Oxidation State Optimization for Maximum Efficiency of NOx Adsorber Catalysts

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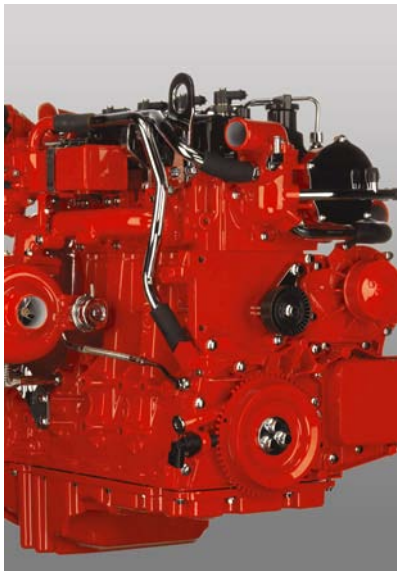
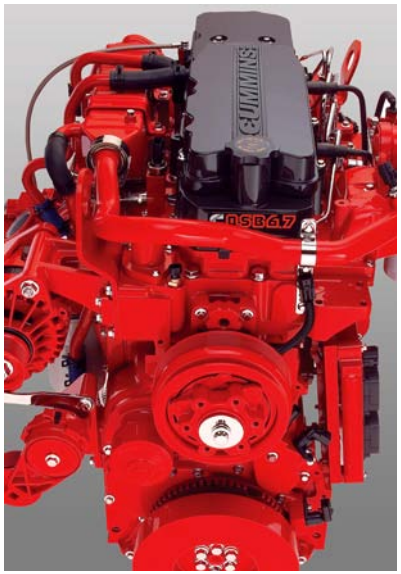
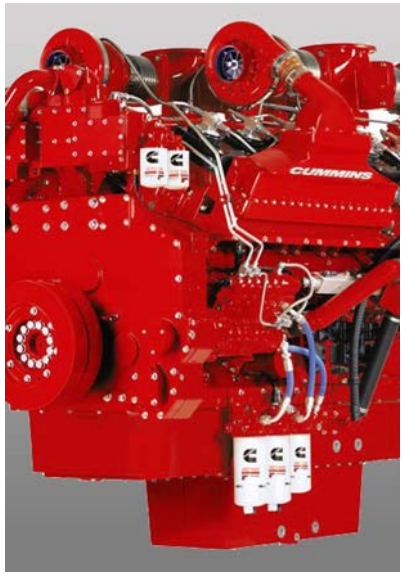
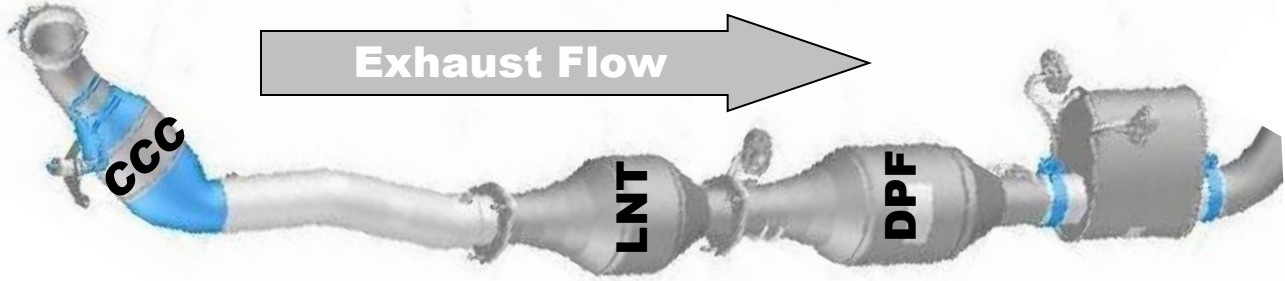





LEV II-ULEV Certified System with Cummins 6.7L Engine and A/T System



System Function	**Close-Coupled Oxidation Catalyst (CCC)**	**Lean NOx Trap Catalyst (LNT)**	**Diesel Particulate Filter (DPF)**
Lean	HC, CO, NO Oxidation	NOx trapping	Soot trapping
De-NOx	Residual O_2 removal In situ POX, WGS	NOx release NOx > N_2 reduction	Regeneration slip species removal
De-SOx	Lean/rich cycling HC oxidation - Heat	Sulfur release HC oxidation - Heat	Regeneration slip species removal
De-Soot	HC oxidation - Heat	HC oxidation - Heat	PM oxidation

- Complex multi-component, multi-functional catalyst
- Major advances in the fundamental understanding and application of the technology

NOx Adsorber Technology

Fundamental challenges[1]:

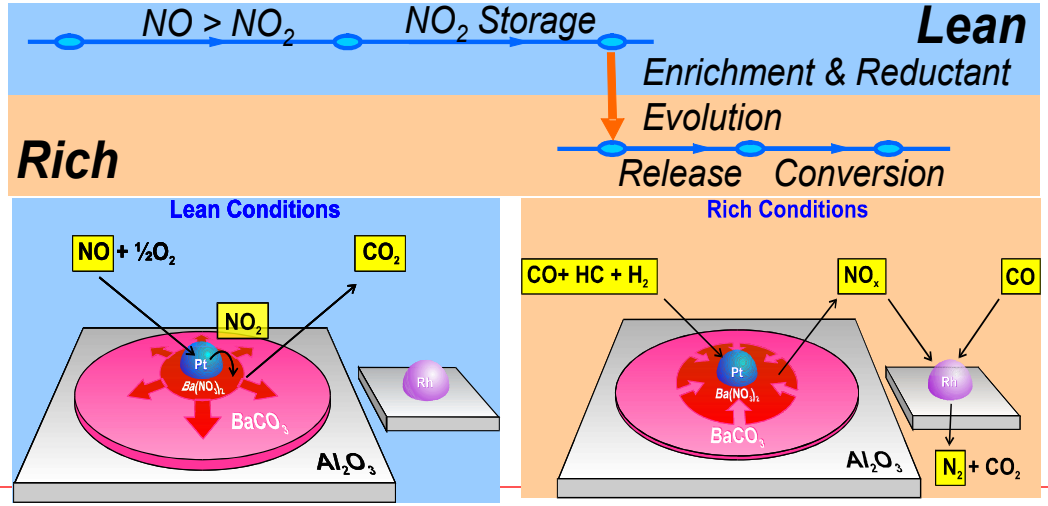
- Multi-component, multi-functional catalyst:
  - At least 3 components, with different functions
  - Both red-ox and acid-base catalyst chemistry
- 5 sequentially-coupled process
- Memory effects

