Reduction of NOx by Plasma-Facilitated Catalysis: An Update on the PNNL-Caterpillar CRADA on Heavy Duty Emissions Reduction

Dr. Christopher L. Aardahl, PNNL

Team Members:

PNNL: C. Habeger, K. Rappe, D. Tran, M. Delgado

Caterpillar Inc.: P. Park, M. Abouzour, L. Balmer, C. Opris, S. Faulkner

DOE-OHVT: G. Singh, J. Fairbanks

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Outline

Background Material

Results

- Commercial vs CRADA Catalysts
  - γ-alumina
  - Ag-doped γ-alumina
- Effect of Reducing Agent Selection on SCR
- Engine Test Preliminary Results

Conclusions and Future Plans

Plasma-Facilitated Catalysis

Step 1. Plasma discharge converts NO to NO_2.
Plasma partially oxidizes some of the HC.
Partially oxidized HC and NO_2 are more reactive.

Step 2. A suitable lean-NOx catalyst (γ-alumina**) is used to convert NO_2 to N_2. Additional HC is required because "active" lean-NOx is a SCR process.

- Dopant Site: $HC + O_2 \rightarrow H_xC_yO_z$
- Alumina Site: $NO_2 + H_xC_yO_z \rightarrow N_2 + H_{x'}C_{y'}O_{z'} + CO_2$

**γ-alumina is active for both reactions.

Plasma Chemistry

Reactions that Dominate Without HC:

$NO + O\bullet \rightarrow NO_2$
$NO_2 + O\bullet \rightarrow NO + O_2$
$NO_2 + \bullet OH \rightarrow HNO_3$

HC Is an O• and •OH Getter:

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

Oxidation Products Form $HO_2\bullet$:

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

$HO_2\bullet$ Reacts Quickly w/NO:

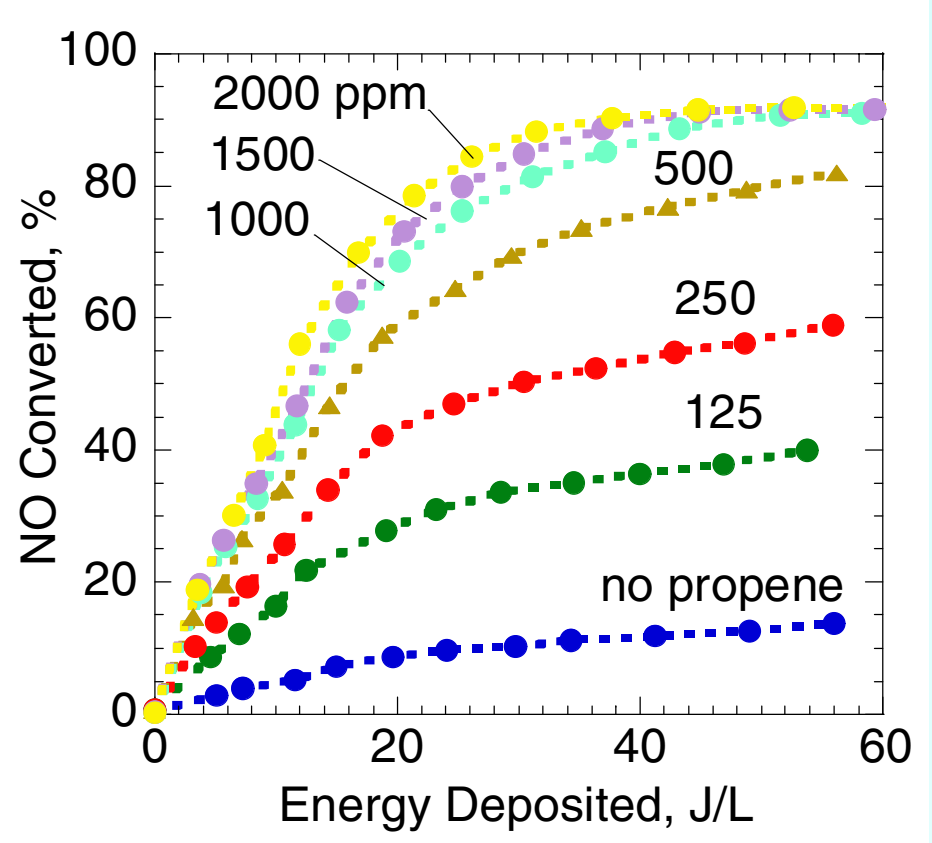
$NO + HO_2\bullet \rightarrow NO_2 + OH\bullet$

NO_2 has Higher Reactivity on Catalysts than NO

Penetrante *et al.* (SAE SP-1395)

