Lean NO_x Trap Deactivation

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Background

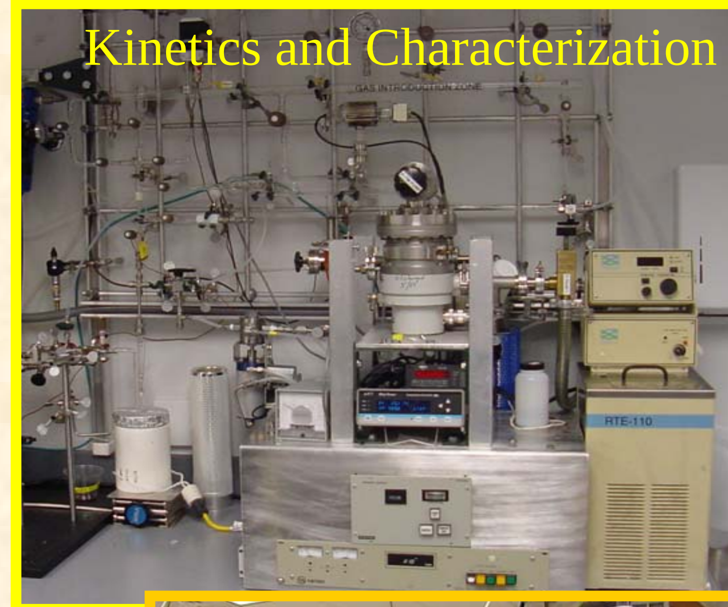
- **LNTs inhibited by poisoning agents**
  - **Lube phosphorous**
  - **Sulfur inhibition and its high temperature removal**
- **Need a better understanding of the deactivation mechanisms that result from treating catalyst**
  - **What impact do oil-born agents have on catalysts?**
  - **What temperature does de-S occur?**
  - **When is the catalyst morphology affected?**
  - **How does the material impact the chemistry?**
- **Transfer this information to teams to:**
  - **improve the material**
  - **improve the desulfation methods**
  - **improve simulation of the processes**

Approach

- **Effort is pre-competitive**
  - **Use model catalysts for majority of study**
  - **Allows sharing of all information**
  - **Compare “fully-formulated” catalysts at manufacturers**
    - **Unable to share all information**
- **Study deactivation mechanism fundamentally**
  - **Complements engine dynamometer experiments and long-term aging**
  - **Investigate activity and its relationship to catalyst components that are not feasible on the engine**
- **Phosphorous, Thermal Aging and Sulfation/Desulfation all studied independently**

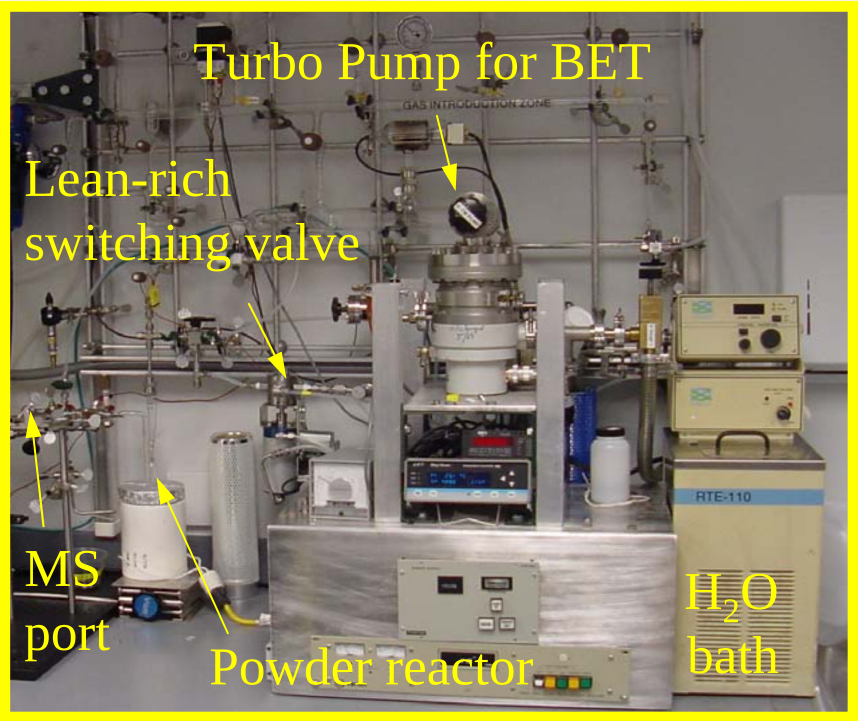
Experimental

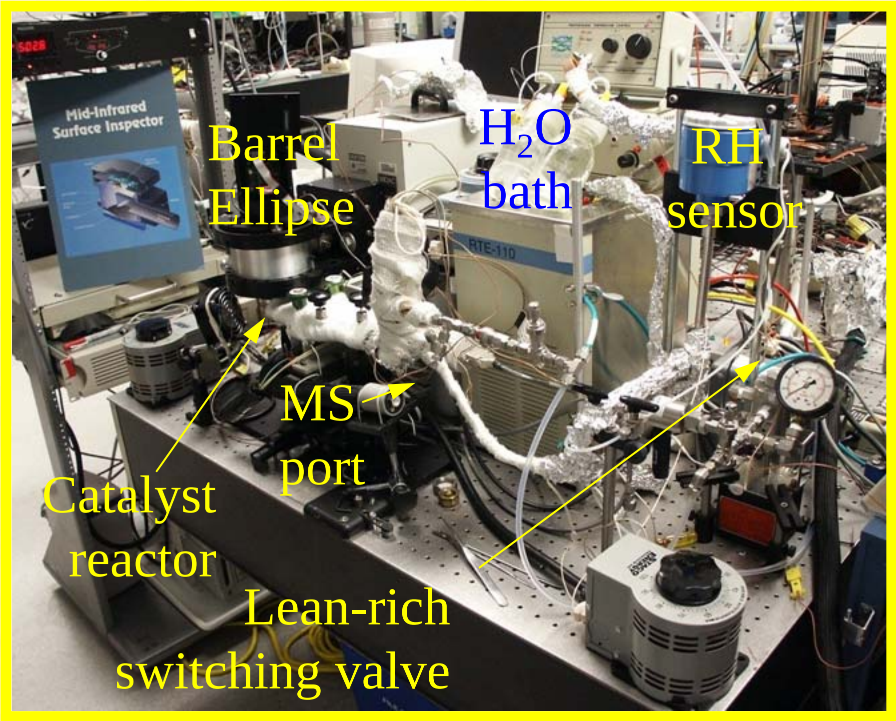
- **Evaluate thermal aging independent of sulfur**
  - **No sulfur on initial catalyst**
  - **Determine T effects up to 900°C**
- **Compare thermal to deactivation from sulfur poisoning and de-S**
- **Multiple analytical techniques**
  - **X-ray Diffraction: morphology changes**
  - **DRIFTS: surface species investigation**
  - **Physisorption/Chemisorption: Pt size, surface area, LNT capacity**
  - **Mass Spectrometry: Activity, TPR, TPD**



Reactor Designs Optimized for LNT Studies

- **Reactors allow key LNT measurements**
  - **fast switching enabled on microreactor and DRIFTS reactor**
    - **equibaric considerations**
  - **pulse chemisorption for faster Pt dispersion measurements**
  - **Allows meaningful short cycle measurements**
  - **Mass spectrometer enabled**





