Plasma-Activated Lean NOx Catalysis for Heavy Duty Diesel Emissions Control

C. Aardahl, J. Birnbaum, K. Rappe, D. Tran (PNNL)

Paul Park (Caterpillar)

Gurpreet Singh (OFVT)

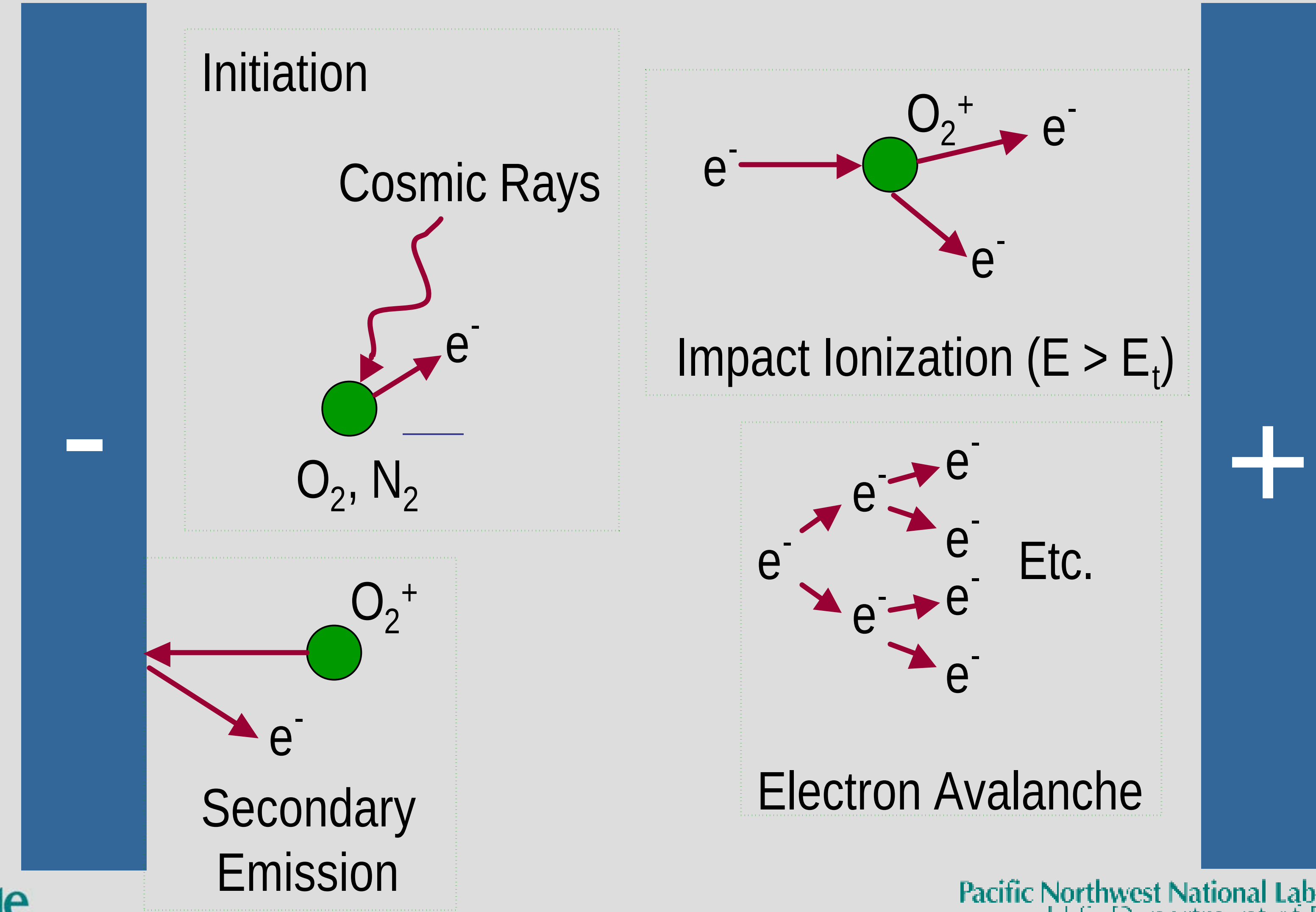
DEER 2002, San Diego, CA

August 29, 2002

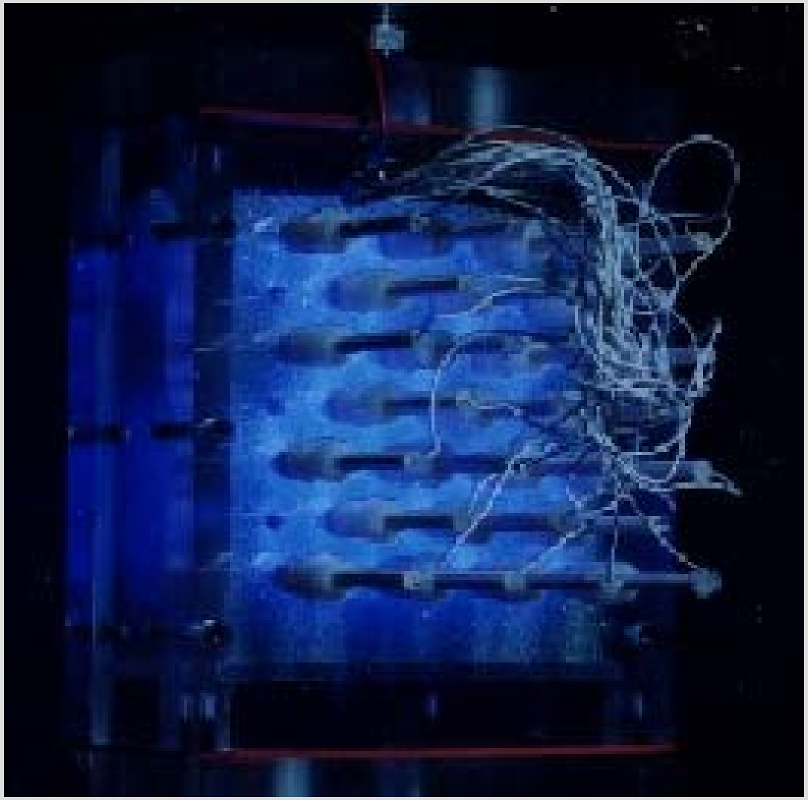
Outline

- Introduction of Non-Thermal Plasma and Plasma Catalysis
- Plasma-Facilitated Lean NOx Catalysis
  - Chemistry
  - Reducing Agent Effects
  - Collaboration with LEP CRADA
  - Aging Studies

Plasma Initiation



Non-Thermal Plasma



Tube Array (Packed Bed)

Cylindrical (Packed Bed)

Plasma-Facilitated Lean NOx Catalysis

- Step 1. Exhaust passed through NTP
  - Selective oxidation of NO to NO_2
  - Partial oxidation of hydrocarbon
- Step 2. NTP-treated exhaust passed over catalyst
  - LD – Zeolites; HD – γ-aluminas (In_2O_3, Ag_2O promoters)
