

Functionality of Commercial NO_x Storage-Reduction Catalysts and the Development of a Representative Model

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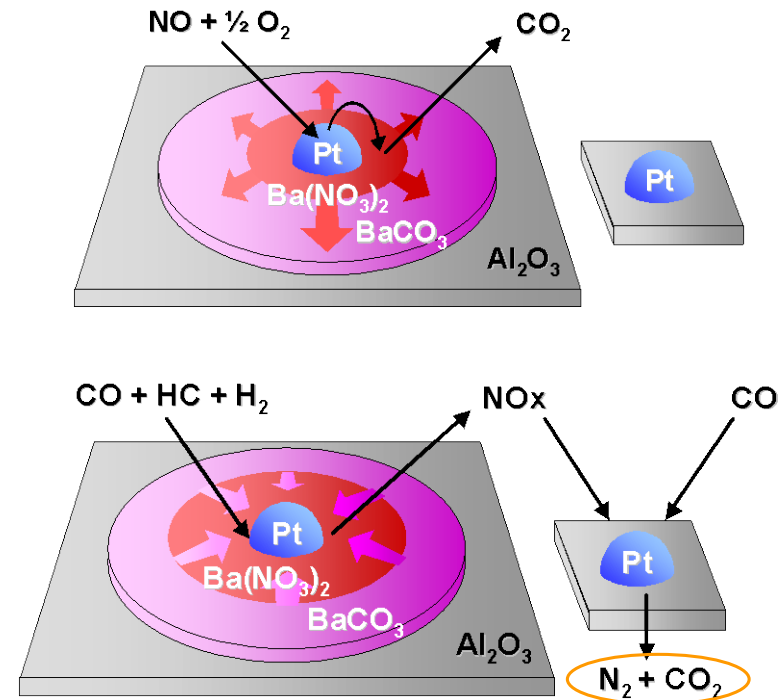
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Commercial LNT/NSR catalysts are complex and challenging to analyze

- Initial LNT/NSR catalyst research focused on model catalysts with well defined roles
- OEMs challenge us to study more realistic catalysts
- CLEERS adoption of Umicore LNT/NSR catalyst
 - Donated by Umicore for full analysis
 - GDI formulation
 - Commercially available catalyst
- What happens when the other components are included in the catalysts?
 - Performance effects
 - Selectivity effects
 - Sulfation and Desulfation
 - Predictability/modeling potential

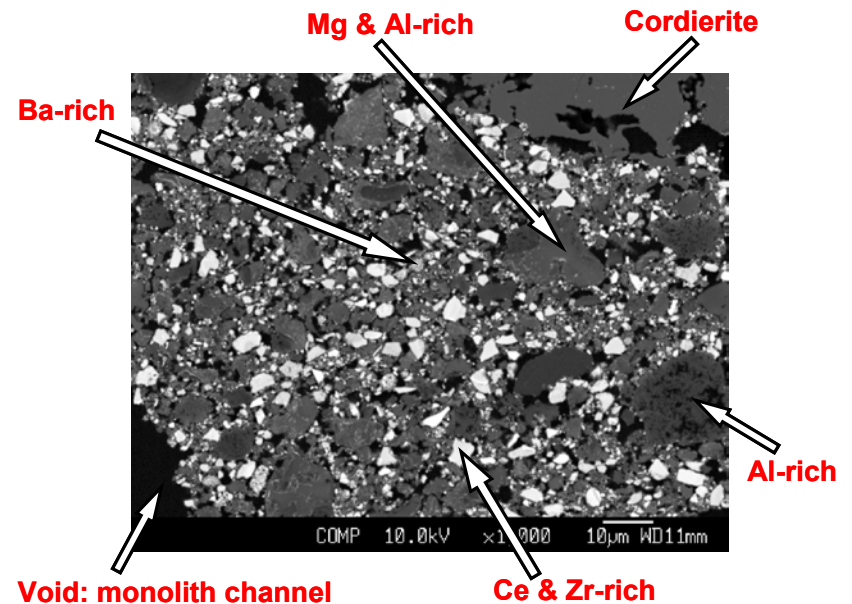
Model catalysts have components with well defined roles



(Images adapted from Johnson Matthey Website)

Commercial catalyst is a complex multicomponent system

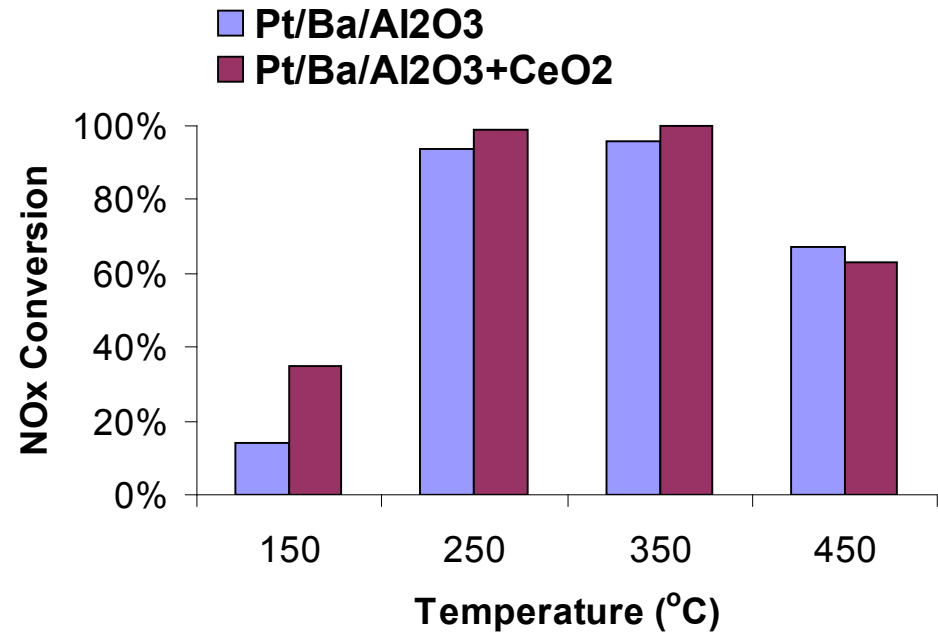
- Ba-based adsorber formulation with Pt, Pd and Rh PGM
- Relies on Al_2O_3 , $\text{CeO}_x\text{-ZrO}_2$, and Mg/Al-oxide as supports
- Key differences:
 - Ba is supported on ceria-zirconia support
 - $\text{Pt/Ba/CeO}_x\text{-ZrO}_2$
(not $\text{Pt/Ba/Al}_2\text{O}_3$)
 - Rh is primarily supported on Alumina
 - Large fraction of washcoat contains low-PGM Mg/Al-oxide



Domain	Composition
Ba-rich	Ba (high), Ce/Zr, Pt, Pd
Ce/Zr-rich	Ba (low), Ce/Zr, Pt, Pd
Al-rich	Al, Rh, Pd
Mg/Al-rich	Mg/Al, Pt, Ce

Inclusion of Ceria results in better NOx conversion at low T than Pt/Ba/Al₂O₃

- Better low temperature properties observed with ceria containing LNTs
 - Observed when:
 - ceria as a support, and
 - with ceria in washcoat
- Nitrates less stable than when using alumina-only as support



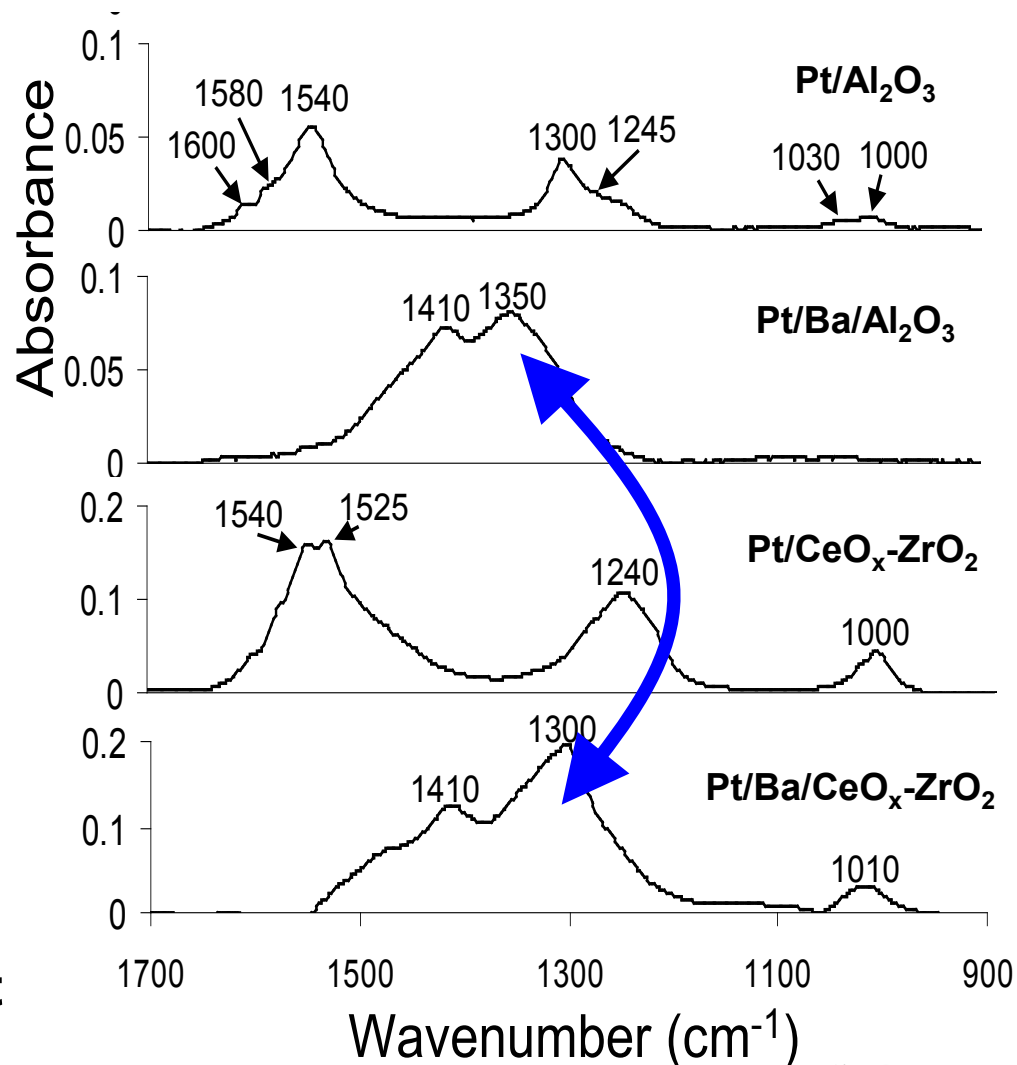
(results from work with Crocker et al. at UK-CAER)

Benefit not without cost...