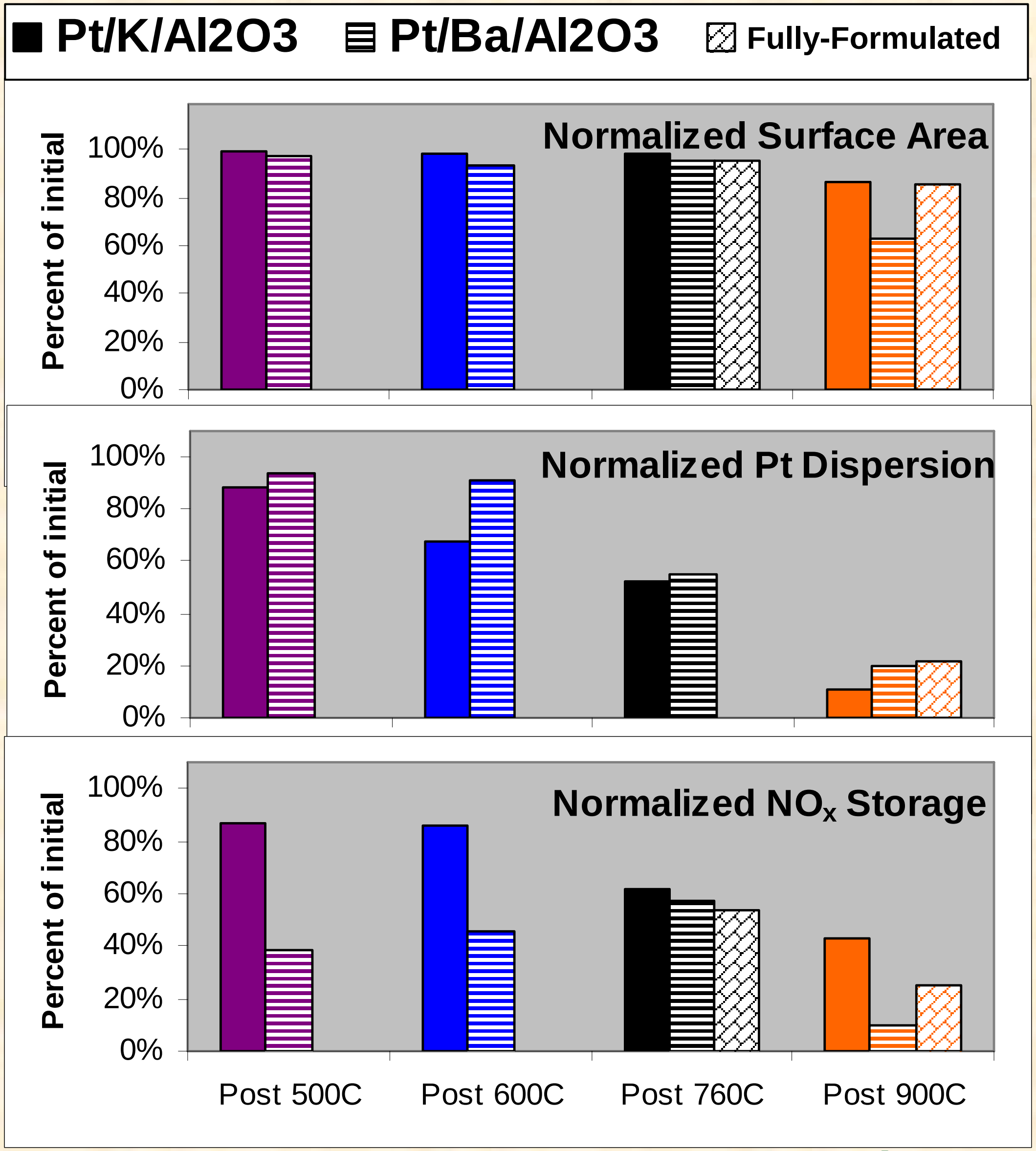
Thermal Aging Study

Experimental Protocol for Thermal Aging

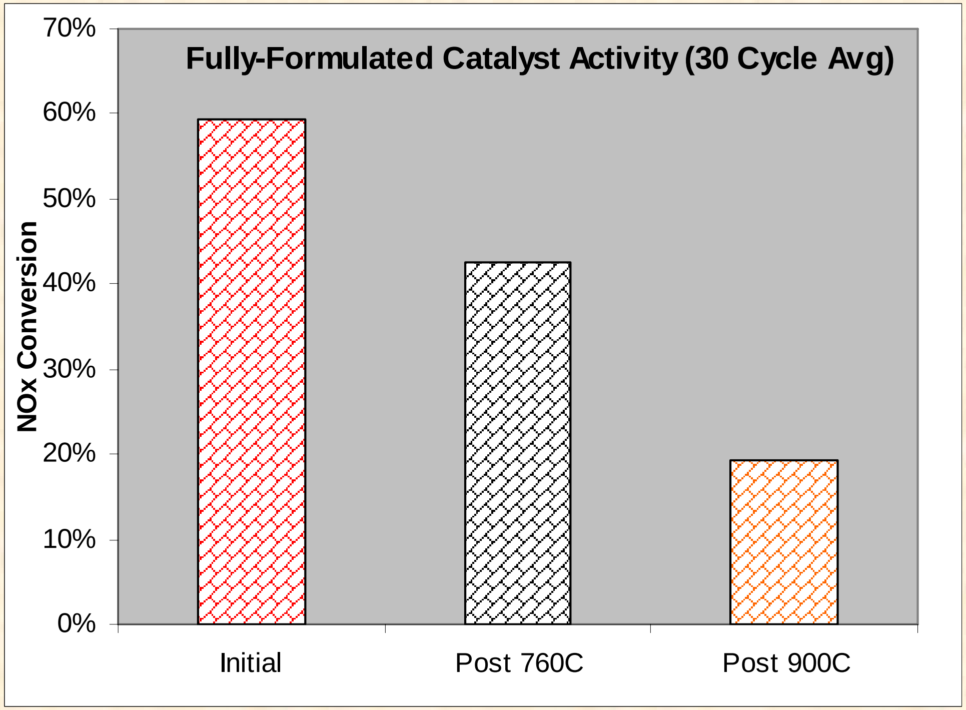
- **Studied Two model powder catalysts**
  - **$Pt/K/Al_2O_3$: 1% Pt, 8% K_2CO_3 on γ-Al_2O_3**
  - **$Pt/Ba/Al_2O_3$: 1% Pt, 20% BaO on γ-Al_2O_3**
  - **~200 g Pt/ft^3 equivalent**
- **Compared Ba-based fully-formulated catalyst**
  - **Washcoated catalyst was ground and sieved for reactor**
- **Aged at 500-900°C**
  - **Cycle between lean and rich (20h)**
- **Characterized effects after each temperature**
  - **Surface Area**
  - **NO_x storage at 15 minutes at 250°C**
  - **Pt size**

Model Catalysts Mimic Fully-Formulated Catalyst

- **All catalysts show similar deactivation after 760 and 900°C**
- **Fully formulated catalyst shows better tolerance than Pt/Ba/Al_2O_3**
  - **Especially for NO storage**
- **Surface area sustained**
  - **Model Ba does decrease compared to fully formulated**
    - **demonstrates effect of stabilizing agent**
- **Pt sintering severe at 760°C**
- **Significant drop in NO_x storage after 760°C**
- **Non-normalized rates available on request**



Thermal Aging Severely Inhibits Activity on Fully-Formulated Catalyst



- **Activity measurements needed for effect of Pt sintering on regeneration**
- **Short Cycle:**
  - **60 s lean, 5 s rich (~fuel penalty 8%)**
  - **Space Velocity: 45k h^{-1}**
  - **Lean: 300ppm NO, 10 % O_2, 5% CO_2, 5% H_2O in Argon (Φ~0.5)**
  - **Rich: 0.9% CO, 0.54% H_2, 5% CO_2, 5% H_2O in Argon (Φ~1.04)**
- **NO_x conversion at 250°C drops by 67% after 900°C**
  - **Un-recoverable loss**

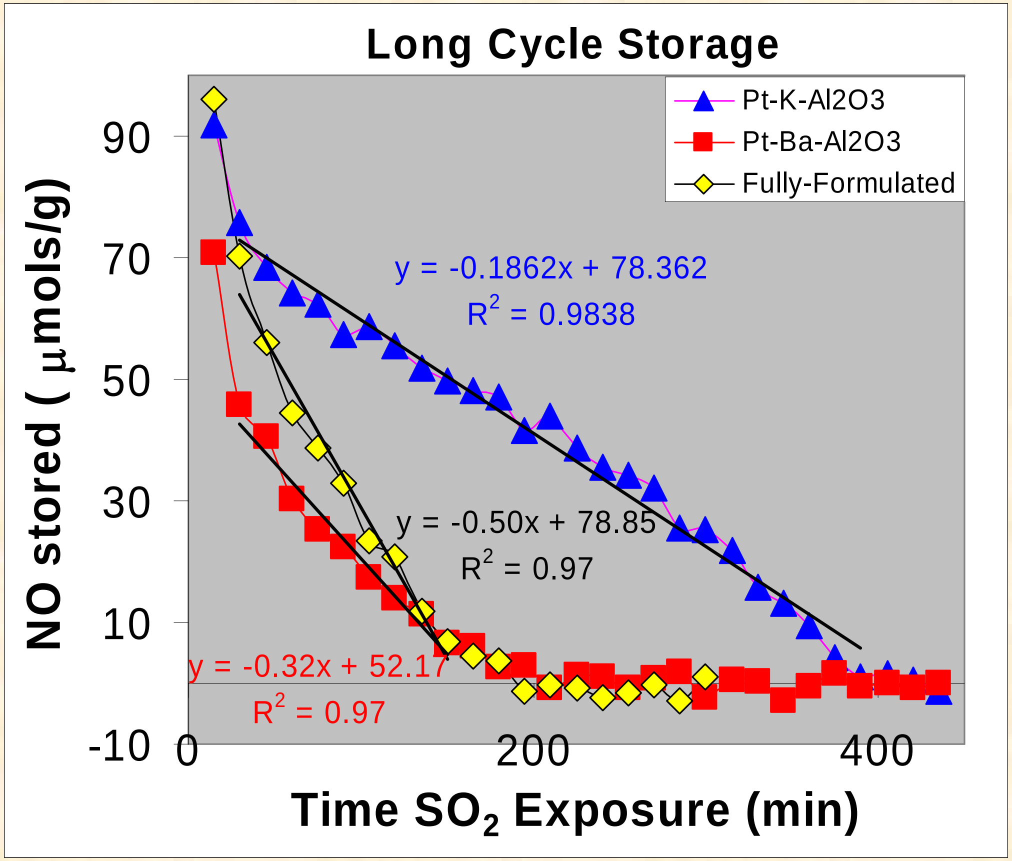
Sulfur Poisoning and Desulfation

Experimental Protocol for Sulfation

- **Two model powder catalysts studied**
  - **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**
  - **~200 g Pt/ft^3 equivalent**
- **Sulfate heavily at 250°C**
  - **Lean conditions with 130 ppm SO_2**
- **Evaluate activity and Characterize**
  - **BET, NO_x storage, Pt exposed, DRIFTS behavior**
  - **Space Velocity: 45k h^{-1}**
  - **Lean: 300ppm NO, 10 % O_2, 5% CO_2, 5% H_2O in Argon (Φ~0.5)**
  - **Rich: 0.9% CO, 0.54% H_2, 5% CO_2, 5% H_2O in Argon (Φ~1.04)**
  - **Total Storage: Dry H_2 purge followed by dry lean operation**
  - **<u>Long Cycle: 15 minutes lean, 10 minutes rich</u>**
  - **<u>Short Cycle: 60 s lean, 5 s rich (~fuel penalty 8%)</u>**
- **Desulfate at 500°C and repeat evaluation**
- **Desulfate at 760°C and repeat evaluation**