Short-term memory
- Amount of NOx on the catalyst
- Spatial profile of reactions

Mid-term memory
- Amount and form of sulfur

Slow, reversible morphological changes
- Ba redistribution
- Ba aluminate formation and break-up
- Oxidation state of Rh

Long-term memory
- Thermal deactivation (Pt sintering, loss of Pt/Ba interface)



Lean (Rh oxidation):

$4Rh + 3O_2 \rightarrow 2Rh_2O_3$

Rich (Rh reduction):

$Rh_2O_3 + 3H_2 \rightarrow 2Rh + 3H_2O$

$Rh_2O_3 + 3CO \rightarrow 2Rh + 3CO_2$

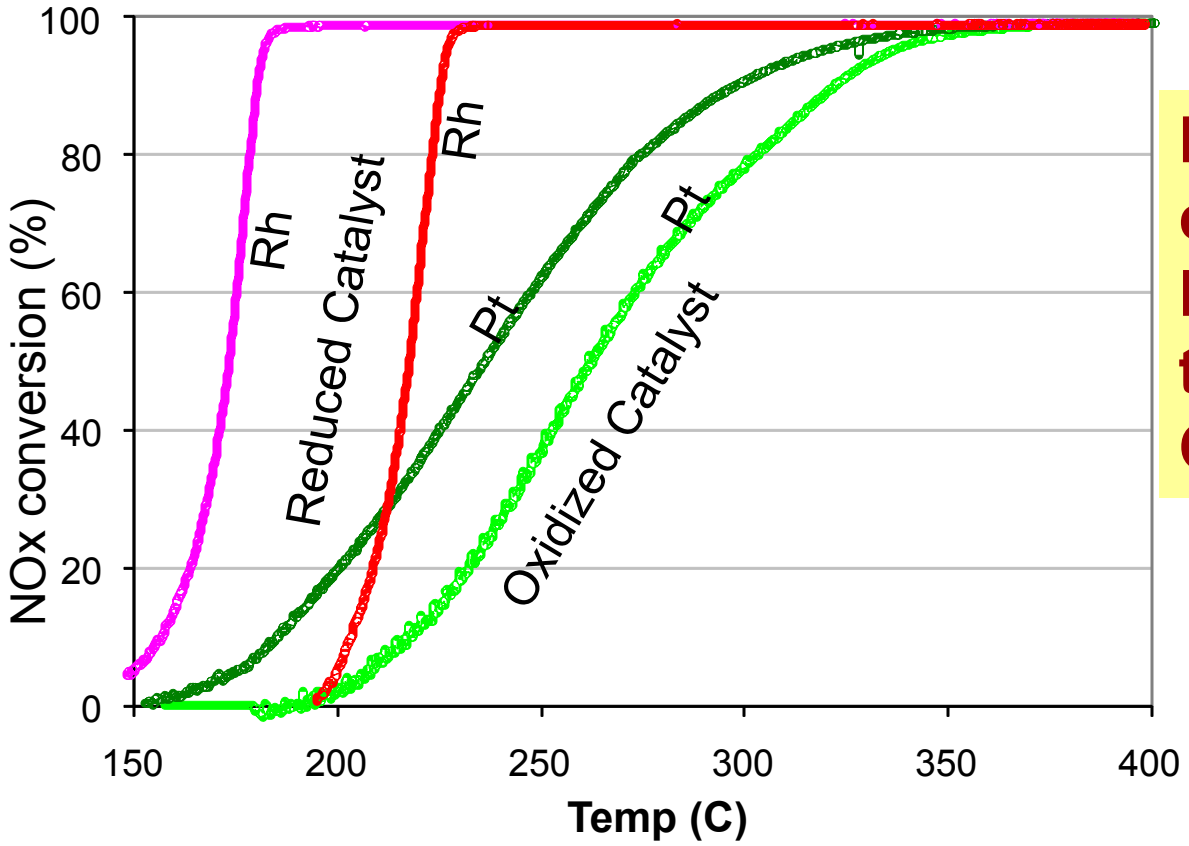
$3Rh_2O_3 + C_3H_6 \rightarrow 6Rh + 3H_2O + 3CO_2$

[1] Epling, Yezerets, Currier et al. "*Overview of the Fundamental Reactions and Degradation Mechanisms of NOx Storage/ Reduction Catalysts*". **Catalysis Reviews**; V46(2004), p.163-245

Outline

- What is the function of Rh in the catalyst (why Rh is important)
- How important is Rh oxidation state
- Rh oxidation
  - temperature and duration
- Rh reduction
  - Role of reductant speciation, temp, richness

Why Rh is Important?