- Ceria stores oxygen that consumes fuel
 - Oxygen storage component (OSC)
 - Lean: CeO₂
 - Rich: Ce₂O₃

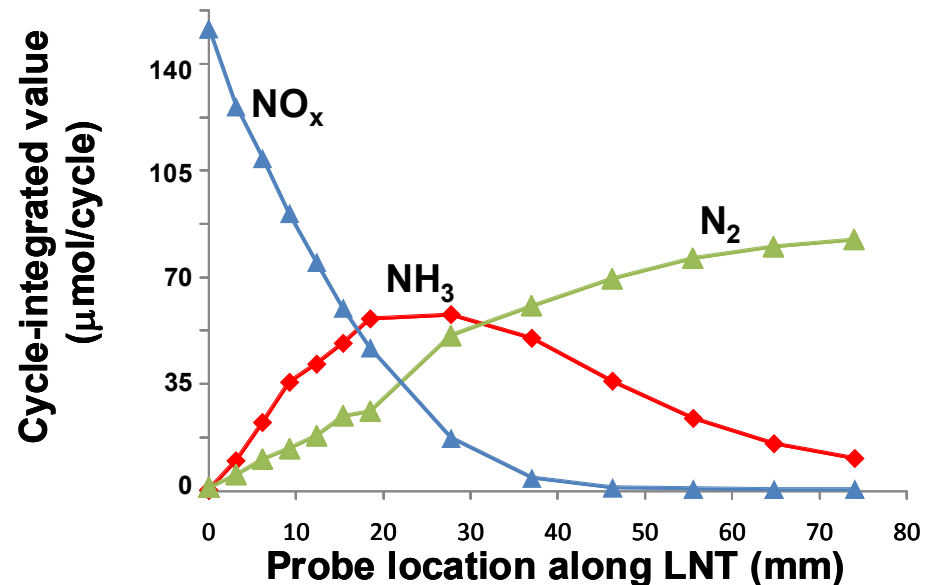
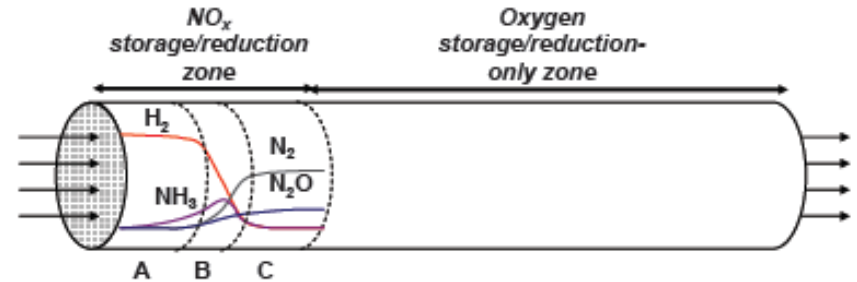
Ceria-Zirconia appears to modify nitrates stored; Peak shift identified

- DRIFT spectra after 30 min of NO_x storage at 200°C
 - 300 ppm NO, 10% O₂, 5% H₂O
- At 200 C, nitrates observed on Ce-Zr support
 - not significant on alumina
- Ba-based nitrate peak locations appear to shift due to support
 - Pt/Ba/Al₂O₃: 1350 & 1410 cm⁻¹
 - Pt/Ba/CeO_xZrO₂: 1300 & 1410 cm⁻¹
- Illustrates impact of adsorber/support interactions



Oxygen storage component impacts selectivity to NO_x reduction products

- NO_x Storage and Reduction (NSR) occurs primarily in front 1/4
- Significant NH₃ is formed when reductant:NO_x ratio is high
 - Typically observed at “reductant front”
 - Breakthrough at similar time as H₂/CO/HC reductant
- Fully oxidized OSC consumes remaining NH₃ in rear of catalyst
 - Reduces tailpipe NH₃
 - Also reduces NH₃ available for SCR reaction in LNT+SCR application

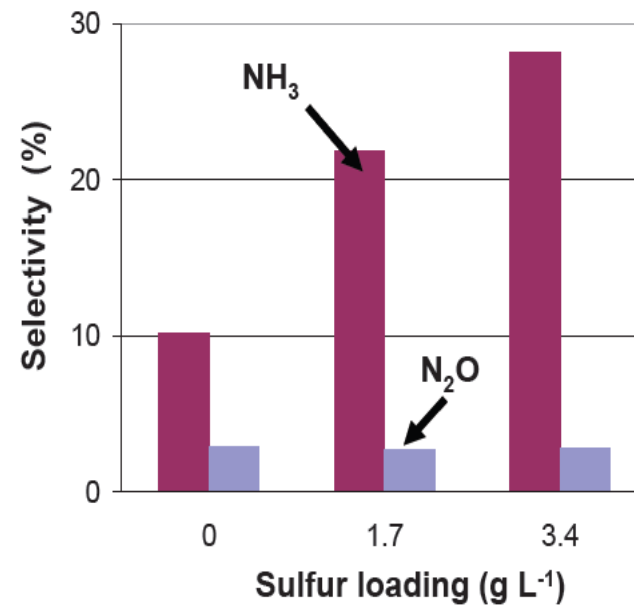
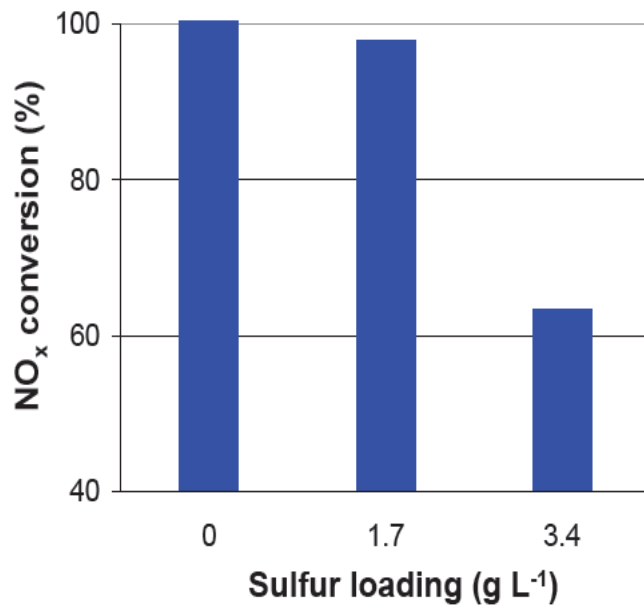