Sulfur Deactiavtion is Approximately Linear on all Catalysts

- **Deactivation is linear after initially steep decline**
- **Deactivation is slower on K-based catalyst**
  - **May only indicate higher maximum capacity**
- **Both Ba-based catalyst show similar behavior**
  - **Model catalyst deactivates faster**

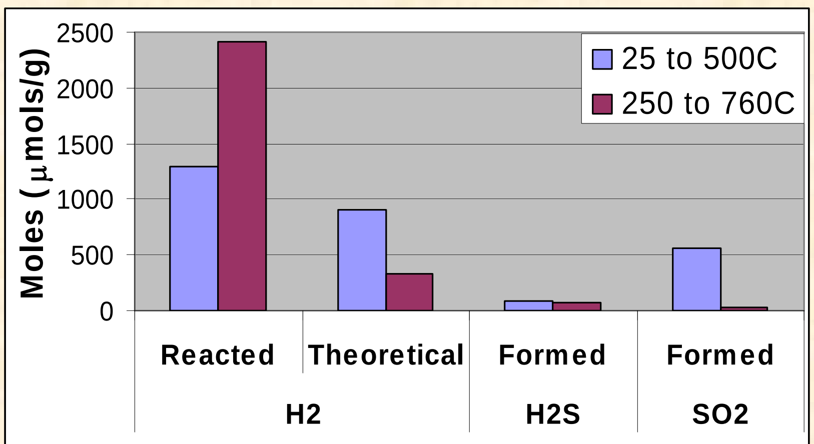


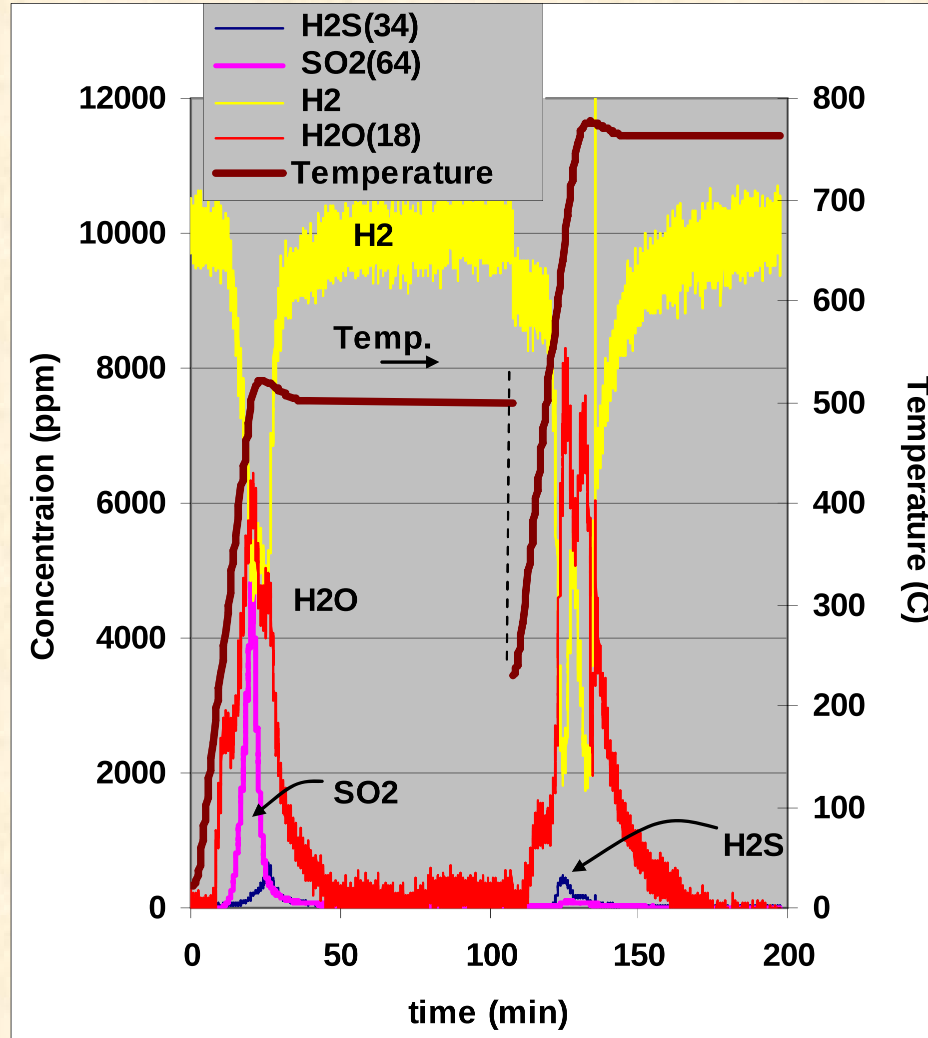
Desulfation at 760°C Releases an Undetected Form of Sulfur

- **$Pt/Ba/Al_2O_3$: little detectable H_2S and SO_x above 500°C**
- **Large Reaction with H_2 doubles NO_x Capacity**
  - **Oxygen source most likely sulfates, but product not detected with mass spectrometer**
- **Desulfation Reactions**

$$4H_2 + BaSO_4 \rightarrow H_2S + 3H_2O + BaO$$

$$H_2 + BaSO_4 \rightarrow SO_2 + H_2O + BaO$$



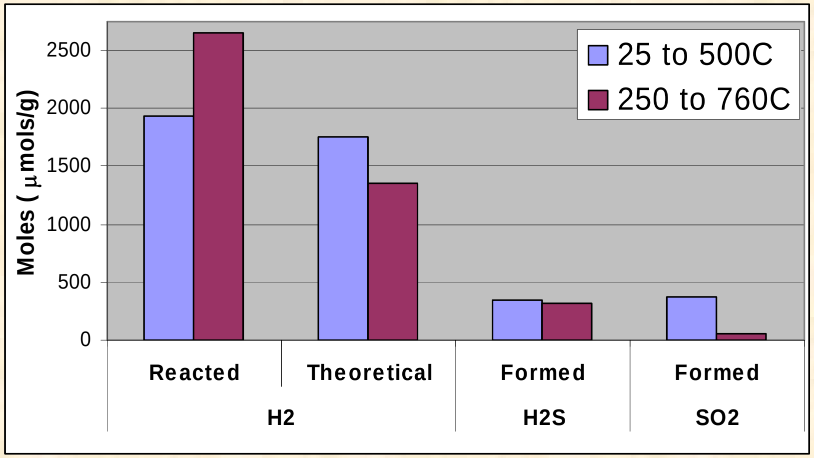


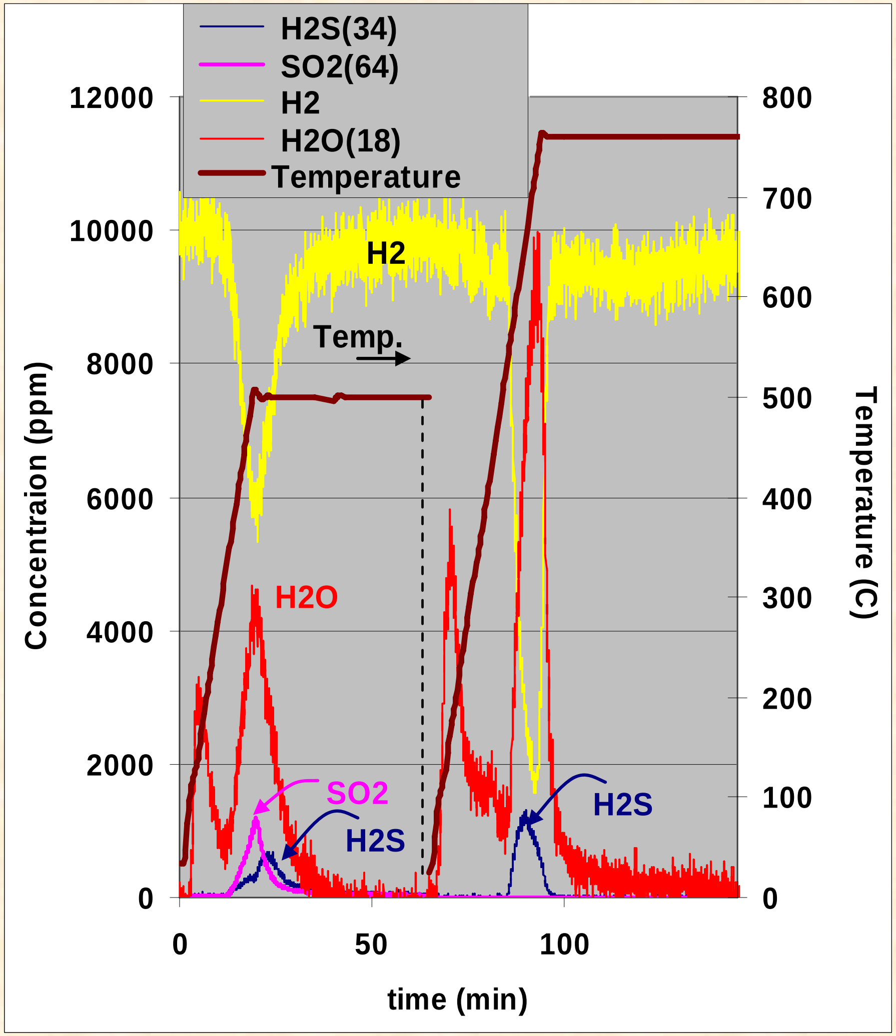
$Pt/K/Al_2O_3$ Also Does not Have Sulfur Equivalent to H_2 Reacted