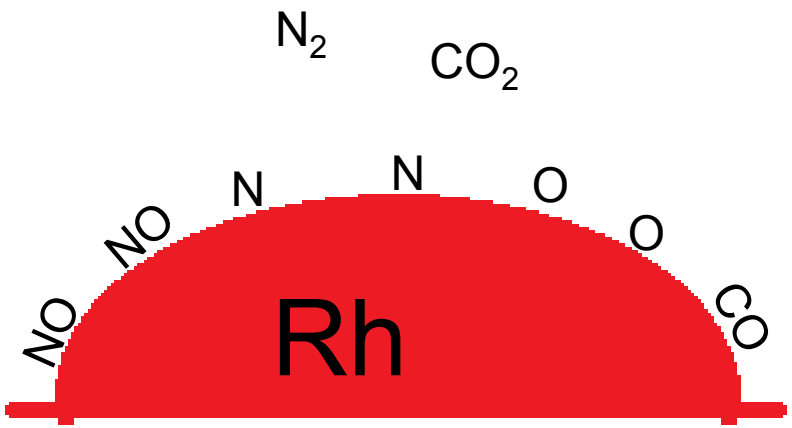


Rh is the key component for NO reduction in the presence of CO

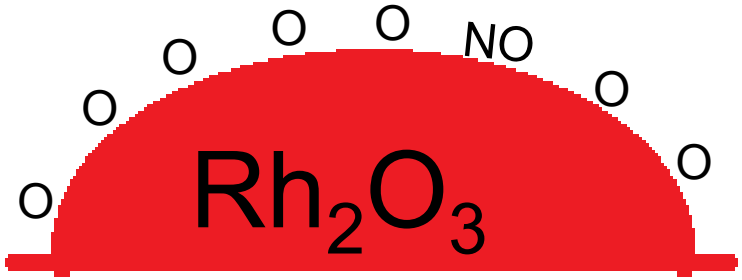
- Reduced metal has better reactivity than oxidized metal.
- Rh is more active than Pt for NO reduction by CO.
- The reactivity of Rh is much more sensitive to its oxidation state than Pt

How Important of Rh Oxidation States

- Rh is the key component for NO reduction in LNT catalysts
- NO dissociation is the rate-limiting step of NO reduction



Reduced Rh



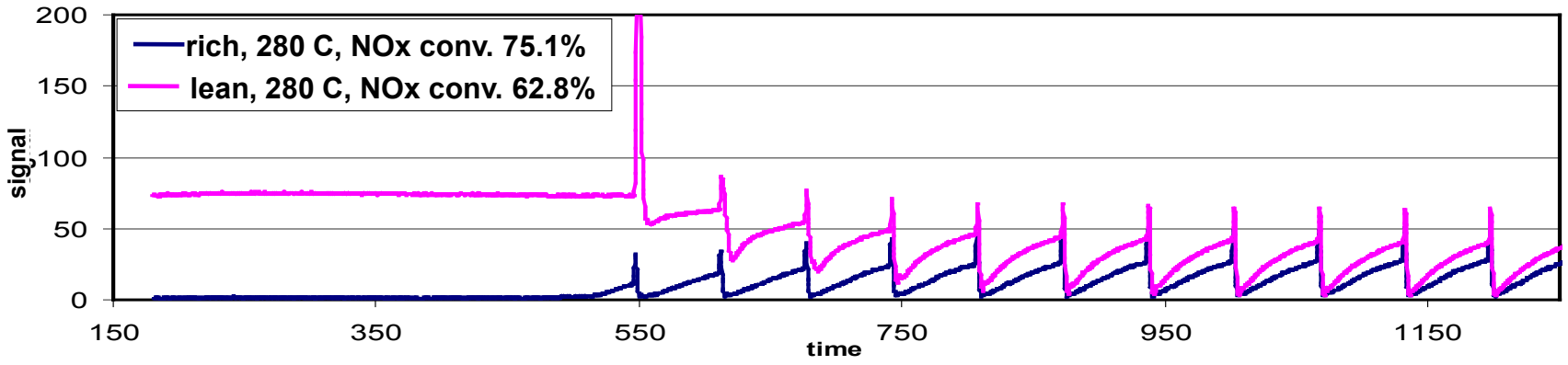
Oxidized Rh

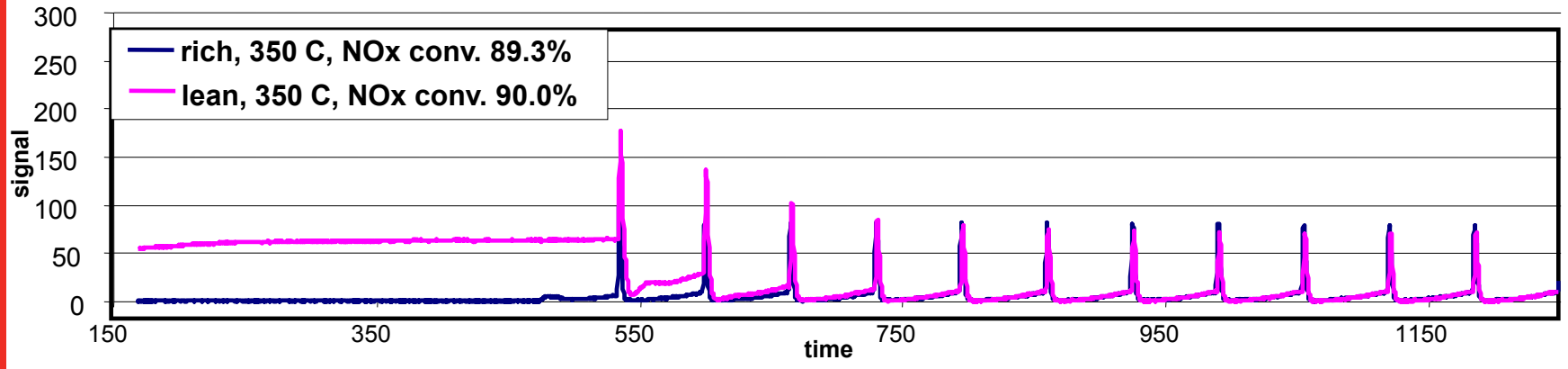
- Oxidized Rh has substantially fewer sites for NO adsorption.
- The adsorbed NO is more difficult to dissociate on the oxidized Rh.
  - Fewer adjacent sites for NO dissociation
  - Thermodynamically less favorable