SULFUR STUDIES and IMPACT

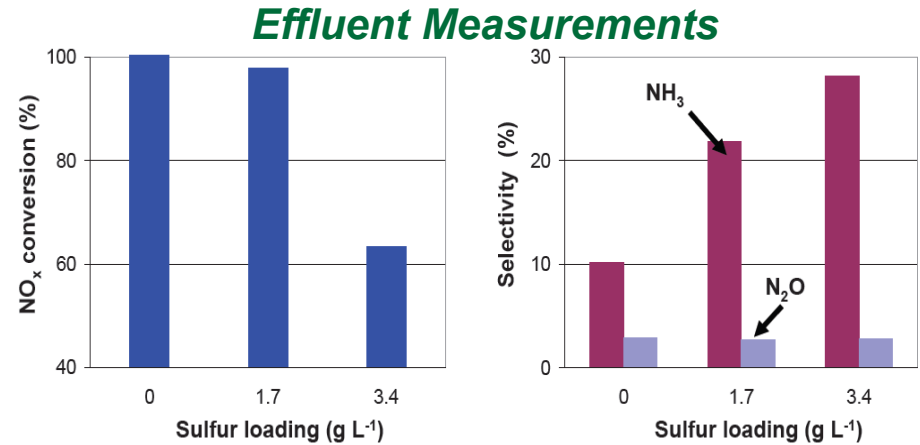
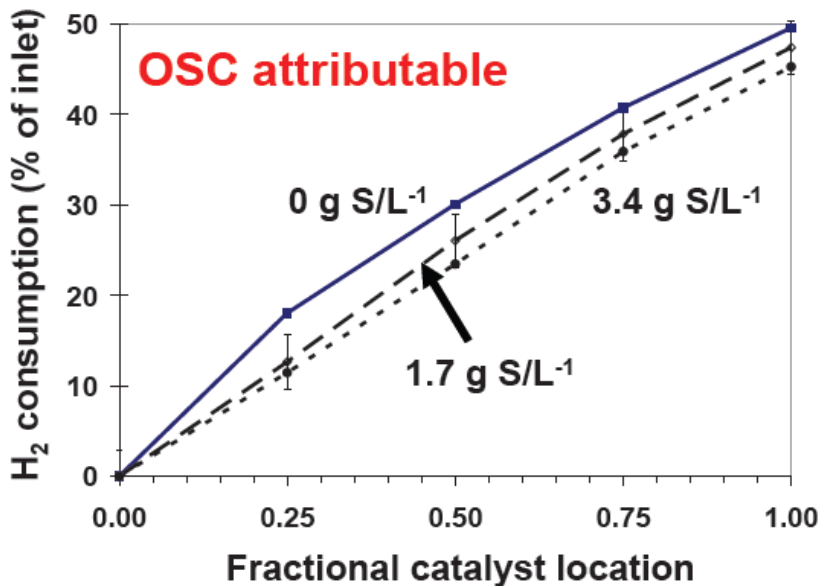
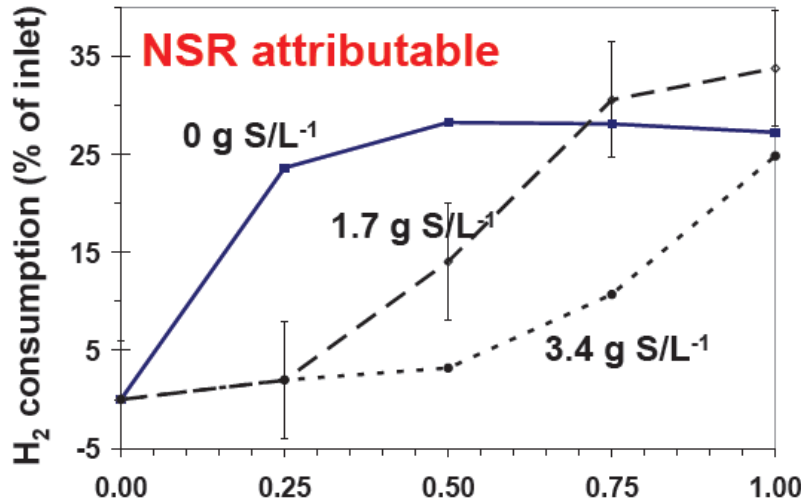
Sulfur impacts both NSR activity and product selectivity

- When sulfur exposure is $>1.7\text{g/L}$, NO_x conversion starts to decrease significantly
- NH_3 increases significantly with each sulfur dosing

Effluent Measurements



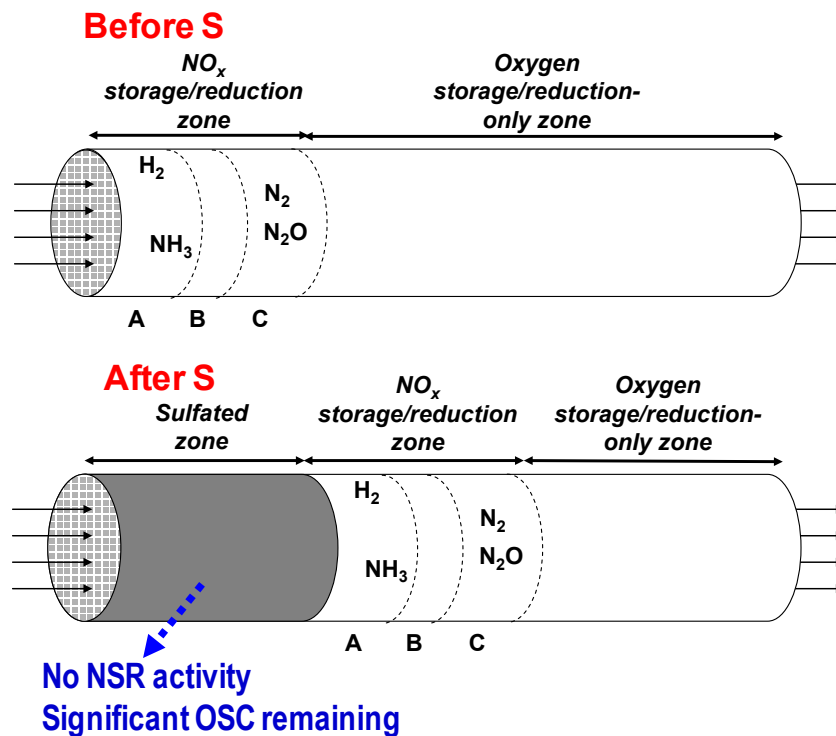
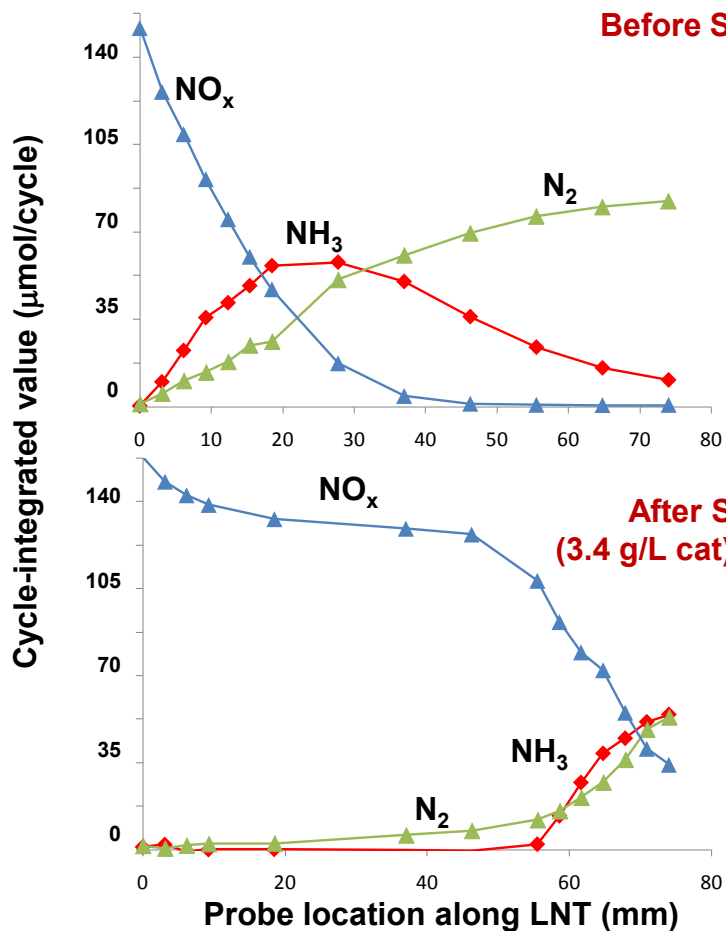
Sulfur impacts NSR activity in plug-like fashion; small distributed impact on OSC



- Only when $S > 1.7 \text{ g/L}$, NO_x conversion starts to decrease
 - Plug-like behavior suggested
- Small impact observed on overall OSC behavior

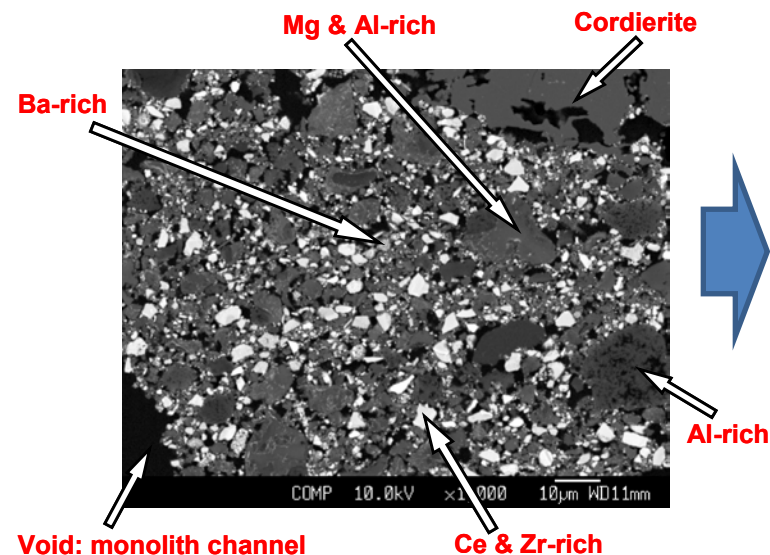
Mechanism of sulfur impact illustrated in detailed intra-catalyst measurements

- Sulfur introduction moves active NO_x storage sites downstream
- As a result, length of OSC-only zone decreases
- More NH₃ exits LNT without being oxidized by OSC



In-depth characterization correlates sulfur concentrations to specific components

Sulfur coordination in front 1/4



Domain	Composition	S content (at.%)
Ba-rich	Ba (high), Ce/Zr, Pt, Pd	7.3
Ce/Zr-rich	Ba (low), Ce/Zr, Pt, Pd	2.1
Al-rich	Al, Rh, Pd	2.4
Mg/Al-rich	Mg/Al, Pt, Ce	1.2



