Lean-NOx Catalyst Development for Diesel Engine Applications

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August 29, 2002

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Advanced Catalyst Technology Program (supported by DOE)

- Program kicked off: 1998
- Support material (alumina) developed:1999
- Metal oxide doped alumina catalysts studied: 2000
- Reaction mechanisms & active sites identified: 2001
- Catalyst formulation developed: 2002
- Full size engine test planned: 2002

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Hydrocarbon Lean-NOx Catalyst Technology

Advantages: on board hydrocarbon
relatively simple system

Disadvantages: low NOx reduction (~30%)
poor hydrothermal stability

Opportunities: non-thermal plasma or HC reformer
improve catalyst performance/durability

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Catalysts for PAC/Lean-NOx System

- Catalyst Materials: γ-Al_2O_3, Metal Oxide/γ- Al_2O_3
- Advantages: - very selective (low fuel penalty)
  - thermally stable (alumina support)
  - inexpensive (no noble metal)
  - suitable for combining with PAC or HC reformer
    - NO → NO_2
    - HC → Oxygenated hydrocarbons
  - flexible formulation (activity, selectivity, durability)

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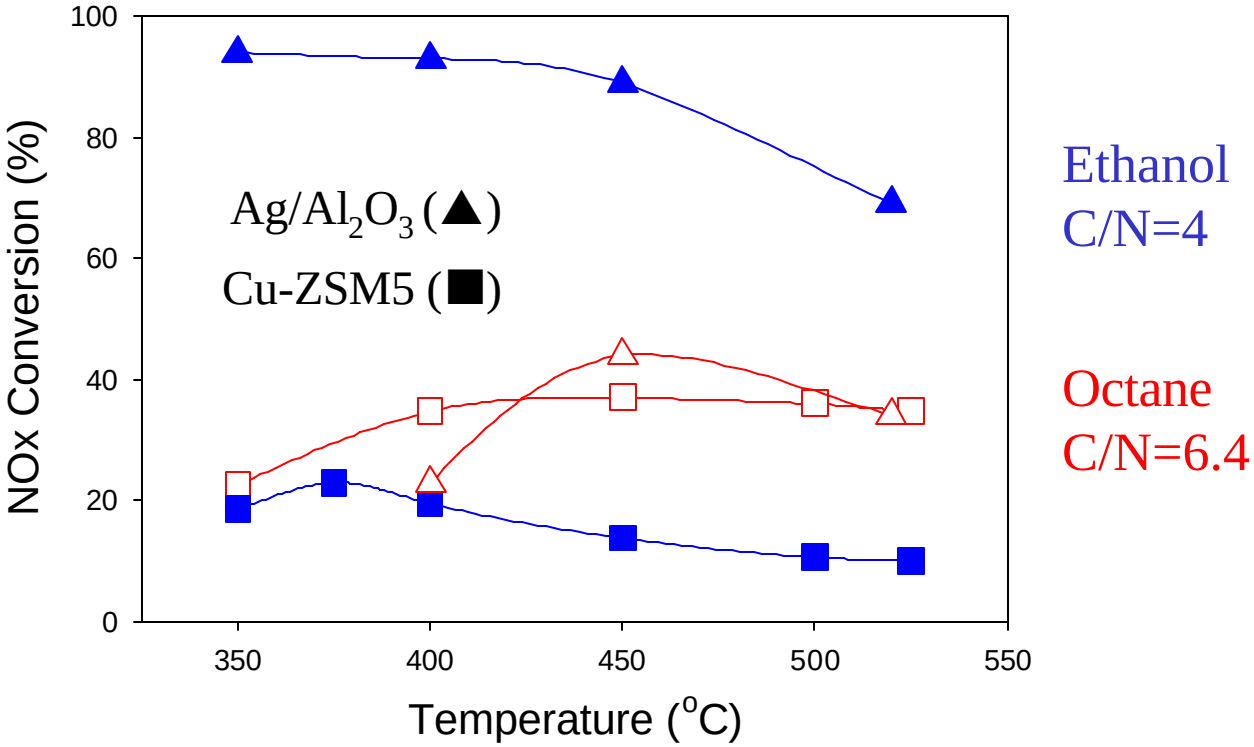
Current Lean-NOx Catalyst Technology

