

Emissions Control for Lean Gasoline Engines

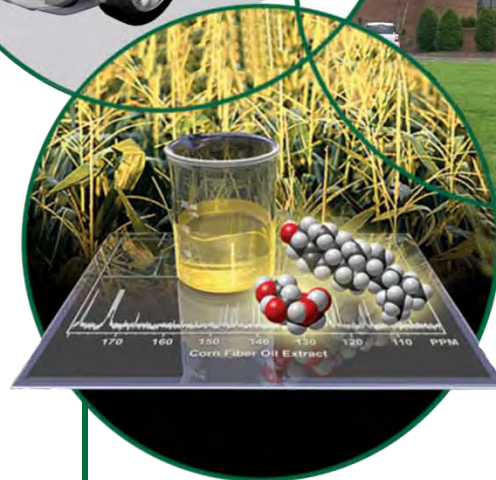
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Pre-Competitive Catalysis Research: Fundamental Studies of Lean NO_x Traps

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ACE033
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Advanced Combustion Engine Program
U.S. Department of Energy



Project Overview

Timeline

- **Projects are ongoing**
 - Refocused each year to address current DOE and industry needs
- **Lean Gasoline**
 - Started in FY10
- **Fundamental Catalysis**
 - Started in FY02

Budget

- **Lean Gasoline**
 - FY10: \$200k
 - FY11: \$200k
- **Precompetitive Catalysis**
 - FY10: \$200k
 - FY11: \$200k
- **Anticipate similar funding for FY12**

Barriers

- **2.3.1B: *Lack of cost-effective emission control***
- **2.3.1C: *Lack of modeling capability for combustion and emission control***
- **2.3.1.D: *Durability***

Collaborators & Partners

- **DOE Vehicle Systems Program**
- **Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS)**
- **General Motors**
- **Center for Nano-phase Material Science (CNMS): BES funded**
- **Umicore: catalyst supplier**

Objectives and Relevance

Improving lean-gasoline vehicles emissions control systems and catalysts, enables significant reduction in petroleum use

- **Objective:**

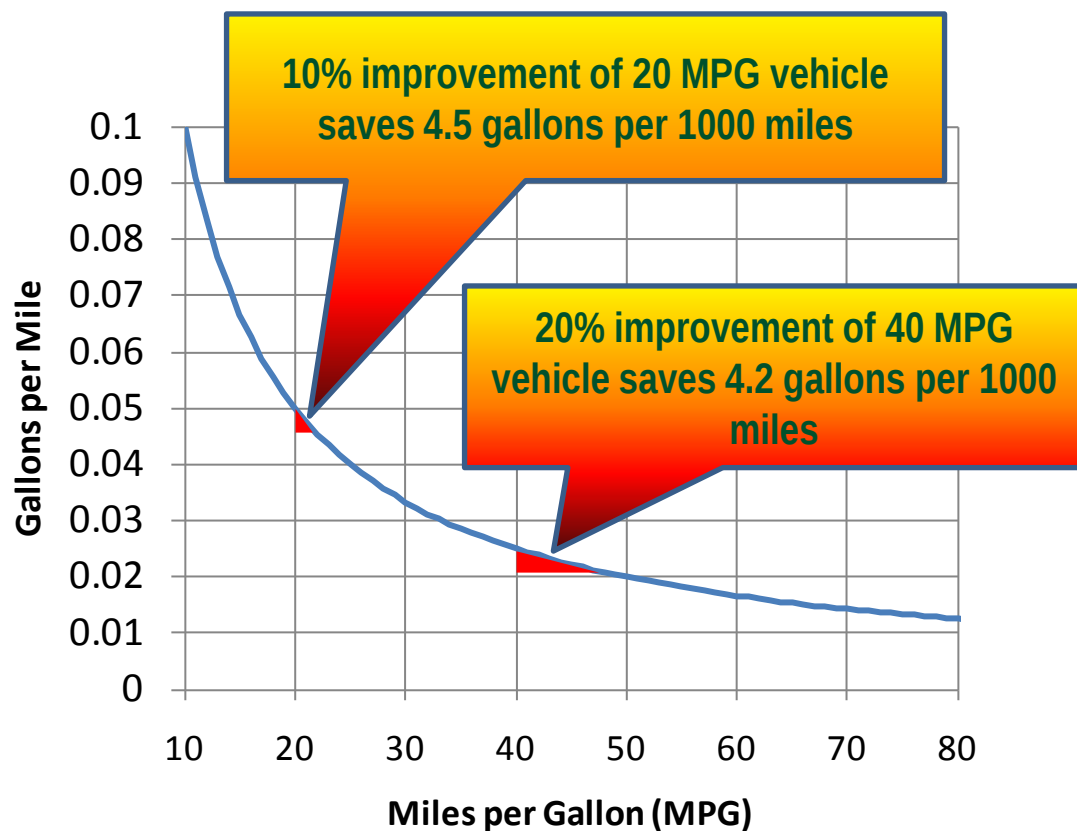
- Address technical challenges of enabling market penetration of lean gasoline engine vehicles by studying emission control approaches to achieve emission regulation compliance
- Investigate methods for improving performance and/or durability of LNTs, such that PGM costs can be reduced

- **Relevance:**

- U.S. passenger car fleet is dominated by gasoline-fueled vehicles.
- Enabling introduction of more efficient lean gasoline engines can provide significant reductions in passenger car fuel consumption
 - thereby lowering petroleum use and reducing greenhouse gases

Making small improvements in fuel economy can significantly decrease overall fuel consumption

- Goals of reduced petroleum consumption and reduced greenhouse gas emissions being addressed by variety of approaches
- Improving from 20 mpg to 22 mpg, 10%, has significant overall impact
 - Saves 300,000,000 barrels gasoline annually
- 10% fuel economy improvement can be achieved with lean gasoline approach
 - Needs more than TWC for emissions control



Lean gasoline vehicles can decrease US gasoline consumption by ~1 million barrels per day

Milestones

- Lean Gasoline

- Characterization of exhaust from the LNT system of a lean gasoline engine vehicle including reductants produced for LNT regeneration and reporting of information to the CLEERS community (9/30/2010).
 - met
- Analysis of lean-rich period modification for enabling lower volume LNTs to reduce the higher concentrations of NO_x associated with lean gasoline engines (9/30/2011).
 - On track

