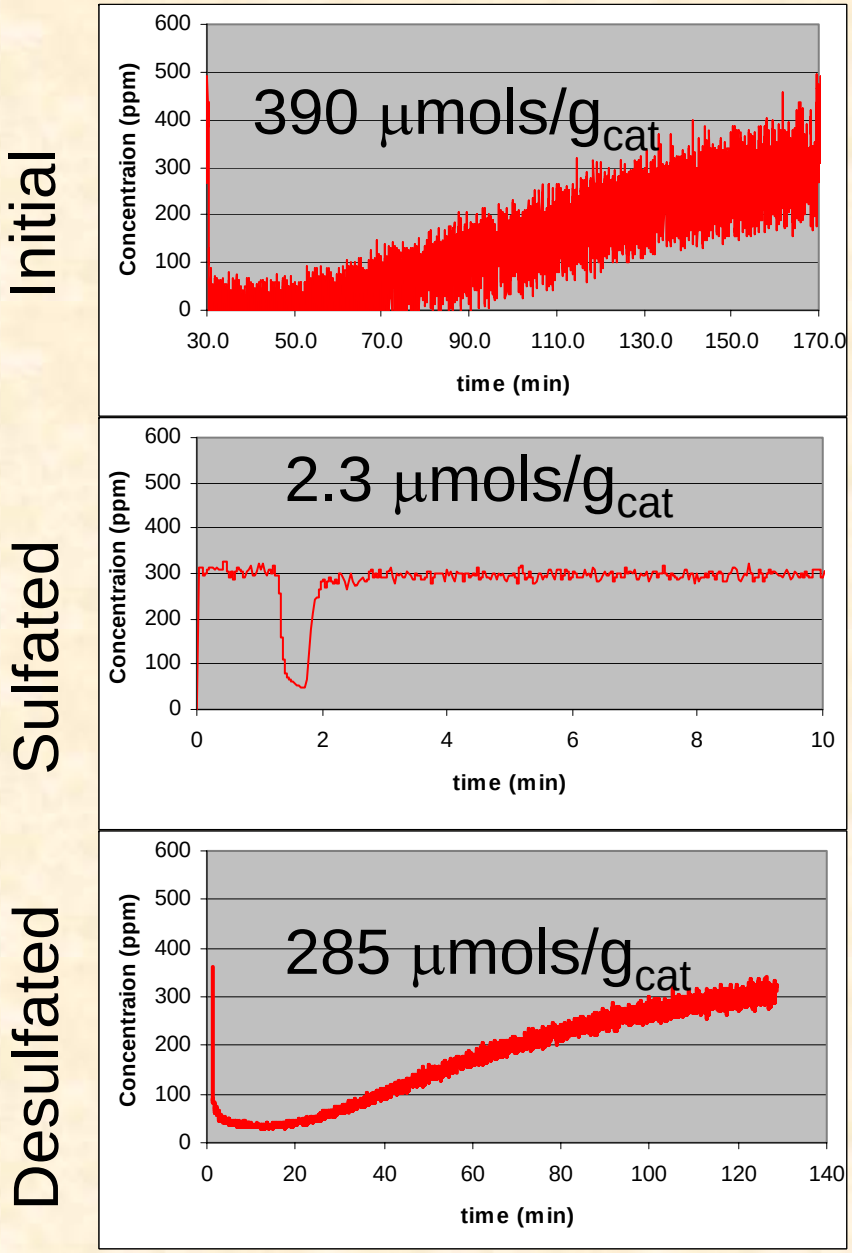
Sulfur Study of $Pt/Ba/Al_2O_3$ and $Pt/K/Al_2O_3$

Sulfur Study

- **Catalysts used**
  - **$Pt/K/Al_2O_3$: 1% Pt, 8% K_2CO_3 on γ-Al_2O_3**
  - **$Pt/Ba/Al_2O_3$: 1% Pt, 20% BaO on γ-Al_2O_3**
- **Steps**
  - **NO_x Storage at 250C (300ppm NO, 10% O_2)**
  - **Sulfate at 250C (140 ppm SO_2 for 20h)**
  - **Post-SO_2 NO_x Storage at 250C**
  - **Desulfate under rich conditions**
  - **Post-desulfation NO_x Storage at 250C**