Ba

Ba sulfation is vigorous leading to plug-like poisoning of NO_x storage sites

→ increasing S

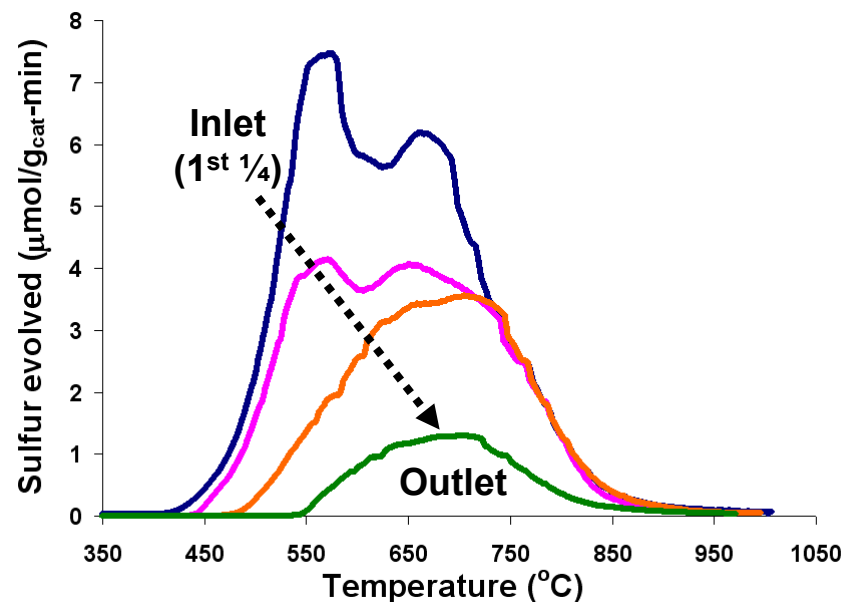
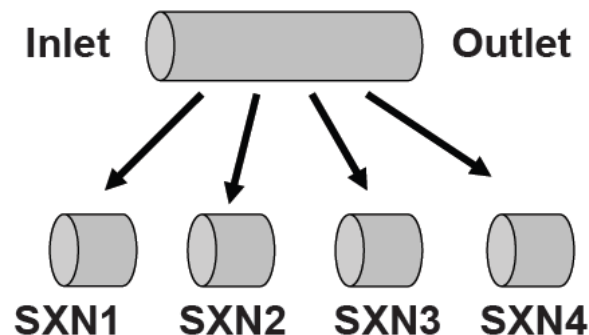
Ce/Zr
Al
Mg/Al

Sulfation of Ce/Zr, Al, Mg/Al is less efficient but significant “S-trap” delaying Ba sulfation

Desulfation profiles further illustrate sulfur associations

- Low temperature peaks decrease from SXN1 to SXN4
 - Sulfur associated with Ce/Zr and Alumina in SXN1 & SXN2
- Only high temperature peaks for SXN3 & SXN 4
 - Primarily Ba-associated sulfur
- Oxygen storage uptake of sulfur (Ce-Zr) is less efficient
 - no low temperature release in SXN4

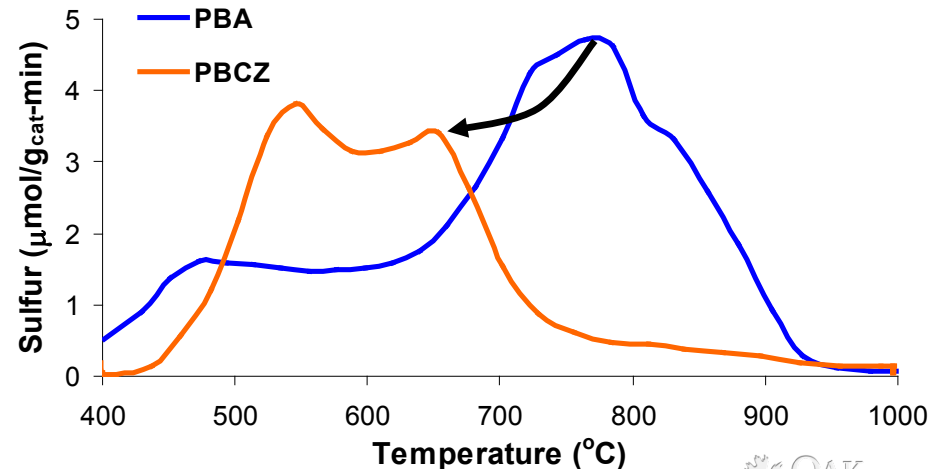
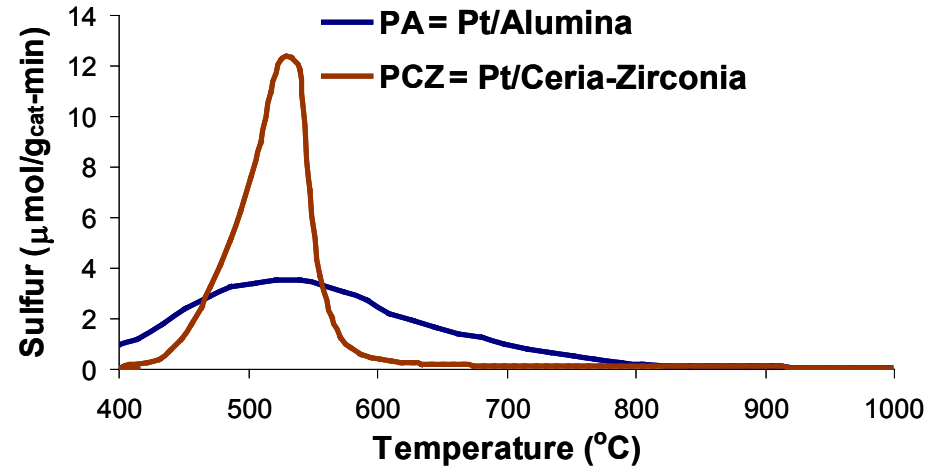
3" Core with 3.4 g S/L loading



Ceria-Zirconia decreases required desulfation temperature significantly

- Onset of SO₂ release is lower for Pt/Al₂O₃, but release profile is broad
 - T_{20%} = 464°C; T_{90%} = 704°C
 - Demonstrates heterogeneity of sites
- Pt/Ceria-Zirconia has sharp release profile
 - T_{20%} = 494°C; T_{90%} = 570°C
- Introducing Ba transforms release profiles
 - Only minor sulfur release observed from alumina supports
 - PBCZ sulfur releases at significantly lower temperature
 - PBA: T_{20%} = 570°C; T_{90%} = 855°C
 - PBCZ: T_{20%} = 535°C; T_{90%} = 797°C

Sulfur release measured during 400-1000°C temperature ramp

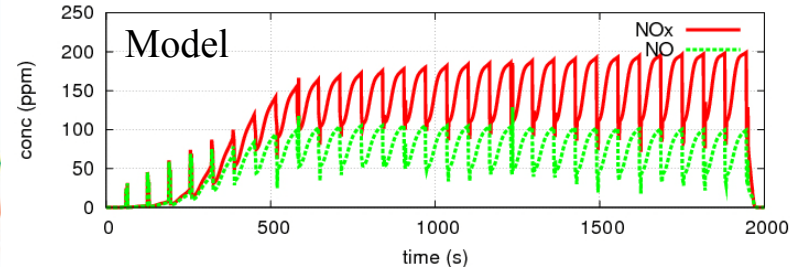
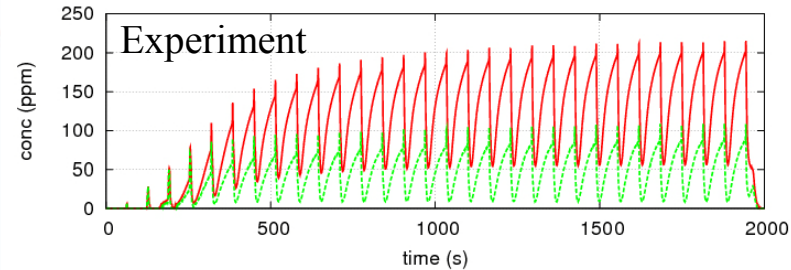
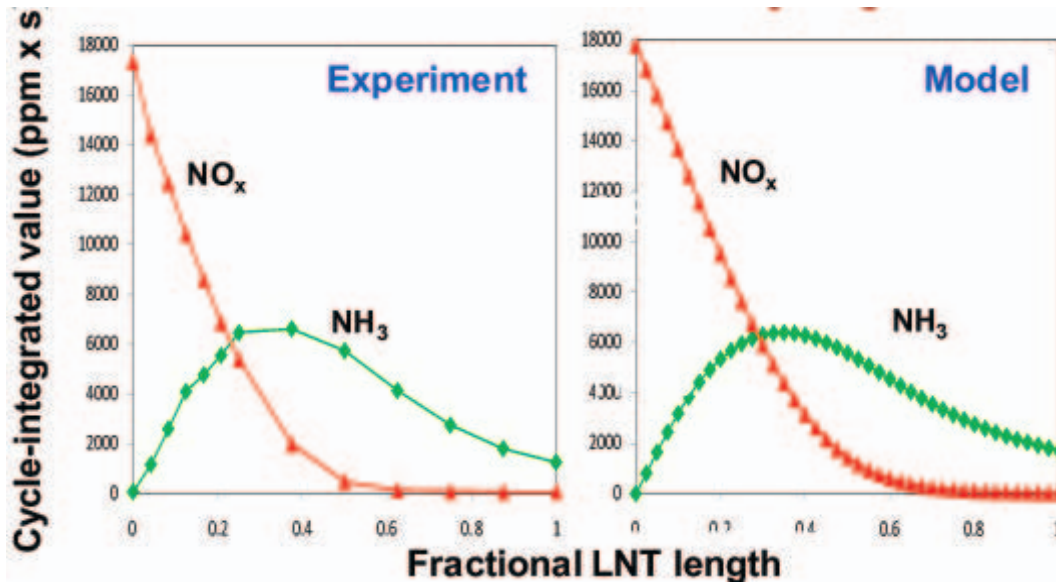
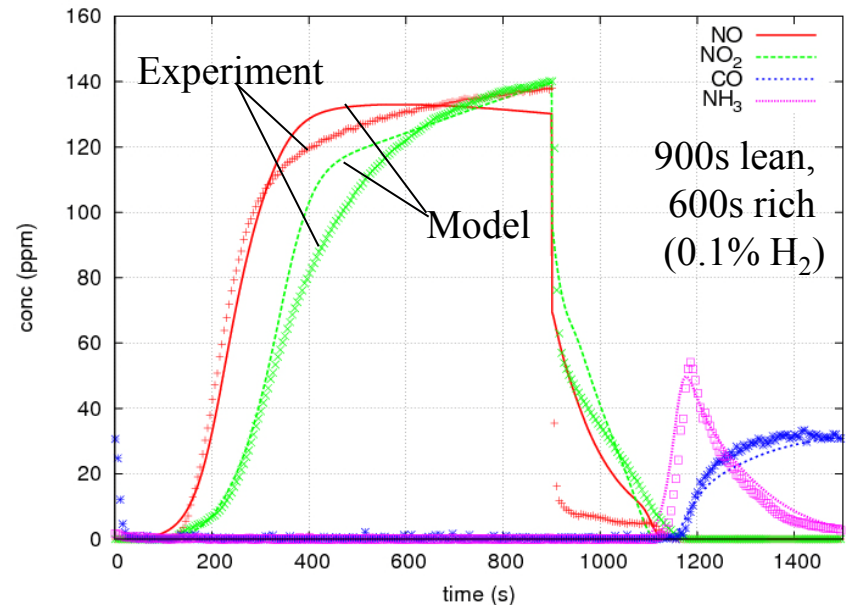