- Fundamental Catalysis

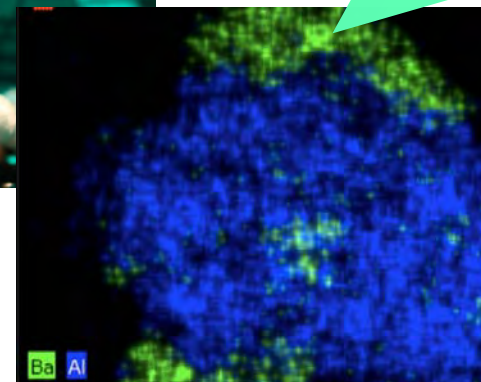
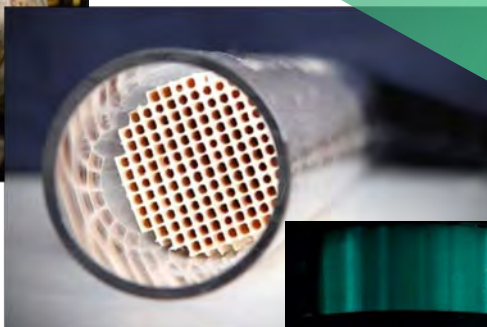
- Publish the collaborative effort with the Center for Nanophase Material Science on Ba-dopant effects on LNT performance (9/30/2010).
 - Published in Catalysis Today
- Publish efforts on Umicore component sulfation/desulfation study (9/30/2010).
 - Submitted to Applied Catalysis B: Environmental
- Investigate performance, sulfation and desulfation of Ca-doped LNTs with a Ca-level between 3 and 9% (9/30/2011).
 - On track

Collaborations and partners

- General Motors
 - loan of Euro spec Lean GDI BMW vehicle
- CLEERS
 - share results and identify research needs
- Umicore
 - Catalyst supplier for the commercial LNT
- University of Kentucky – Center for Applied Energy Research
 - Collaborators on the ceria studies
- Center for Nanophase Materials Science (CNMS)
 - Basic Energy Science funded user facility at ORNL
 - Prepared doped storage materials
 - Performed materials characterization
- High Temperature Materials Laboratory (HTML)
 - ORNL user facility funded by EERE
 - Materials characterization and microscopy

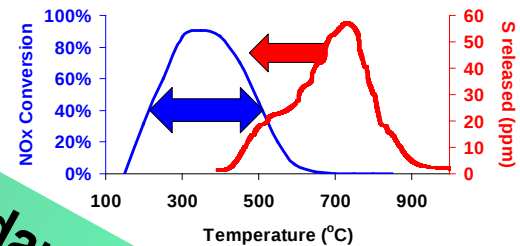
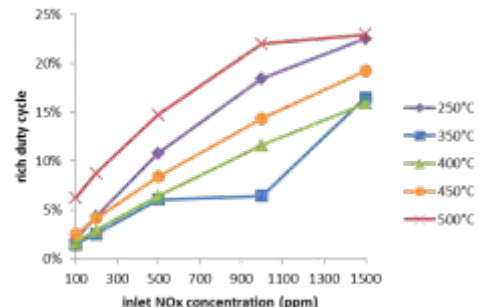
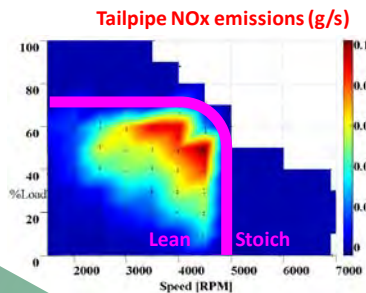


Approach



Lean Gasoline

Fundamental Catalysis



- Study emission control devices using multi-platform approach
 - Balance of real and fully-controlled
 - Vehicle/engine/bench/powder formulations
- Range of devices studied
 - LNT, SCR, TWC, HC-trap + Combinations of each
 - Primarily rely on industrially supplied catalysts
 - Also employ novel catalyst formulations or model components
- Communicate results with CLEERS being a primary conduit for information exchange

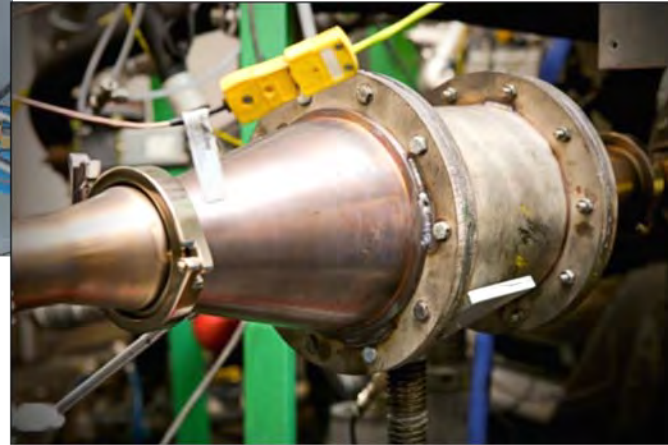
Summary of Technical Accomplishments

- Lean Gasoline

- Characterized exhaust and analyzed all data from lean-gasoline vehicle which uses TWC + LNT technology
- Identified challenging conditions associated with lean gasoline operation using bench flow reactor with CLEERS reference LNT
- Progressed towards installation of a modern lean gasoline engine suitable for engine dynamometer studies
 - Awarded subcontract to Drivven to develop full pass controller and engine sensor calibration; Initial chassis lab diagnostics of critical signals complete
 - Resolved export/import hurdles and procured dyno-ready engine identical to the European lean gasoline BMW 120i vehicle

- Fundamental Catalysis

- Identified catalyst improvement with dispersion of ceria on alumina support
- Identified impact of sulfur on Ca and Ca+Ba doped LNT catalysts
- Designed new DRIFTS reactor for simultaneous surface analysis and gas-phase measurements