500ppm NOx, 500ppm CO, 8% CO_2, 9% O_2, 7% water, 1”x3” core, 50,000 h^{-1}



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Hydrocarbon Reformation by Non-thermal Plasma

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Slip Stream Engine Test Cell

3126B 190 hp engine
Fuel: ULSD

Catalyst: 0.049 & 0.22 L
Load: High & Road
Reductant: C_3H_6, MtOH
ULS Diesel
Conc.: 3000-6000 ppm C_1
Plasma Power: 0-60 J/L
Temp.: 300, 400, 500 ^oC
S.V.: 6,000 - 100,000 h^{-1}

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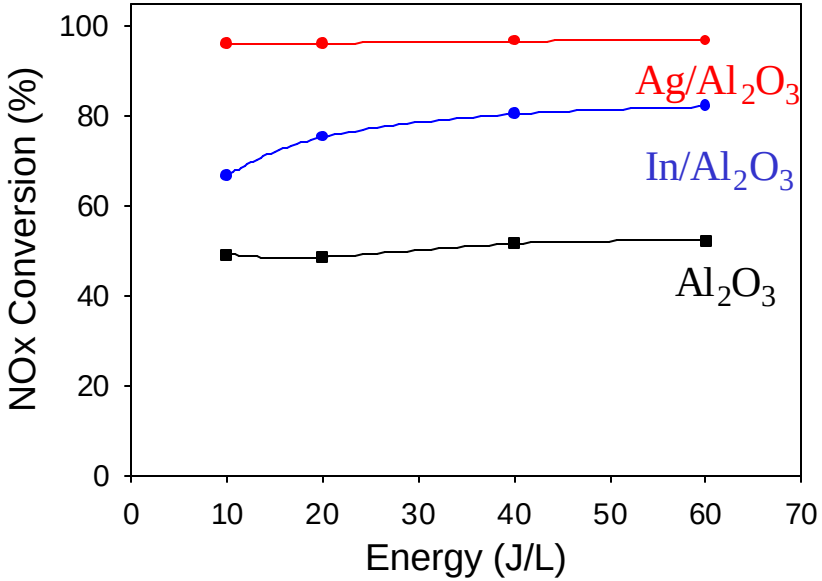
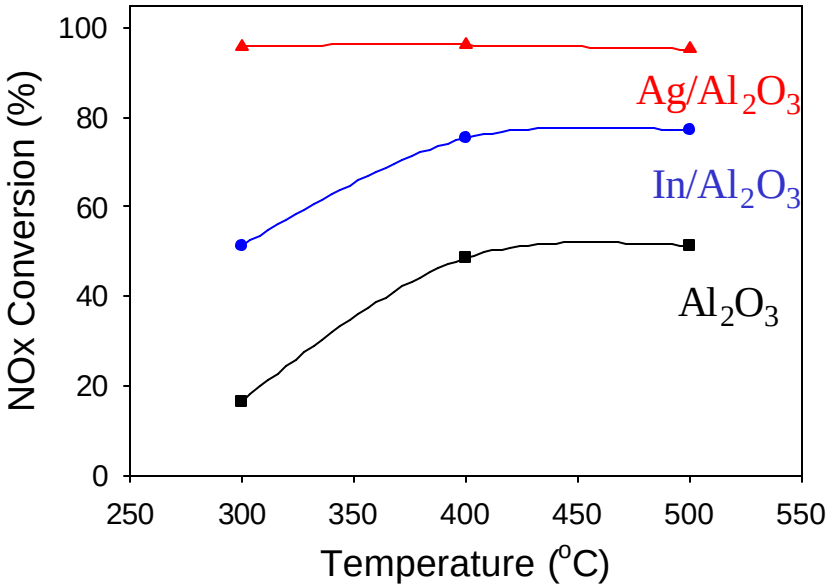
Slip Stream Engine Test Results