  - NO & NO_2 reduced to N_2
  - Consumption of hydrocarbons

Plasma-Facilitated deNOx

- Advantages
  - Sulfur tolerant
  - Tunable through power deposition
  - High conversion can be obtained

- Challenges for Heavy Duty
  - Broad temperature range required
  - High flow rate and NOx level
  - Durability
  - Low HC level in exhaust
  - 3% fuel penalty target

Plasma Chemistry

Reactions that dominate without HC:

$NO + O\bullet$ ® NO_2
$NO_2 + O\bullet$ ® $NO + O_2$
$NO_2 + \bullet OH$ ® HNO_3 → High power (no HC)

Net = NO stable

HC is an O• and •OH getter:

$C_3H_6 + O\bullet$ ® $\bullet C_2H_5 + HCO\bullet$
$C_3H_6 + O\bullet$ ® $\bullet CH_2CO + \bullet CH_3 + H\bullet$
$C_3H_6 + \bullet OH$ ® $C_3H_5 + H_2O$
$C_3H_6 + \bullet OH$ ® C_3H_6OH

Partial oxidation of HC

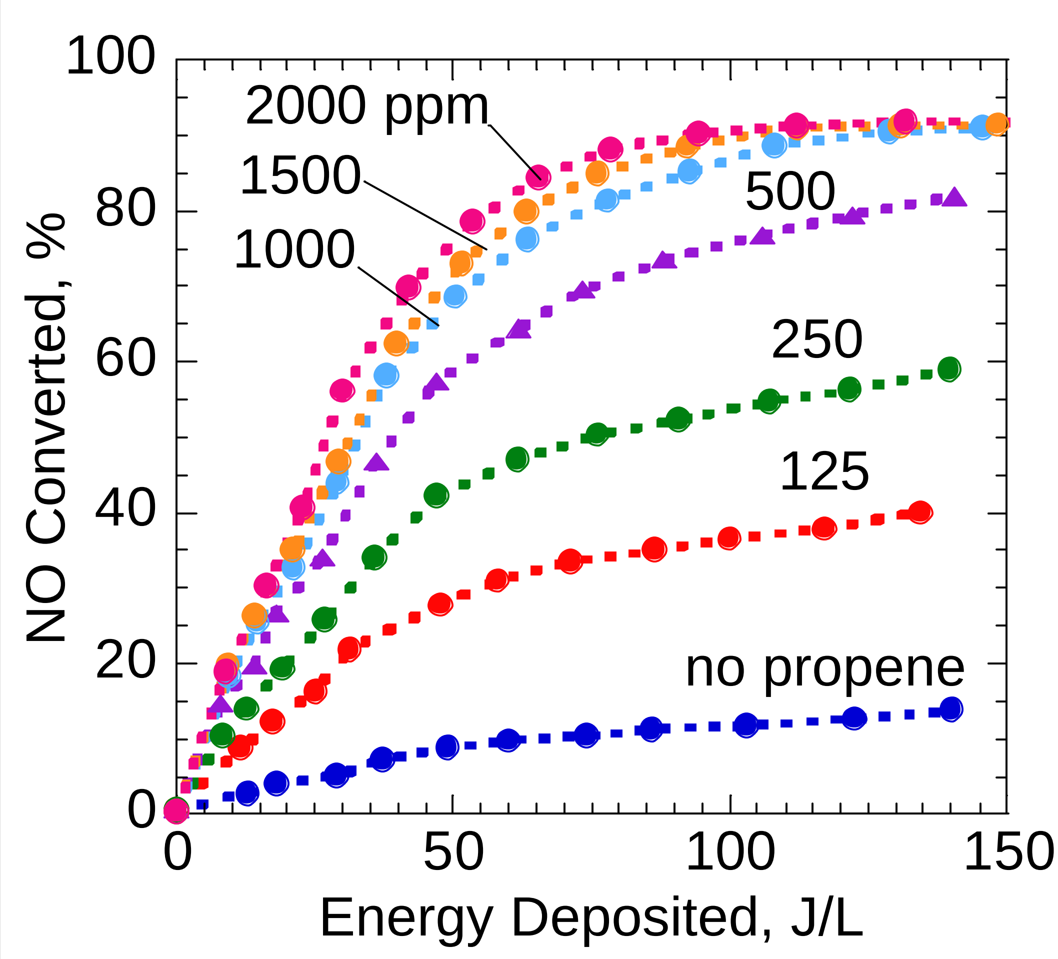
Further degradation Of HC forms $HO_2\bullet$:

$CH_3O\bullet + O_2$ ® $CH_2O + HO_2\bullet$
$HCO\bullet + O_2$ ® $CO + HO_2\bullet$
$H\bullet + O_2$ ® $HO_2\bullet$

$HO_2\bullet$ reacts quickly w/NO:

$NO + HO_2\bullet$ ® $NO_2 + OH\bullet$ → Stable NO_2

Plasma Treatment of Simulated Exhaust



T = 350°C

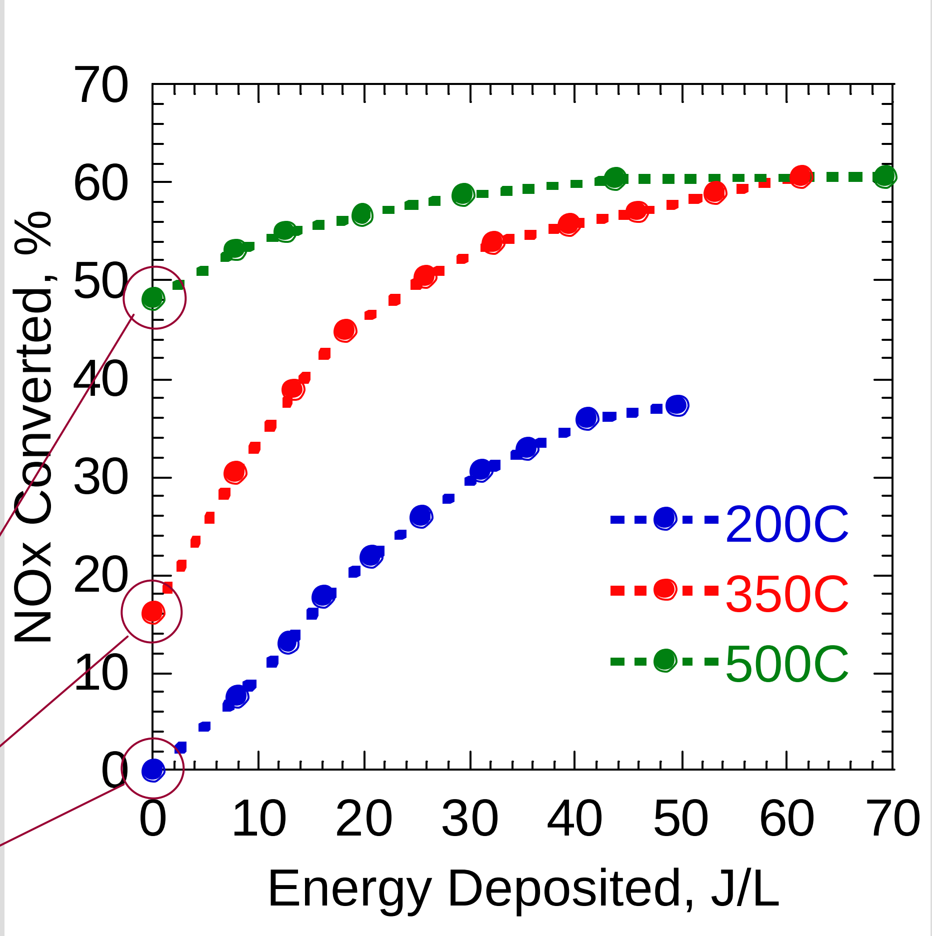
500 ppm NO
300 ppm CO
8% CO_2
1.5% H_2O
20 ppm SO_2
9% O_2
N_2 Balance