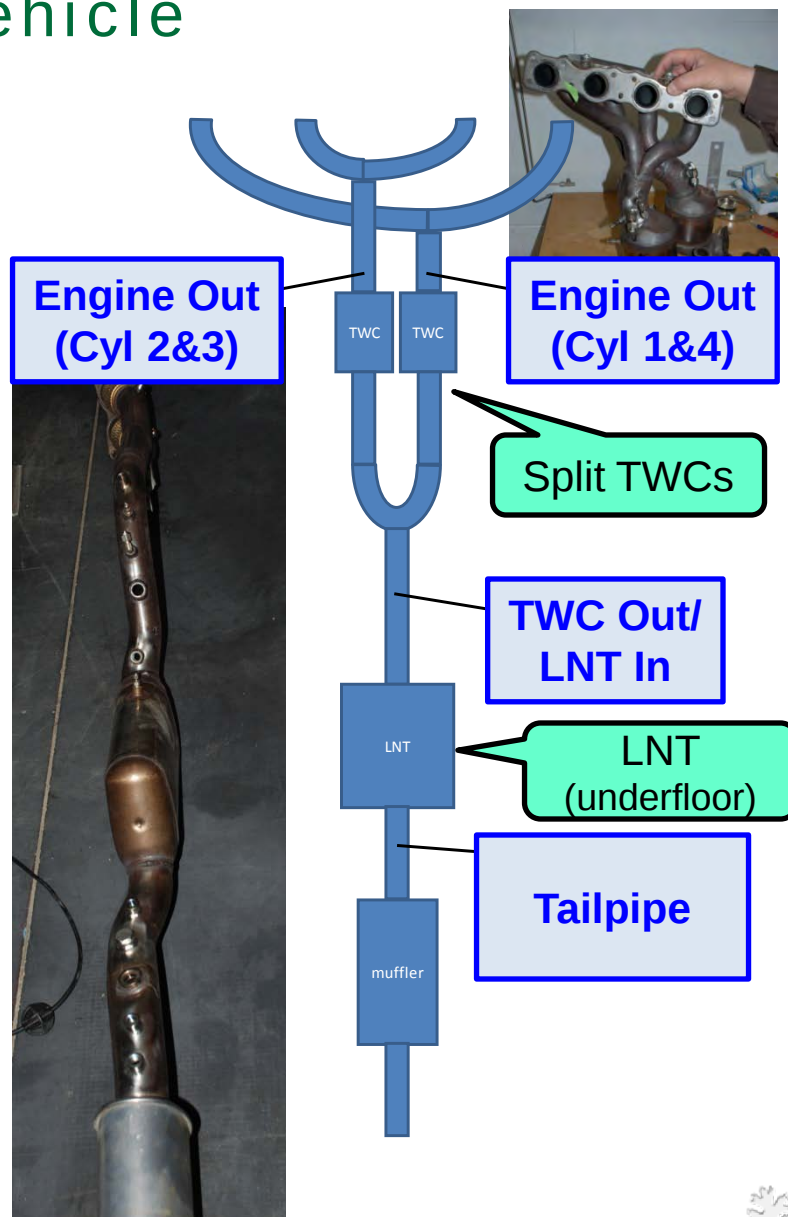


Emissions Control for Lean Gasoline Engines

VEHICLE AND ENGINE-BASED STUDIES

Layout of Emissions control system of European lean gasoline BMW 120i vehicle

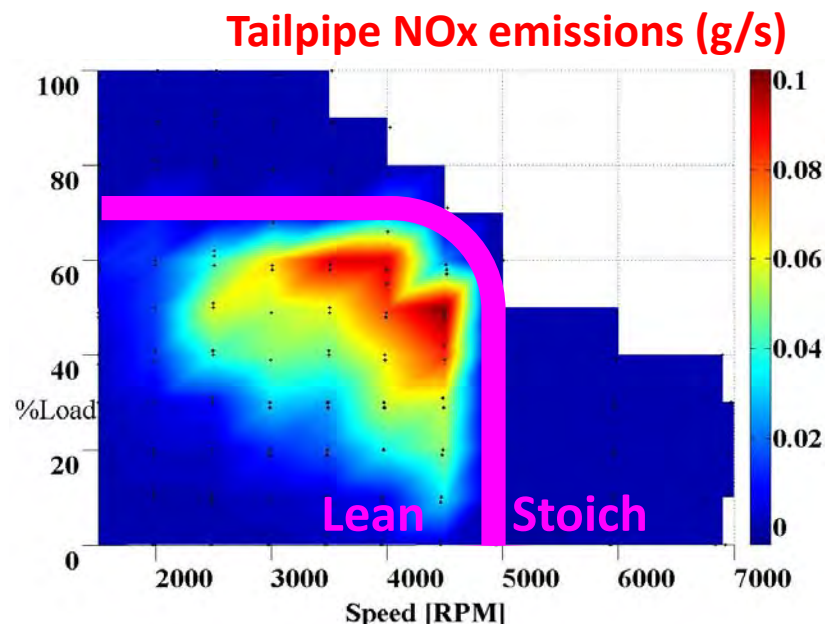
- Emissions and Reductant Speciation
- UEGOs for both exhaust manifold legs
- Conventional emissions analyzers at engine out and tailpipe positions
- Reductant focused emissions analysis at LNT inlet position
 - FTIR (NO , NO_2 , N_2O , NH_3 , HCs, CO, etc)
 - SpaciMS (H_2 , O_2)



4-15% Fuel Economy Benefit but Challenge of Emissions Exceeding U.S. Regulation Levels

- Vehicle designed to meet emissions levels required by European regulations
- NOx emission levels exceed U.S. Tier II Bin 5, 0.05 g/mile at 50k miles
 - Bin 2 → 0.02 g/mile
- NOx emissions during lean operation are problematic
- Particulate matter (PM) emissions may also be of concern with respect to particle number regulations*

*see SAE 2010-01-2117, SAE 2010-01-2129, SAE 2010-01-2125, etc.