- **Another reaction is probably responsible for desulfation**
  - **Non H_2S, SO_x product**
  - **Elemental S (Claus rxn) possible**
- **Lack of S in Effluent does <u>not</u> indicate De-S is complete**
- **Desulfation Reactions**

$$4H_2 + K_2SO_4 \rightarrow H_2S + 3H_2O + K_2O$$

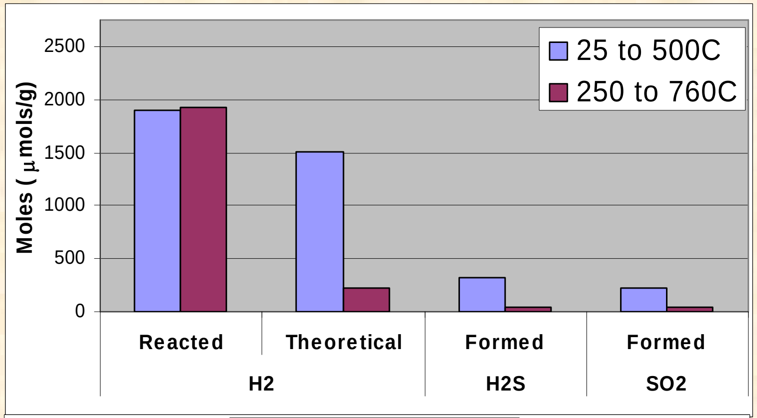
$$H_2 + K_2SO_4 \rightarrow SO_2 + H_2O + K_2O$$

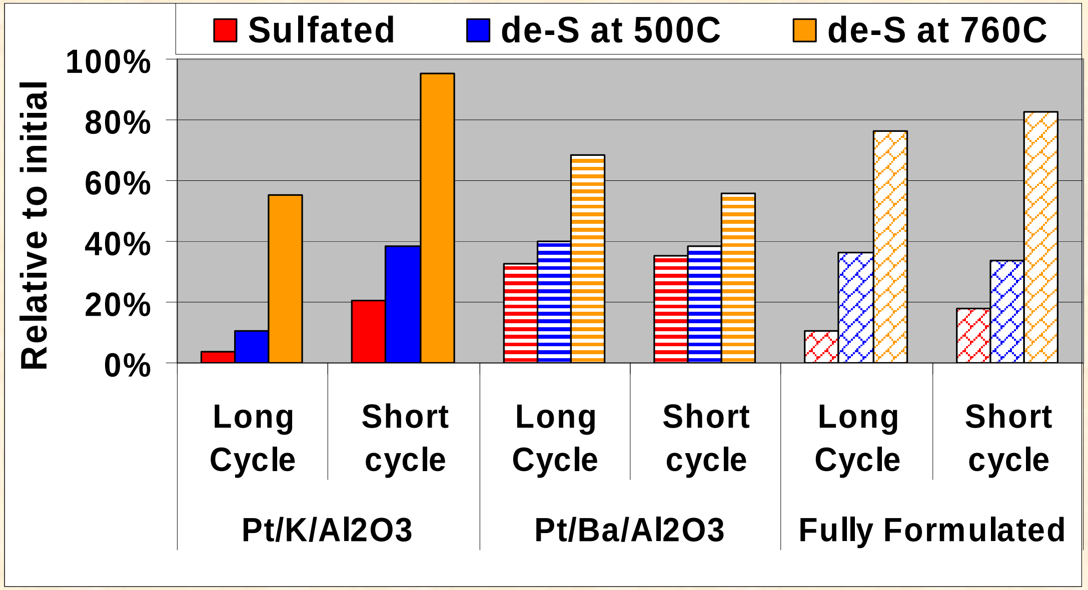


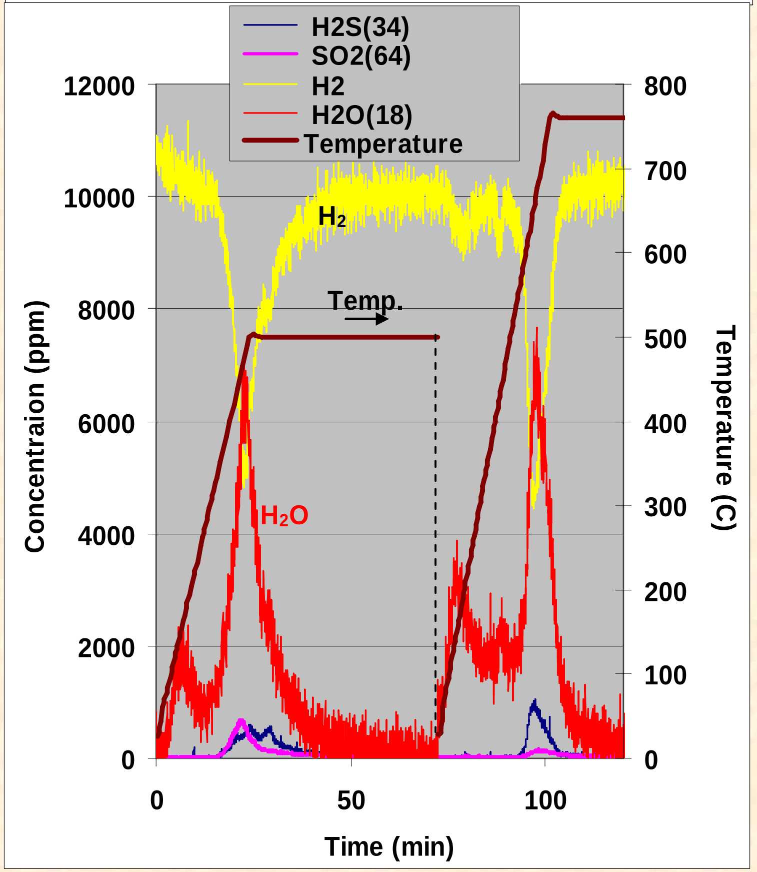


Fully-Formulated Catalyst Shows Similar Effects

- **Sulfur discrepancy above 500C still apparent**
  - **Significantly more H_2S observed below 500C**
- **80% Short cycle conversion nearly completely recovered**