NO to NO_2 (Plasma): Effect of HC Level

350°C – Propene Added

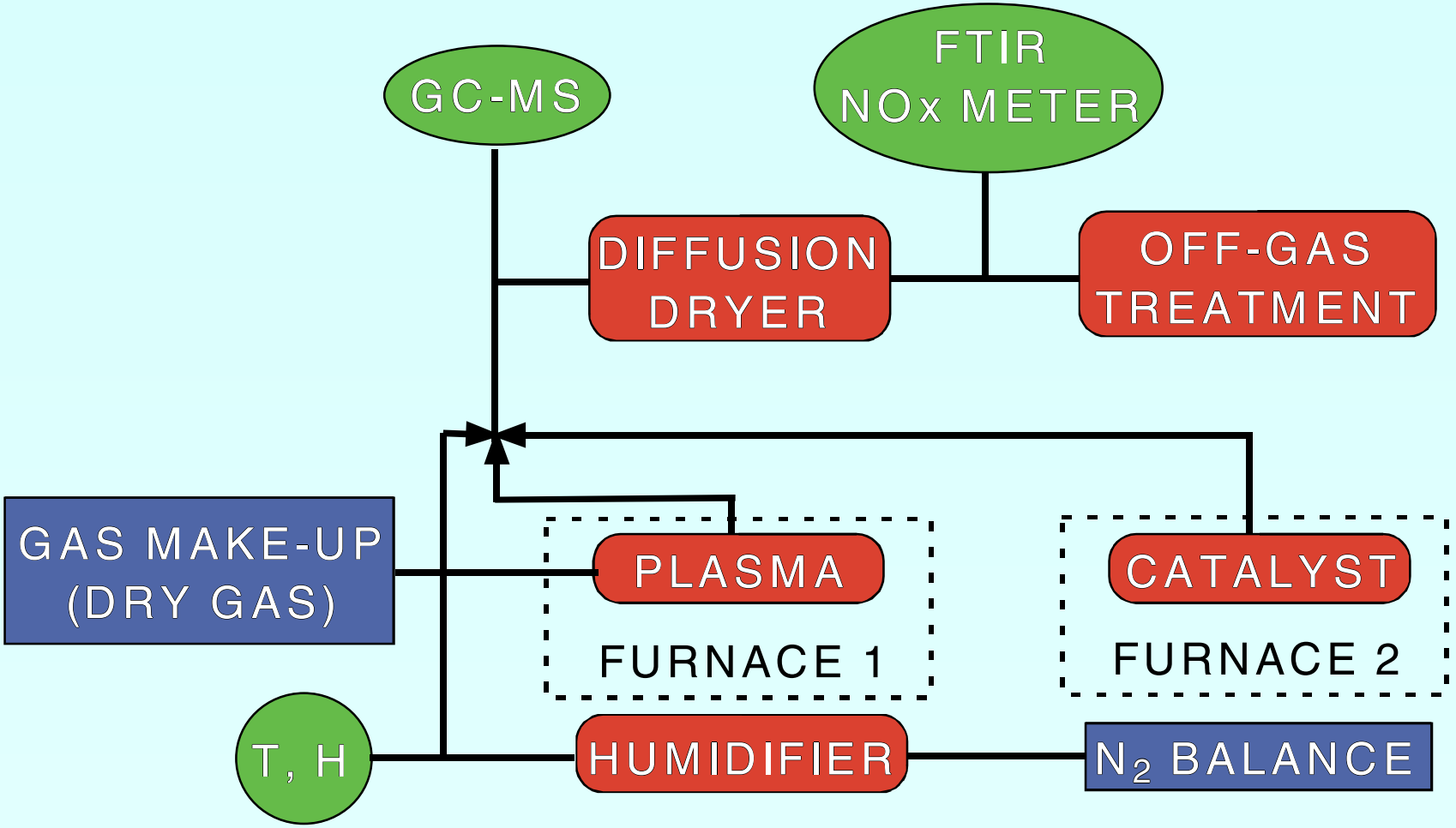


HC is required for conversion of NO to NO_2.

6:1 C_1:NOx sufficient for maximum conversion.

Slight energy gain for higher HC levels for 10-45 J/L.

Process Flow Sheet



Bench Test Conditions

Make-Up

NO	500 ppm
SO_2	0/2/20 ppm
O_2	9%
CO	300 ppm
HC	6000 ppm C_1
CO_2	8%
H_2O	1.5%
N_2	balance
C:N	12

