Heavy-Duty NOx Emissions Control: Reformer-Assisted vs. Plasma-Facilitated Lean NOx Catalysis

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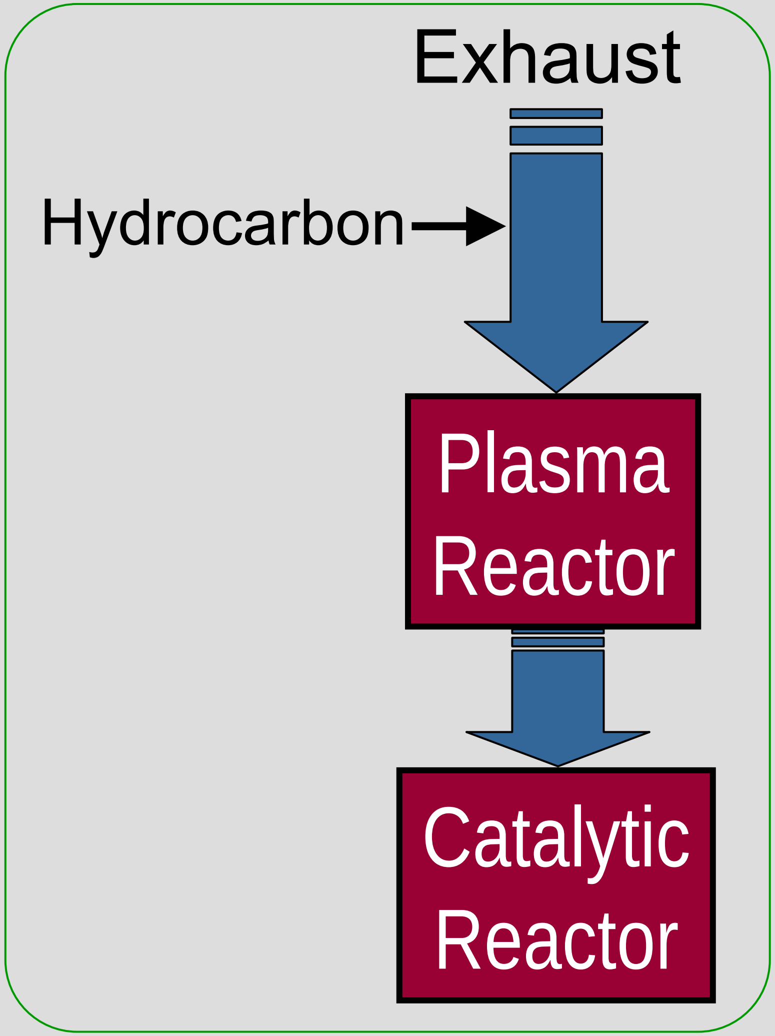
Outline

- Background
  - Flowsheets
  - Motivation for examination reformers
  - Suitable reformation approaches
  - Current work
- Data on reformer-assisted lean NOx catalysis
  - HC speciation using plasma reformer w/C_3H_6
  - Ag_xO/γ-Al_2O_3
  - Ba/zeolite-Y $\rightarrow$ Ag_xO/γ-Al_2O_3
- Comparison between PFC and RAC
- Summary and future plans