Plasma-Catalysis:
Thermal vs. Plasma Activation

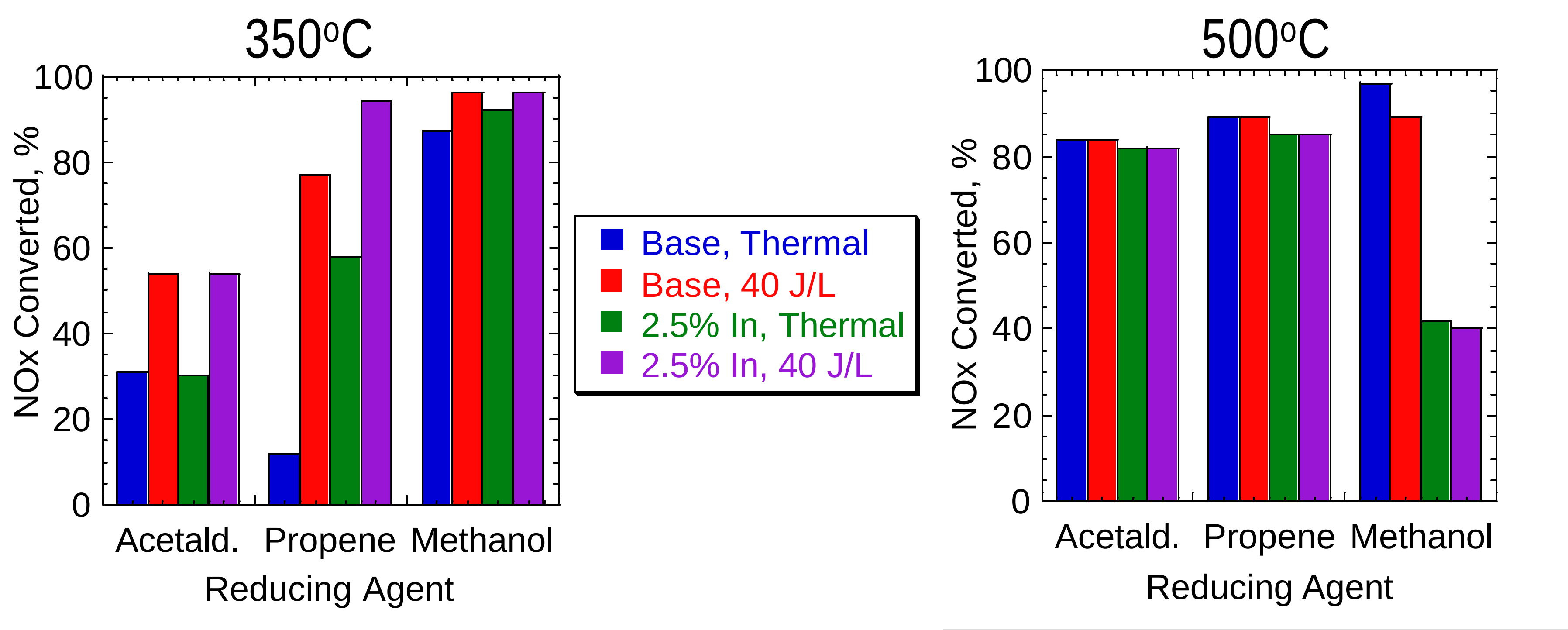
Energy Deposited =
Power/Flow Rate

Plasma-Facilitated
Activity Reported at a
Given Energy
Deposition

Thermal Catalytic Activity



Influence of Plasma and Dopants



- 350ºC: plasma and promoter have positive impact and are synergistic.
- 500ºC: plasma is a non-factor and addition of metals has negative impact. Base material is sufficiently thermally active at these temperatures and plasma has no impact. Metal promotion results in excess HC combustion and less NOx reduction.