***Improved Lean
NOx catalysis
required for
deployment of
lean gasoline
vehicles***

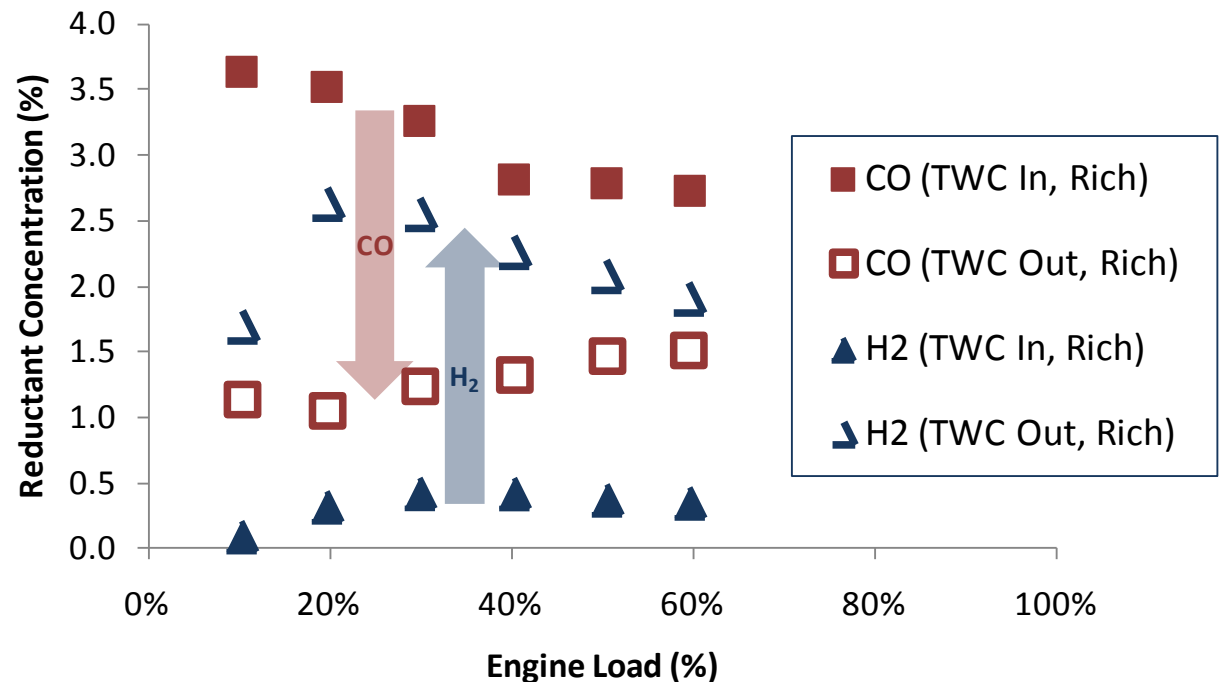
Drive Cycle	Fuel Economy Improvement**	NOx Emissions (g/mile)
FTP	10.0%	0.11
HFET	14.6%	0.11
US06	4.4%	0.35

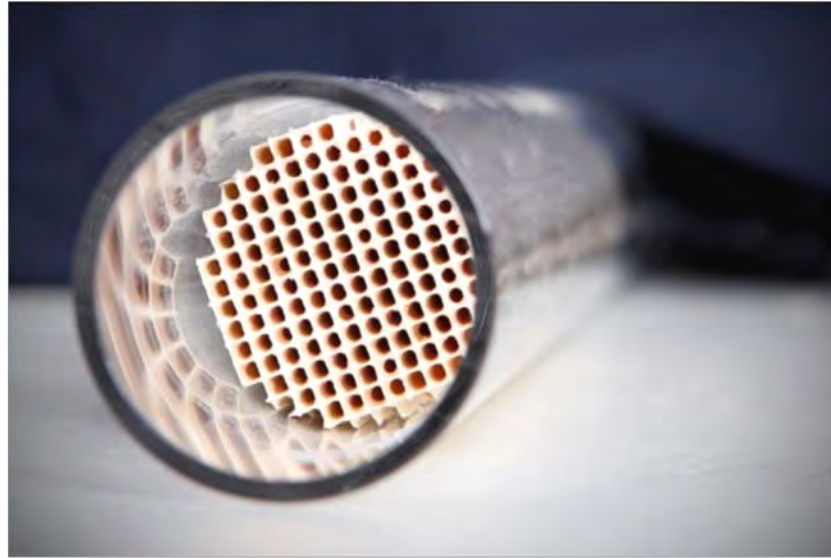
****comparing stoichiometric operation to lean**

TWC Affects Reductant Mix

- MY2008 BMW 120i vehicle uses TWC + LNT for European emissions compliance
- Analysis of CO and H₂ before and after TWCs shows that TWC is affecting mixture of reductants
 - data from 3500 rpm shown
- CO levels decrease over TWCs while H₂ levels increase
 - TWC is converting CO to H₂ via the Water-Gas-Shift reaction