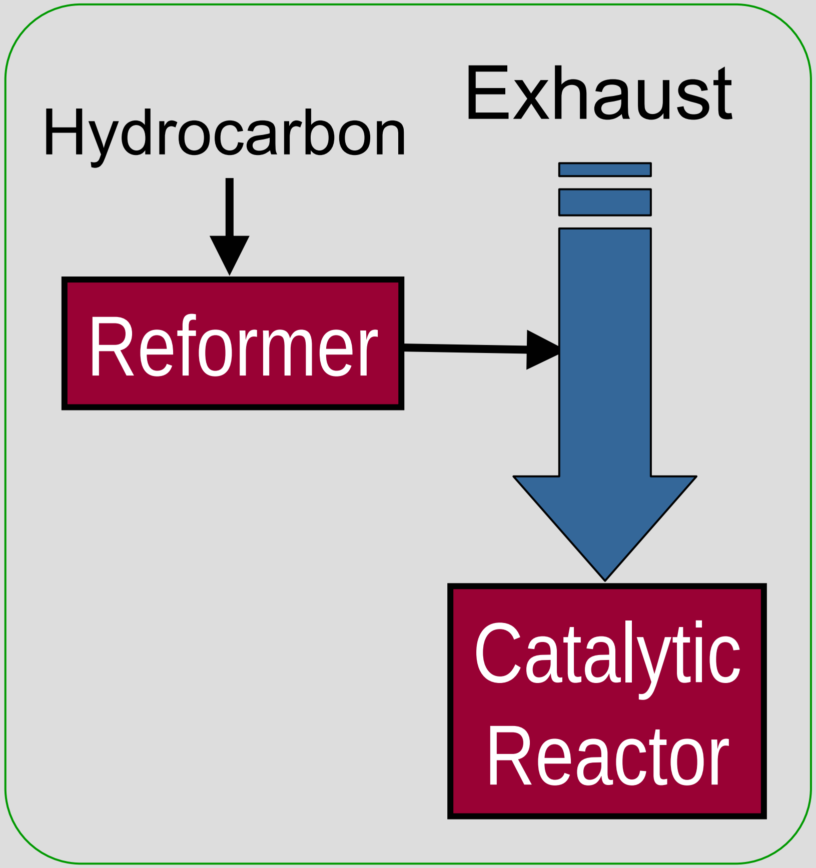
Plasma-Facilitated Lean NOx

- Step 1. Exhaust passed through NTP
  - Selective oxidation of NO to NO_2
  - Partial oxidation of hydrocarbon
- Step 2. NTP-treated exhaust passed over lean NOx catalyst
  - LD – zeolites; HD –alumina
  - NO & NO_2 reduced to N_2
  - Consumption of hydrocarbons