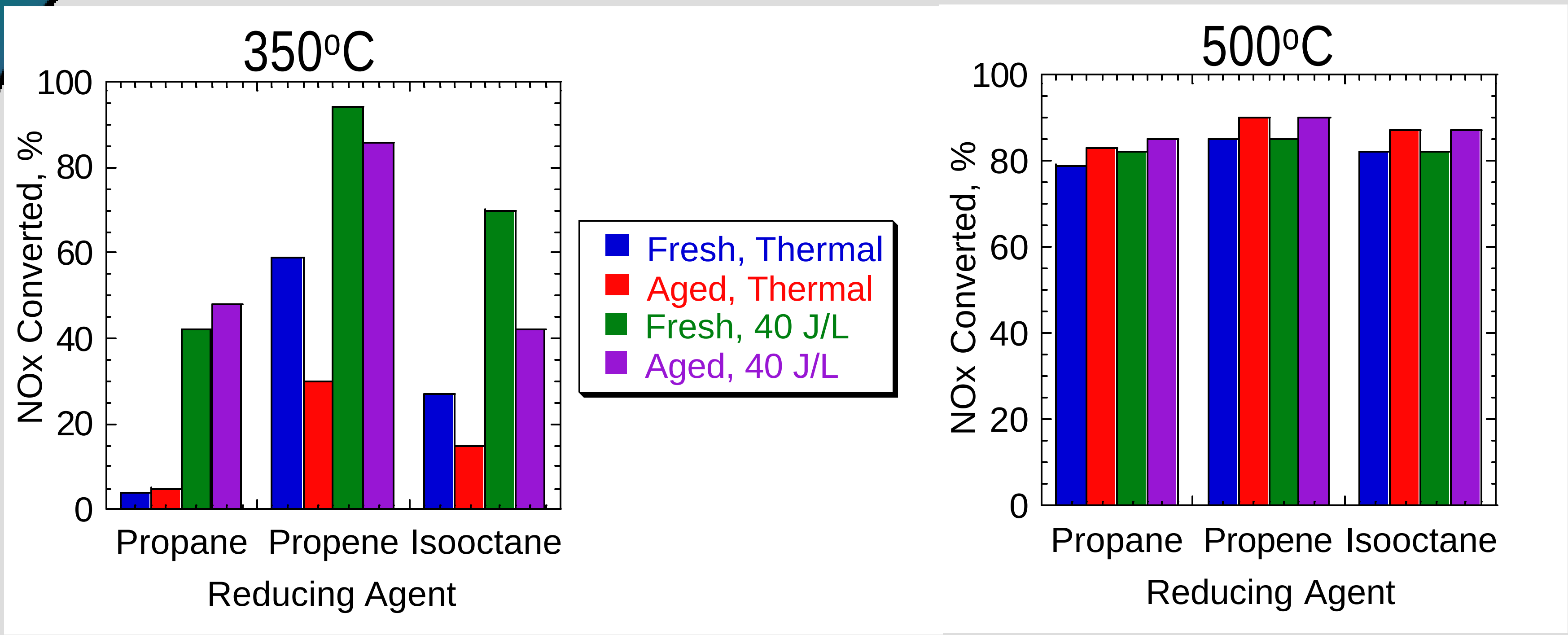
Plasma Activation & Metal Promotion

- Main Benefit: Production of oxygenated HCs results in increased NOx reduction.
  - Aldehydes
  - Alcohols
  - Enals
  - Enols
  - etc.
- Secondary Benefit: Conversion of NO to NO_2, which is advantageous over certain catalysts.
  - Current studies indicate may be a significant factor over aged catalysts.

Catalyst Aging

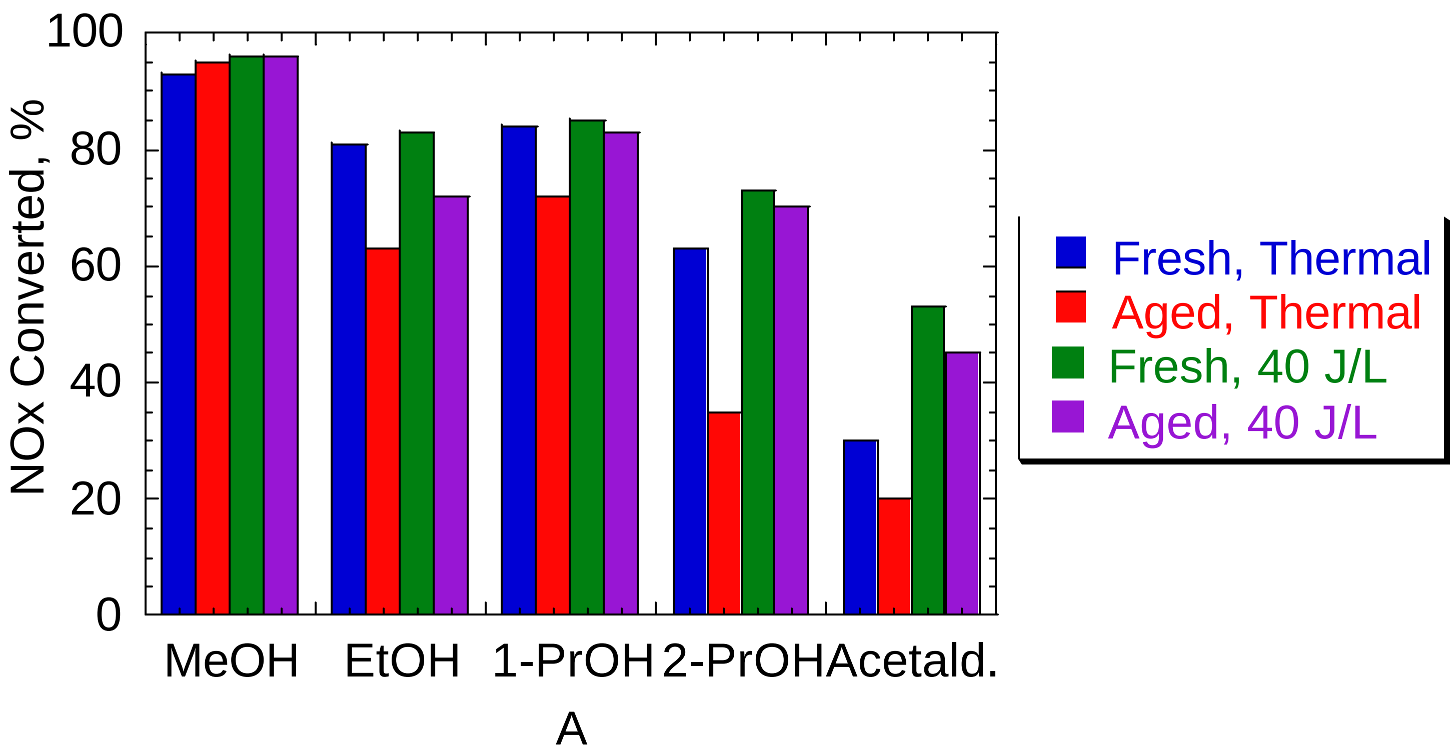
- Protocol - 250 hours at 520^{o}C continuous flow:
  - 30 ppm SO_2
  - 500 ppm NO
  - 7% O_2
  - 7% H_2O
  - Balance N_2
- Equivalent experimental conditions used to compare fresh and aged materials.