Granger et al, *J. Catal.* **175** (1998) 194-203

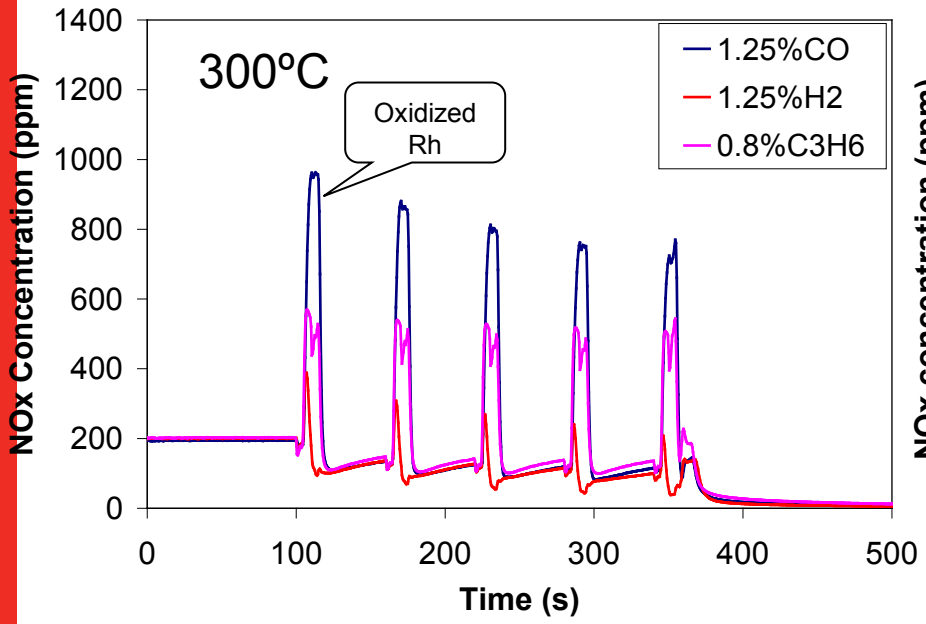
Effect of Temperature on *"Memory" of* Rh Function

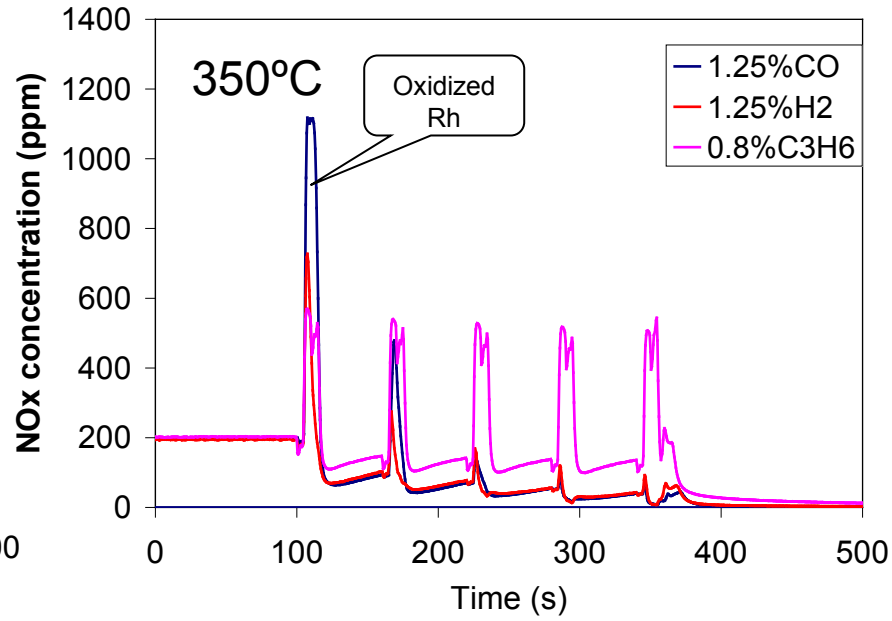
- The reduced Rh is more active of NO reduction than oxidized Rh.
- The memory effect is highly dependant on temperature