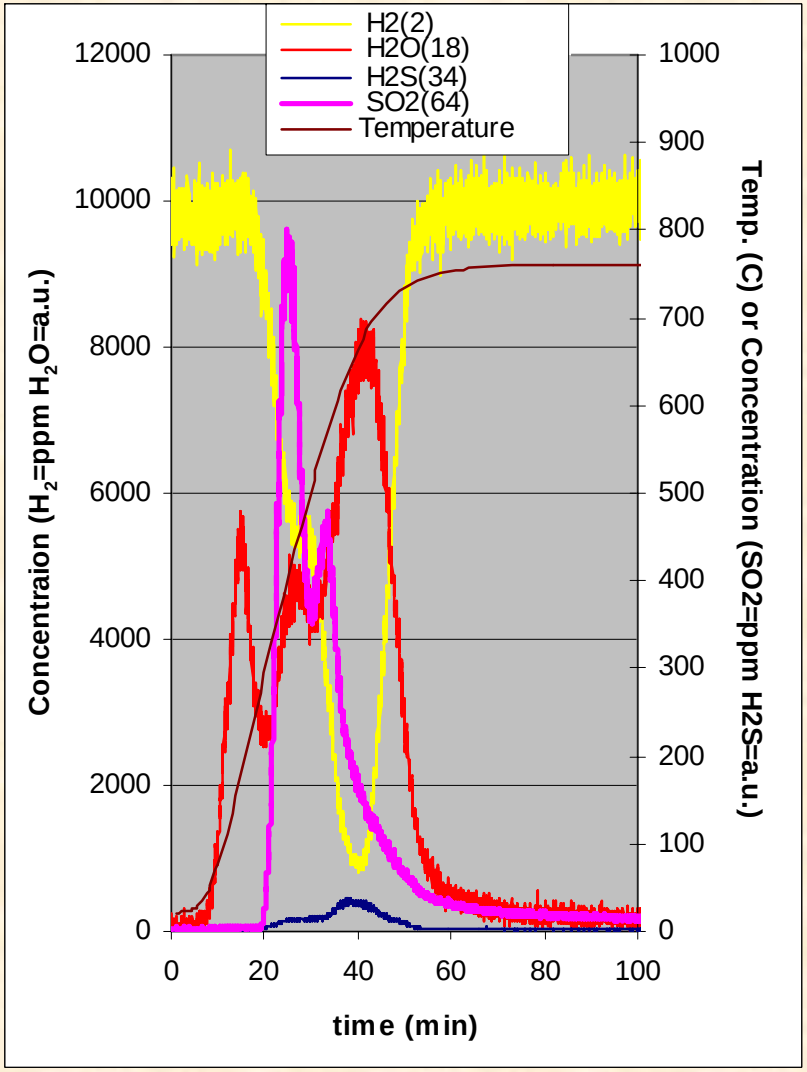
NO_x Storage on $Pt/K/Al_2O_3$

- **Nearly all of the storage capacity removed by sulfation**
- **73% regained after desulfation**



Desulfation of $Pt/K/Al_2O_3$

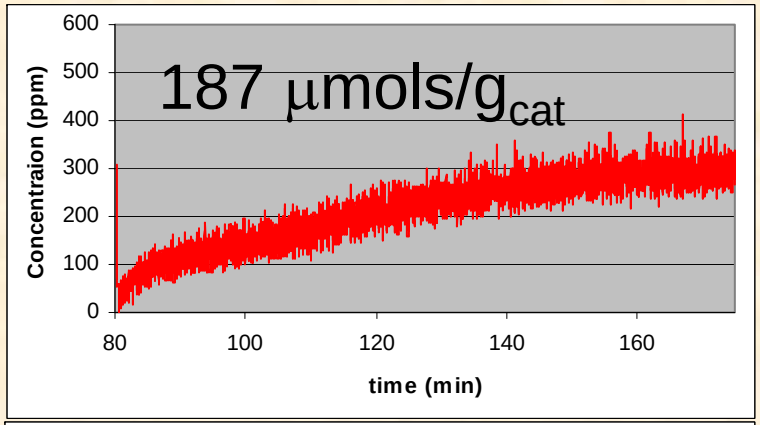
- **1% H_2 at 30k h^{-1}**
- **Two desulfation peaks observed**
  - **SO_2 peaks reach maximum at 435C and 575C**
  - **H_2S peaks reach maximum at 435C and 675C**
- **This desulfation recovers 73% of NO_x capacity**