Goal: bring all of the findings into an accurate yet functional global model

- Surrogate Pt/BaCO₃/Ce₂O₃/Al₂O₃ formulation
 - Basic functions of NO_x and oxygen storage are modeled
 - noble metal activity modeled using Pt
- Features :
 - Track 6 gas species
 - NO, NO₂, O₂, H₂, CO, NH₃
 - Track 7 surface species
 - BaCO₃, BaO-NO₂, BaO-NO₃, Ba(NO₃)₂, BaO-O, Ce₂O₃, CeO₂
 - Catalytic reactions on PGM
 - Two types of sites need to capture slow and fast cycling performance
 - NO_x storage on fast, in vicinity of PGM, and regular BaCO₃
 - Heats of reaction included in the simulations
 - Ceria and alumina can store NO_x at low temperatures
 - All reversible reactions are thermodynamically consistent

Sample model results at 300°C

- Model predicts long and short cycling performance with one set of parameters
- NO_x is released from sorbent sites
 - due to removal of NO_x (g) or
 - reductant spill-over from Pt
- NO_x is reduced to N₂/NH₃ at Pt



Summary

- **Complex catalyst systems can be studied, fully analyzed and modeled**
 - **As expected, the general functionality and chemistry is similar, but model parameters need to be adjusted based on formulation**
- **Compared to an alumina supported LNT, Ceria-Zirconia:**
 - **Increases NO_x conversion at low temperature**
 - **Decreases NH₃ selectivity/slip**
 - **Decreases desulfation temperature**
- **Sulfation increases NH₃ release/breakthrough and proceeds:**
 - **in a plug-like fashion with respect to NSR**
 - **in a distributed fashion for OSC**

Presentations and Publications on Umicore LNT

- J.A. Pihl, J.E. Parks II, C.S. Daw, T.W. Root, "Experimental studies of N species selectivity during regeneration of lean NOx traps," SAE 2006 Transactions Journal of Engines, 2006-01-3441 (2006).
- R.S. Larson, V.K. Chakravarthy, J.A. Pihl, C.S. Daw, "Modeling Chemistry in Lean NOx Traps Under Reducing Conditions," SAE Technical Paper 2006-01-3446 (2006).
- J.-S. Choi, W.P. Partridge, C.S. Daw, "Sulfur impact on NOx storage, oxygen storage, and ammonia breakthrough during cyclic lean/rich operation of a commercial lean NOx trap", Applied Catalysis B: Environmental 77 (2007) 145.
- R.S. Larson, J.A. Pihl, V.K. Chakravarthy, T.J. Toops, and C.S. Daw, "Microkinetic modeling of lean NOx trap chemistry under reducing conditions," Catalysis Today 136, 104-120 (2008).
- J.-S. Choi, W.P. Partridge, J.A. Pihl C.S. Daw, "Sulfur and temperature effects on the spatial distribution of reactions inside a lean NOx trap and resulting changes in global performance", Catalysis Today 136 (2008) 173.
- J.-S. Choi, W.P. Partridge, M.J. Lance, L.R. Walker, J.A. Pihl, T.J. Toops, C.E.A. Finney, C.S. Daw, "Nature and spatial distribution of sulfur species in a sulfated barium-based commercial lean NOx trap catalyst", Catalysis Today 151 (2010) 354.
- N.A. Ottinger, T.J. Toops, J.T. Roop, J.A. Pihl, J.-S. Choi, W.P. Partridge "Nitrate and Sulfate Storage and Stability on Lean NOx Trap Components", in preparation for submission to Applied Catalysis B.

- J.-S. Choi, J.A. Pihl, W.P. Partridge, V.K. Chakravarthy, T.J. Toops, C.S. Daw, "Factors Affecting LNT NH3 Selectivity", Presented at 13th Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) Workshop, Dearborn, MI, April 20-22, 2010.
- T.J. Toops, N.A. Ottinger, J.T. Roop, J.A. Pihl, J.-S. Choi, W.P. Partridge "Sulfate Storage and Stability on Lean NOx Trap Components", Presented at 13th Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) Workshop, Dearborn, MI, April 20-22, 2010.
- J.-S. Choi, W.P. Partridge, N.A. Ottinger, J.A. Pihl, T.J. Toops, C. Finney, M. Lance, C. Stuart Daw, "Types, Spatial Distribution, Stability, and Performance Impact of Sulfur on a Lean NOx Trap Catalyst", American Institute for Chemical Engineers (AIChE) Annual Meeting, November 8-13, 2009.
- J.-S. Choi, W.P. Partridge, N.A. Ottinger, J.A. Pihl, T.J. Toops, C. Stuart Daw, "Impact of Stepwise Desulfation on the Performance of a Ba-Based Commercial Lean NOx Trap Catalyst", 21st North American Catalysis Society Meeting, San Francisco, CA, June 7-12, 2009.
- J.A. Pihl, N.A. Ottinger, J.-S. Choi, T.J. Toops, "CLEERS Coordination & Development of Catalyst Process Kinetic Data", 2009 Department of Energy (DOE) Annual Merit Review - Vehicle Technologies Program, Crystal City, VA, May 21, 2009.
- J.-S. Choi, W.P. Partridge, N.A. Ottinger, J.A. Pihl, T.J. Toops, M. Lance, C. Finney, C. Stuart Daw, "Stepwise Desulfation and its Impact on LNT Performance - Study of CLEERS Reference Catalyst", 12th Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) Workshop, Dearborn, MI, April 28-30, 2009.
- J.-S. Choi, W.P. Partridge, J.A. Pihl, T.J. Toops, M.J. Lance, C.E.A. Finney, V.K. Chakravarthy, C.S. Daw, "Correlation between spatiotemporal distribution of reactions and global performance of a commercial lean NOx trap catalyst at varying sulfation stages", oral presentation at the 5th International Conference on Environmental Catalysis, Belfast, United Kingdom, August 31-September 3, 2008.
- J.-S. Choi, W.P. Partridge, J.A. Pihl, T.J. Toops, M.J. Lance, C.E.A. Finney, V.K. Chakravarthy, and C.S. Daw, "Experimental studies of LNT sulfation and desulfation with the Umicore reference catalyst", oral presentation at the DOE CLEERS (Crosscut Lean Exhaust Emissions Reduction Simulations) Focus Group Teleconference, April 10, 2008.
- J.-S. Choi, W.P. Partridge, J.A. Pihl, M. Lance, L. Walker, C. Finney, K. Chakravarthy, V. Prikhodko, C.S. Daw "CLEERS Coordination and Development of Catalyst Process Kinetic Data", DOE- Office of Vehicle Technologies Annual Merit Review, Bethesda, MD, February 2008.

Acknowledgements

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- **Commercially available LNT catalysts supplied by Umicore**
- **EPMA performed at ORNL's High Temperature Materials Laboratory (HTML)**