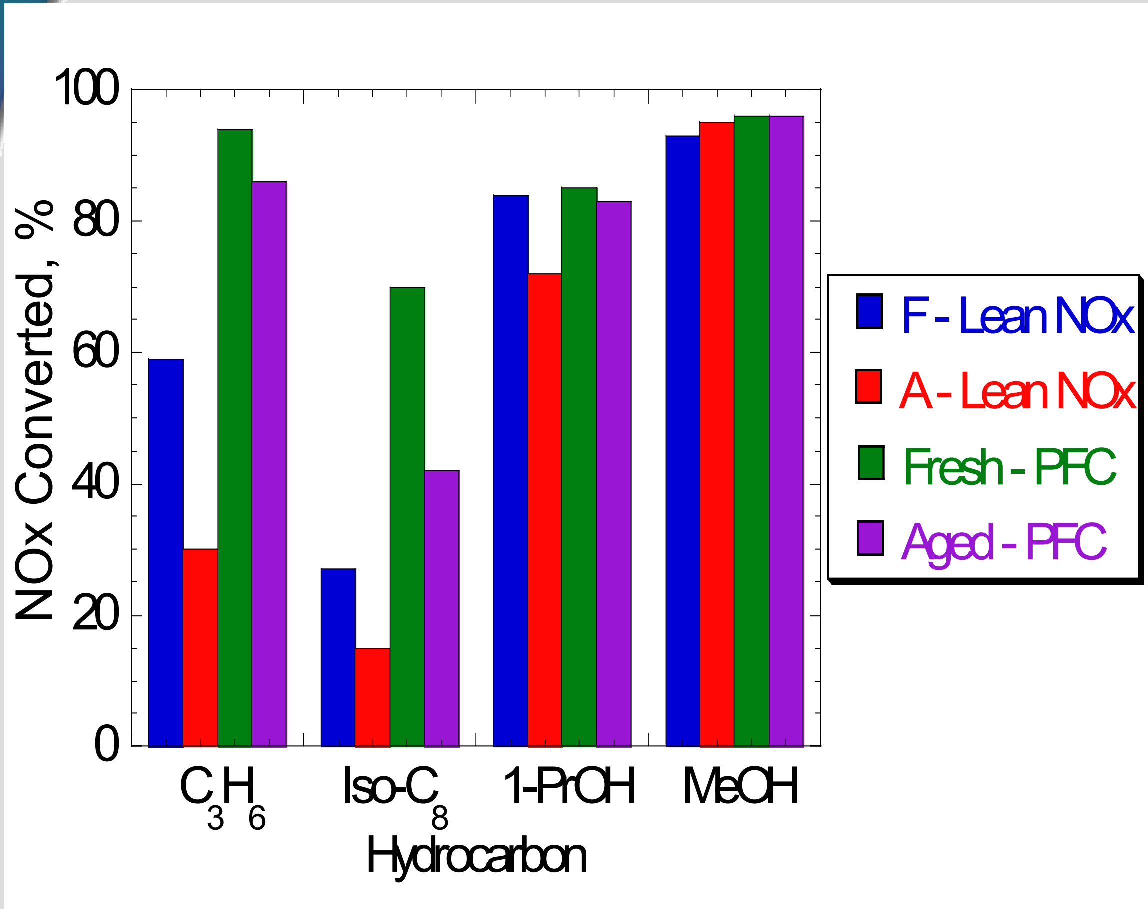
Reformer-Assisted Lean NOx

- Step 1. Hydrocarbon is treated in a side stream
  - Partial oxidation of hydrocarbon
- Step 2. Treated HC injected in to the exhaust prior to lean NOx catalyst
  - NO reduced to N_2
  - Consumption of hydrocarbons
  - Active catalyst should be similar to PFC



Motivation for RAC

350^oC: $In_xO/\gamma\text{-}Al_2O_3$



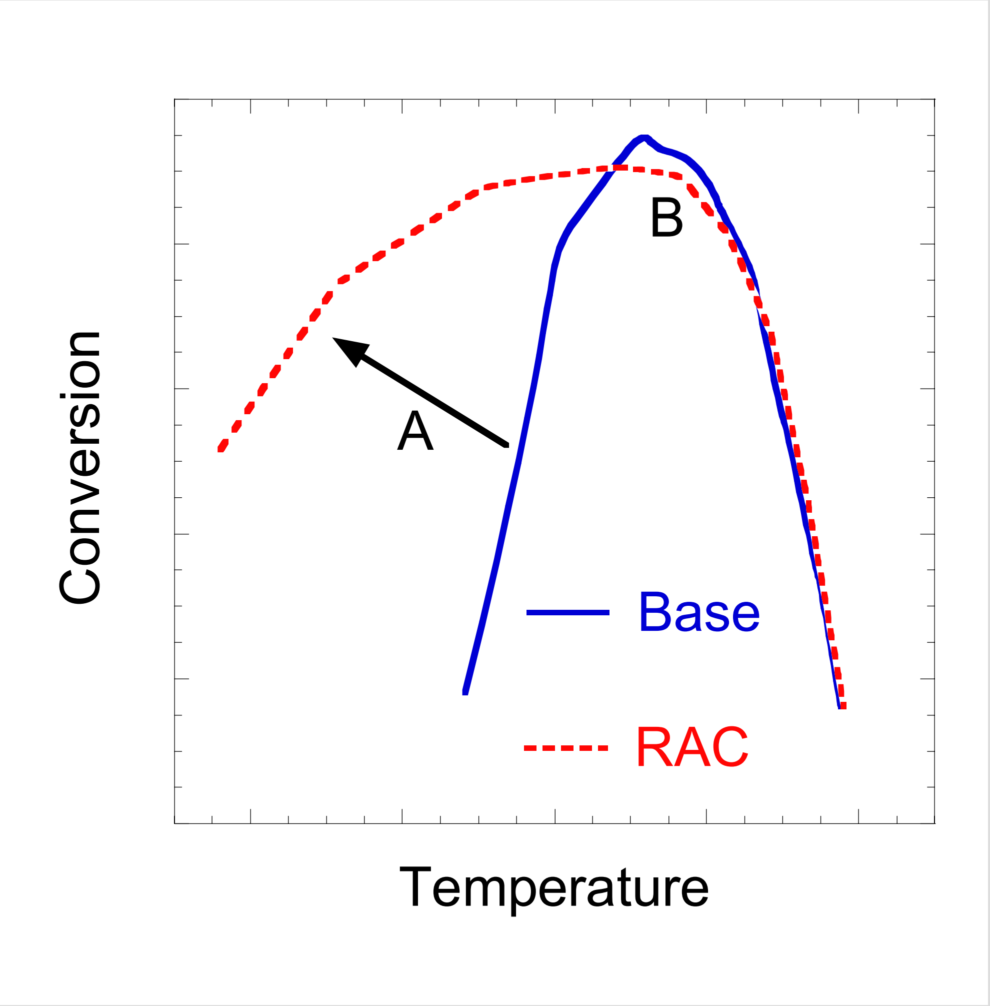
- Oxygenates result in higher activity on lean NOx catalysts
- Temperature range for high catalyst activity broadened
- Sulfur tolerance with oxygenates is better
- Potential to reduce energy cost (fuel penalty) and reduce the size of the system as a whole

Equal C_1:NOx basis. Aging in 30 ppm SO_2, 7% H_2O, 500 ppm NO, 7% O_2 for 250 Hrs.

What to Expect From RAC?