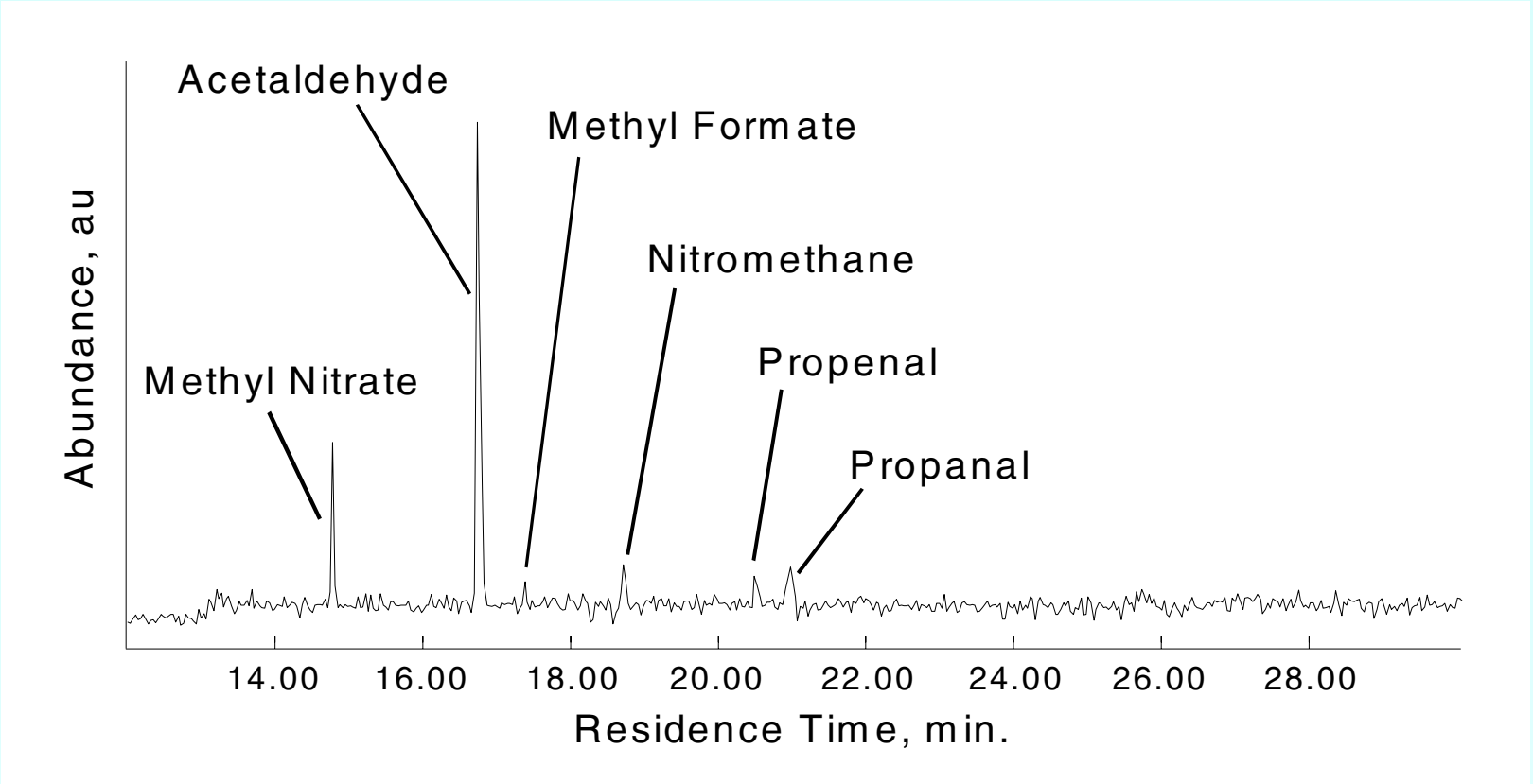
Catalyst: 1 gram

Bulk Sp. Grav.: 0.25–0.40

Flowrate: 1 SLM

Space Velocity:
15,000–25,000 1/hr

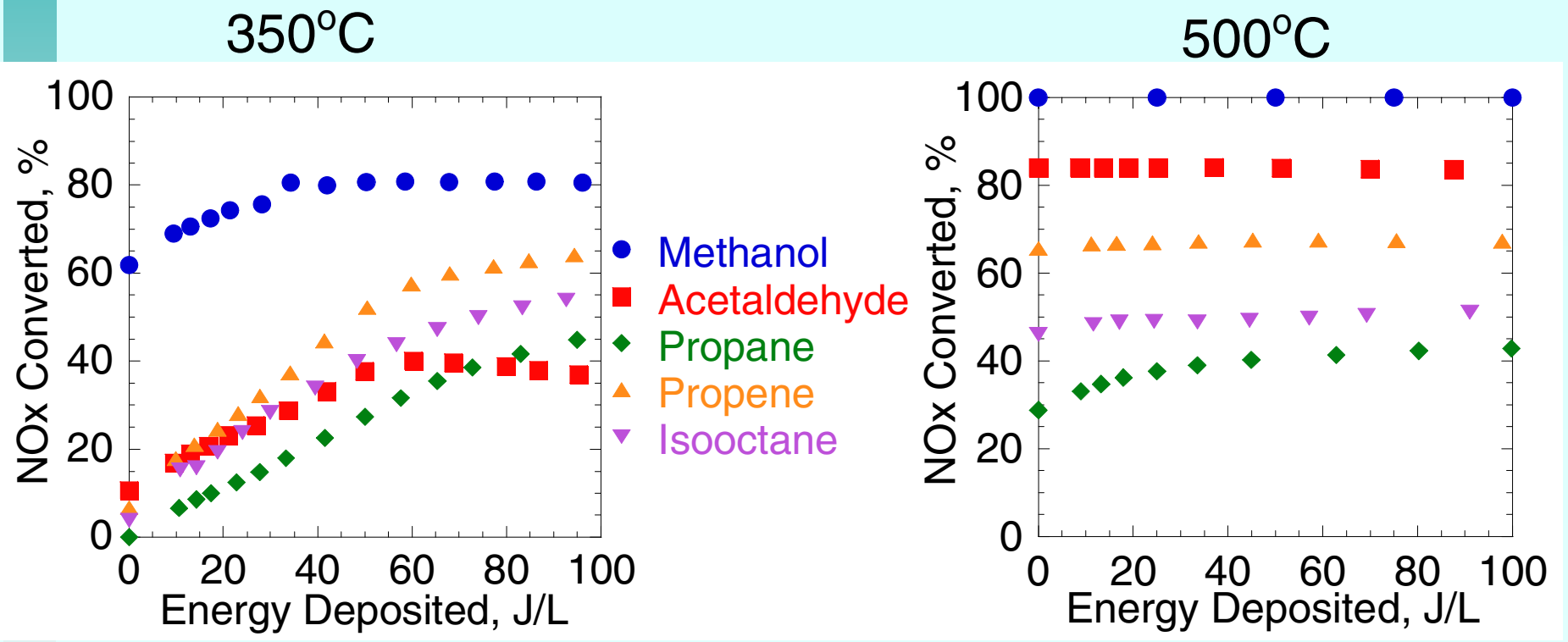
Plasma** - Partially Oxidized HCs (GC-MS*)