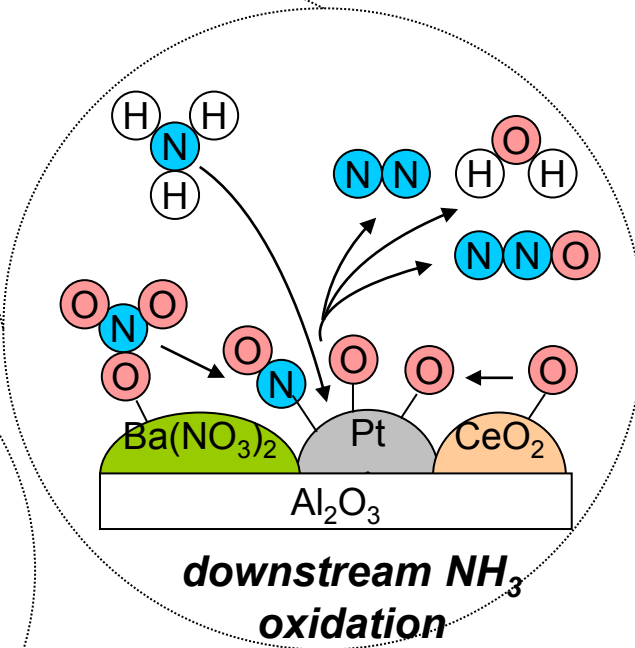
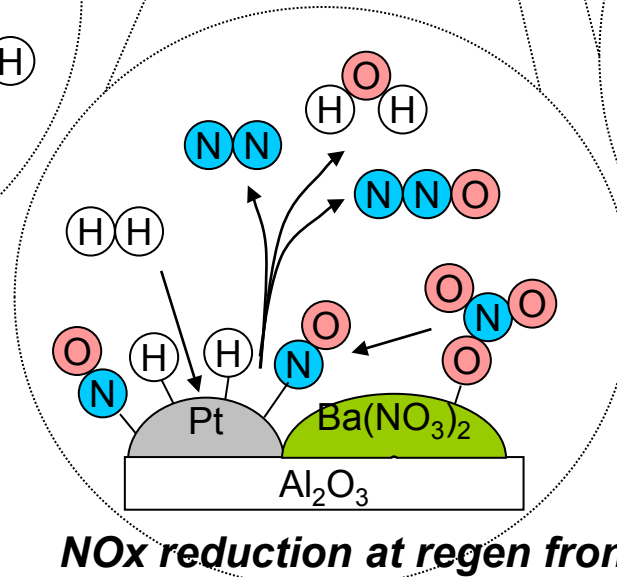
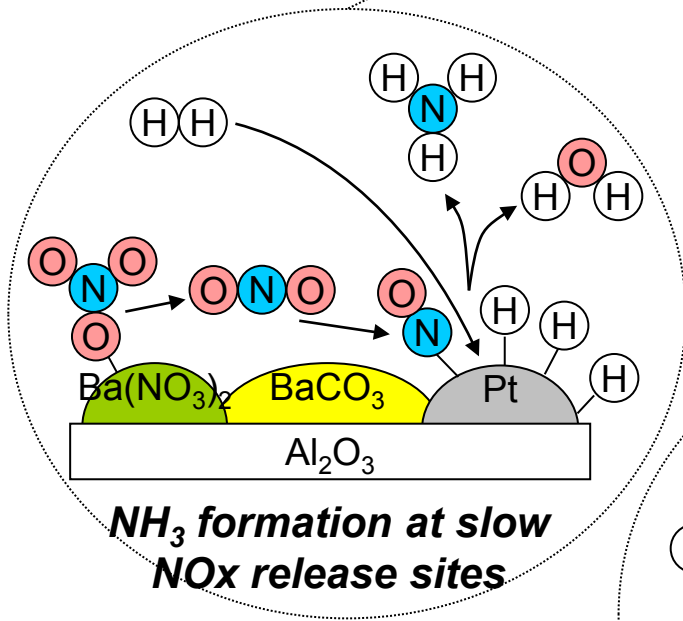
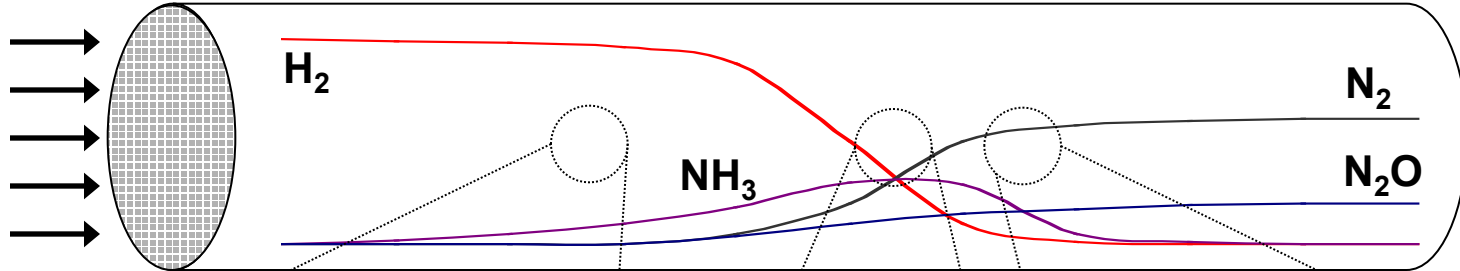
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Additional slides

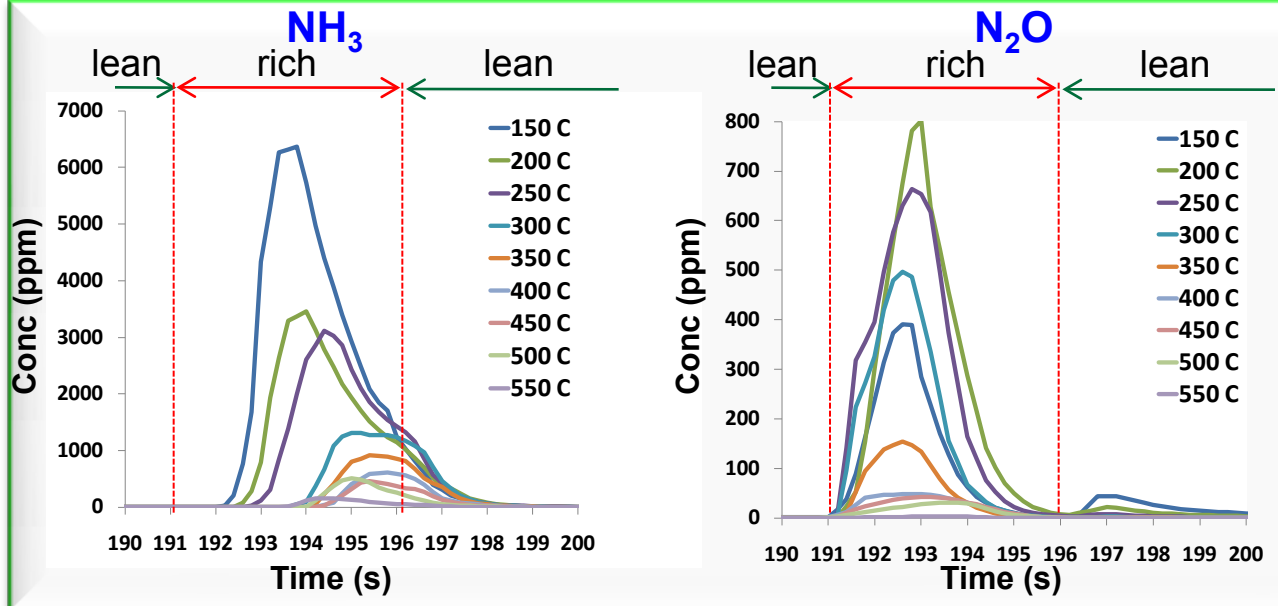
Regeneration Mechanism Development

“snapshot” of expected gas concentration profile inside monolith

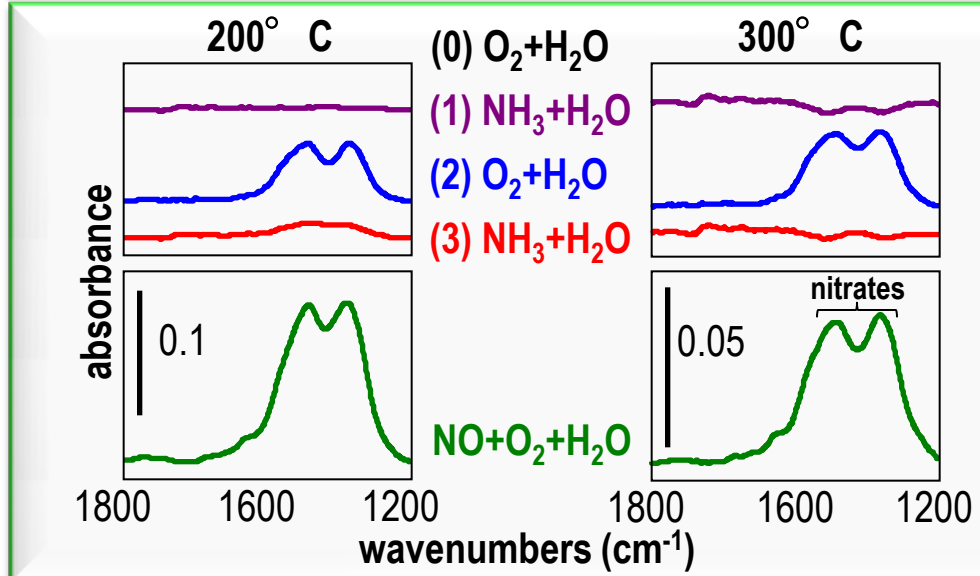


Result Highlights: LNT Research (4/5)

- Initial results reveal some key NH_3 features to be captured by models



- Bench reactor (CLEERS LNT)**
60/5-s lean/rich cycling
- **Wide NH_3 peaks**
significant NH_3 formation behind regen front
 - **N_2O at rich \rightarrow lean**
indicate NH_3 storage & oxidation