Road Load Condition (75% Load) with 2000ppm C_3H_6 at 10,000 h^{-1}

Temperature at 400 °C



Plasma Energy at 20 J/L



- **Minimum plasma energy**
- **Broad temperature window**

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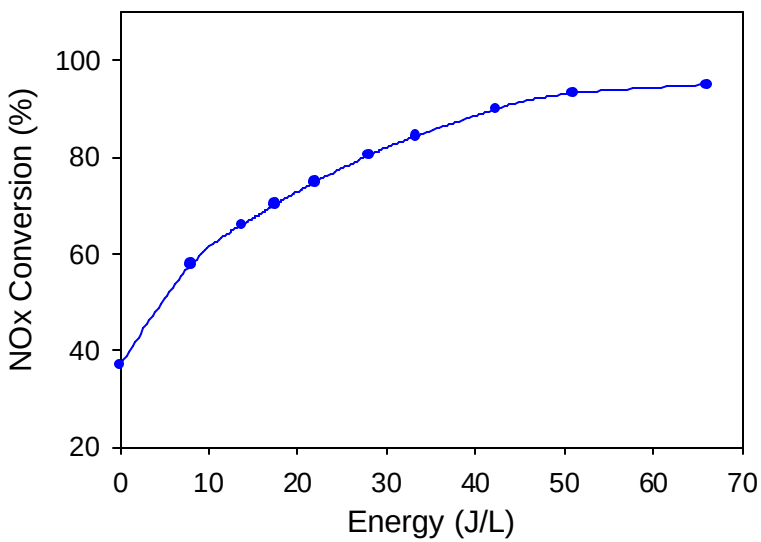
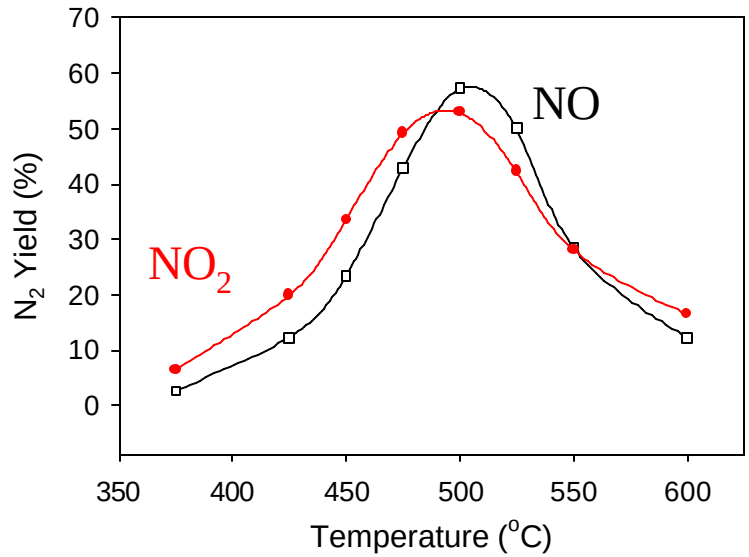
Plasma Assisted Catalysis

Plasma assisted catalysis: Ag/Al_2O_3



NOx reduction over Ag/Al_2O_3



- **Plasma improves a silver catalyst performance.**
- **NOx reduction over the catalyst is independent on NOx species.**
- **Plasma provides better reductant to the catalyst (oxygenates)**