- A) Major benefit is broadening the active temperature window due to higher reactivity of oxygenates over catalyst at lower temperatures

- B) May be a slight loss in maximum level of reduction due to lower C_1:NOx over catalyst



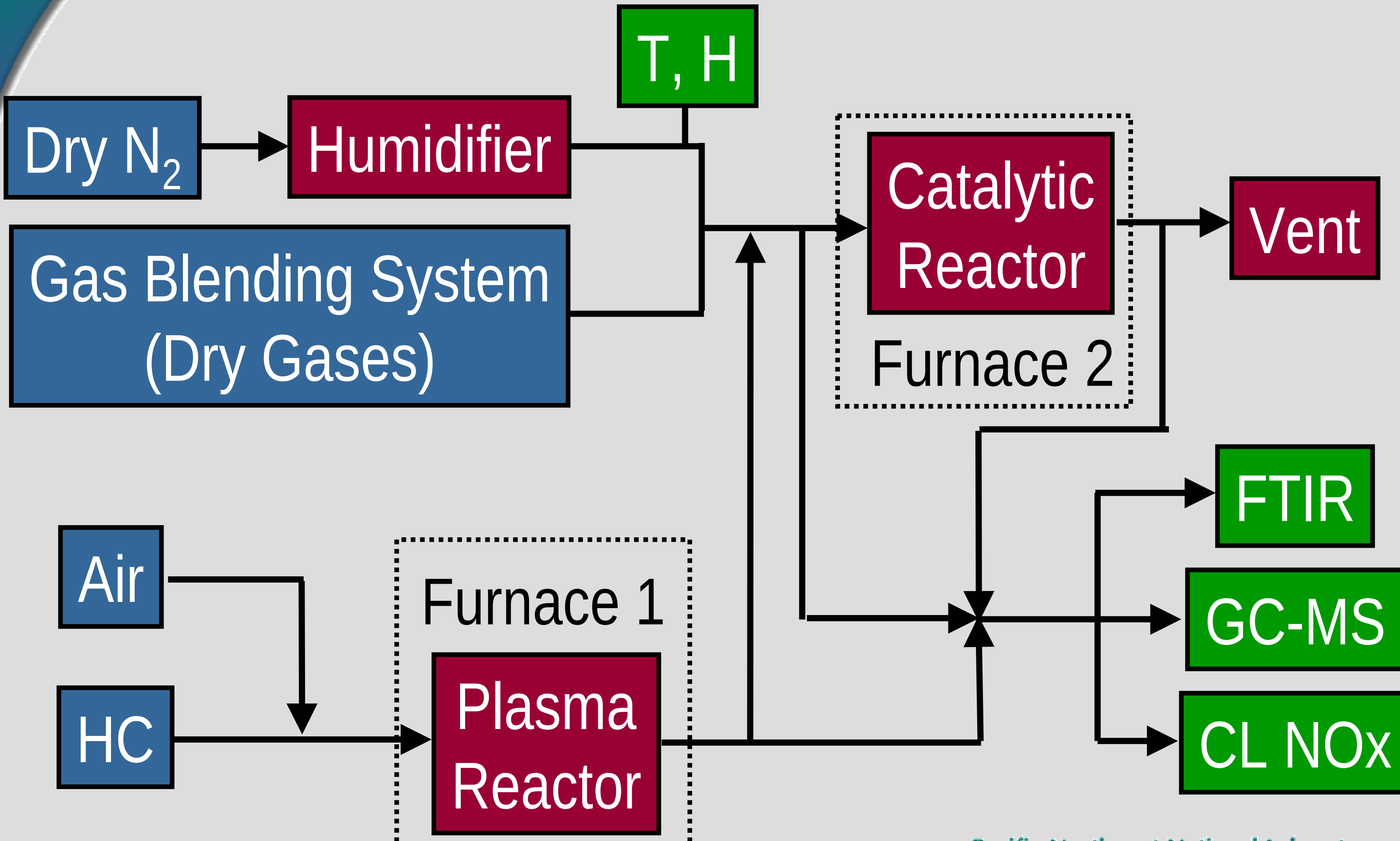
Reformer Options

- NTP alone
- NTP-catalyst combinations
- Thermal catalytic reformers
  - Partial oxidation of alkanes
  - Reform fuel to H_2/CO and use synthesis chemistry to obtain desired reducing agent