*Methanol and formaldehyde also present
**2000 ppm propene in simulated exhaust stream

Alternative SCR Agents

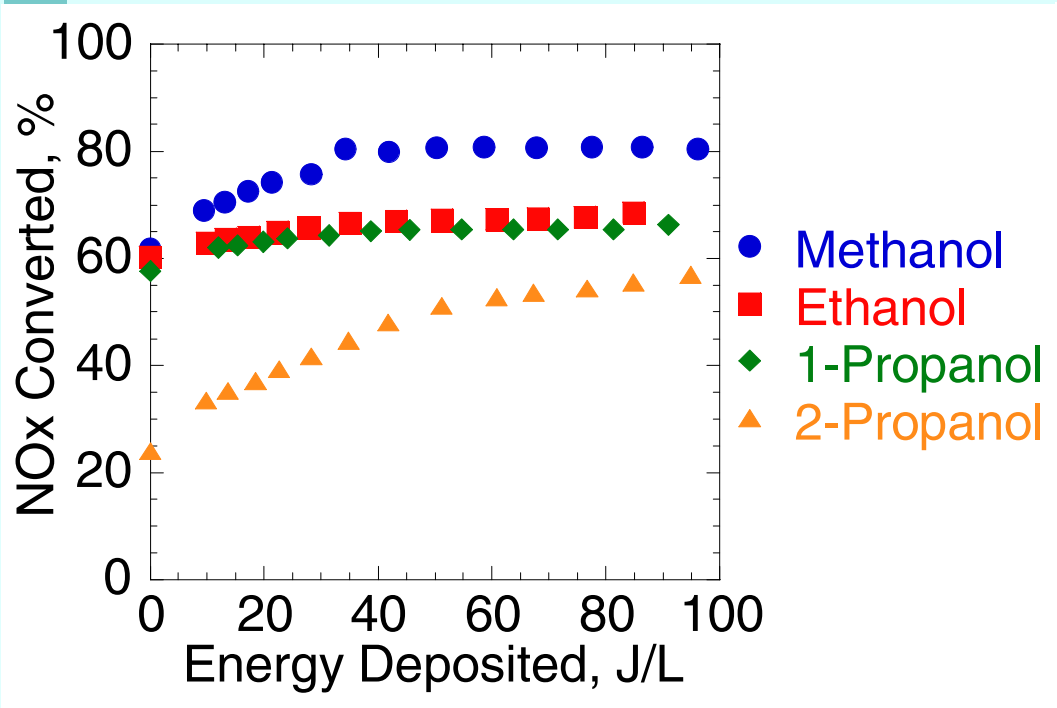
Commercial γ-alumina with 2000 ppm eq. C_3 (12:1 C:N)



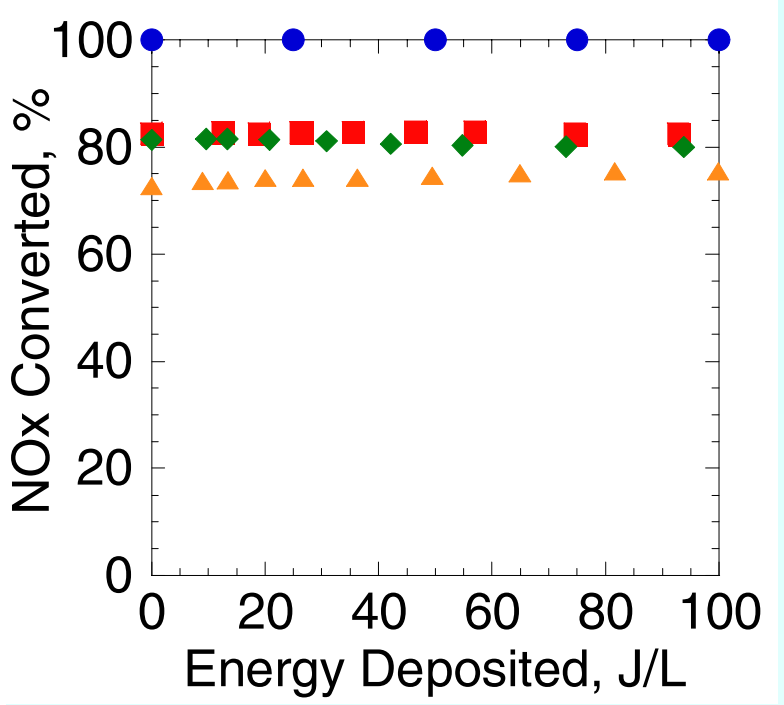
Alcohols as SCR Agents

Commercial γ-alumina 2000 ppm Equivalent C_3 (12:1 C:N)