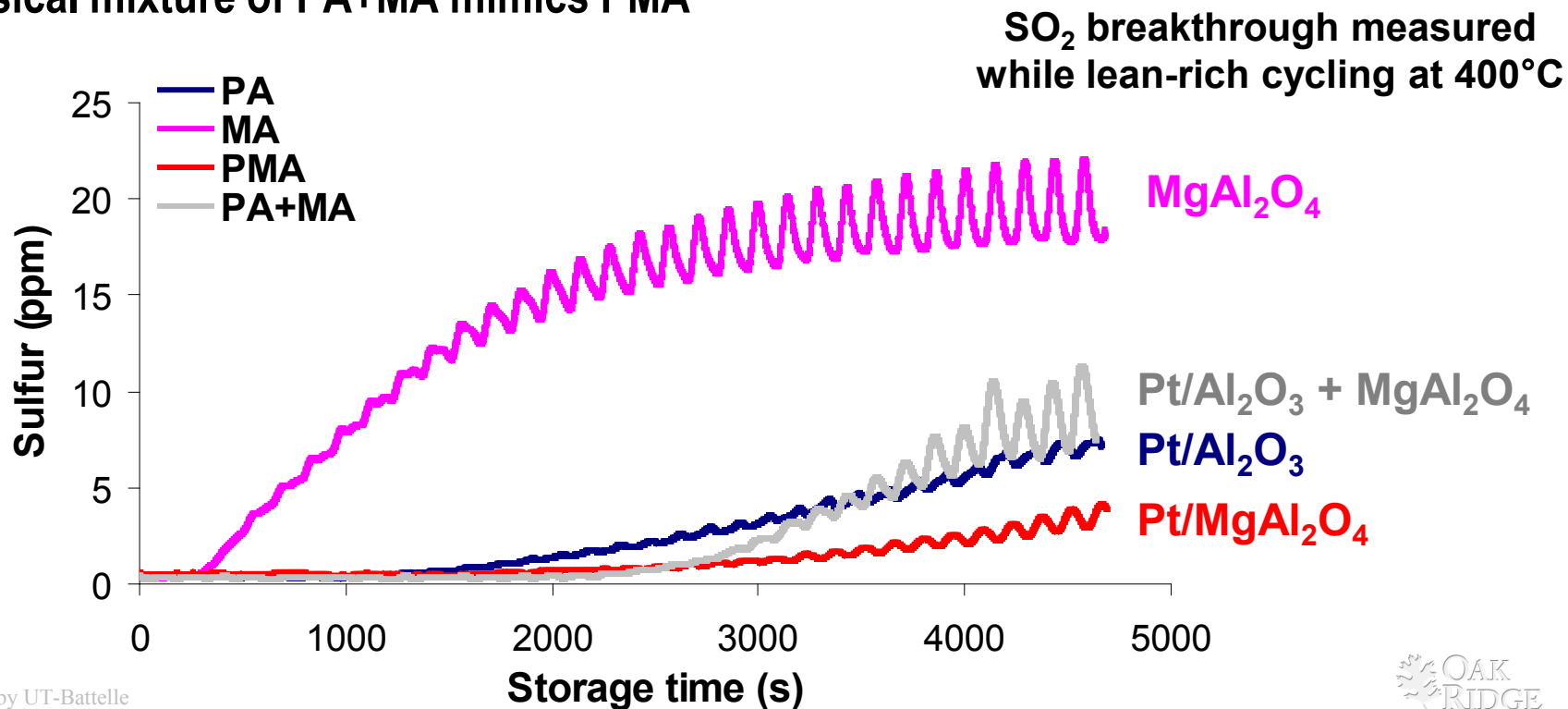
- DRIFTS (Pt/Ba/Al₂O₃)**
- **NH_3 storage on surface**
 - **NH_3 oxidation by**
 - OSC (during regeneration)
 - O_2 (inception of subsequent lean)
 - **NH_3 storage as nitrates indicates**
possible axial redistribution of NO_x via NH_3

Several studies have shown contribution of Ceria in mixtures with Pt/Ba/Alumina

- Low temperature improvement with ceria
- Multi-valent properties of ceria results in oxygen storage
 - Impacts nitrogen-based products and selectivity
 - Decreased NH₃ slip
- Water gas-shift activity: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$
- Improved durability
- Sulfur detected on ceria in physical mixtures
 - Lower desulfation temperature

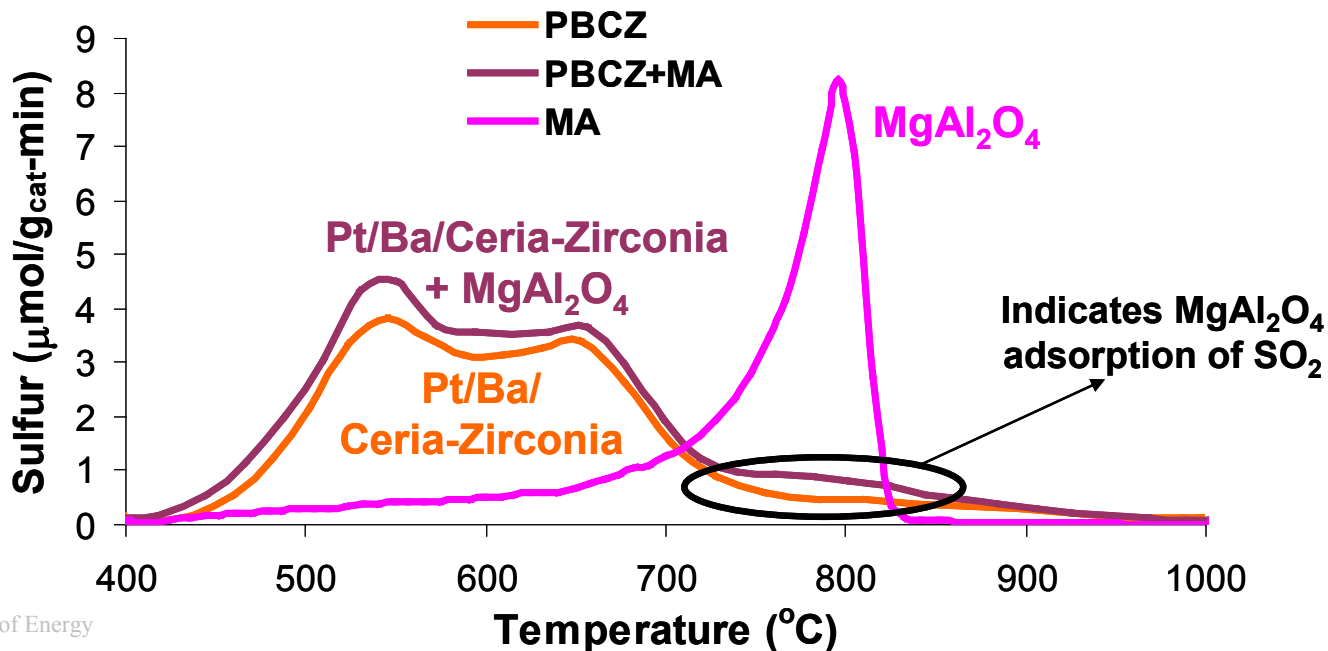
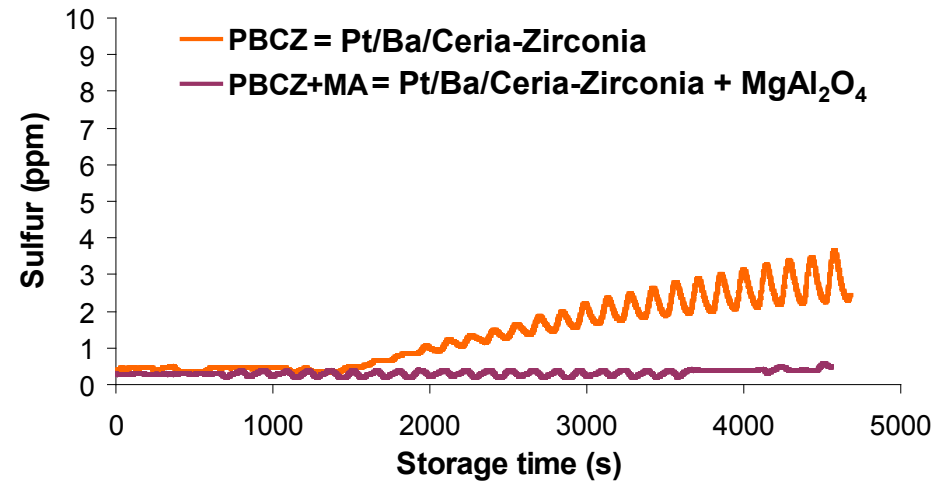
Umicore catalyst has high MgAl_2O_4 content but mechanism of benefit is unknown

- Up to 40%wt MgAl_2O_4 (MA) in the washcoat
- Not strongly-coordinated with platinum group metals (PGM)
- Sulfation profile on MA-only results in fast SO_2 breakthrough
 - With PGM, it is an effective SO_2 trap (PMA)
- Physical mixture of PA+MA mimics PMA