***TWC increases
H₂ availability
for LNT under
periodic rich
conditions***



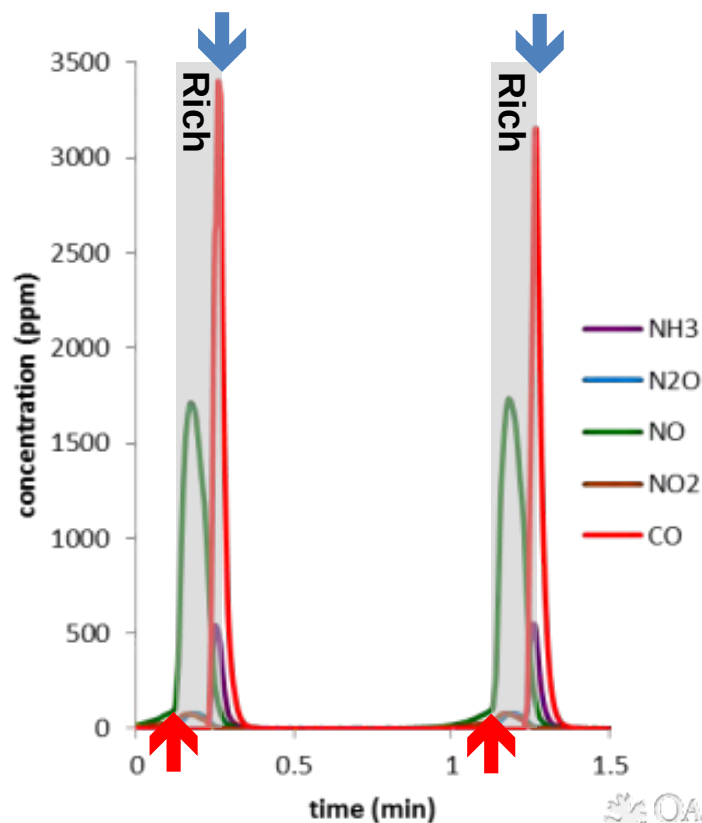


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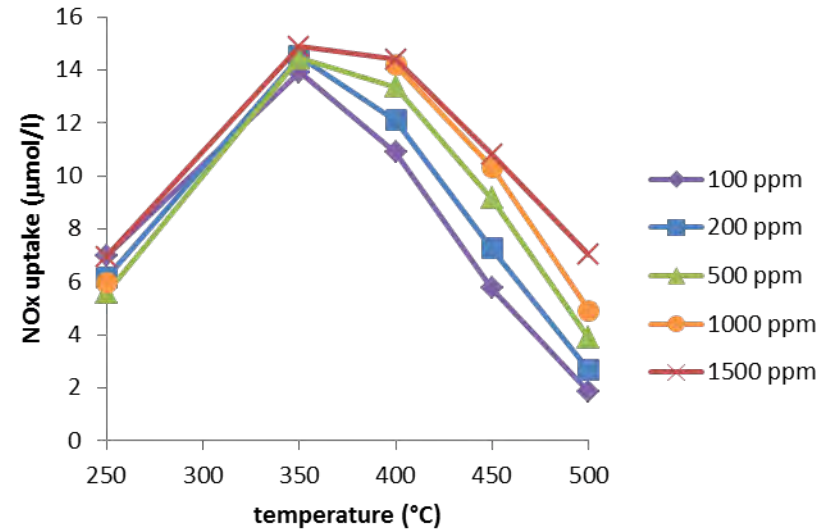
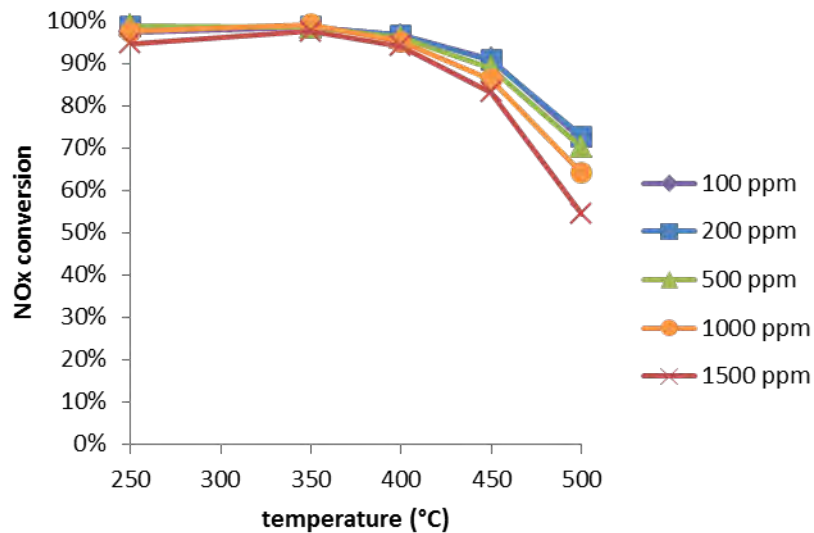
BENCH REACTOR STUDIES

Studied effects of high temperature and high NOx on LNT operation

- Key questions:
 - Is there sufficient storage capacity at lean GDI exhaust temperatures to achieve reasonable NOx conversion?
 - Does increased equilibrium storage capacity compensate for higher inlet NOx?
- Catalyst: CLEERS reference LNT (Umicore GDI)
- Space velocity: 25,000 hr⁻¹
- Operation: feedback controlled cycles
 - Switch lean to rich (↑): FTIR NOx > 10 ppm
 - If 10% inlet NOx used, results were identical
 - minimum: 20 sec
 - rich to lean (↓): downstream UEGO rich AFR
 - corresponds to reductant breakthrough
 - goal: complete regeneration
 - minimum: 3 sec

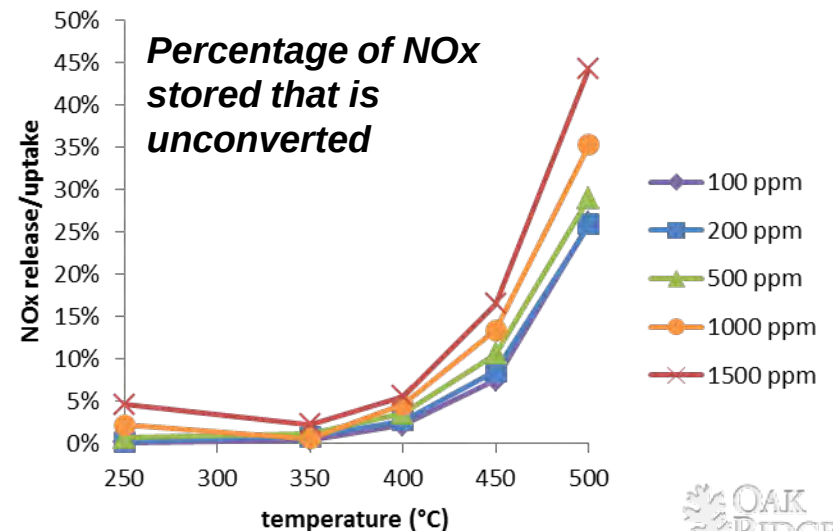


High temperature conversion efficiency limited by rich NOx slip

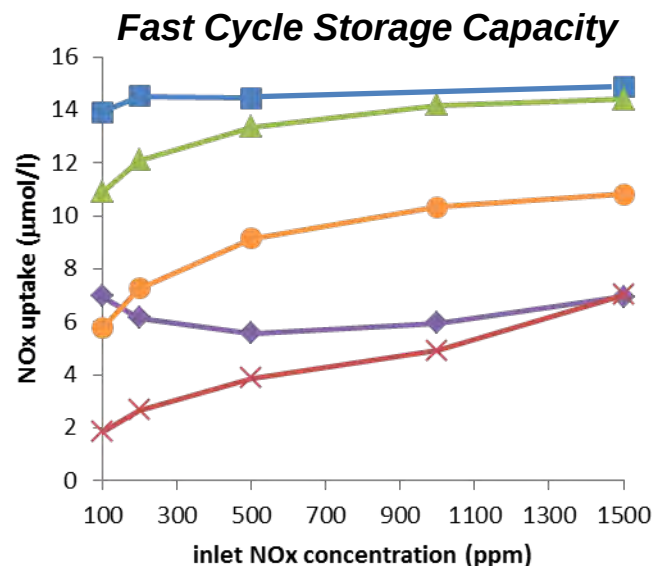
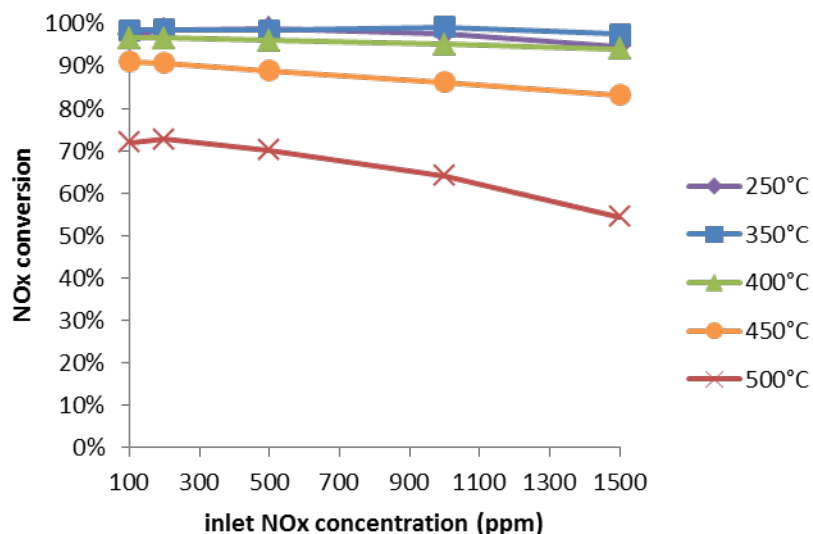