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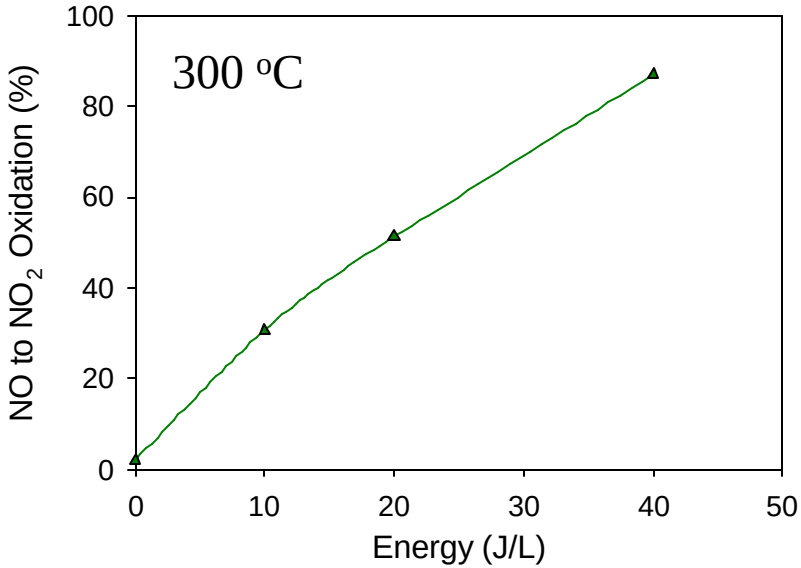
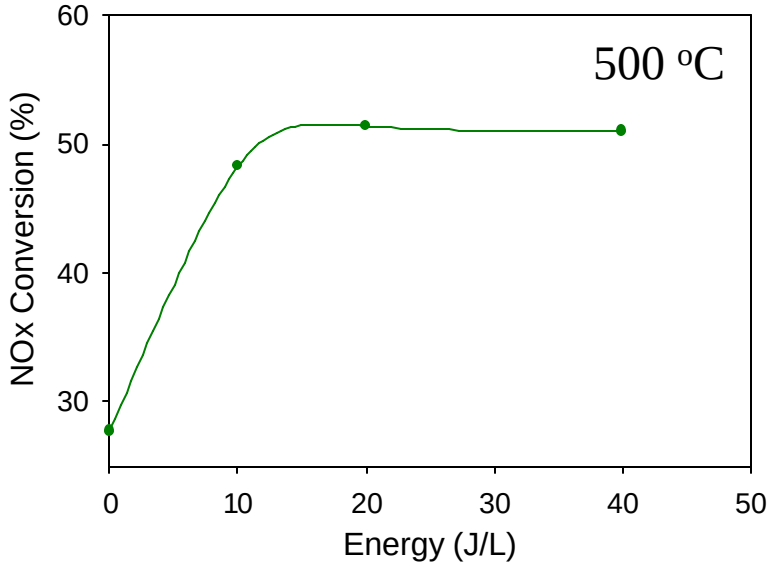
Plasma Assisted Catalysis-Continue

Road Load Condition (75% Load) with 2000ppm C_3H_6 at 10,000 h^{-1}

Plasma Reactor



Catalyst Reactor



- **NOx conversion is not proportional to NO oxidation to NO_2.**
- **Oxygenated hydrocarbons produced may limit NOx reduction.**

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Hydrocarbon Reformation by Catalyst Formulation