Aging: Hydrocarbons (In-Alumina)



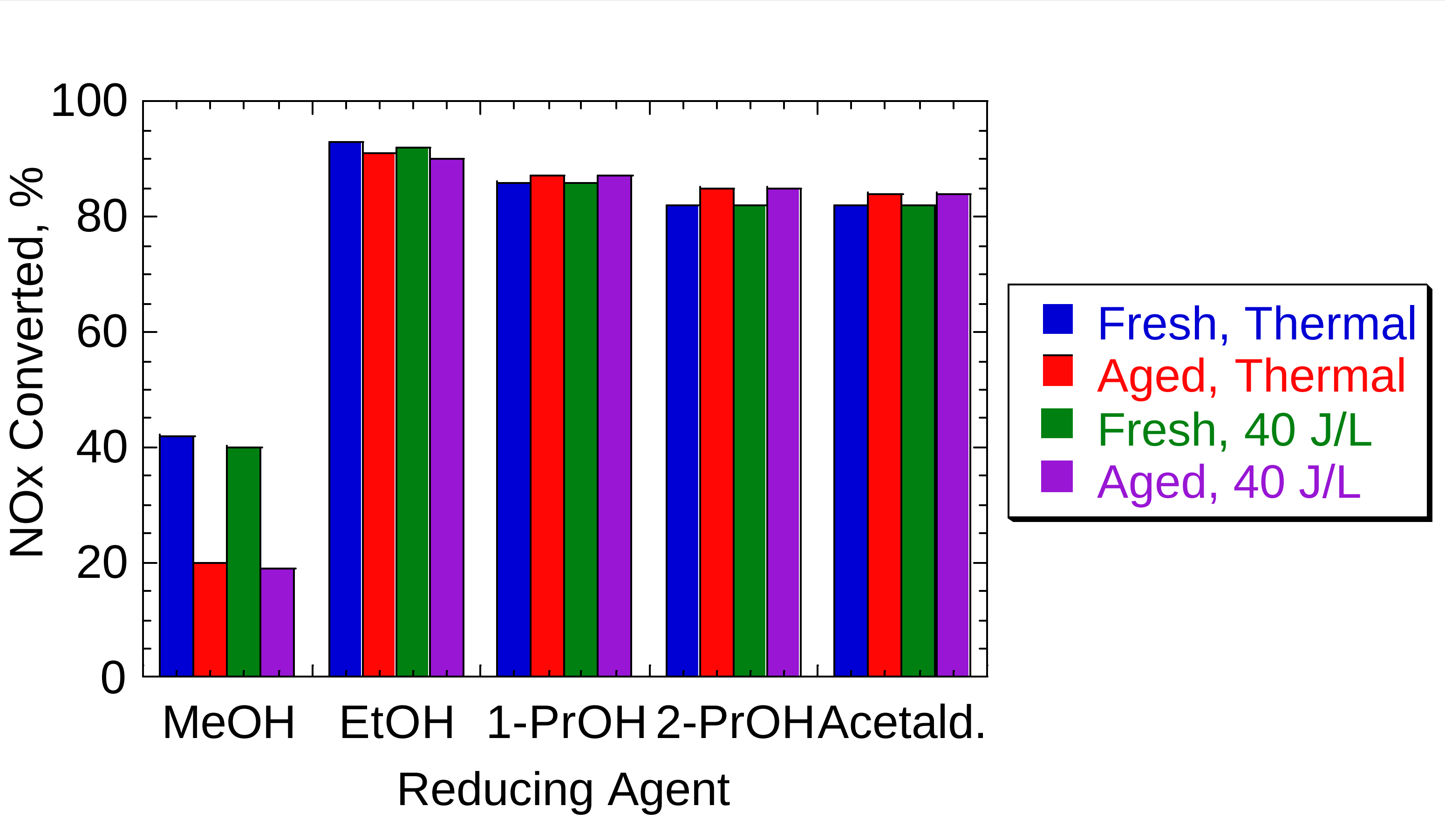
- 350°C: Aging has significant impact on thermal conversion. Plasma assist results in significant preservation of activity for propene. Possible that on the aged surface NO_2 is need to preserve reactivity.
- 500°C: Plasma is a non-factor. Aging results in increased activity.