- Conversion strongly dependent on temperature
 - drops sharply above 450C
- Measurable NOx storage at 500C
- 25-45% stored NOx released during rich pulse exits LNT unconverted (NOx “puff”)

Improving high temperature performance requires stabilizing surface nitrates to slow their release during regeneration

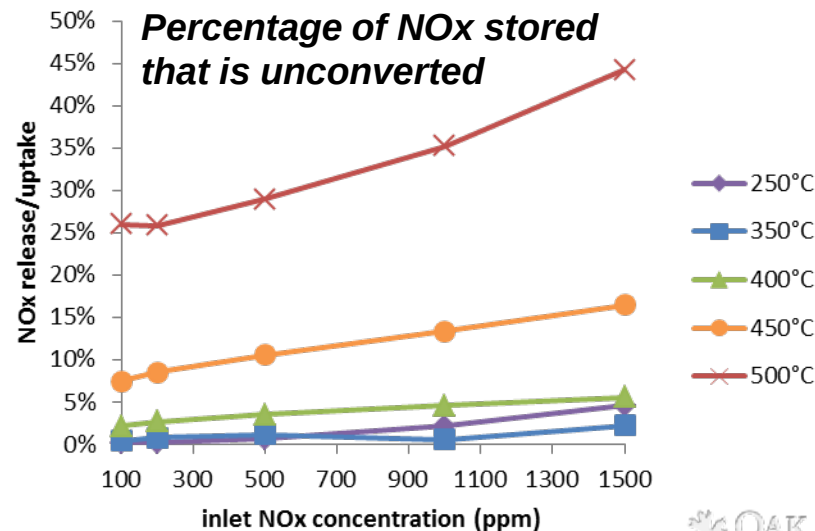


Higher NOx concentrations increase both capacity and rich NOx slip



- Fast cycle storage capacity increases with inlet NOx
- NOx puff also increases, particularly at high temperature
- Net effect: decrease in conversion efficiency with increasing inlet NOx

Increased storage capacity with higher inlet NOx is offset by increased rich NOx slip



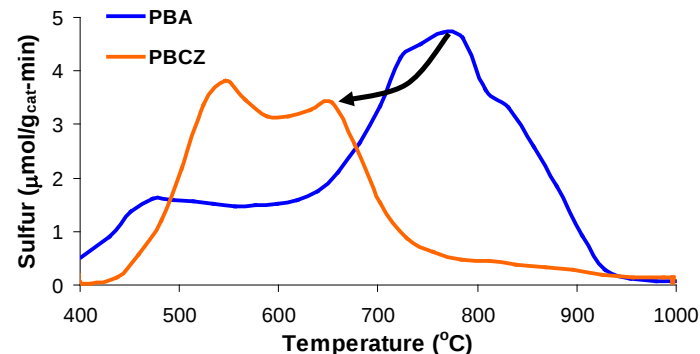


Fundamental Catalysis

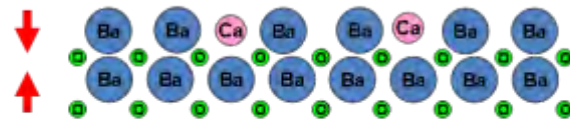
MICROREACTOR AND SURFACE STUDIES

Catalyst formulations and support effects on performance and desulfation being studied

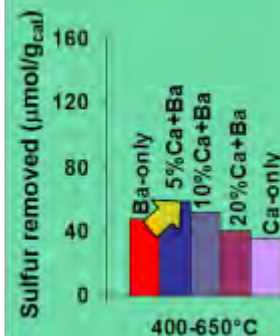
- Support effects
 - Shown to dramatically effect desulfation temperature
 - Synergistic effects being demonstrated...effects on Ba phase
- Catalyst formulation studies looking at impact of Ca on performance and desulfation
 - Shown Ca doping effects performance
 - Ca-only increase temperature window
 - Looking at effects of sulfur on performance and desulfation
- Also, implementing new DRIFTS techniques to allow investigations under realistic conditions



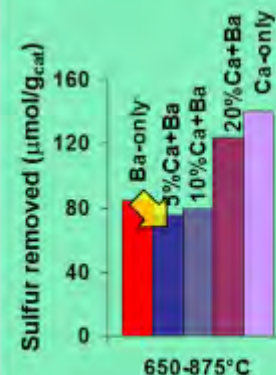
Substitution of Ca into Ba LNT changes lattice spacing, increases strain, changes behavior