Ongoing Work of Interest

- First record: Engelhard USP #6176078
- PNNL-Caterpillar CRADA (Aardahl): Plasma-based oxygenate production
- GM (Schmieg): Thermal catalytic oxygenate production (LEP CRADA with PNNL)
- LANL (Borup) POx for olefin production from fuel
- Catalytica, NOxTech: Fuel reformers/converters for aftertreatment
- Potential sources of syngas
  - DOE-EERE Hydrogen Program: POx-LANL; Autothermal-ANL; SMR-PNNL
  - MIT (Bromberg): Plasmatrons
  - Seimens (Hammer), several others: Plasma SMR
  - Delphi (Fisher), Univ. Minn. (Schmidt): Millisecond POx

Bench Scale RAC System



Stream Compositions

- Catalytic Reactor
  - Simulated exhaust composed of 2% water, 8% CO_2, 9% O_2, 500 ppm NO, and 300 ppm CO.
  - Steady-state data taken: constant reactor temperature and reformer conditions for a given point.
  - 3 grams of catalyst and 3 SLM flow.
    - Ag_xO/γ-alumina
    - Ba/zeolite Y → Ag_xO/γ-alumina

- Reformer
  - Feed streams are house air and propene.
  - Propene rate fed to the reformer maintains constant propene to NOx ratio of 4 in the catalytic reactor. Values reported are feed ratios only, not actual HC:NOx levels in the catalytic reactor.
  - 1:1 to 15:1 C-to-O ratios examined
  - Reformer held at 500^{o}C and 6 kJ/L

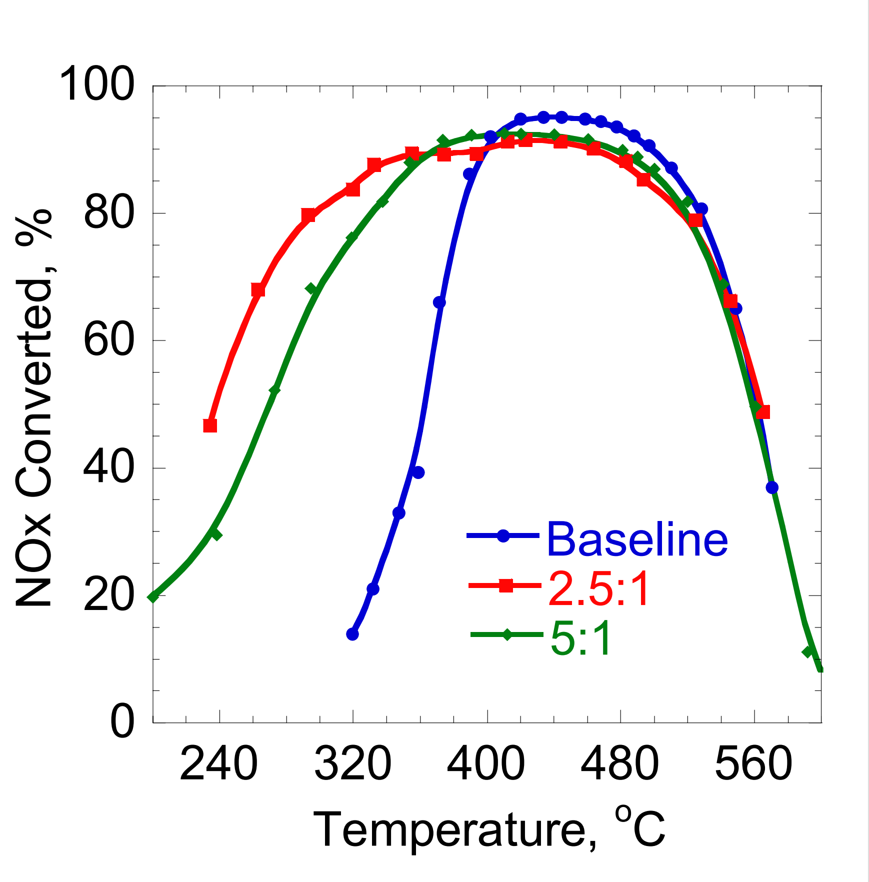
Reformer Chemistry for C_3H_6

- Higher energy density produces more oxygenates
- Observed compounds include acetaldehyde, propylene oxide, propanal, acetone, 2-propenal, 2-propanol, formaldehyde, methanol, ethanol, 1-propanol, 2-propen-1-ol, 1-hydroxy-2-propanone, carboxylic acids
- Higher power shifts alcohol production to somewhat higher C:O ratios
- Single pass propene conversion is less than 20% for conditions used.
- Limited CO_2 production at high C:O ratio. Selectivity deteriorates heavily below C:O = 2. Complete C balance still needed.