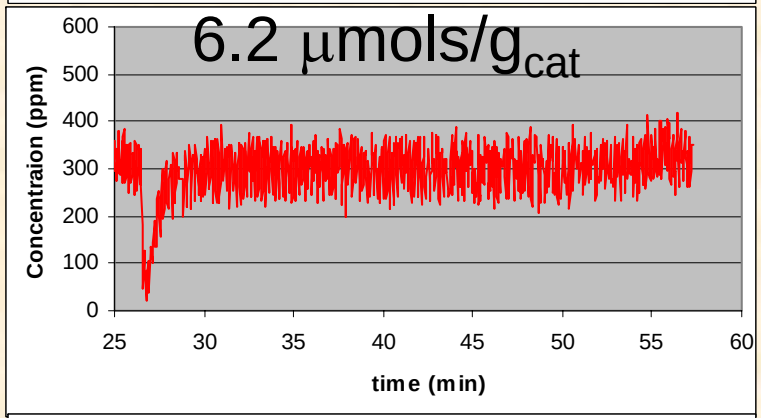
NO_x Storage on $Pt/Ba/Al_2O_3$

- **Nearly all of the storage capacity removed by sulfation**
- **75% regained after desulfation**

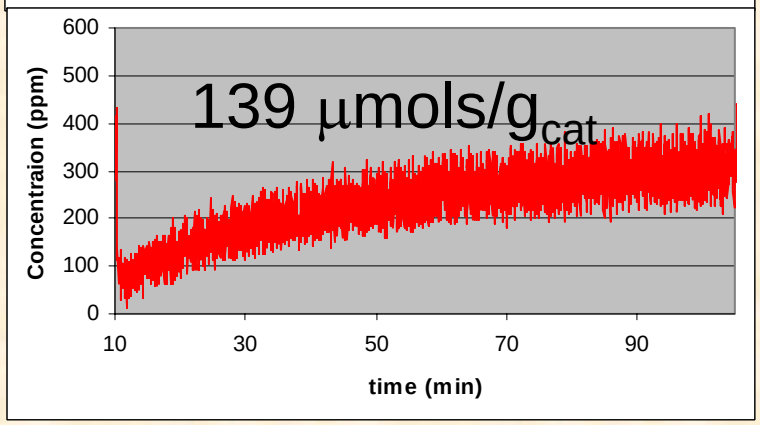
Initial



Sulfated

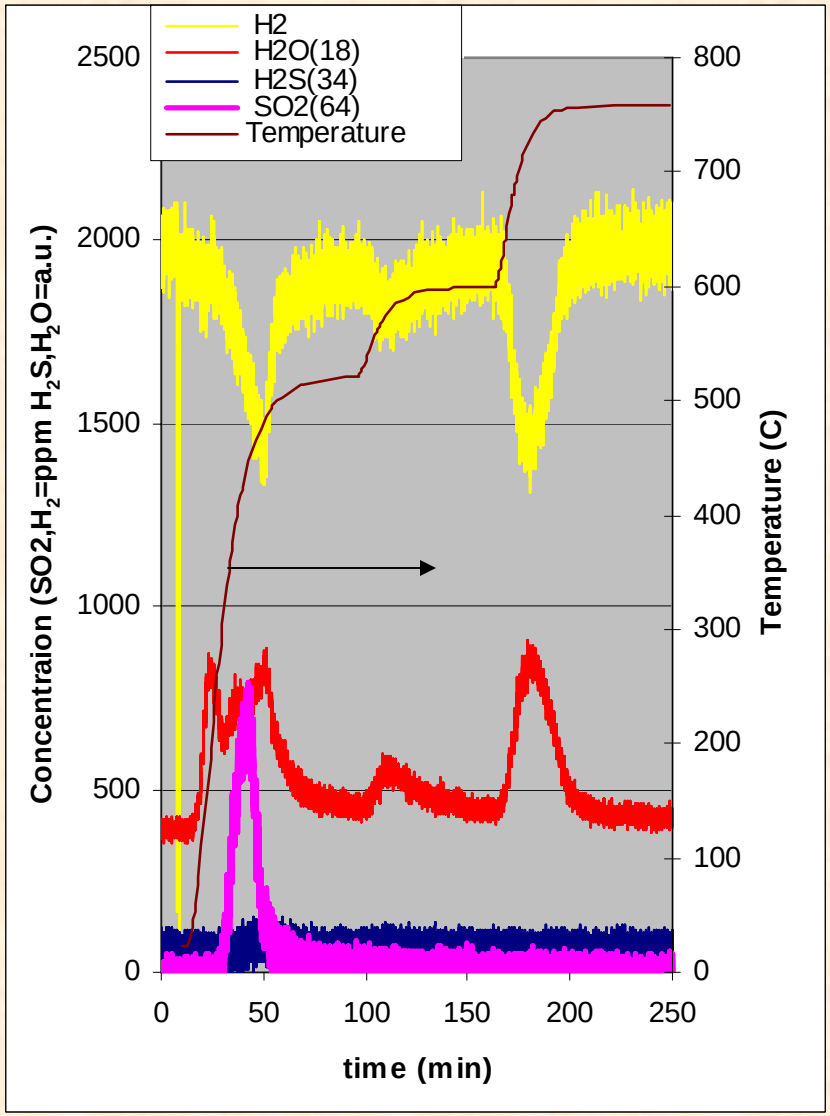


Desulfated



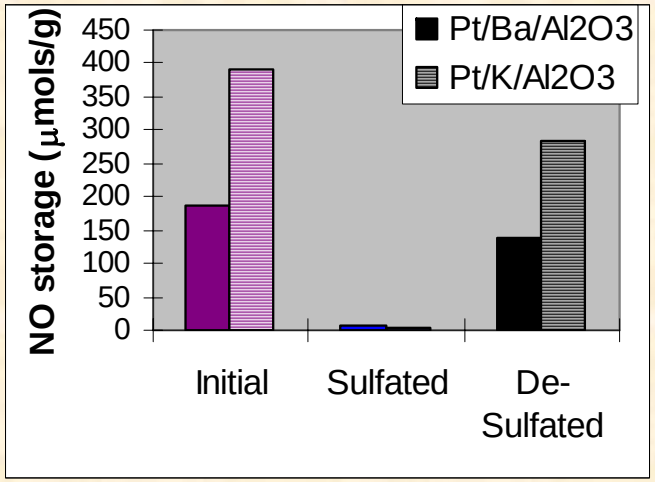
Desulfation of $Pt/Ba/Al_2O_3$

- **1% H_2 at 30k h^{-1}**
- **Only one desulfation peak observed**
  - **SO_2 with a peak max at 450C**
  - **H_2S peak also apparent near 500C**
- **This desulfation recovers 75% of NO_x capacity**
- **Subsequent experiments on Englehard's Ba-based model LNT desulfated similar to $Pt/K/Al_2O_3$**



Sulfur Summary

- **Model Ba catalyst achieves full desulfation by 500C**
  - **Very surprising; typical desulfation T is >750C**
  - **Englehard's model LNT shows de-S for T>500C**
- **75% Recovery of storage capacity is typical of thermal deactivation experiments too**



	$Pt/Ba/Al_2O_3$	$Pt/K/Al_2O_3$	
Pt loading	1%	1%	
Storage loading	20%	8.01%	
Surface area	100	150	m^2/g_{cat}
Initial NO_x stored	187	390	$\mu mol/g_{cat}$
NO_x stored on fully sulfated catalyst	6.2	2.3	$\mu mol/g_{cat}$
Percent decrease	97%	99%	
Post De-sulfation NO_x storage	139	285	$\mu mol/g_{cat}$
Percent decrease	25%	27%	