5-10% Ca results in destabilization of sulfates

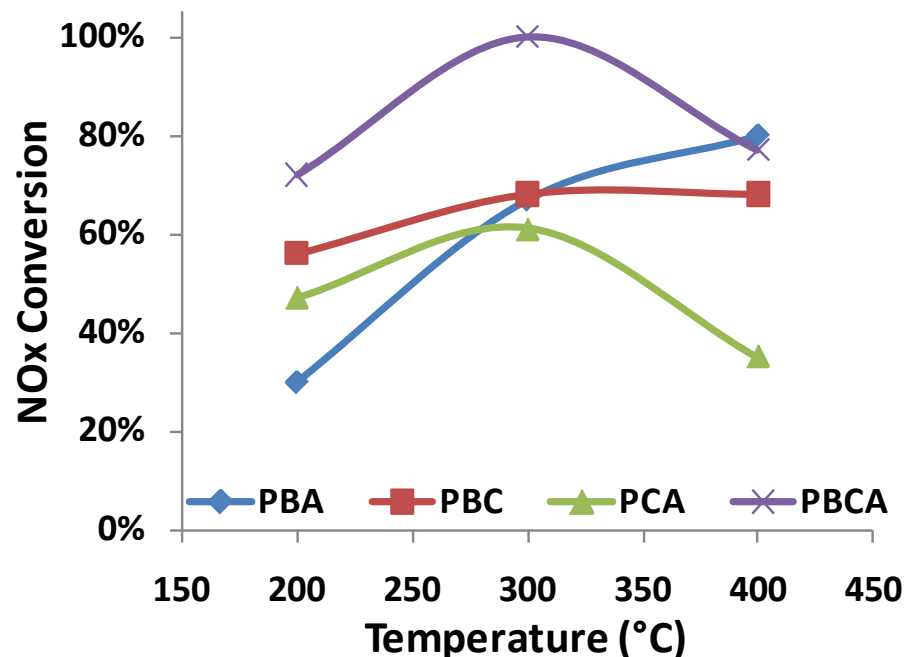


Higher than 20% Ca results in more stable sulfates



Supporting Ba + Ce on Al_2O_3 support improves NO_x conversion at low temperatures

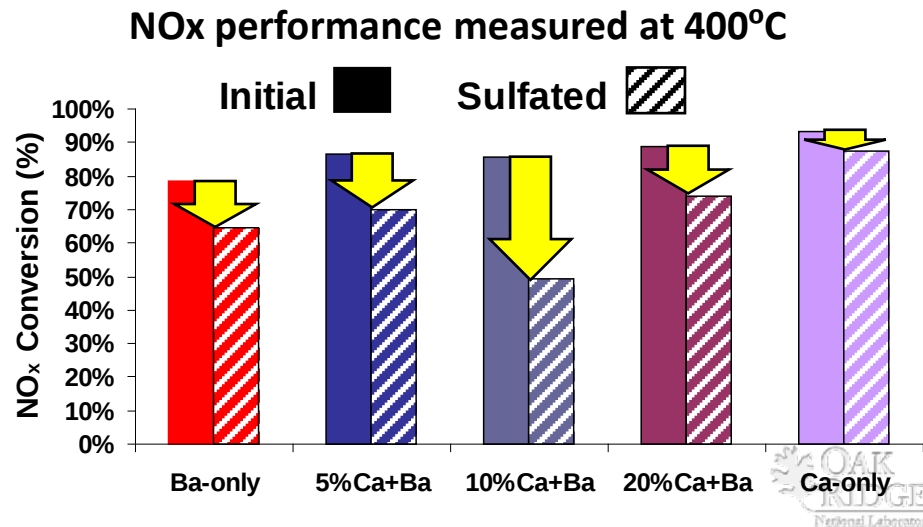
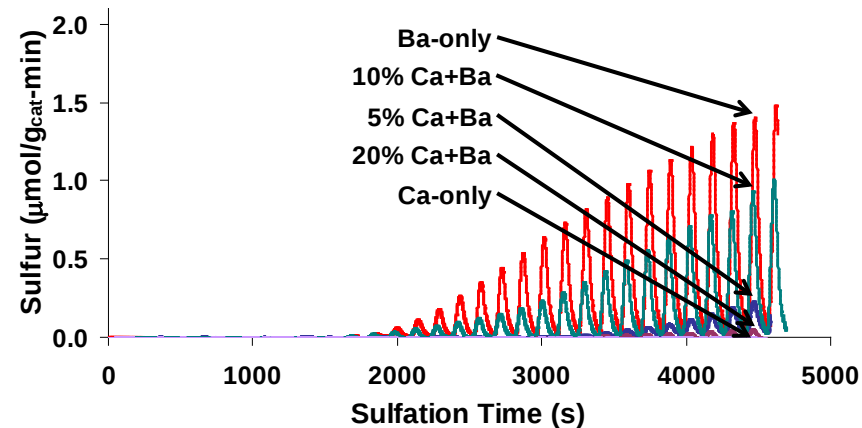
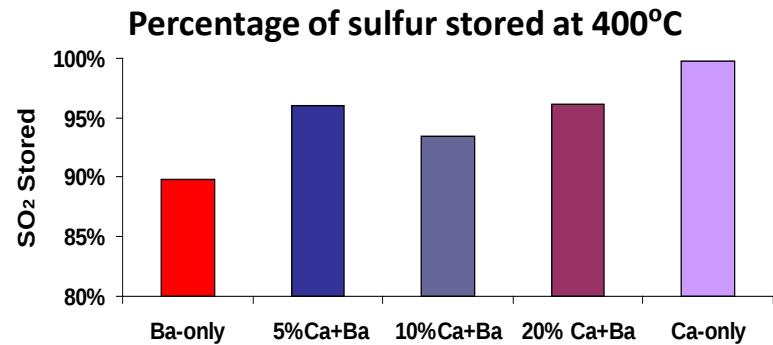
- Catalysts prepared and studied
 - PBA: 1%Pt / 10%BaO / Al_2O_3
 - PBC: 1%Pt/10%BaO/ CeO_2
 - PCA: 1%Pt / 25% CeO_2 / Al_2O_3
 - PBCA: 1%Pt / 10%BaO / 25% CeO_2 / Al_2O_3
- Catalysts evaluated in a micro-reactor under lean-rich cycling conditions
 - Lean (120s): 300 ppm NO, 8% O_2 , 5% H_2O + CO_2
 - Rich (12s): 1.1%CO, 0.6% H_2 , 5% H_2O + CO_2
 - GHSV of 30,000 h^{-1}
- Dispersing Ceria and Baria on Alumina yields synergistic effect
 - Alumina aids ceria dispersion
- Ceria also known to decrease Ba-based desulfation temperature significantly



Underlying support can impact performance significantly and is important variable