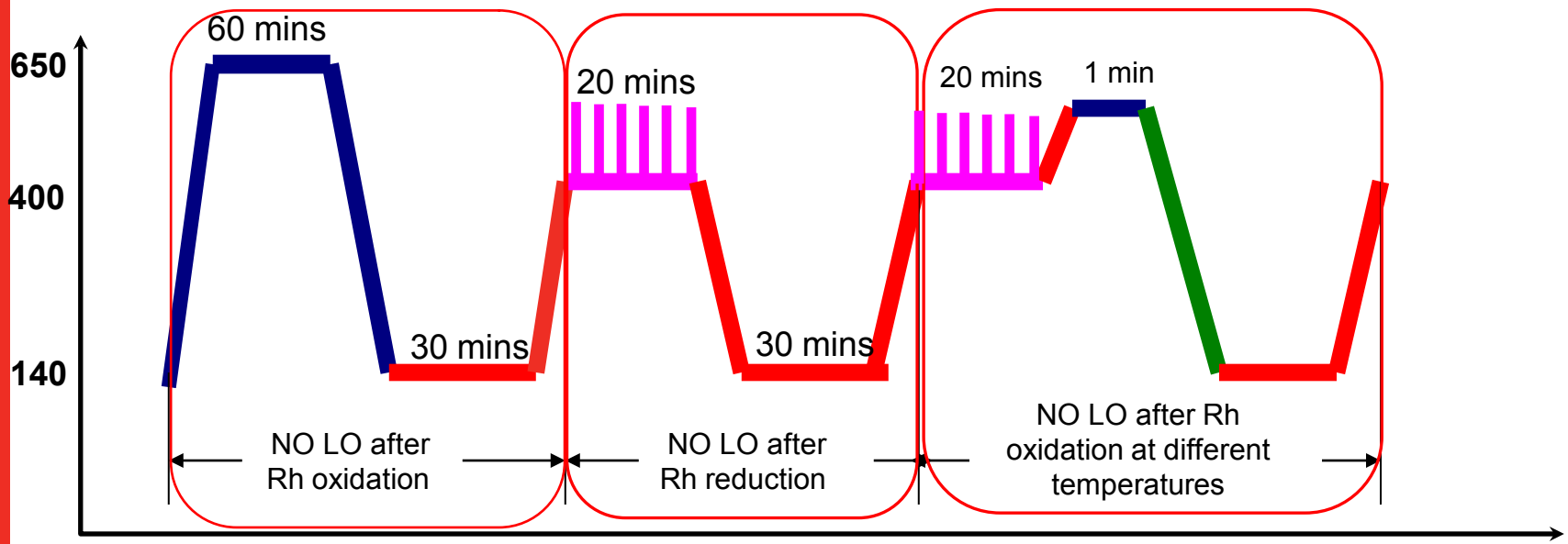
Effect of Reductant Type on *"Memory" of* Rh Function





- H_2 is very effective for both NOx release and NOx conversion to N_2.
- CO is effective for NOx release but not as effective for NOx conversion to N_2, compared with H_2
- C_3H_6 is not effective for either NOx release or NOx conversion.

Experimental Procedure



Lean

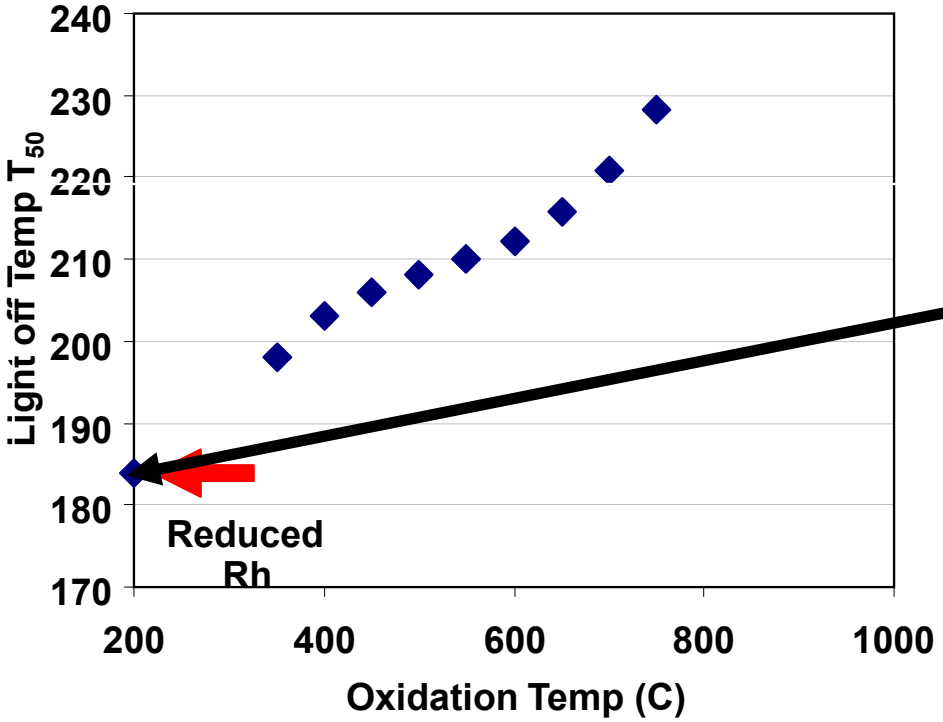
Rich

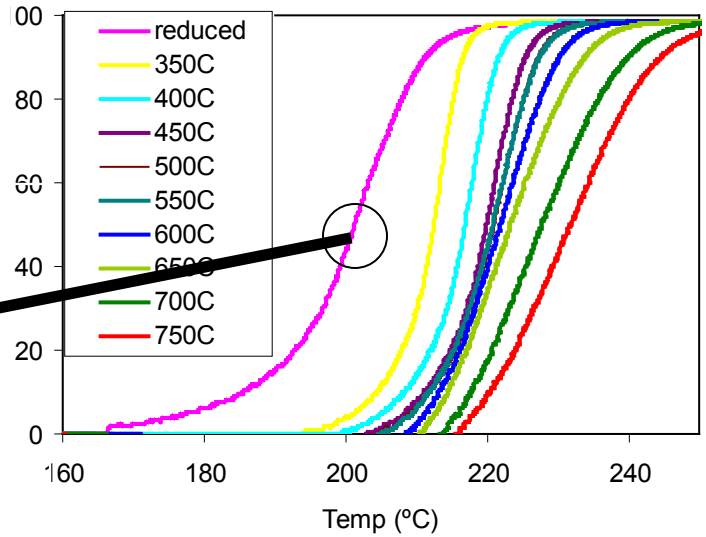
50s Lean/ 10s Rich

He

Gas species	Rich	Lean
NOx	200 ppm	200 ppm
C_3H_6	2000 ppm	-
H_2	1.25%	-
CO	4.00%	-
O_2	0.00 %	5%
H_2O	5 %	5 %
CO_2	5 %	5 %