Sulfation/Desulfation of Umicore-like sample suggests Mg-Al adsorbs SO₂

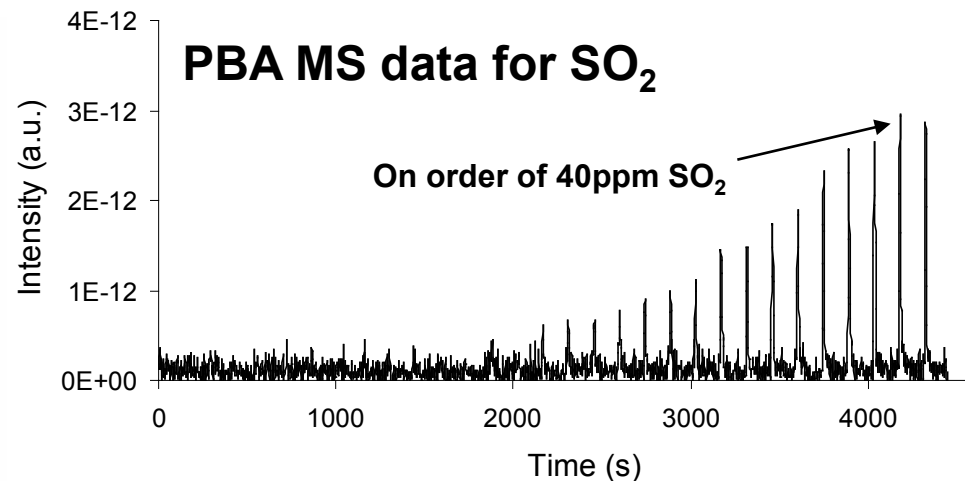
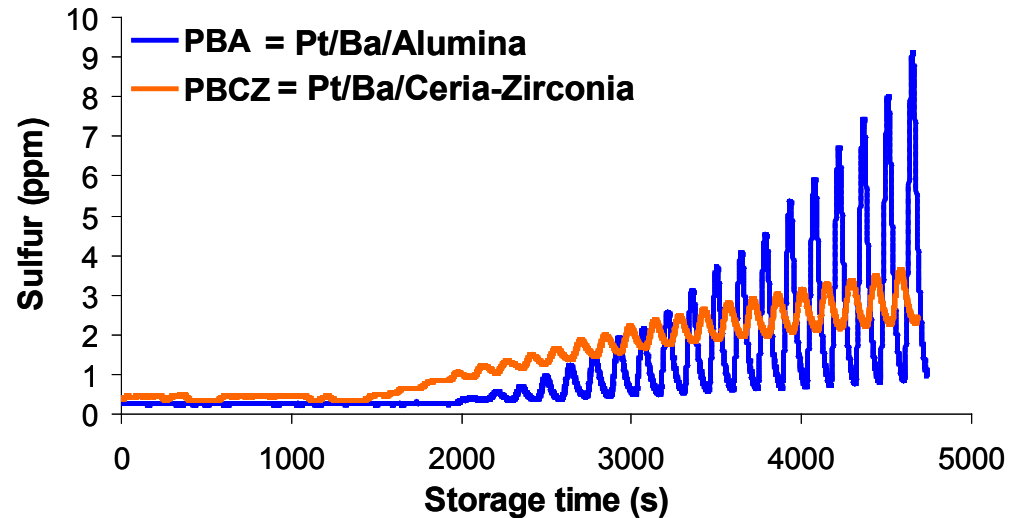
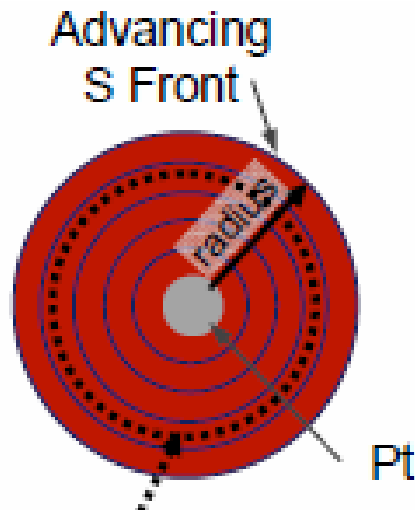
- PBCZ+MA most closely mimics Umicore formulation
- Additional sulfur stored on PBCZ+MA
- Desulfation shows small amount of extra SO₂ released at ~800 C
 - Mg-Al phase participates in sulfur trapping and perhaps transport



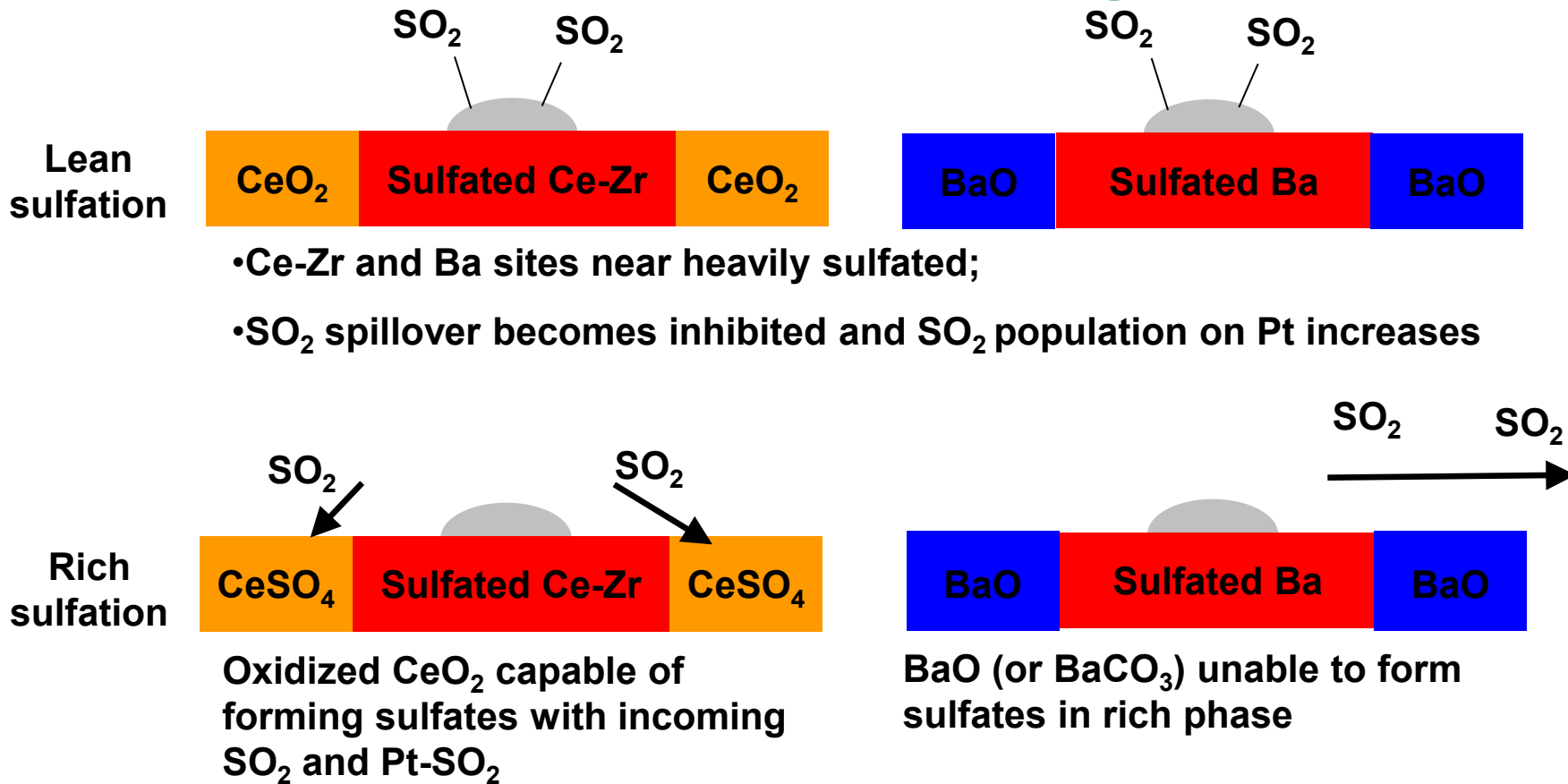
Why does sulfur pulse during cycling on Pt/Ba/Alumina but not on Pt/Ba/Ceria-Zirconia?

- Always flowing 30 ppm SO₂
 - Both lean and rich cycles
- No SO₂ breakthrough on PCZ
 - Impact of stored oxygen
- PBA has minimal oxygen storage
 - Sharp releases possibly due to SO₂ on Pt unable to spillover
- PBCZ has muted release
 - Mixed effects

Ba sites heavily sulfated; SO₂ spillover becomes inhibited



Proposed scheme: oxygen storage in ceria enables sulfation during rich phase



- Ce-Zr and Ba sites near heavily sulfated;
- SO₂ spillover becomes inhibited and SO₂ population on Pt increases

- SO₂ in feed, and on Pt, reacts w/ stored oxygen, forms sulfate

- For PBA, SO₂ on Pt and in rich feed leaves reactor
- For PBCZ, some of the desorbed and incoming SO₂ readsorbs on ceria

ORNL global LNT model

- L-H kinetics of Pt (no storage on any kind) calibrated using TR data (Pihl thesis)
 - $\text{NO} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{NO}_2$
 - $\text{NO}_x + \text{H}_2/\text{CO}/\text{NH}_3 \rightleftharpoons \text{NO}/\text{N}_2/\text{NH}_3$ (several steps of this kind)
 - **NO_x storage release at all sites (disproportionation)**
 - $\text{BaCO}_3 + \text{NO}_2 \rightleftharpoons \text{BaO-NO}_2 + \text{CO}_2$
 - $\text{BaO-NO}_2 \rightleftharpoons \text{BaO-O} + \text{NO}$
 - $\text{BaO-O} + \text{NO}_2 \rightleftharpoons \text{BaO-NO}_3$ (surface species)
 - $\text{BaO-NO}_3 + \text{NO}_2 \rightleftharpoons \text{Ba(NO}_3)_2$ (perhaps a pure compound)
 - Calibrated using long cycle data (CLEERS protocol) with no reductant
 - **Spill over Pt that facilitates fast storage (on roughly 28% of the sites)**
 - $\text{BaCO}_3 + \text{O}_2 \rightleftharpoons \text{BaO-O} + \text{CO}_2$ (mediated by Pt)
 - Thermodynamically consistent with NO oxidation on Pt and first 2 steps of disproportionation
 - Calibrated using long cycle data (CLEERS protocol) with no reductant
 - **Regen reactions :**
 - $\text{BaO-NO}_x + \text{H}_2/\text{CO}/\text{NH}_3 + \text{CO}_2 \Rightarrow \text{BaCO}_3 + \text{NO}_x + \text{H}_2\text{O}$
 - Calibrated using long cycle data (CLEERS protocol with (CO+H₂) reductant mix
 - Individual effects of CO and H₂ can not be accounted for quantitatively (assume both are equivalent for now)
- Short cycles used for verification only, parameters remain the same (no further adjustment)**