Ca-only has better NO_x conversion at 400°C and minimally impacted by S

- Series of catalysts studied to investigate impact of formulation
 - Focus on NO_x conversion and sulfur
- Sulfur exposure shown: 5.5 mg S/g_{cat}
- At 400°C, Ca-only LNT is the most sulfur adsorbant storage material
 - Ba-only releases the most sulfur during rich cycle at 400°C
- Ca-only is most tolerant LNT to sulfur
- Sulfur tolerance is important factor
 - LNT can go further between de-S
 - Fewer desulfations
 - less fuel consumed
 - less impact on PGM
 - less initial PGM needed

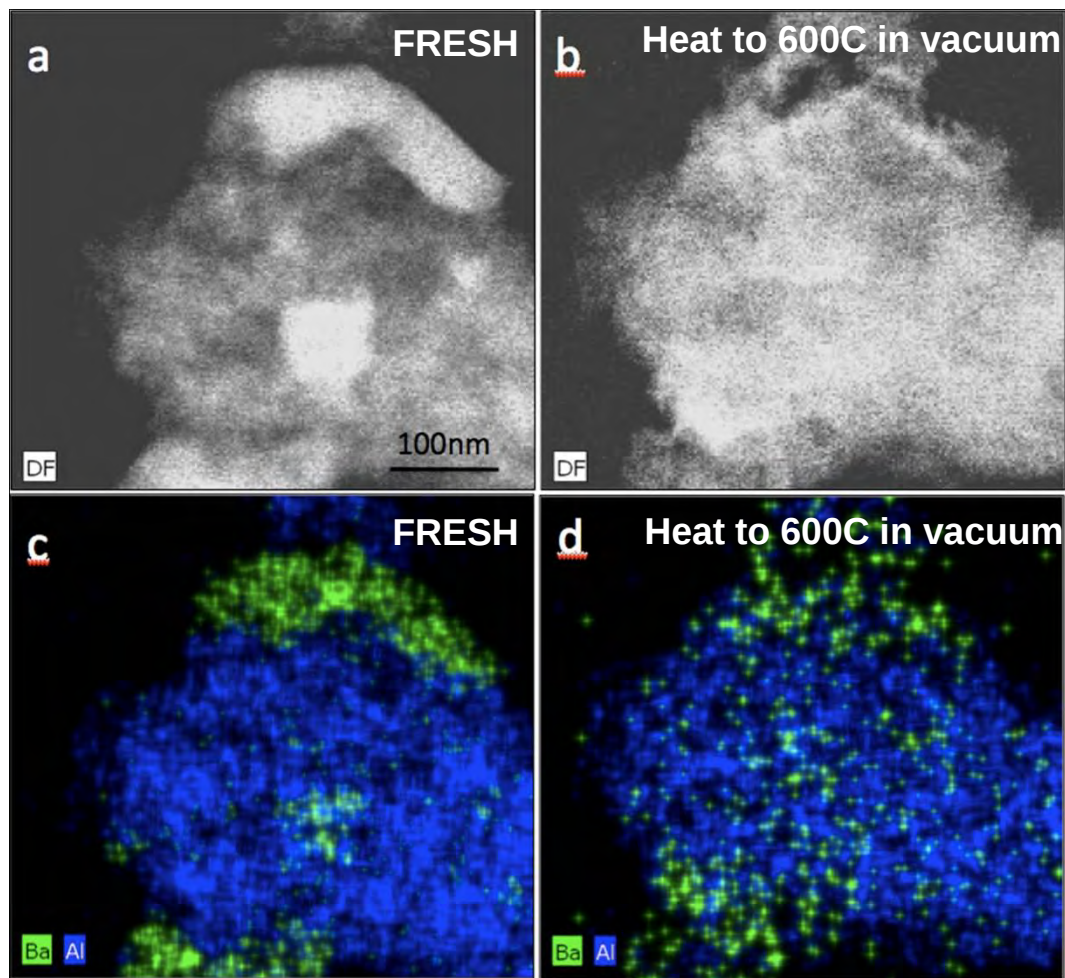


Future work

- Resources focused on developing lean gasoline engine platform with controls
- Continue bench flow reactor studies of LNTs and include sulfur
- Study NH_3 formation by Three-way Catalysts (for NH_3 -SCR potential)
- Evaluation of additional Ca levels and Pt levels
- Team with catalyst supplier to apply new formulations to washcoats for full evaluation
- Incorporation of in-situ microscopy to understand contact of storage phase to support and as a mixed metal oxide
 - Heated stage allows detailed study of particles under realistic conditions

Preliminary microscopy study with heated stage

- Imaging catalyst samples with aberration-corrected electron microscope (ACEM) at HTML
- Heated stage allows in-situ heating
 - Including $O_2 + H_2O$
- Energy-dispersive x-ray spectroscopy (EDS) allows elemental distributions to be mapped at the nanometer level
 - heating under vacuum at 600°C leads to Baria crystallite dispersion
 - HOWEVER, in AIR Ba phase is stable up to 800°C .
 - Catalyst systems must be studied under realistic environments
- Approach to be used with sulfated and multi-phase catalysts



a-b) Dark-field images before (a) and after (b) heating catalyst for 10min at 600°C . The bright areas are the barium-rich phase; c-d) elemental maps showing the re-dispersion of the barium-rich phase after heating.

Summary

- **Relevance:** Improving lean-gasoline vehicles emissions control systems and catalysts, enables significant reduction petroleum use
- **Approach:** Study emission control devices using multi-platform approach
 - Balance of real and fully-controlled
 - Vehicle /engine/bench/powder formulations
- **Collaborations:** Industrial (GM and Umicore), University (UK-CAER), and other federally funded research organizations (BES-CNMS and EERE-HTML)
- **Technical Accomplishments:**
 - Characterized exhaust and analyzed all data from lean-gasoline vehicle which uses TWC + LNT technology
 - Identified challenging conditions associated with lean gasoline operation using bench flow reactor with CLEERS reference
 - Identified catalyst improvement with dispersion of ceria on alumina support
 - Identified improved sulfur tolerance through LNT formulation investigation
- **Future Work:**
 - Resources focused on developing lean gasoline engine platform with controls
 - Bench flow reactor studies of LNTs and TWC (for NH_3 -SCR potential)
 - Team with catalyst supplier to apply new formulations to washcoats for full evaluation

Technical back-up slides

reactor details and yields

- Space velocity: 25000 hr⁻¹
- Gas composition:
 - rich: 2.3% H₂, 1.5% CO
 - lean: x ppm NO, 8% O₂
 - both: 8.3% CO₂, 7.7% H₂O