Effect of Temperature on Rh Oxidation

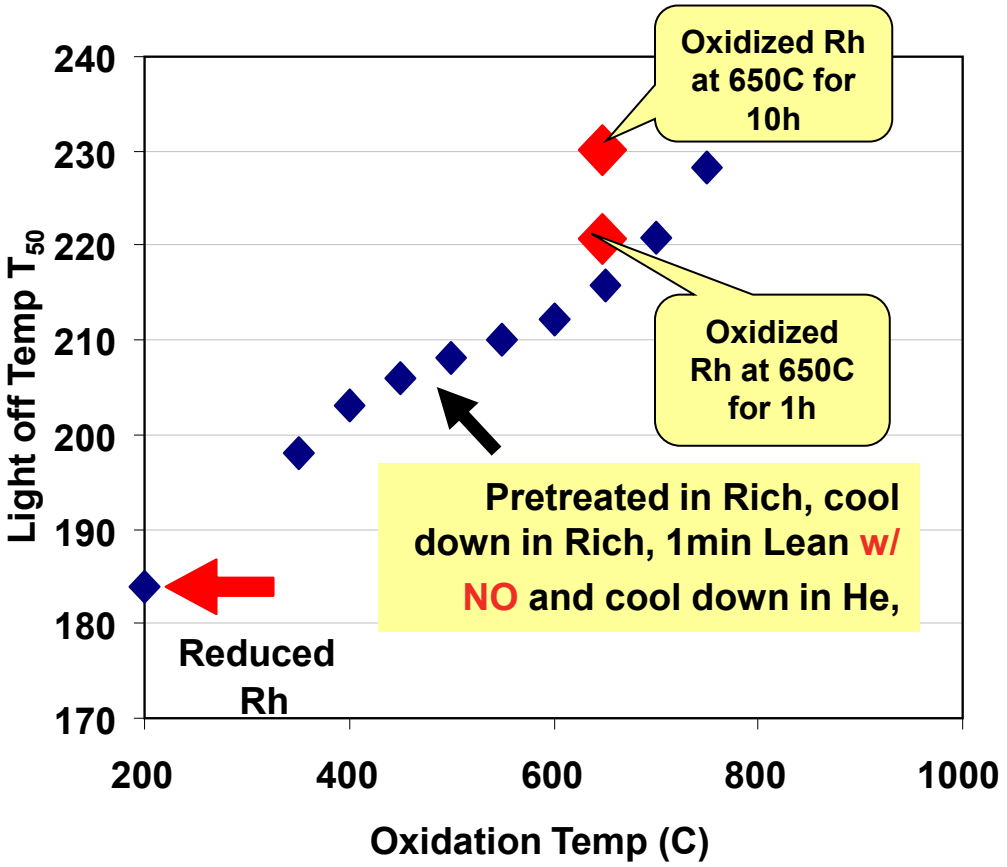


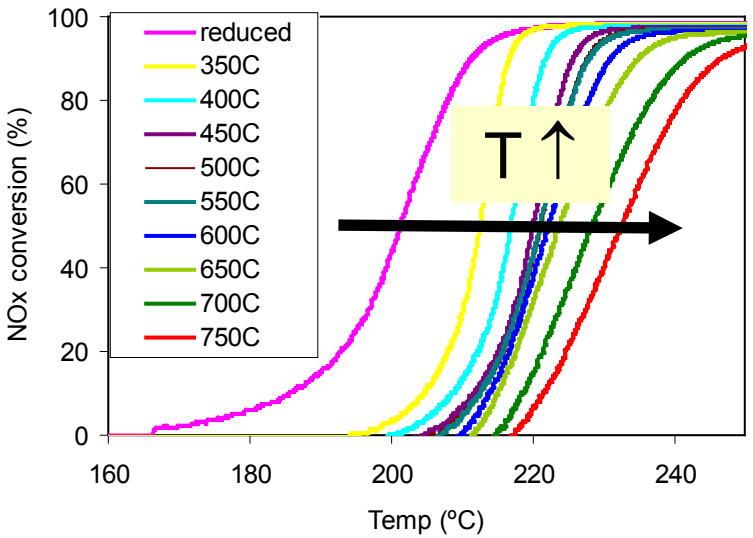


- Reduced Rh: pretreat sample at 400C, 20 L/R cycles with NO and cool down in rich condition to 140C w/o NO

- T_{50} = 184°C for reduced Rh vs. T_{50}=223°C for oxidized Rh
- One-minute lean exposure at high temperature can cause Rh oxidation