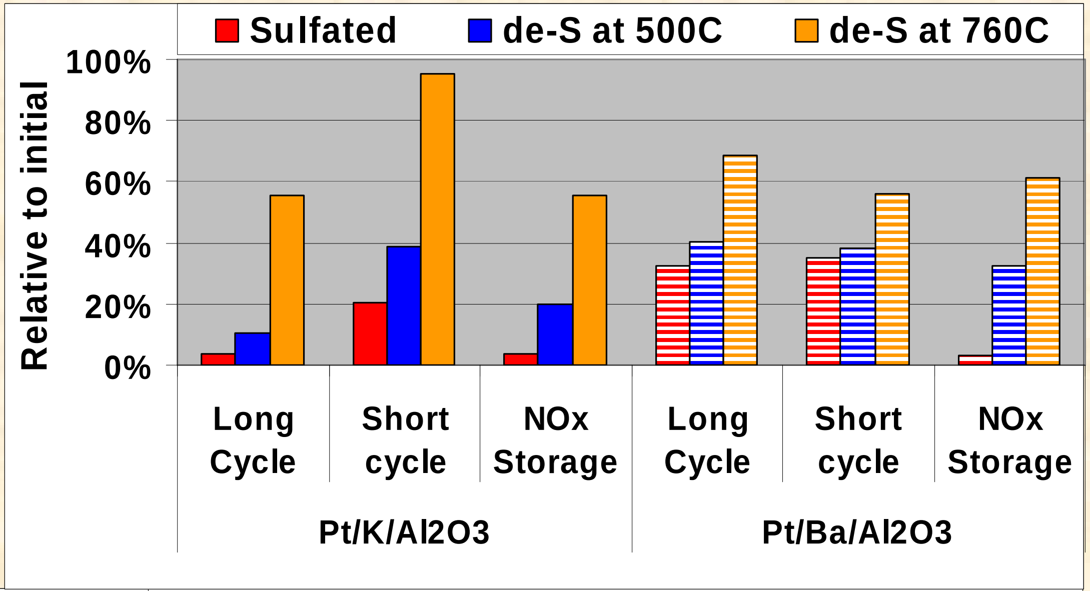


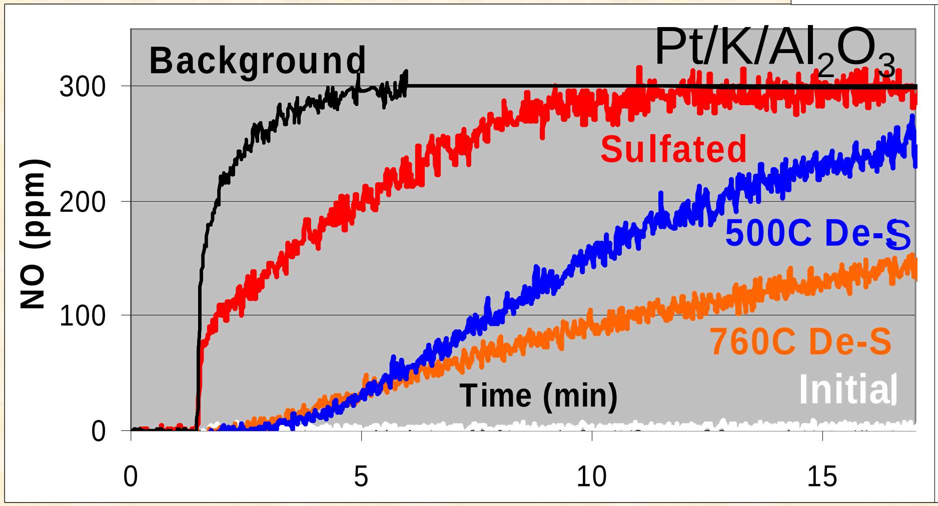


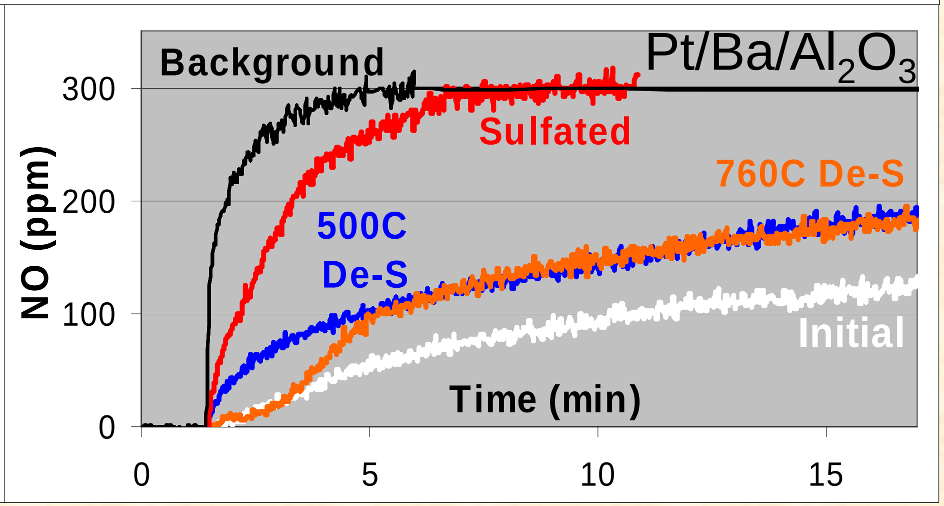


Desulfation Recovers Fast-Storage Sites

- **Some gains after each desulfation**
- **NO_x storage impacted the most**
  - **Total storage still low after desulfation**
  - **Long cycle analogous to total storage**
    - **15m lean/10m rich**
- **Short Cycle is analogous to typical engine**
  - **60s lean/5s rich**
  - **Recovered 95% of activity**

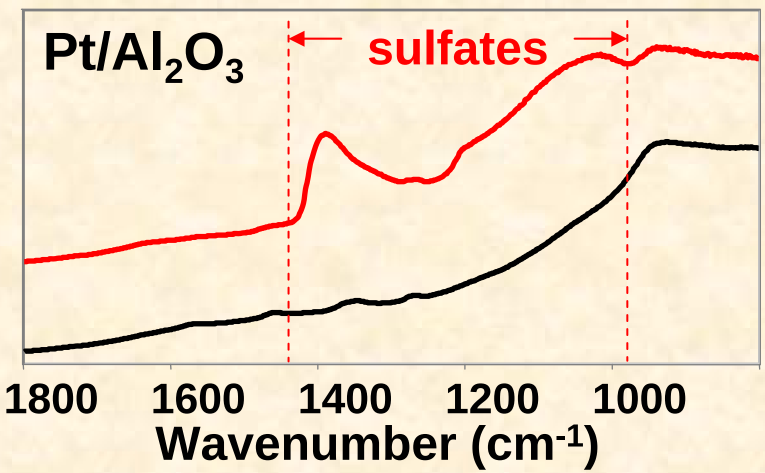


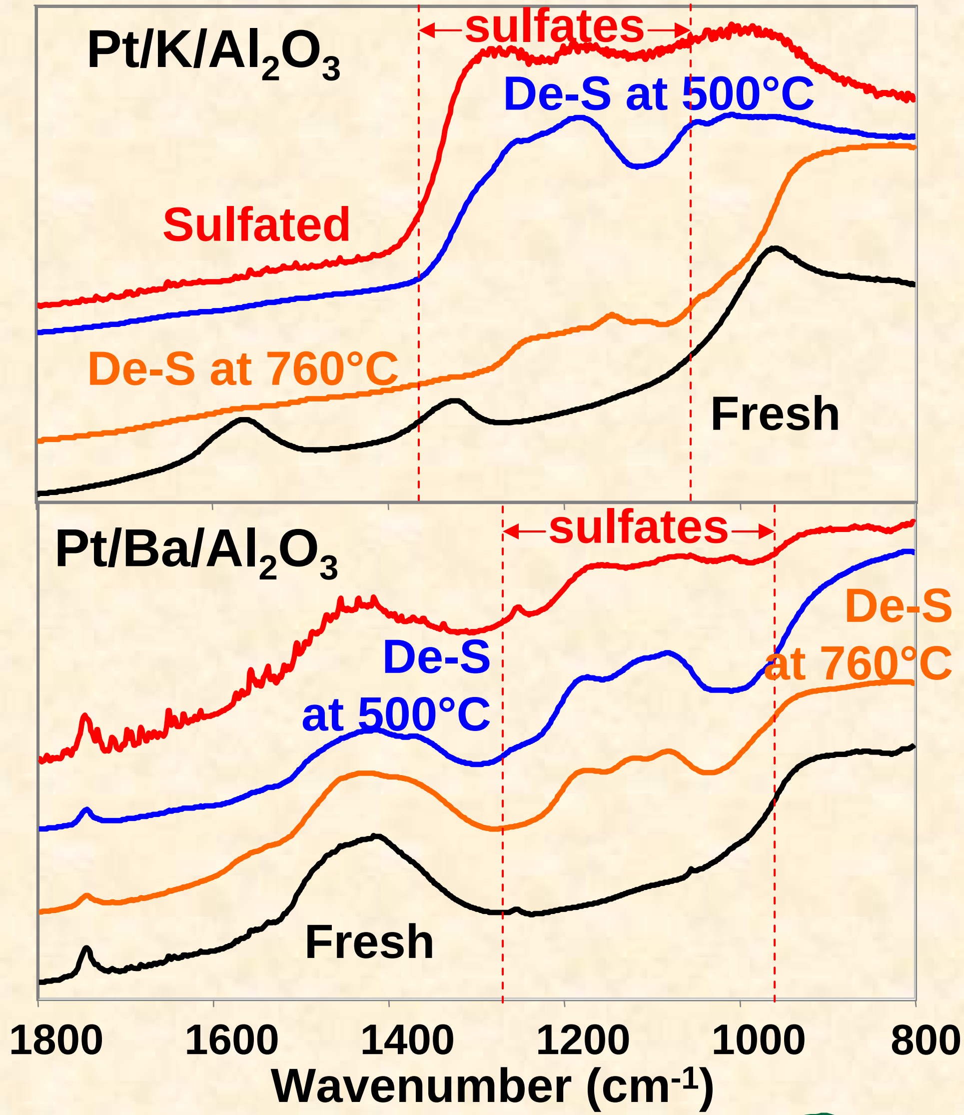




DRIFTS: Desulfation Incomplete

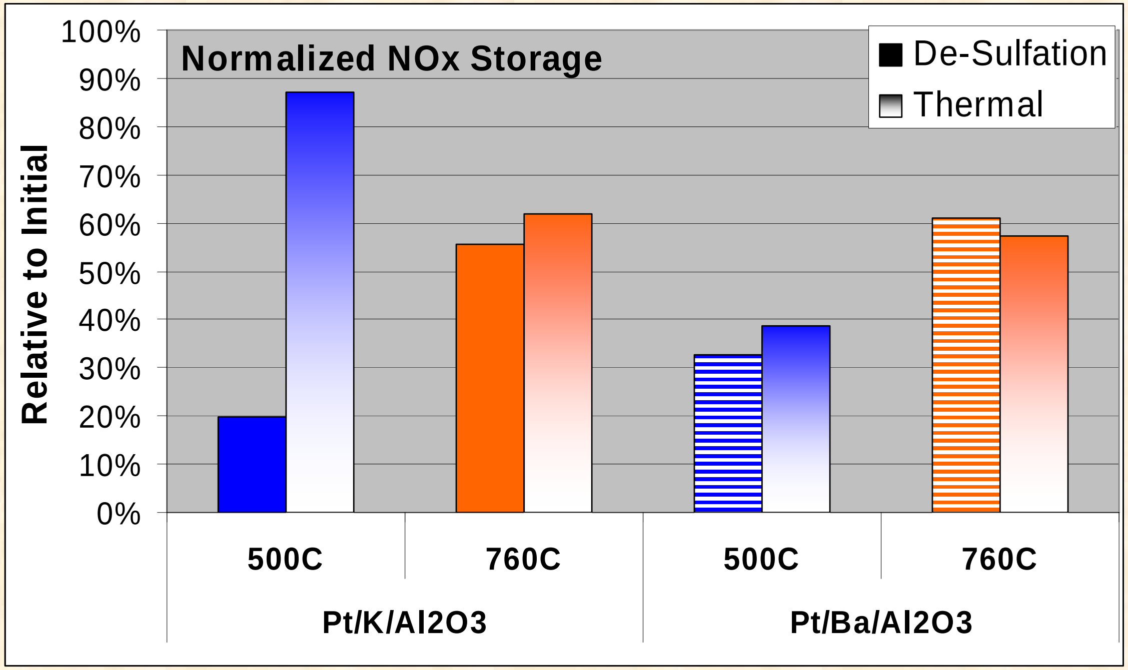
- **Long desulfation at 760°C does not fully remove S on either LNT**
- **Pt-Al_2O_3 sulfate have different absorptions**
  - **Peaks at 1390, 1200, 1080 cm^{-1}**
  - **Sulfur removal below 500°C not necessarily Al_2O_3 based**
- **Suggests Ba relies significantly on slow storage sites versus surface sites (even during fast cycling)**
  - **importance of adsorber dispersion**
  - **Surface sulfates more quickly removed**