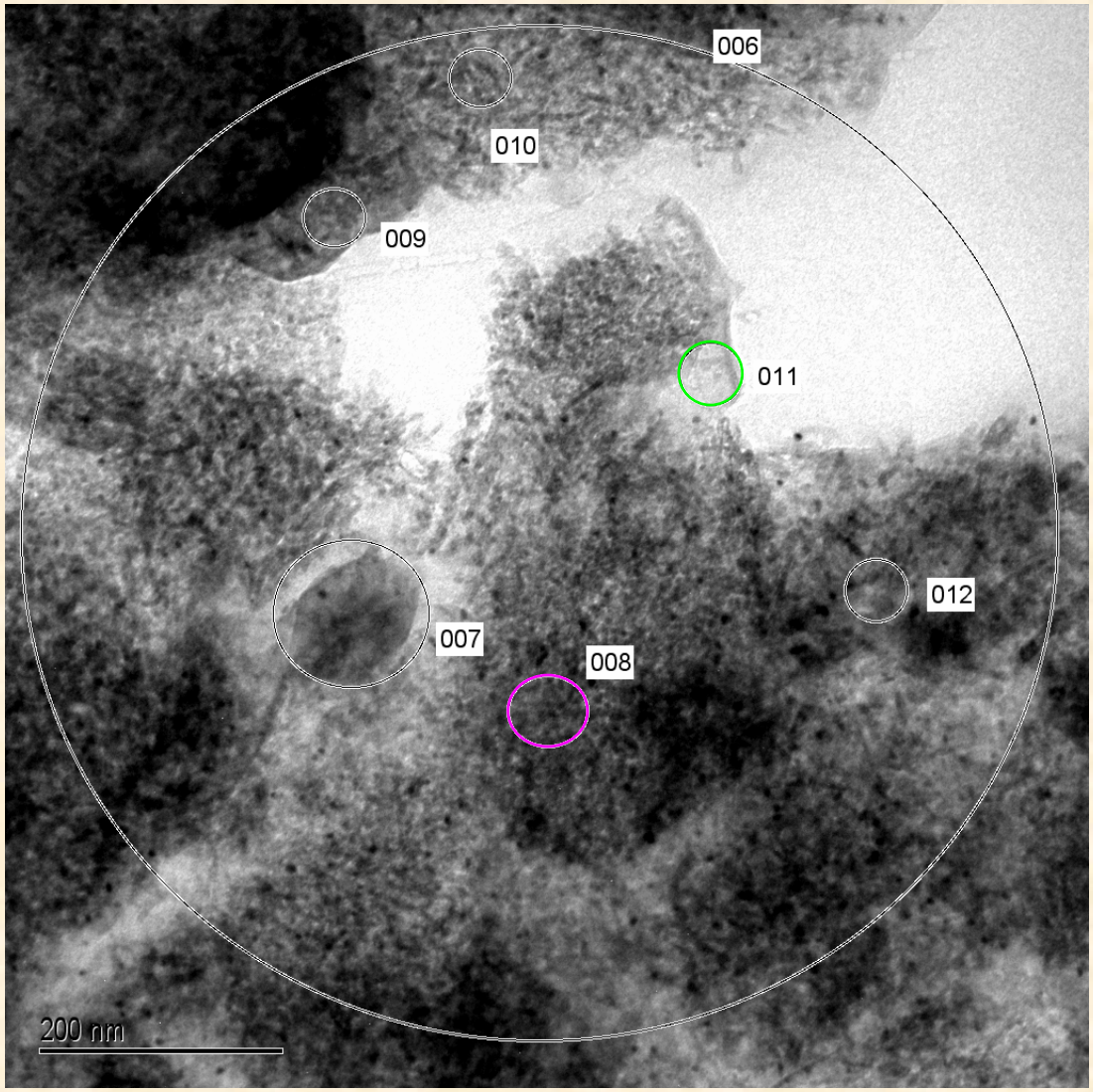
Summary

- **Mechanistic findings for NO_x storage**
  - **NO is only significantly adsorbed on sites near Pt**
  - **NO_2 does not adsorb as a nitrite**
  - **NO_2(g) can adsorb readily with/without Pt present**
  - **Nitrites not observed above 200C**
- **Regeneration Findings**
  - **CO must be activated for regeneration**
- **Thermal deactivation findings**
  - **K (50%) and Ba (90%) capacity after 900C**
  - **Pt size more stable on Ba at 900C**
    - **Ba may mask Pt at T>760C**
- **Sulfur deactivation findings**
  - **About 75% of the posioning effects of SO_2 are replensihed after desulfation; similar to thermal aging**
  - **Low desulfation Temp. for Ba suggests further analysis**

Future Work

- **Elucidate chemistry of catalyst regeneration with flow-through reactor**
  - **Include O_2 as a variable in regeneration investigation**
- **Sulfur-based deactivation/desulfation mechanisms**
  - **Elucidate LNT capacity for SO_x, chemical form of sulfur-based species, and ability of NO_x to compete for storage sites**
  - **Elucidate the desulfation temperatures and how they relate to the thermal deactivation results presented here**

Catalyst Morphology Characterization at ORNL's HTML



- **TEM Image of K-based NOx Absorber Catalyst**
  - **Catalyst Was Not Aged**
  - **Precious Metals Finely Dispersed Over Washcoat**
  - **Majority of K Sorbate Finely Dispersed**
  - **Some Amorphous K Deposits Occur at Interfaces**
  - **Future Studies Will Characterize Aged Catalysts**
  - **Performed by Karren More**