Effect of Temp on Rh Oxidation

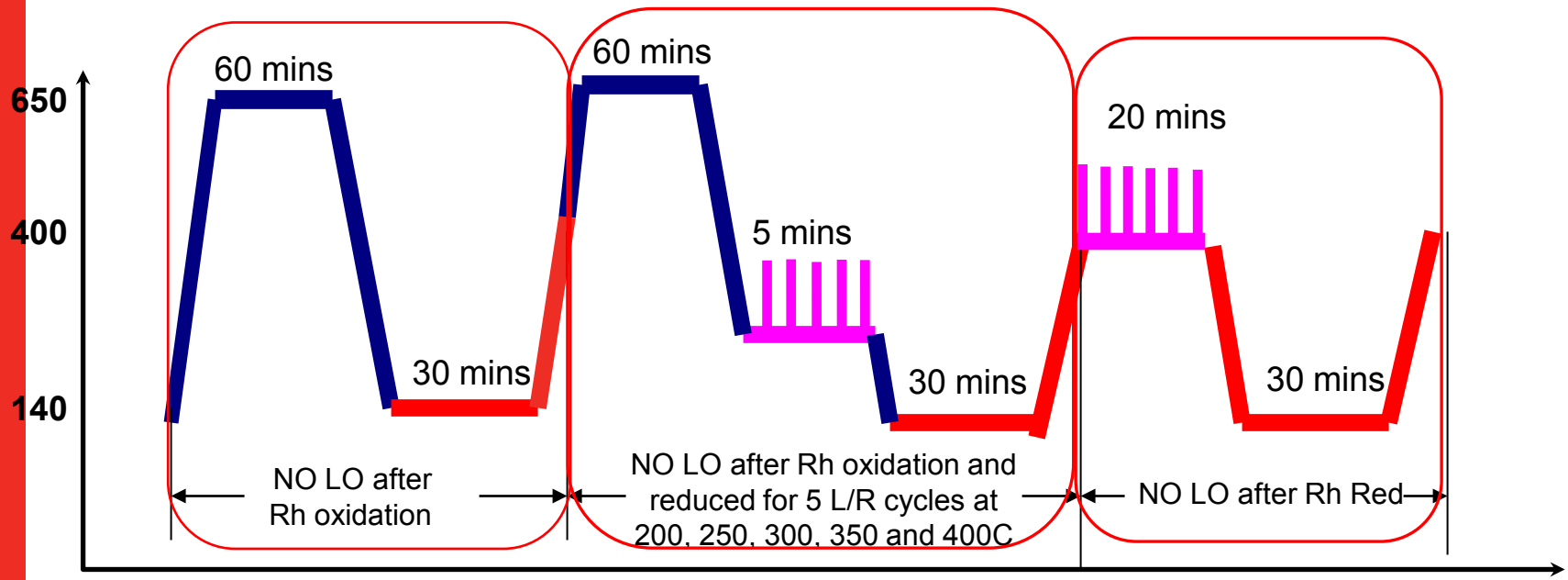




•Reduced Rh: pretreat sample at 400C, 20 L/R cycles with NO and cool down in rich condition to 140C w/o NO

- T_{50} = 184°C for reduced Rh vs. T_{50} = 230°C for oxidized Rh
- One-minute lean exposure at high temperature can cause Rh oxidation