Effects from Thermal Aging Primary Deactivation above ~700°C

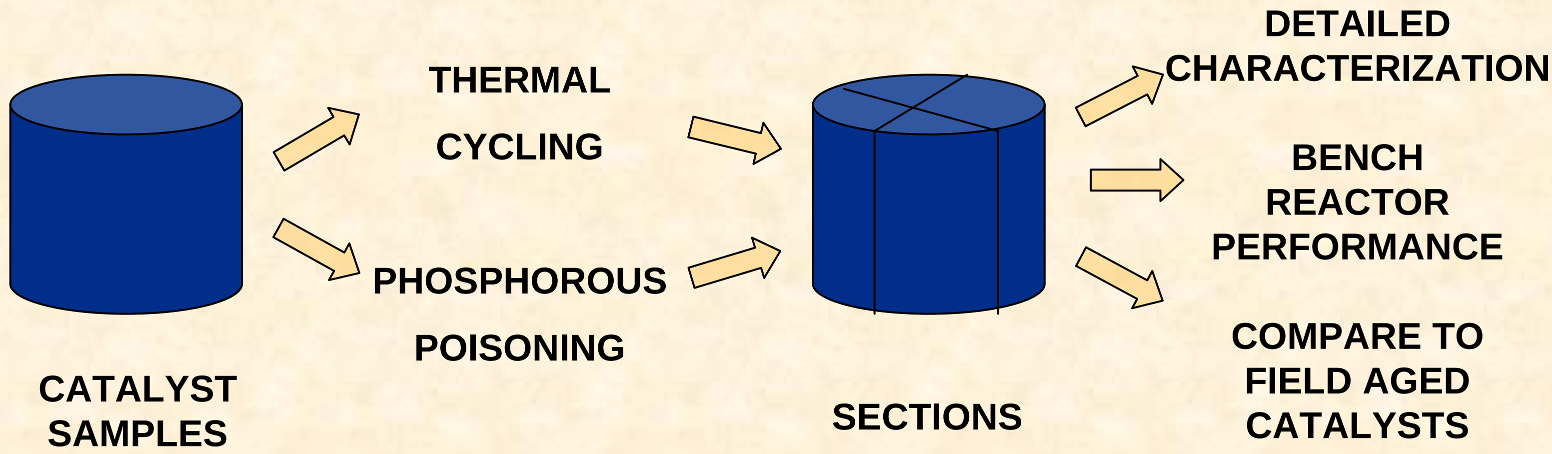
- **Catalysts desulfated at 760°C (1-2h) have similar capacity to thermally aged catalysts (20h)**
  - **Even though they are not fully desulfated**
  - **Activity tests needed to verify effect**
- **Sulfur dominates deactivation at 500°C**
- **Overheating is worse than leaving some Sulfur**
- **Suggests long, mild desulfation has benefits to short, harsh strategy**



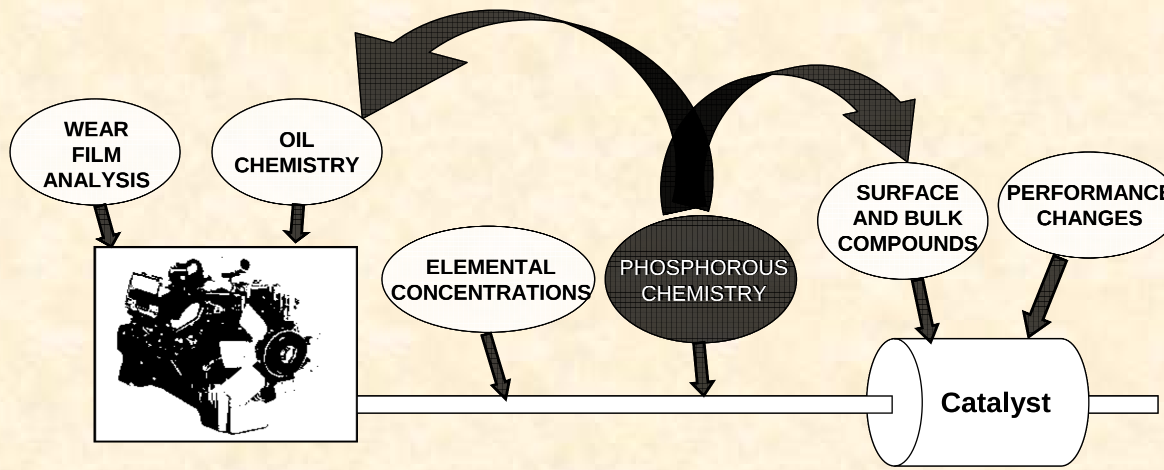
Rapid Aging Protocol:

Oil-Borne Agents

Approach - Accelerated Aging



ZDDP (Zinc dialkyl-dithio-phosphate) Experiments

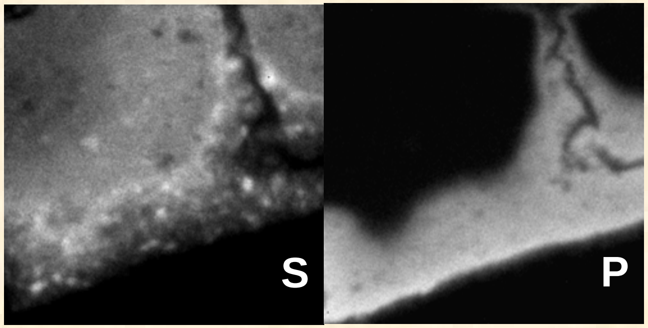


ZDDP in Lube Oil Inhibits Catalyst with P and S

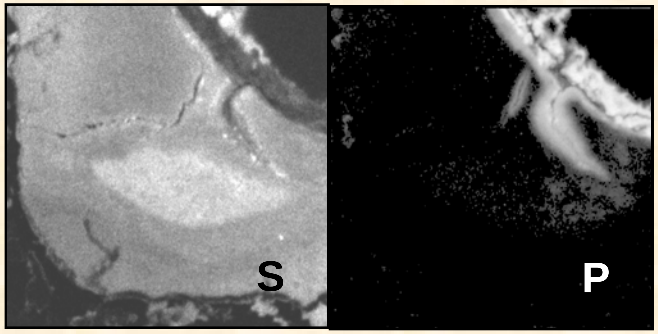
CATALYST	Sulfur collection efficiency, %	Phosphorous collection efficiency, %	Zinc collection efficiency, %
INTAKE MANIFOLD INJECTION	11.26	10.40	0.08
EXHAUST MANIFOLD INJECTION	16.47	28.93	9.76
DISSOLVED IN FUEL	20.41	12.04	0.16

- **P impacts more in exhaust-born oil**
  - **~120% rise in light-off Temp w/3g ZDDP**
- **Sulfur impacts more in fuel-born oil**
  - **~80% rise in light-off Temp w/3g ZDDP**
- **More details available:**
  - **SAE 2005-01-1758; buntingbg@ornl.gov**

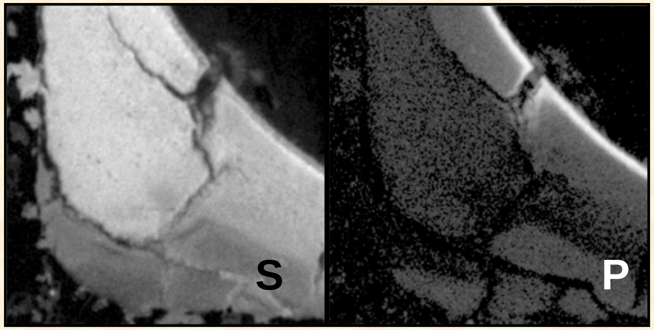
Added at intake



Added in exhaust

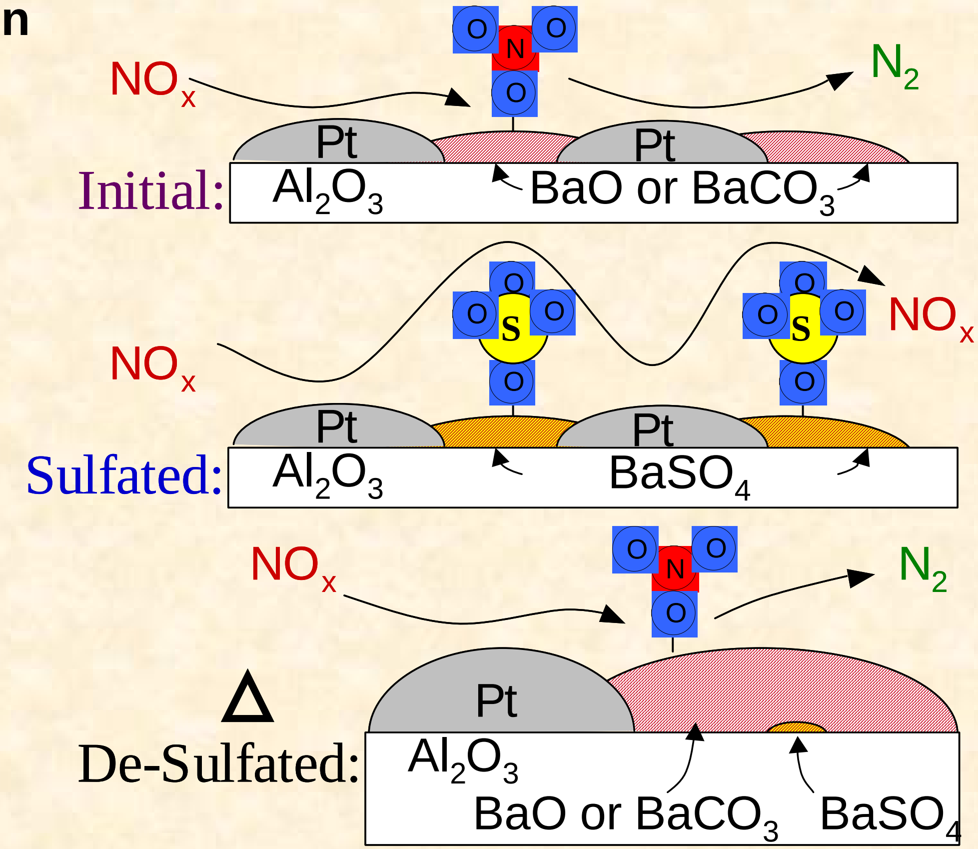


Added in fuel



Summary

- **Thermal aging is primary mechanism of LNT deactivation**
- **Desulfation is slow**
  - **most likely never results in a S-free catalyst**
  - **Surface sulfates removed quickly**
  - **Bulk Sulfates linger**
  - **However, significant activity is restored**
- **H_2S and SO_2 are not only desulfation products**
- **Moderate desulfation key to LNT longevity**
- **S and P from oil have shown effect on DOC**
  - **LNTs also susceptible**