K Concentration via X-Ray Analysis (a.u.):
Position 011: 560
Position 008: 120
Noise Level: 10

$Pt/K/Al_2O_3$ compares favorably with other NO_x adsorber catalysts under similar conditions

Temp. (C)	Adsorption time	Gas Components	Adsorbed NOx ($\mu mol/g_{cat}$)	($\mu mol/m^2$)
$Pt(1.0\%)/K(4.5\%)/\gamma\text{-}Al_2O_3$				
250	sat (~17h)	300 ppm NO-12% O_2-bal N_2	936	6.2
250	1h	300 ppm NO-12% O_2-bal N_2	797	5.3
250	1h	Standard + 5% CO_2 + 5% H_2O	658	4.4
250	1 min	300 ppm NO-12% O_2-bal N_2	215	1.4
250	1 min	Standard + 5% CO_2 + 5% H_2O	283	1.9
Pt(0.72%)/Rh(0.14%)/Ba/La/Washcoat				
250	sat (~2h)	500 ppm NO-7% O_2-bal N_2	333	-
$Pt(0.76\%)/Ba(15\%)/\gamma\text{-}Al_2O_3$				
250	sat (~20min)	1000 ppm NO + 3% O_2 + bal He	379	-
250	sat (~20min)	Standard + 0.3% CO_2 + 1% H_2O	166	-
250	~3 min	1000 ppm NO + 3% O_2 + bal He	181	-
250	~3 min	Standard + 0.3% CO_2 + 1% H_2O	97	-
$Rh(1.0\%)/CaO(5\%)/\gamma\text{-}Al_2O_3$				
300	3 min		5000	14.4
		1000 ppm NO + 7% O_2 + bal He		
300	1 min	1000 ppm NO + 7% O_2 + bal He	1700	4.9
$Pt(1.0\%)/CaO(5\%)/\gamma\text{-}Al_2O_3$				
300	3 min		3400	9.8
		1000 ppm NO + 7% O_2 + bal He		
300	1 min	1000 ppm NO + 7% O_2 + bal He	1380	4.0
$Pd(1.0\%)/CaO(5\%)/\gamma\text{-}Al_2O_3$				
300	3 min		1660	4.8
		1000 ppm NO + 7% O_2 + bal He		
300	1 min	1000 ppm NO + 7% O_2 + bal He	660	1.9
$CaO(5\%)/\gamma\text{-}Al_2O_3$				
300	3 min		820	2.4
		1000 ppm NO + 7% O_2 + bal He		
300	1 min	1000 ppm NO + 7% O_2 + bal He	220	0.6

Presentations and Publications

Presentations:

- "NO_x Adsorption on $Pt/K/Al_2O_3$ and the Quantitative Effects of CO_2 and H_2O", **Third Joint meeting of the US section of the Combustion Institute, Chicago, March 16-19, 2003.**
  - **Paper available at http://feerc.ornl.gov/publications/toops5.pdf**
- "Quantified *in-situ* DRIFTS Analysis of NO_x Adsorption on $Pt/K/Al_2O_3$ in the Presence of CO_2 and H_2O", **The 2003 Meeting of the North American Catalysis Society.**
- "NO_x Adsorption of $Pt/K/Al_2O_3$ in the Presence of CO_2 and H_2O: an *In-situ* DRIFTS Study", **6th DOE CLEERS Workshop, Warren, MI, 2003.**
- "Lean NOX Trap Chemical Behavior and Thermal Deactivation Effects", **7th DOE Crosscut Workshop on Lean Emissions Reduction Simulation (CLEERS)**, June 16-17, 2004.
- "NO_x Adsorption of $Pt/K/Al_2O_3$ in the Presence of CO_2 and H_2O: an *In-situ* DRIFTS Study", **4th DOE National Laboratory Catalysis Conference, Oak Ridge, TN, 2003.**

Presentations:

- "Quantification of the *in-situ* DRIFT Spectra of Pt/K/gamma-Al_2O_3 NO_x Adsorber Catalysts", **Applied Catalysis B: Environmental**, in print.
- "Quantified NO_X adsorption on Pt/K/gamma-Al_2O_3 and the Effects of CO_2 and H_2O", **Applied Catalysis B: Environmental**, in print.