Experimental Procedure



Lean

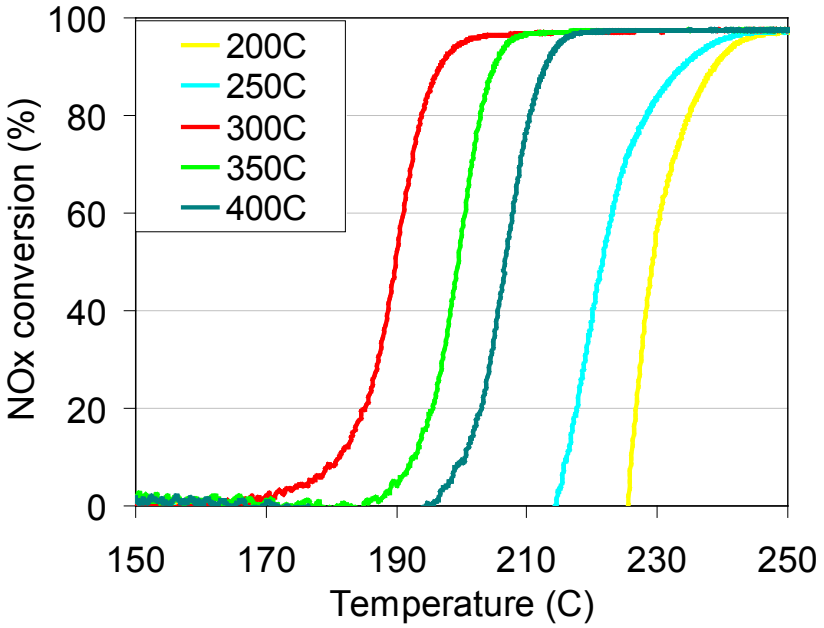
Rich

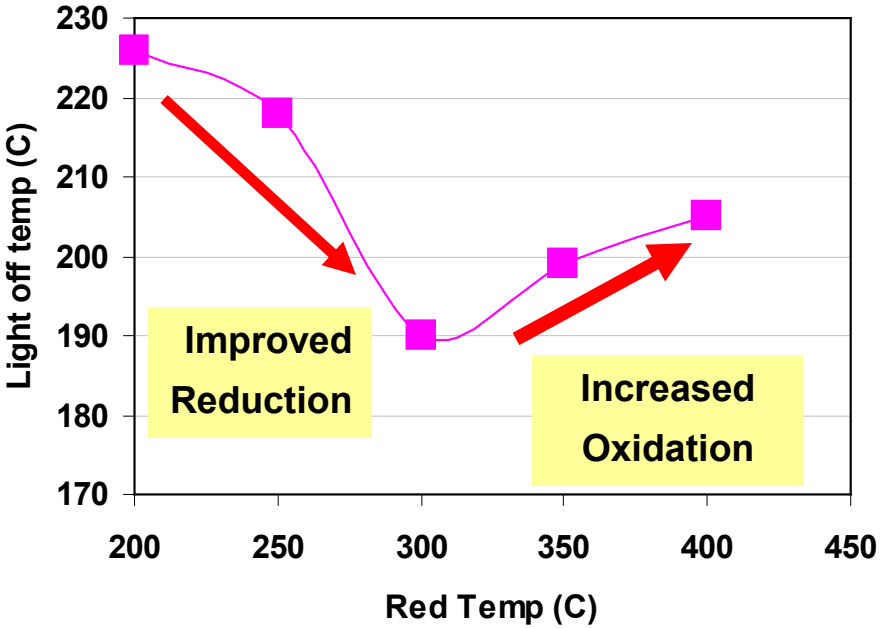
50s Lean/ 10s Rich

He

Gas species	Rich	Lean
NOx	200 ppm	200 ppm
C_3H_6	2000 ppm	-
H_2	1.25%	-
CO	4.00%	-
O_2	0.00 %	5%
H_2O	5 %	5 %
CO_2	5 %	5 %

Effect of Temp on Rh Reduction During L/R Cycling

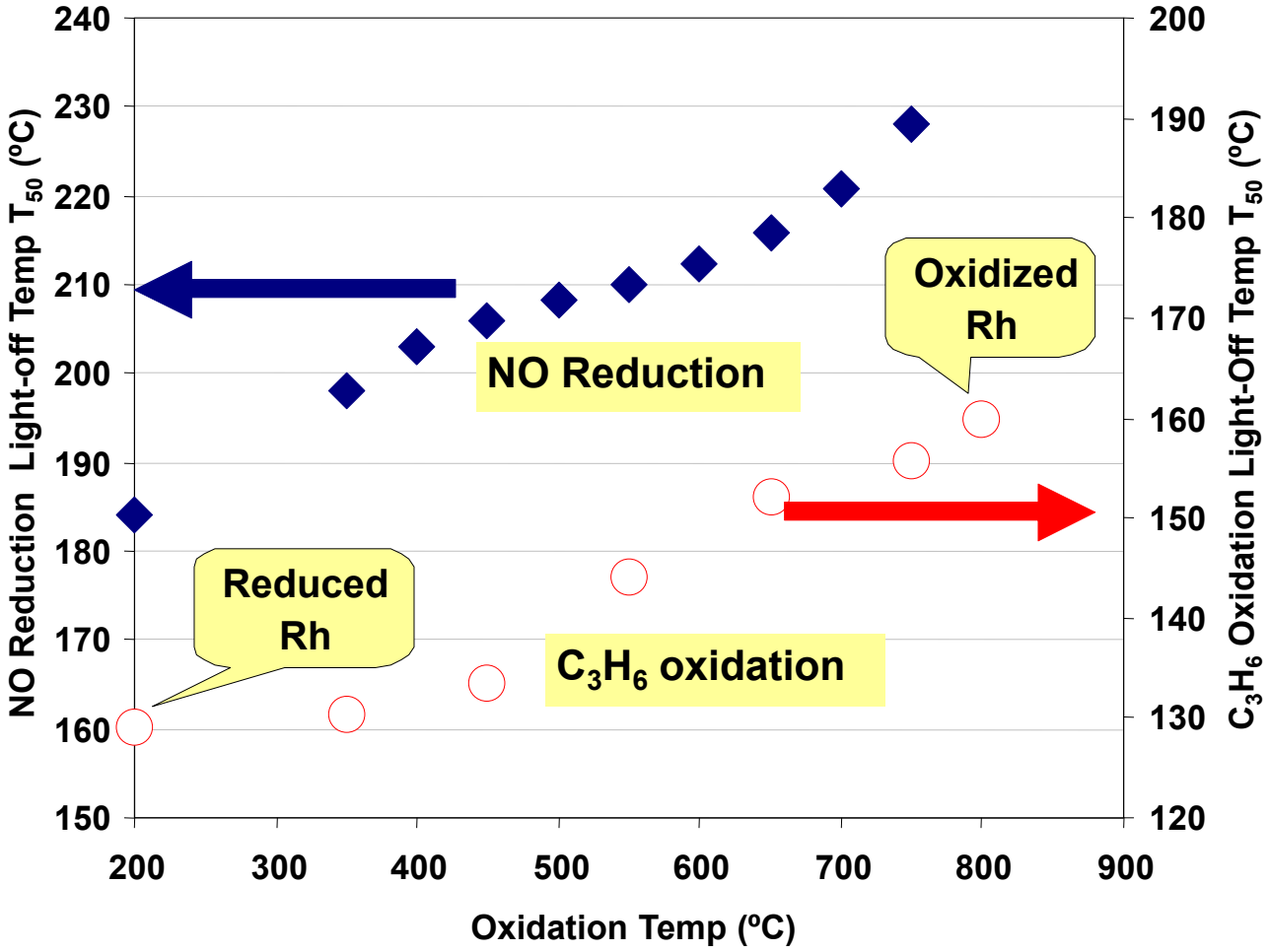




- The Rh reach its most reduced state at 300ºC.
- The exposure to temperature higher than 300ºC will partially oxidize the reduced Rh.

Note: NO present during the lean oxidation at 650C, cool down to target temp and 5 L/R cycles at the target temperature.

Effect of Rh Redox States on C_3H_6 Oxidation



- Rh oxidation state affects both NO reduction and HC oxidation on NOx adsorber catalyst.

Summary

- Continued improvements in the understanding of the underlying chemistry of LNT operation and lifecycle offer opportunities for further system efficiency improvements
  - Operation
  - Catalyst design

Catalyst Technology Team

- **Cummins**
  - Neal Currier
  - Aleksey Yezerets

Johnson Matthey

- Haiying Chen
- Howard Hess
- Shadab Mulla

Many other colleagues at Cummins and JM