RAC Results: $Ag_xO/\gamma\text{-}Al_2O_3$

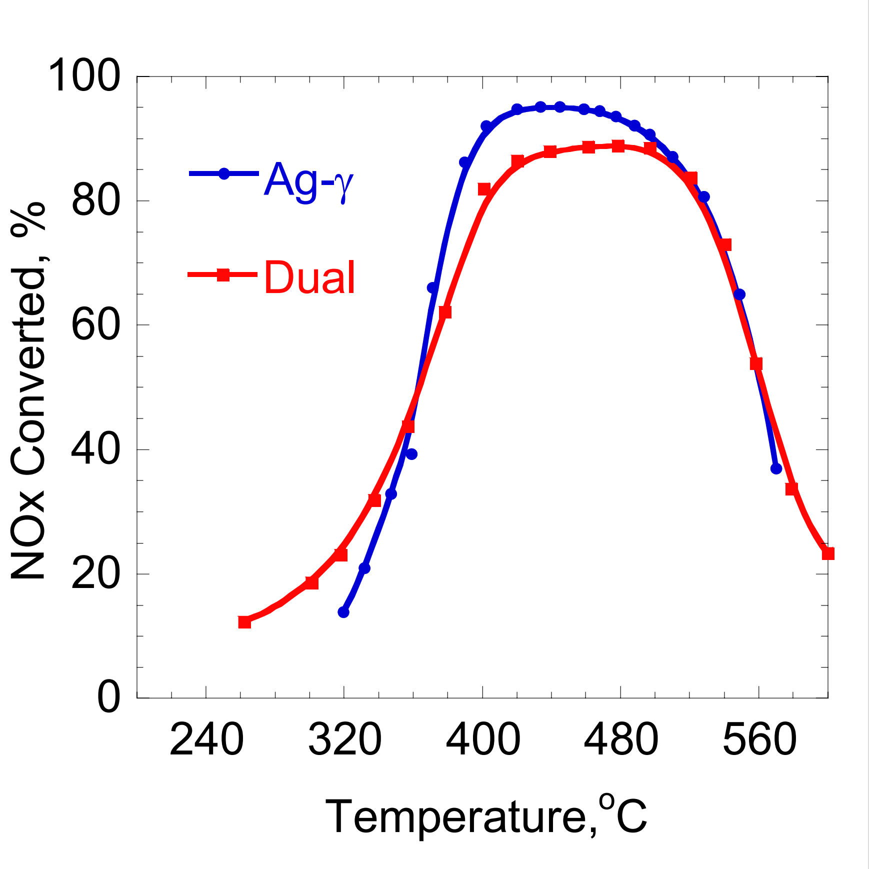
- Baseline is equivalent to lean NOx catalysis – no reformation
- As expected, temperature window broadened with slight loss in peak NOx reduction efficiency
- SV = 22000 1/hr

Reformer Operation: 500°C, 6 kJ/L



Lean NOx: Dual System vs Single Catalyst

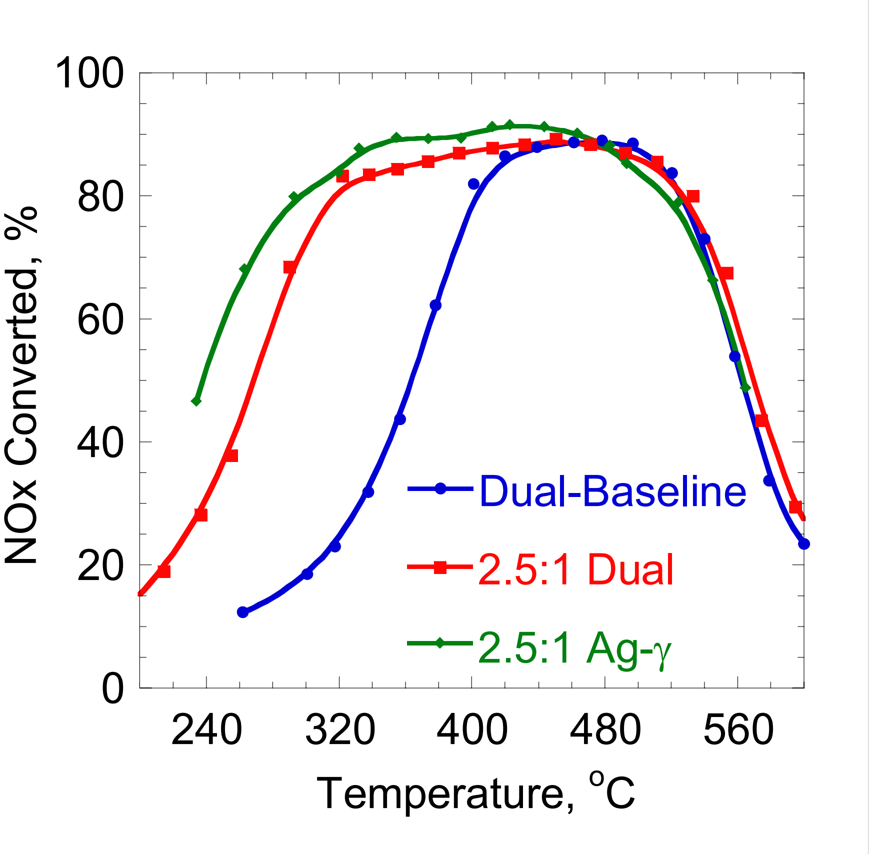
- Ag-γ ≡ $Ag_xO/\gamma\text{-}Al_2O_3$
- Dual catalyst represents Ba/zeolite Y followed by Ag-γ (SV = 28000 1/hr; SV= 44000 based on Ag-γ alone)
- Total amount of catalyst by weight is the same for each case
- Drop in maximum effiency due to SV effect. Ba/zeolite Y is not active with propene feed