350°C



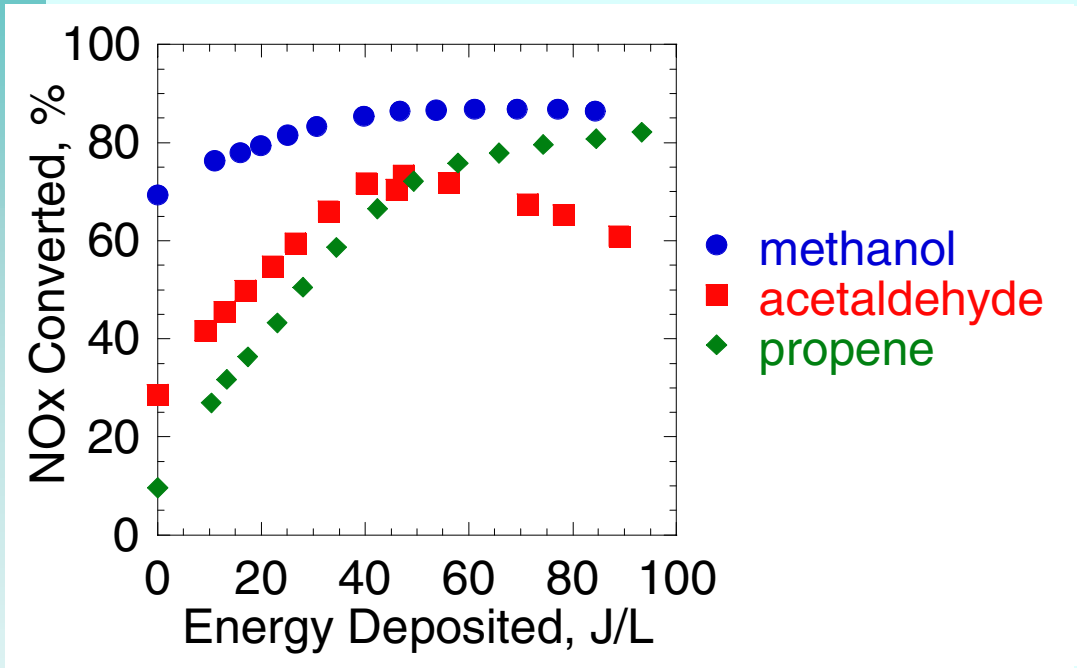
500°C



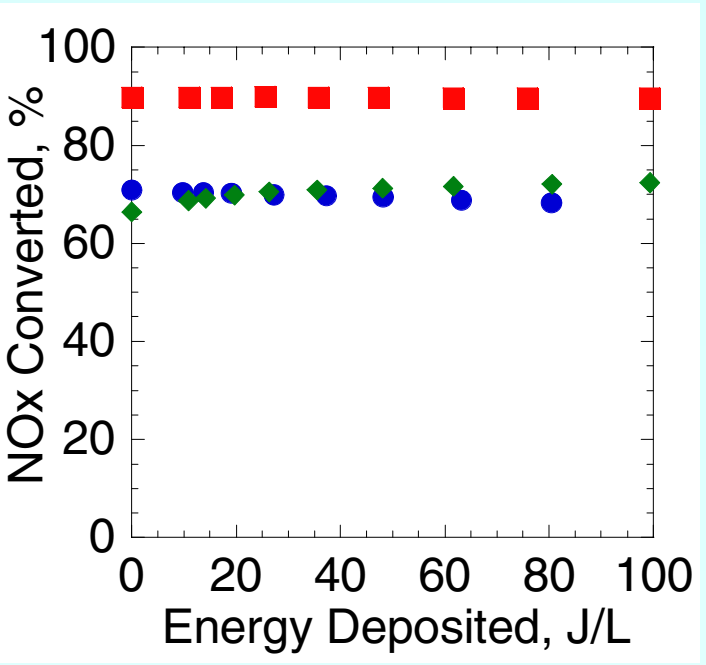
Alternative SCR Agents (w/Ag)