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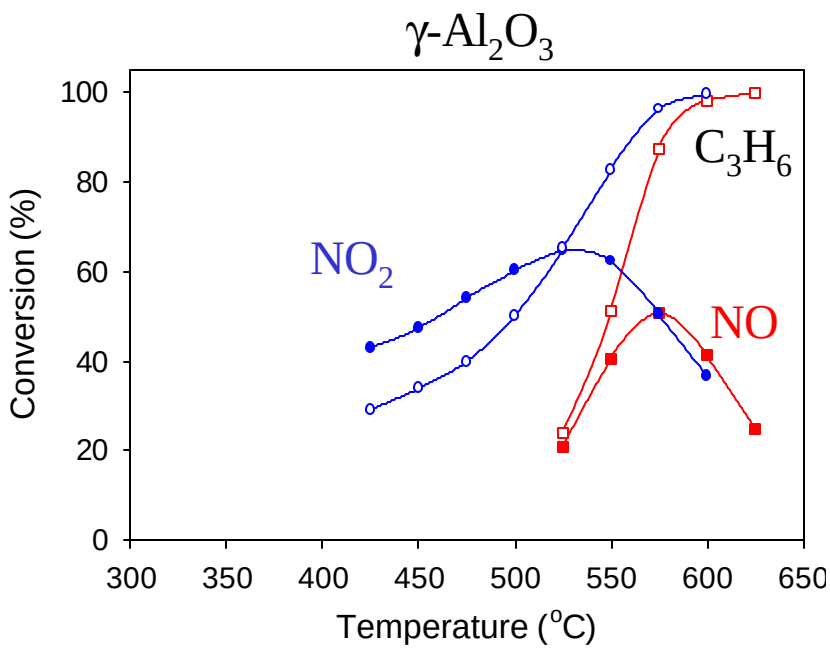
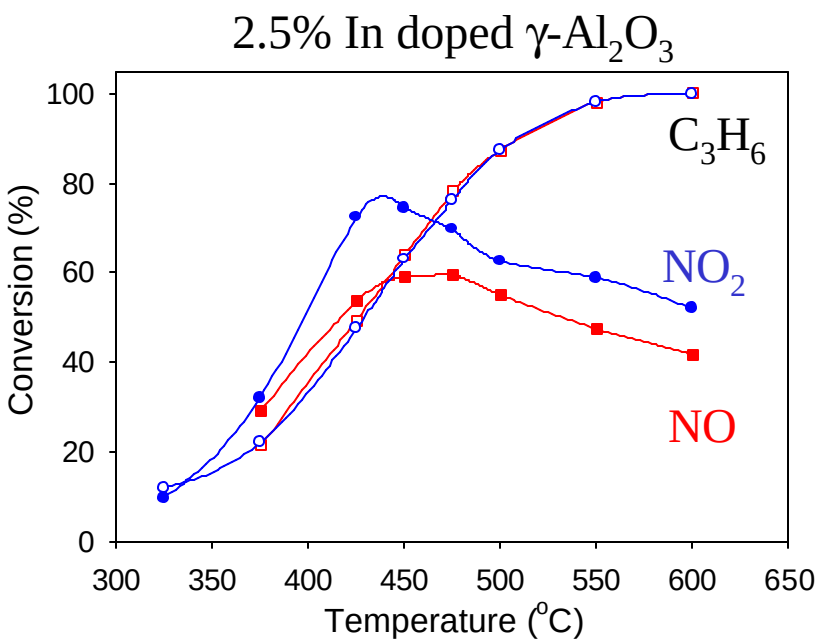
Catalytic Performance of In_2O_3/Al_2O_3: NOx/C_3H_6

0.1% NOx, 0.1% Propene, 7% H_2O, 9% O_2, 30,000h^{-1}





When indium is doped on alumina,

- **NOx reduction is less dependent on NOx species.**
- **HC conversion is constant.**

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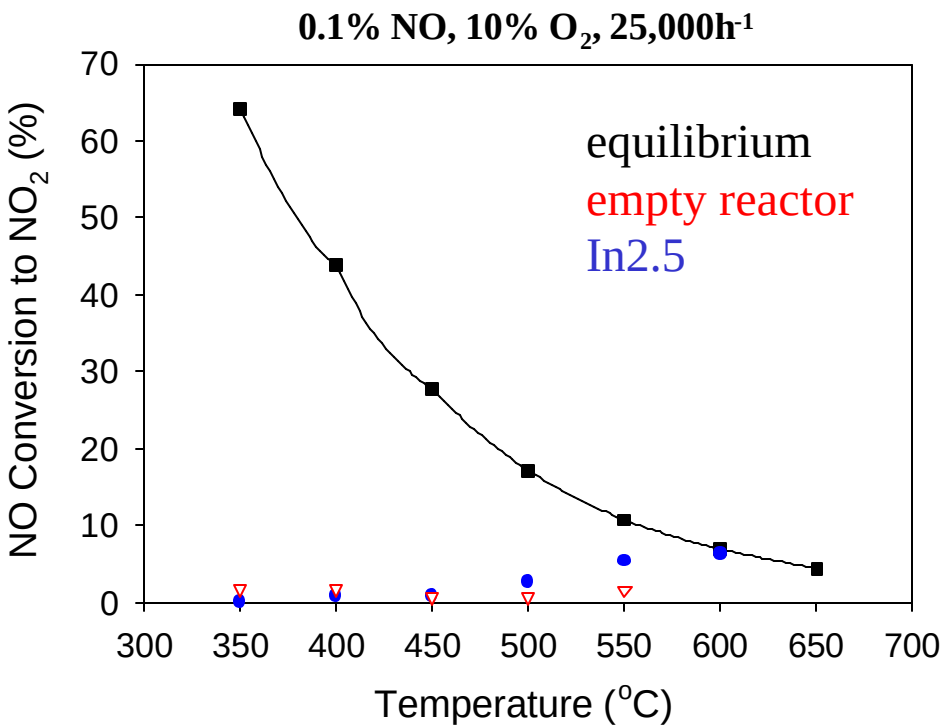
NO oxidation over In_2O_3/Al_2O_3