RAC for Dual Catalyst System

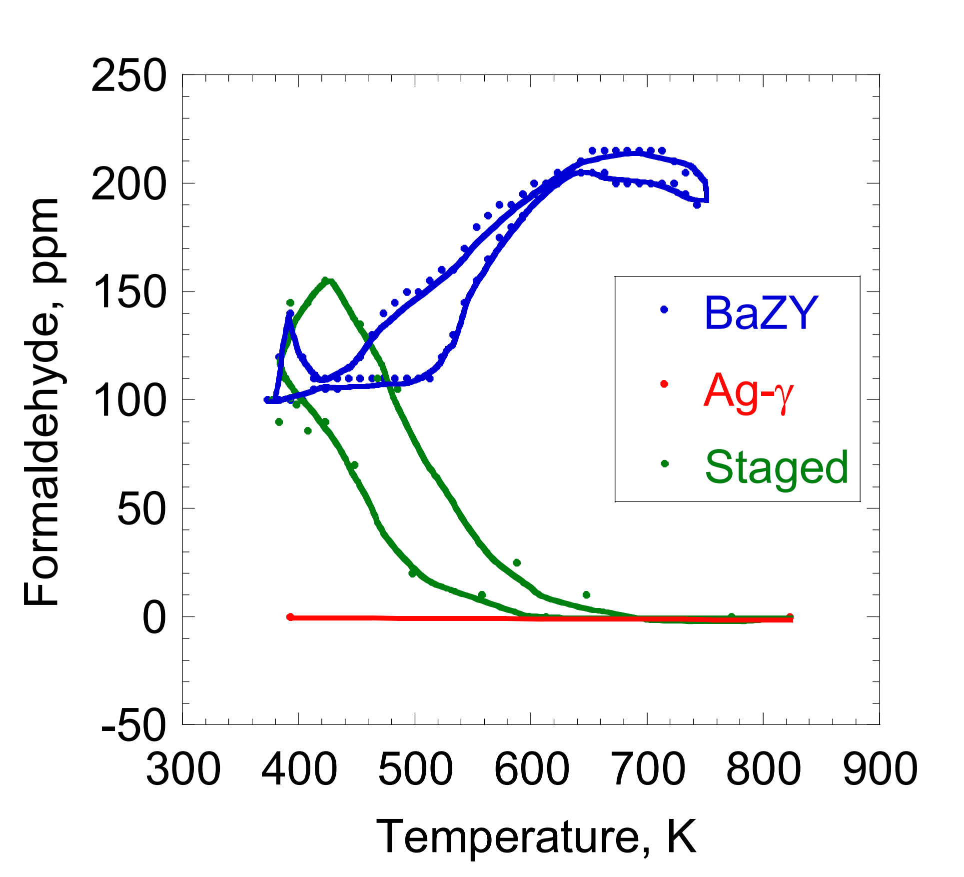
- Reformation shows improvement from lean NOx baseline.
- Dual catalyst not better than Ag-γ alone.
- Likely that Ba/zeolite Y is not active with reformate as reducing agent.
- Drop in NOx conversion in dual catalyst from Ag-γ due to SV effect.