Aging: Oxygenates (350ºC: In-Alumina)



- Significant hit on thermal efficiency with aging (exception is methanol).
- For the most part activity is recovered with plasma assist. Further indication of NO_2 being significant player on aged catalyst.

Aging: Oxygenates (500^{o}C: In-Alumina)



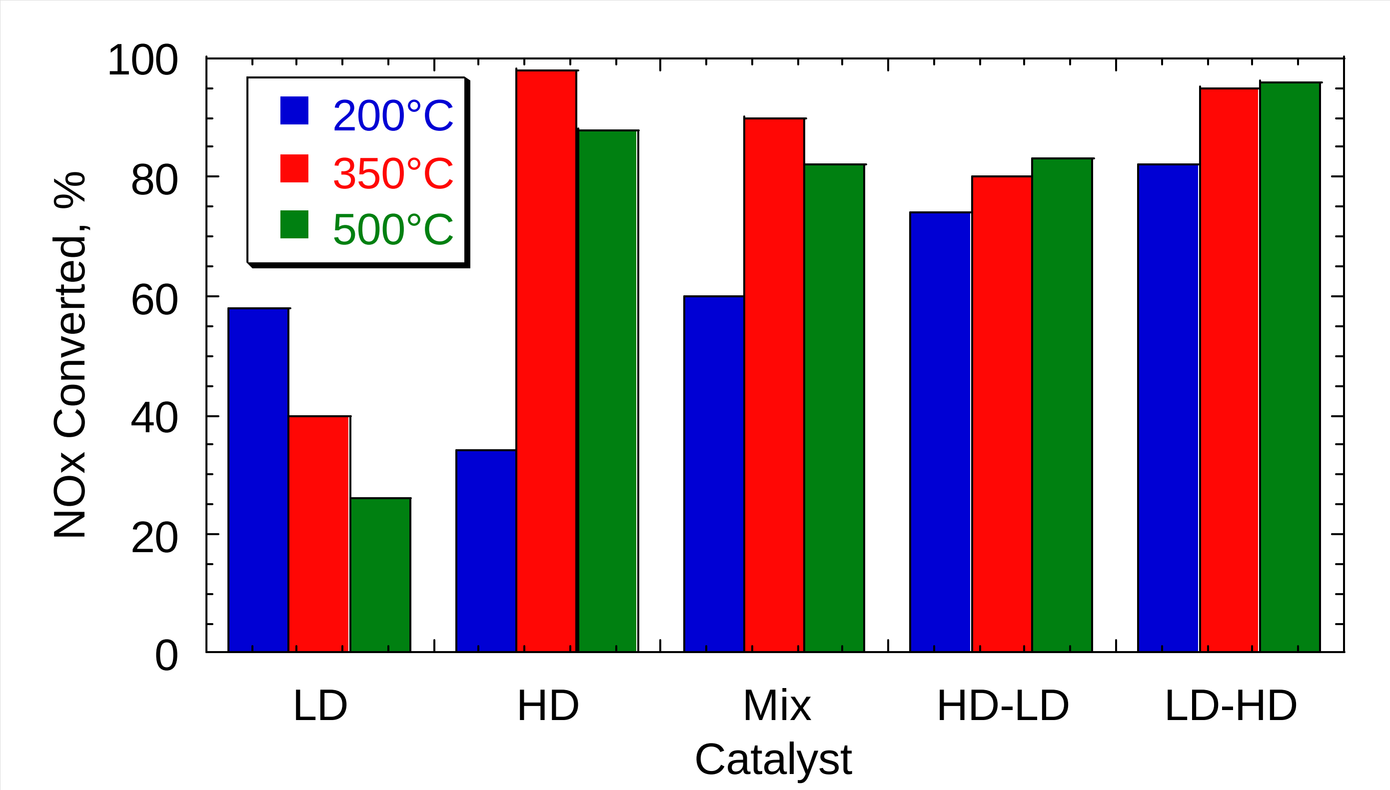
- Little effect due to aging observed, except in the case of methanol.
- Plasma has little impact. Consistent with other results at 500^{o}C.

Catalyst Exchange with LEP CRADA

- John Hoard (Ford): Transient plasma testing looking at temperature cycles (100 – 500°C)
- Russ Tonkyn (PNNL): Nitrogen balance testing
- Paul Park (Caterpillar): Testing catalyst combinations for lean-NOx activity
- Chris Aardahl (PNNL): Plasma testing of catalyst combinations with alternate HCs

3 combinations: LD/HD mix, HD→LD, LD→HD

Broad Temperature Coverage with Mix (Steady-State Performance)