Future Work

- Shift Focus to DRIFTS-based analysis, especially with respect to desulfation
- Expand temperature range (200 and 500°C)
- Further characterize catalysts with respect to sulfation
  - Does strongly bound sulfur poison rapid sites quickly? Or is it stable?
- Sulfate catalysts and titrate desulfation
  - Goal is to establish method for removing sulfur in near Pt
    - Establish with detailed characterization
    - Work with modeling effort to infer rate of surface migration
- Make thermally aged catalysts available for modeling effort
  - Establish criteria for Pt-size, Adsorber surface area, and relative proximities and their effects on LNT kinetics
  - How well does activity correlate with Adsorber/PM interface
- Finalize *in-situ* DRIFTS reactor for washcoated samples
  - Enables translation along channel
  - Successful design reasonably simulates flow/temperature
  - Incorporate spatiotemporal diagnostics of Spaci-MS

Recent Publications and Upcoming Presentations

- "Quantification of the *in-situ* DRIFT Spectra of Pt/K/gamma-Al_2O_3 NO_x Adsorber Catalysts", **Appl. Catal. B, 58:3-4 (2005) 245.**
- "Quantified NO_X adsorption on Pt/K/gamma-Al_2O_3 and the Effects of CO_2 and H_2O", **Appl. Catal. B, 58:3-4 (2005) 255.**
- **"NO_X Adsorption Routes on Pt/K/Al_2O_3",** will be presented at 19th NACS meeting (Wednesday)
  - **Selected for publication in Catalysis Today**
- **Poster Presentation of LNT deactivation and ZDDP Poisoning at 19th NAM (Tuesday night)**
- **Contact: tjtoops@ornl.gov, (865)-946-1207**

Engine Aging Procedure

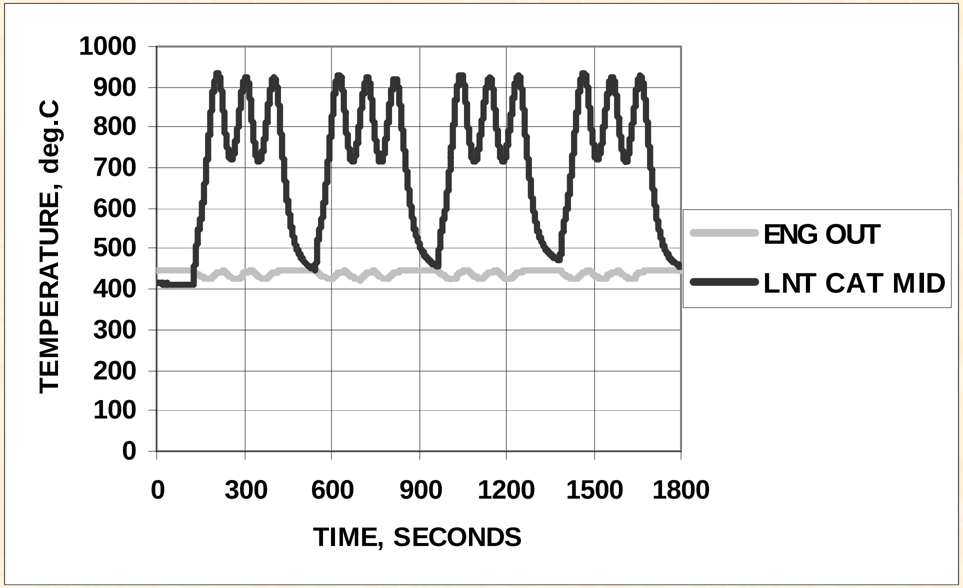
- Temperature and cycle times generated from industrial survey
- Performance evaluations under similar conditions
  - 4 sec rich (target 13:1 A/F)
  - 20 sec lean
  - 60K h^{-1} SV
  - 400 deg.C
  - 800 ppm NO_X

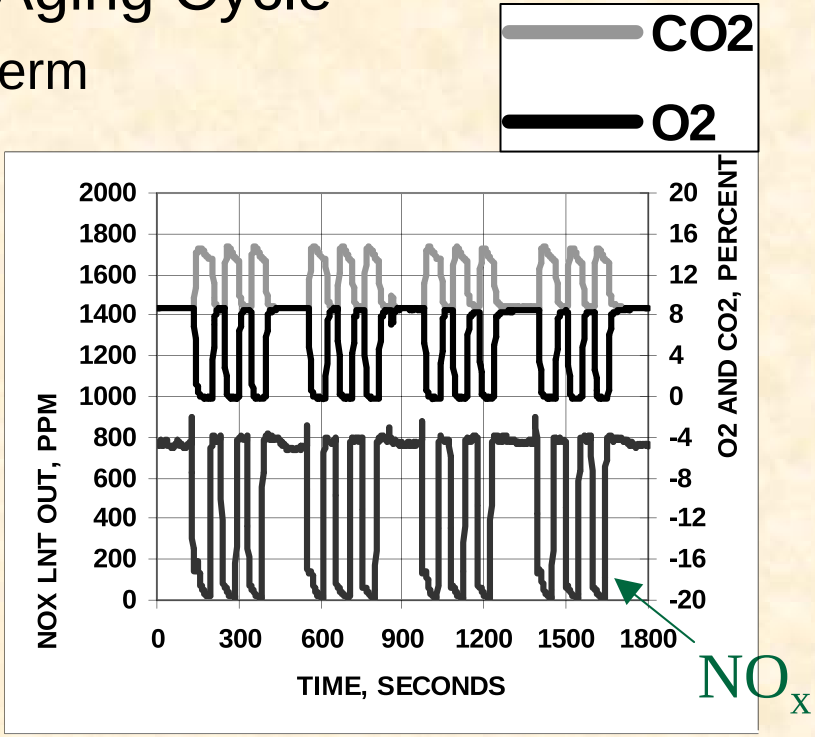
HOURS AGING	NUMBER OF AGING CYCLES	TARGET TEMPERATURE		
		700 deg.C	800 deg.C	900 deg.C
20	80	X	X	X
6	24	X	X	X
2	8	X	X	X

- Engine aging
  - 400 C base temperature
  - 120 sec lean
  - 30-120 sec rich
    - Switched to lean when target temperature rich
    - Large exotherm (100 C) after lean transition

Engines Exhibits Exotherms in Aging Cycle

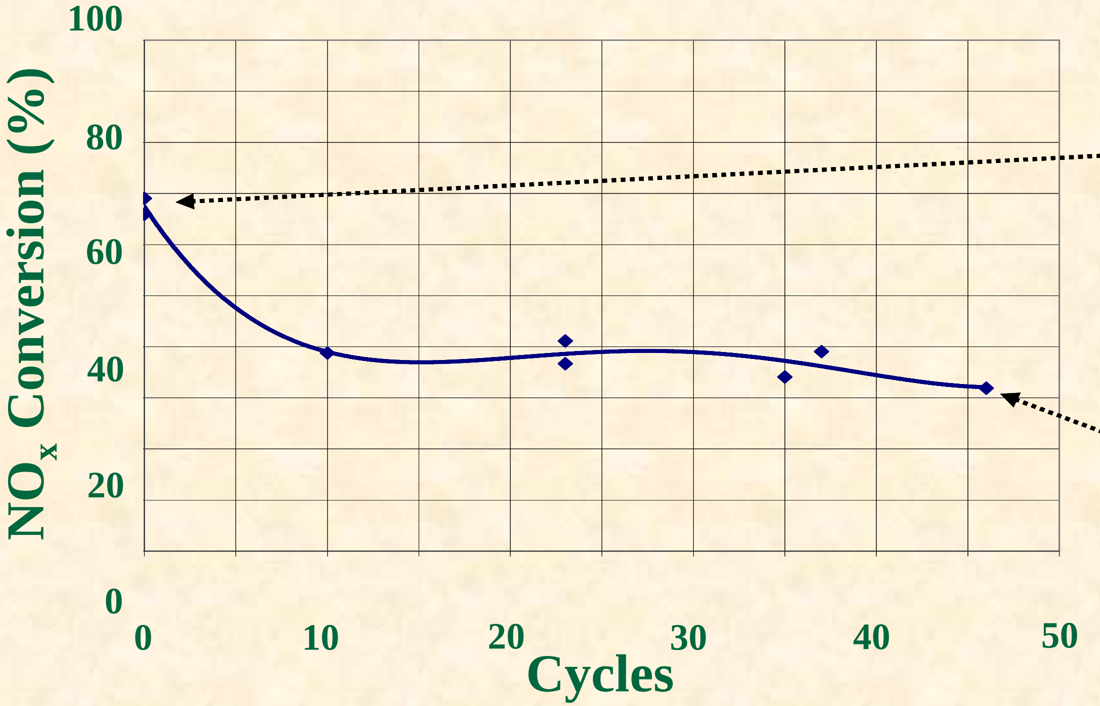
- Typical Engine Lean / Rich Aging Cycle
  - 800C target with a 920C exotherm