Reformer Operation: 500°C, 6 kJ/L



Impact of Oxygenate Speciation

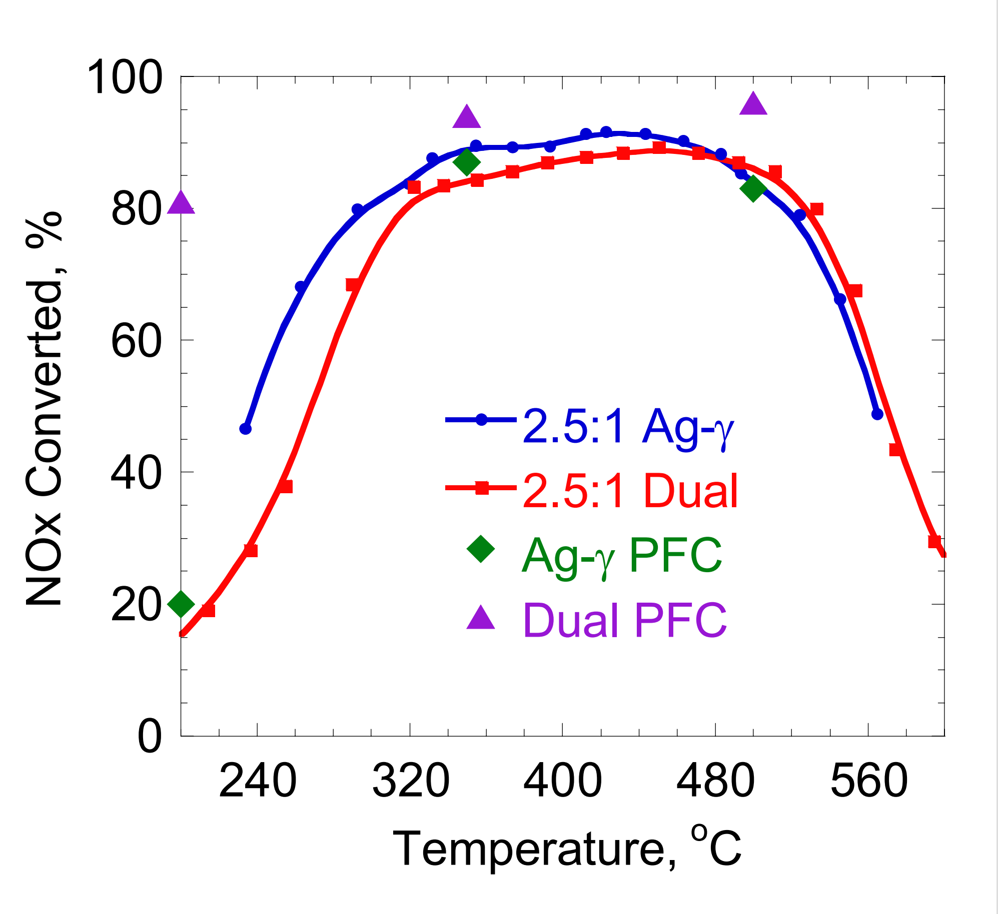
- RAC shows positive results for $Ag_xO/\gamma\text{-}Al_2O_3$, but not for the staged catalyst system with Ba/zeolite Y.
- **Hypothesis**: Oxygenates produced in the plasma can participate in the deNOx chemistry over alumina, but not the zeolite.
- Observed before with formaldehyde.



Data taken by J. Hoard (Ford Research Labs)

Comparison: PFC vs RAC

- In the case of Ag-γ, RAC is equivalent to PFC (40 J/L).
- Still advantages for the dual catalyst system in using PFC.



Summary

- Reformer-assisted lean NOx catalysis (RAC) is equivalent or better than plasma-facilitated catalysis (PFC) over $Ag_xO/\gamma\text{-}Al_2O_3$.
- The configuration of RAC used here (air:HC) was not successful in promoting NOx reduction over Ba/zeolite Y. Other species in exhaust may be key to make ample amounts of acetaldehyde.

Outlook

- Currently looking at larger alkanes (dodecane and hexadecane) in the bench system
  - Fuel vaporizer required
  - Line heating an issue
  - Coking an issue?
- Catalytic NTP reforming could benefit
  - System is simple
  - Chemistry is not so simple
- Provided continued improvement examined, RAC will be examined at full scale during transient PFC testing at Caterpillar Tech. Center in Spring-Summer 2004.