- In_2O_3 does not oxidize NO to NO_2.
- HC reformation over indium site enhances NOx reduction

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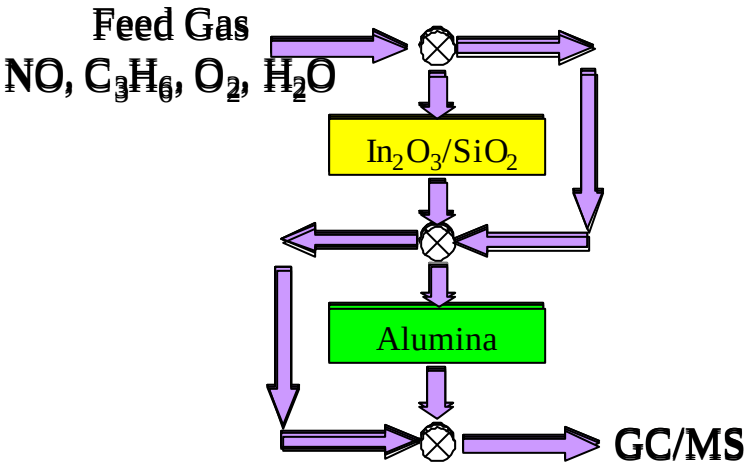
Reaction Mechanism of In_2O_3/Al_2O_3

Dual Bed System



Products

- Acetaldehyde (CH_3CHO)
- Acrolein (CH_2=CH-CHO)
- No N_2 produced

- N_2

- $3xN_2$

Roles of active sites

- **In_2O_3 : Stable oxygenated hydrocarbons**
- **Al_2O_3 : NO reduction to N_2**

Park et al. J. Catal. Vol. 210, No. 1, 97-105, 2002

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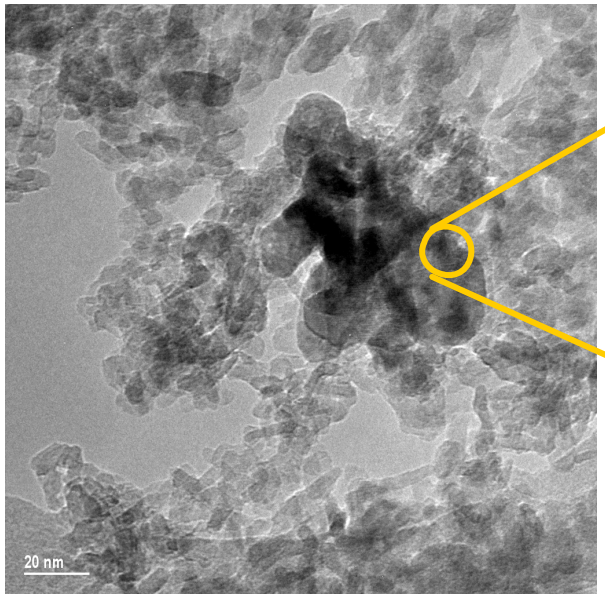
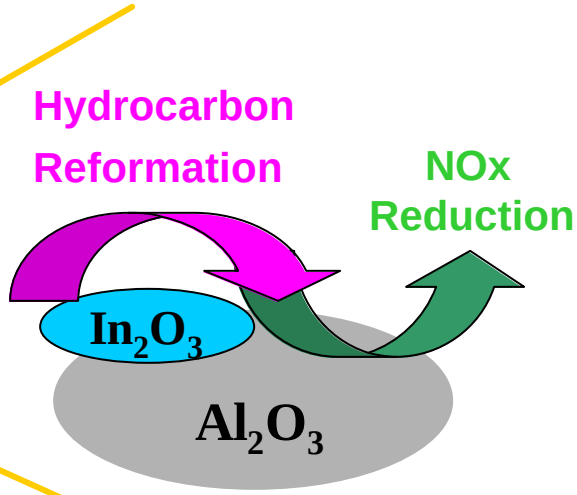
Two Active Sites in Lean-NOx Catalysts