Commercial γ-alumina (Ag): 2000 ppm Eq. C_3

350°C



500°C



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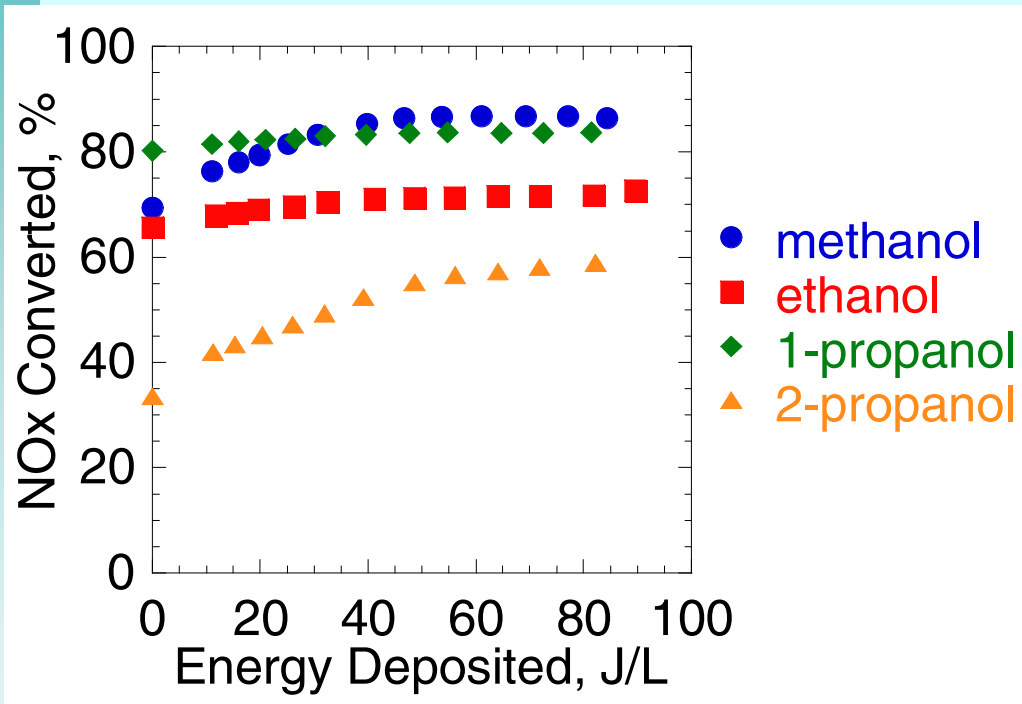
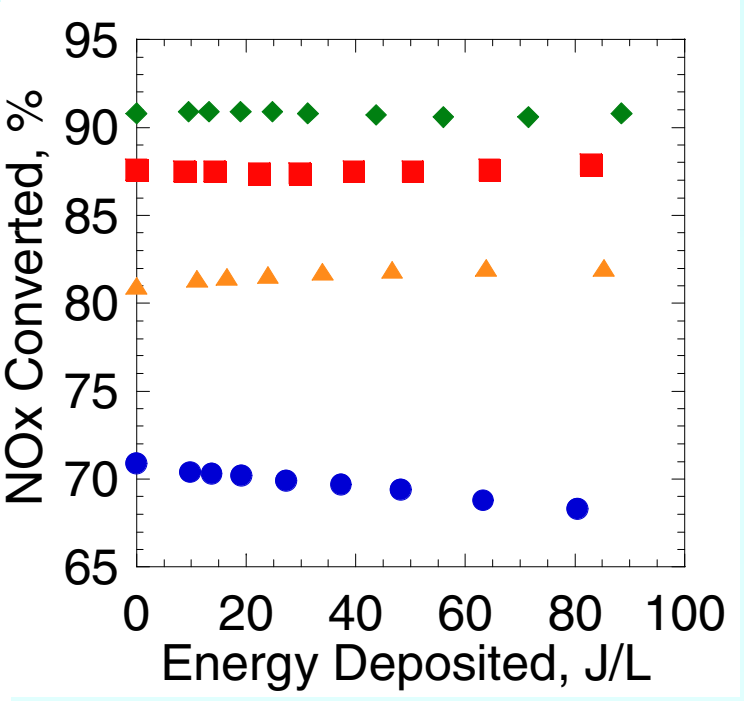