50 J/L; 2000 ppm C_3H_6; 1 SLM; 1 g each catalyst

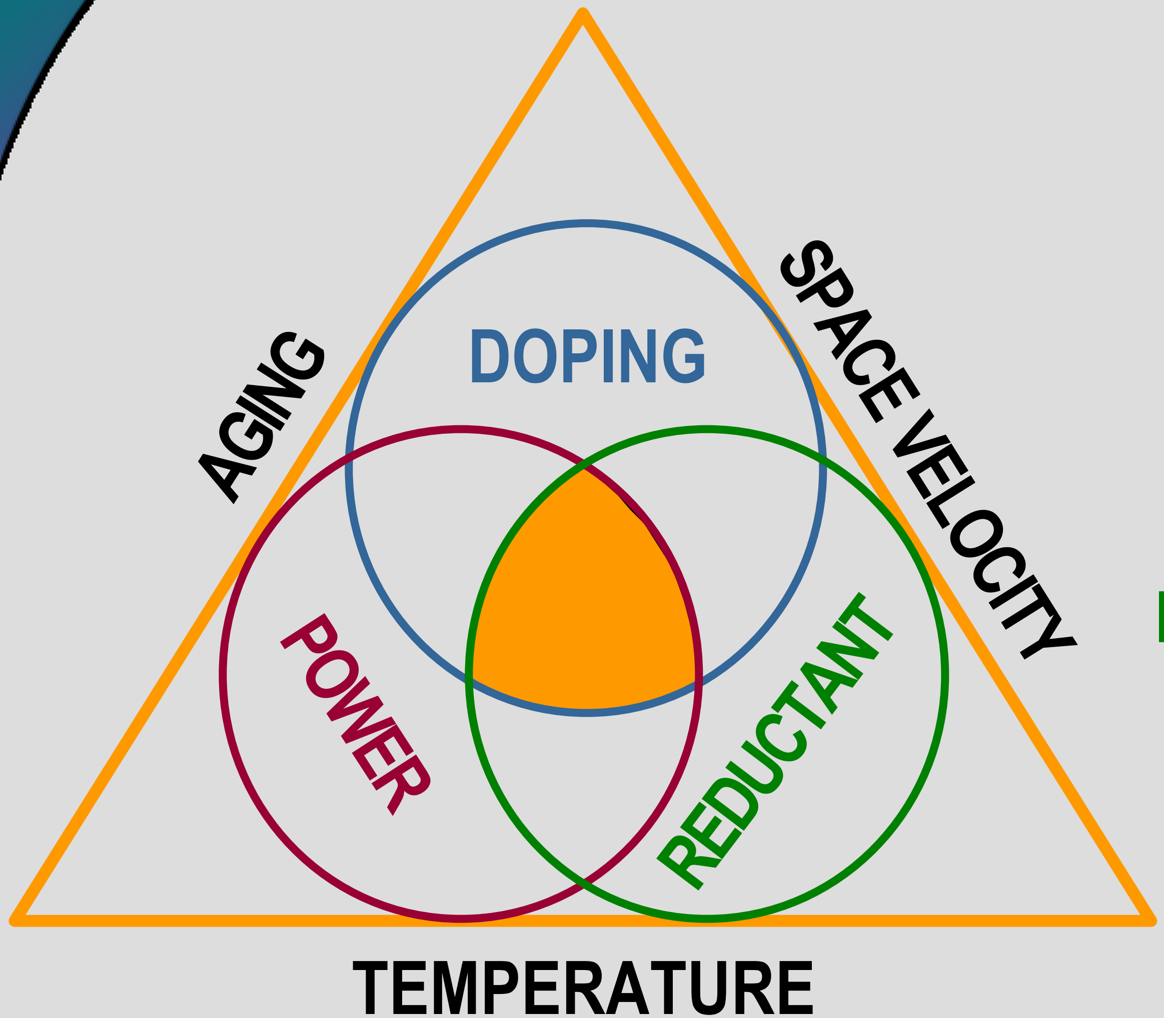
Why is Order Important?

- Widely accepted that C_2 and greater aldehydes are critical intermediates on LD (Data presented by LEP CRADA: SAE Spring F&L Meeting).
- Experiments on HD do not indicate that acetaldehyde is critical to NOx reduction; however, formaldehyde does appear to enhance activity significantly over HD (Data from Caterpillar CRADA and European groups: SAE Spring F&L).
- Hypothesis: LD cannot utilize CH_2O produced in plasma and over catalyst. HD can utilize this HC, so order is critical for HC maximum HC utilization and lowest fuel penalty.

Conclusions

- Aging studies show that activity lost in thermal operation can be recovered using plasma assist with many hydrocarbons. Such results indicate that NO_2 formation may be critical for NOx conversion over aged catalytic systems.
- Large gains in efficiency could be obtained by conversion of fuel to oxygenated compounds.
- Light and heavy duty catalyst formulations can be combined to produce broad temperature coverage. Order of the catalysts is important to utilize HC.

Final Message:
System Optimization is Complex!!



Issues

Power - Reforming

Power - NO → NO_2

Dopant Choice & Level

Reductant Choice & Level

Future Expectations

- Significant focus on conversion enhancement at high space velocity.
- More focus on transient experiments.
- Growing collaboration opportunities between the CRADAs.