NO_x Conversion Decreases Rapidly

- NO_x Activity drops precipitously
  - 43% decrease in conversion after 10 cycles
  - 54% after 46 cycles
- Surface Area and Pt/Rh size Affected

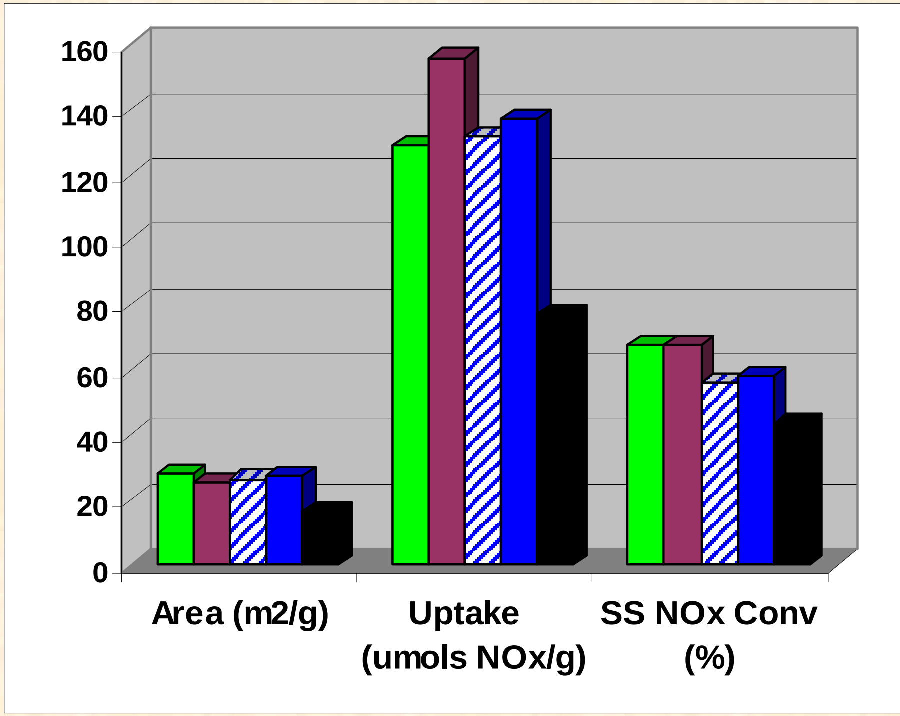


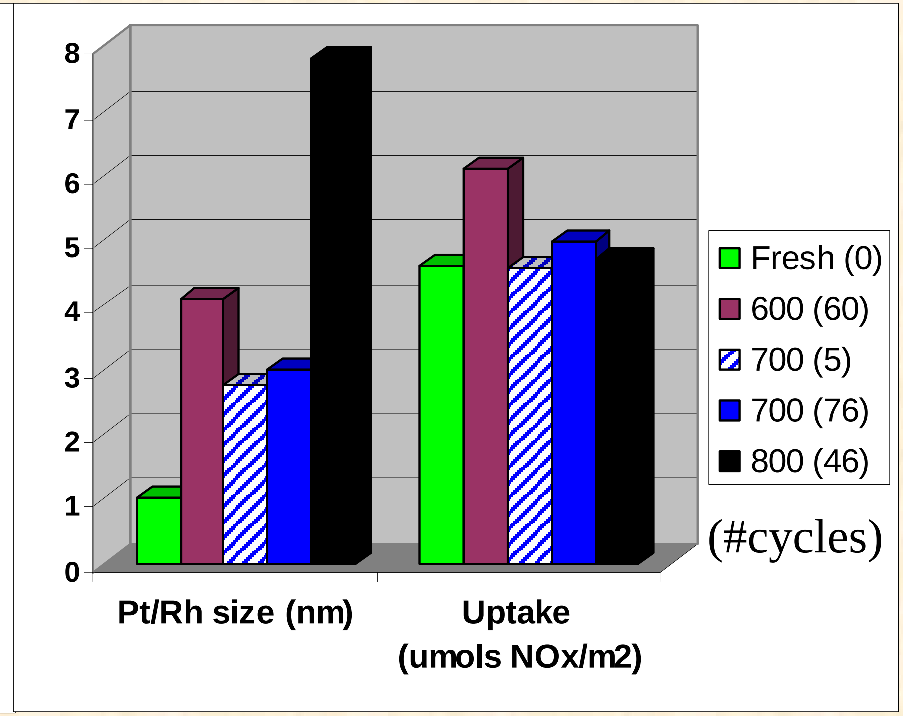
Fresh Catalyst
Surface Area: 32 m^2/g
Pt/Rh size: 1-4 nm
NO_x storage: 126 μmols/g
4.5 μmols/m^2

Aged Catalyst (46 cycles)
Surface Area: 17 m^2/g
Pt/Rh size: 7-20 nm
NO_x storage: 78 μmols/g
4.8 μmols/m^2

Powder Reactor Storage Capacity Drop Primarily a Surface Area Effect

- Surface Area and total NO_x uptake per gram drops for 800C
- Normalized uptake per m^2 stays constant
- Pt/Rh size relates to kinetics and future tests



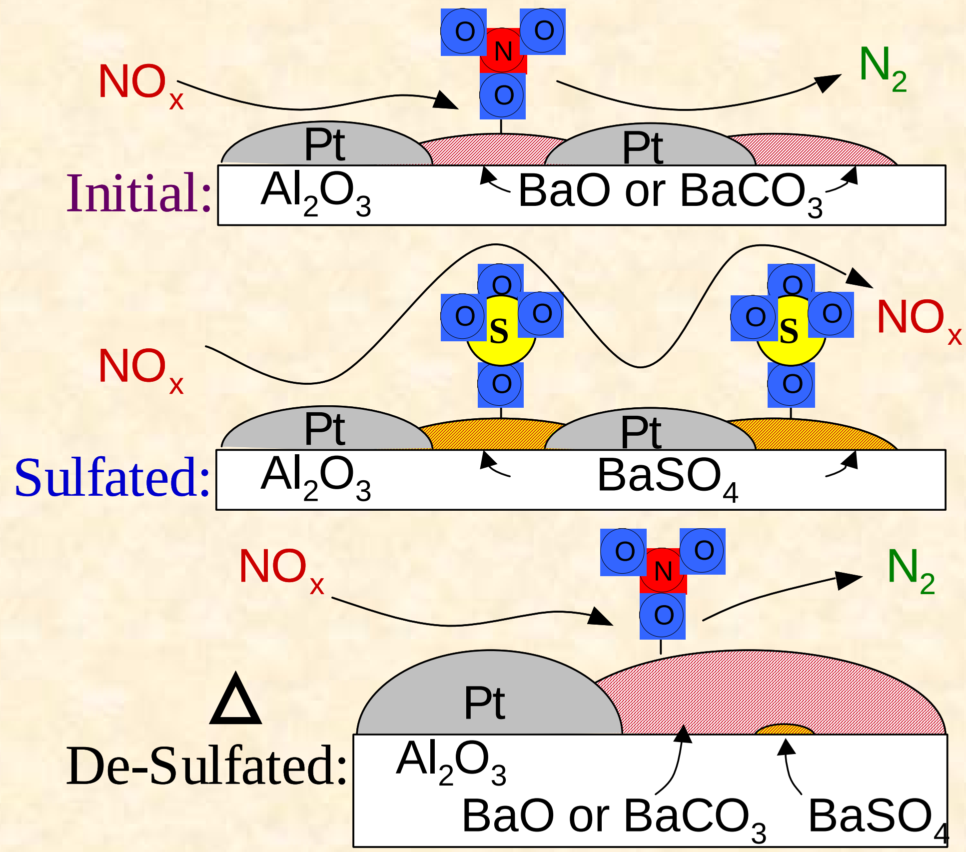


Summary of Literature*

- **Even low Sulfur fuels will eventually completely deactivate LNTs if unmitigated**
- **Sulfur affects both precious metals and adsorber**
  - **Sulfates form more readily in lean conditions**
  - **Poison precious metals more effectively in rich**
- **H_2S, SO_2, and CO-S all effectively poison LNTS**
- **Catalyst components affect desulfation Temperature**
  - **Ba-based LNTs desorb at lower T than K-based**
- **H_2 is most effective desulfation reductant**
  - **Tests with CO require H_2O for effective de-S (WGS)**

*** - references available on request**

- **Are slow adsorption sites bulk or just sites away from Pt?**



Pt/K/Al_2O_3 Sulfation with DRIFTS

- **Long Cycling at 250°C with 100 ppm SO_2 in lean flow**
- **Nitrates and Sulfates initially compete for sites**
- **Sulfates dominate after a couple of cycles: 1100, 1050 cm^{-1}**
- **CO adsorbed on Pt**

Lean Spectra detailing peak assignments	Movie of long lean to rich cycle on K with H_2O and CO_2
Rich Spectra detailing peak assignments	Movie of long lean to rich cycle on K with H_2O and CO_2 plus SO_2

Engine also Suggests Greater Deactivation from Thermal Aging

- **Engine Background (Jim Parks Talk)**
  - **Barium-Based LNT; heavily sulfated (equivalent of 7k miles)**
  - **Engine desulfated for 10-20 minutes at 500-800°C (50°C increments)**
- **Heavily desulfating with temperature excursions greater than 900°C only recovered 60% of initial activity**
  - **The 40% reduction in activity is permanent**