500°C



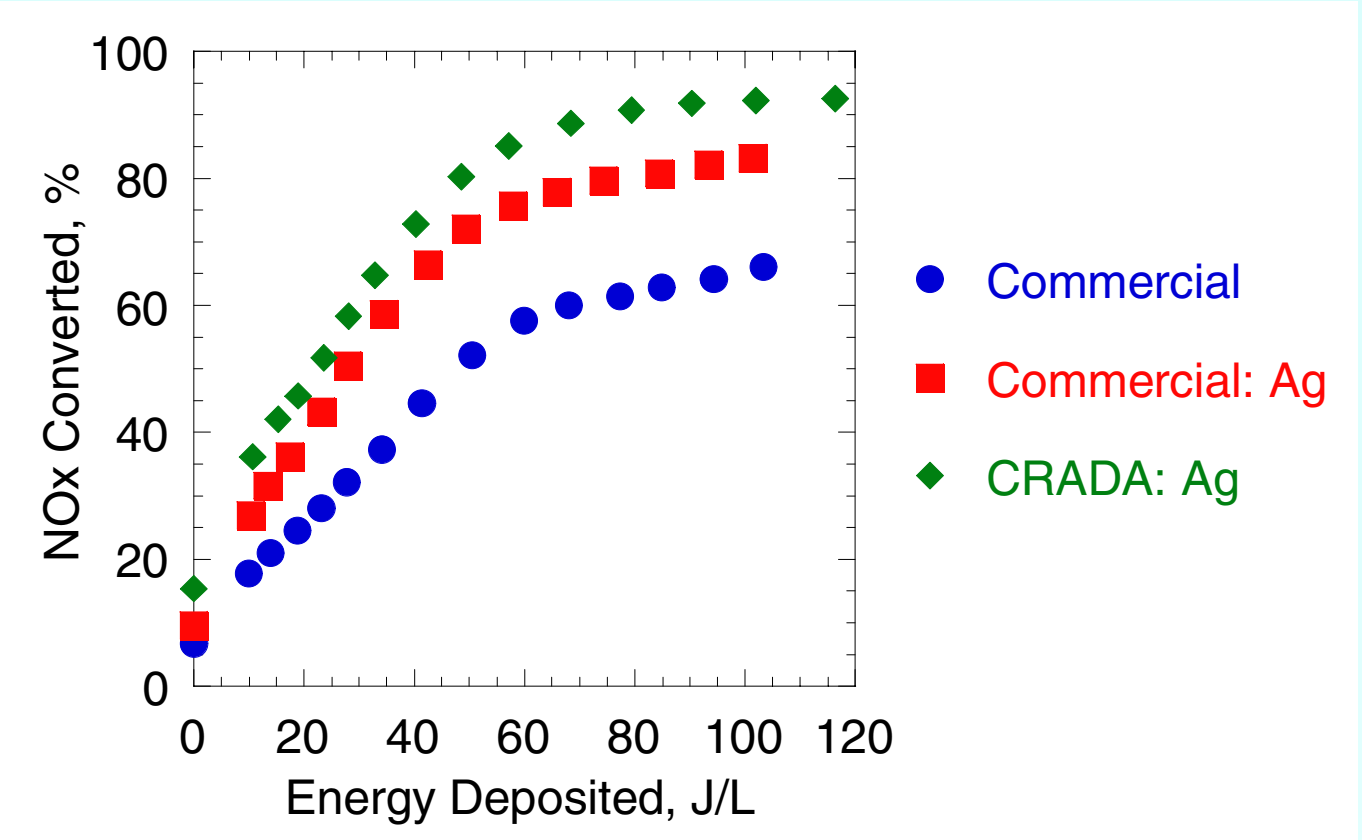
SCR Agent Summary

- Partial oxidation is good: alcohols and aldehydes (higher T)
- Presence of unsaturations is desirable
- Primary alcohols perform better than secondary alcohols
- For fully saturated HC, larger molecules are better
- No data on aromatic or phenolic compounds…needed!
- Activity of SCR agent consistent with generic “reactivity”

Commercial vs. CRADA: γ-Alumina:Ag

Propene Addition – 350°C

Best Commercial - 12:1 C_1:NOx CRADA – 9:1 C_1:NOx



Engine Test: Specifications

Engine

CAT 3126B – 15 ppm sulfur fuel

Flow Conditions

0.5 – 2 CFM slipstream with HC added

Reductants: propene, methanol, and low sulfur fuel

Catalysts Examined

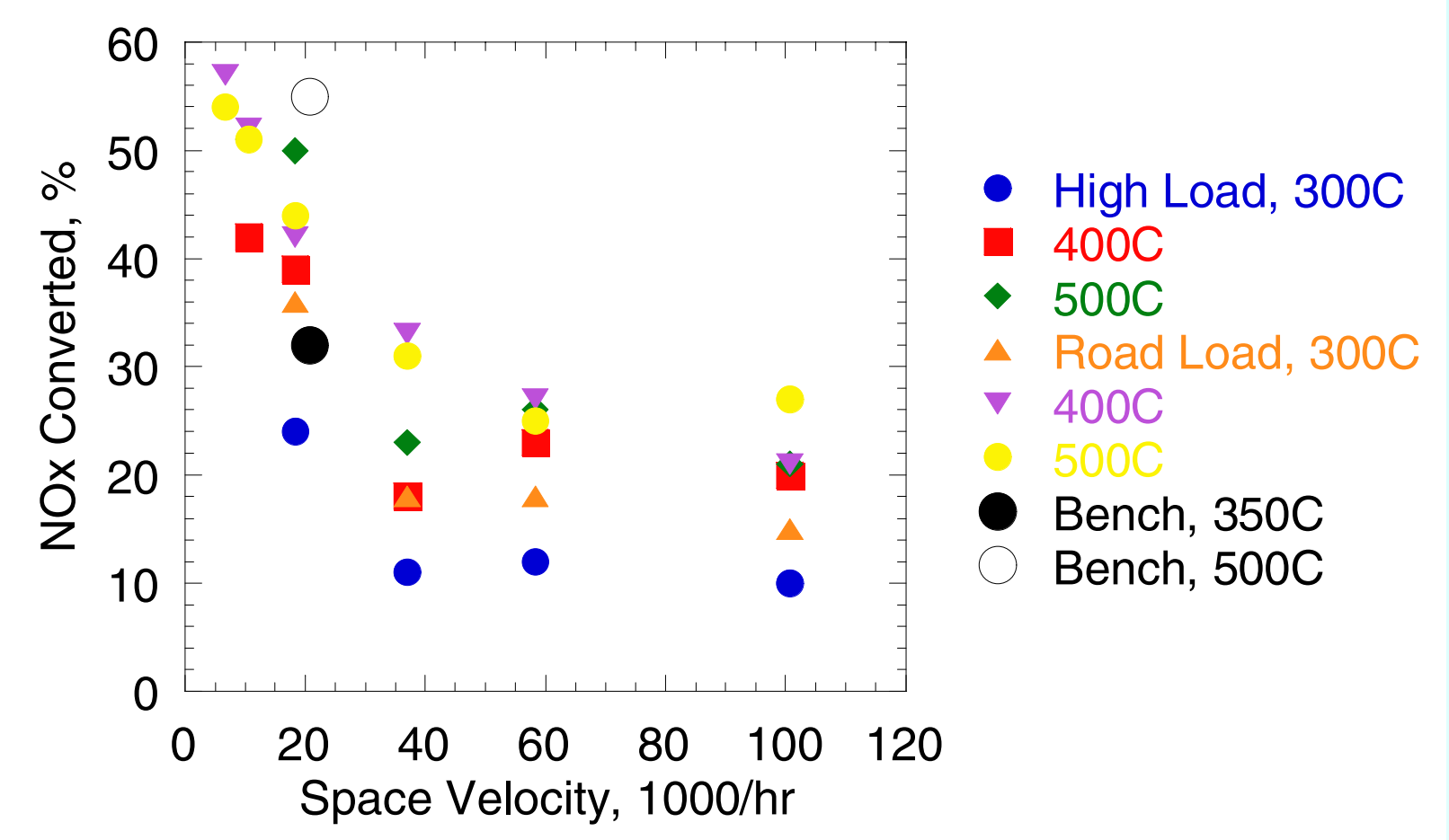
Cordierite Monoliths (volumes of 40 and 220 ml)