TEM image of In_2O_3/Al_2O_3





- Optimize each active component independently
- Leads to new & improved catalyst formulations

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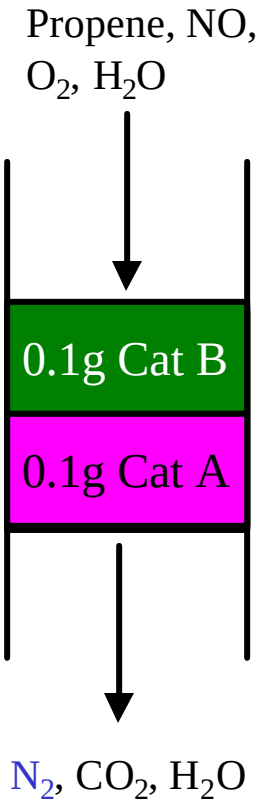
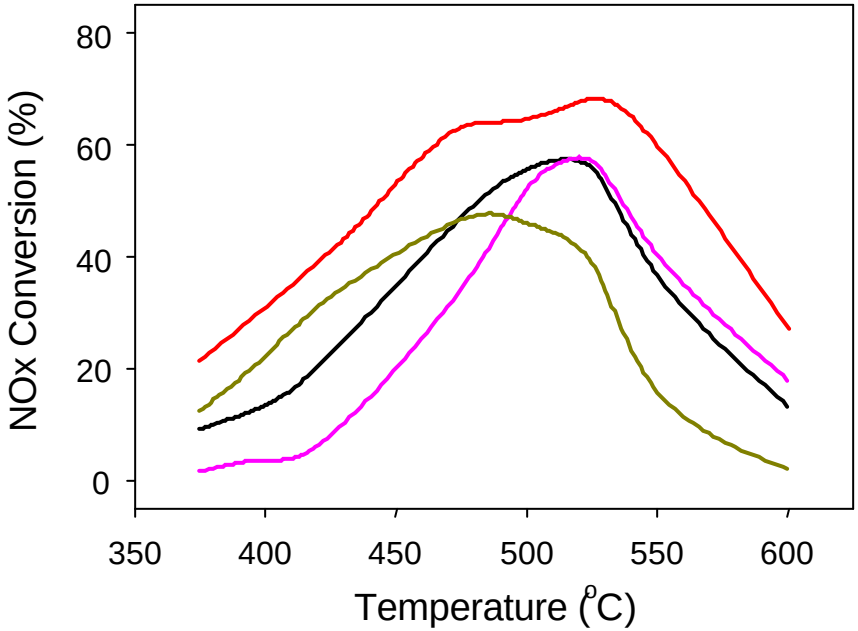
Development of Catalyst Formulation



NO Reduction Results
(C/N=3, 9% O_2, 7% H_2O, 30,000h^{-1})



- **High performance catalyst formulation: high NOx reduction wide temperature window**

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Summary

- Hydrocarbon reformation is a key to improve Lean-NOx catalysis
  - plasma assisted catalyst { plasma: NOx & HC activation; catalyst: NOx reduction }
  - reformation function integrated in catalyst formulation
    - first catalyst: HC activation
    - second catalyst: NOx reduction
- Tailored reaction mechanism leads a new catalyst development.
- Catalyst formulations suitable for PAC & Lean-NOx Catalyst were identified.

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Acknowledgements

CRADA: Caterpillar Inc. & PNNL

PNNL(EMSL): Mr. Mark Engelhard (XPS)

Mr. David McCready (XRD)

ORNL: Dr. Lawrence F. Allard (TEM)

DOE: Mr. Gurpreet Singh

Dr. Sidney Diamond

Dr. D. Ray Johnson (ORNL)

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