Space Velocity = 7000/hr – 100000/hr

Coatings: γ-alumina and doped γ-alumina (Ag, others)

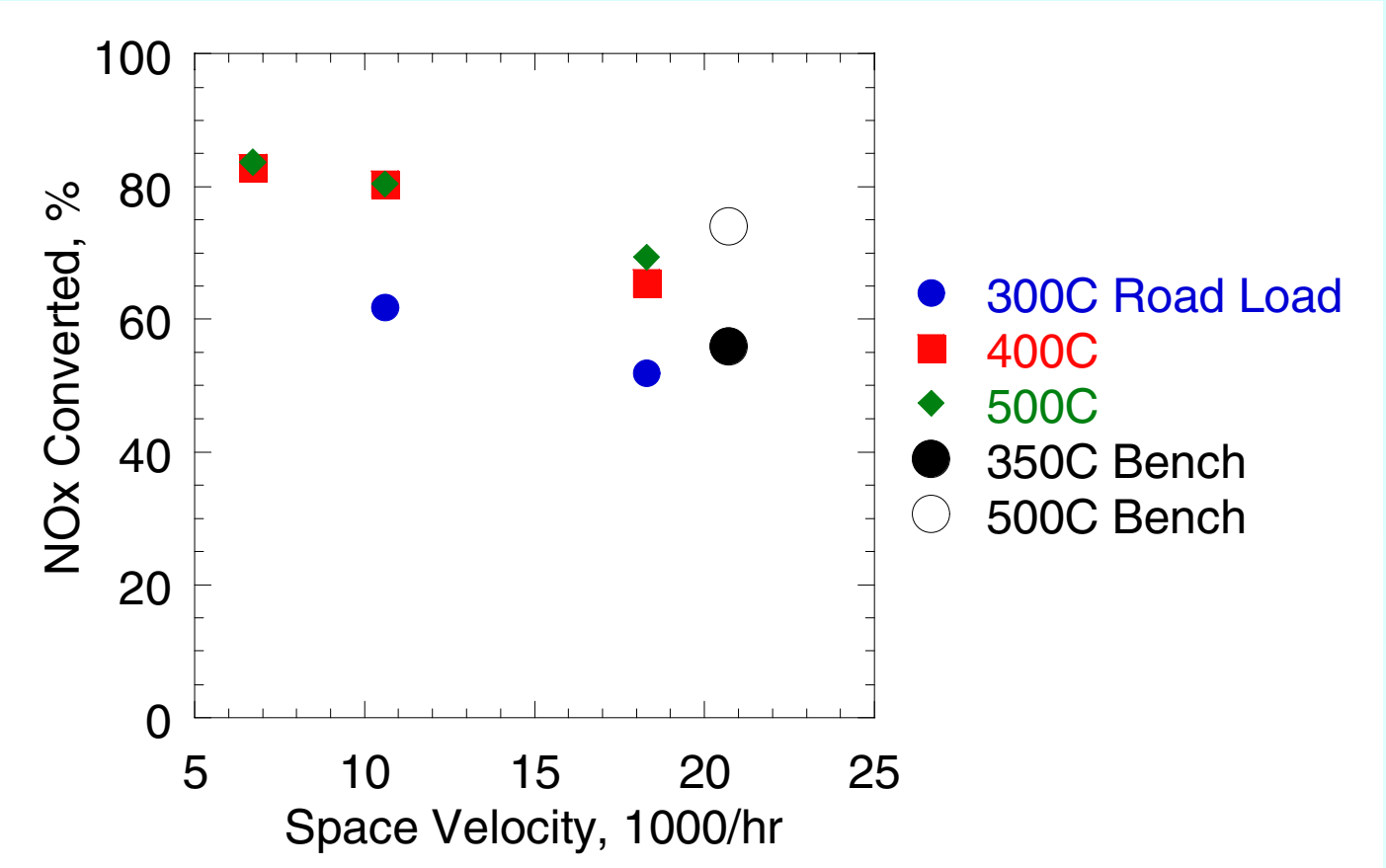
γ-Alumina Performance

CRADA formulation with 2000 ppm propene



Performance of Doped γ-Alumina

CRADA Formulation: Dopant #2 – 2000 ppm Propene



Conclusions

1. There are more active reducing agents than propene, and in many cases they are more practical.

2. Alcohol functionality shows best activity.

3. Engine tests are ongoing, and preliminary data is consistent with bench results on simulated exhaust.

Future Work

1. Need to test the mixture of γ-alumina catalysts developed in this CRADA along with 200-300°C catalysts from OAAT programs (zeolites).

2. Need to work on a compact, full-scale plasma reactor configuration applicable to heavy-duty. Must withstand operation temperatures to at least 600°C.

3. Need to examine whether diesel may be reformed to alcohol functionality (high conversion and selective partial oxidation of HCs is the *holy grail* of organic synthesis) or catalytically cracked to unsaturated species.

Future Work

4. Need to develop stable ultra-high surface area catalyst substrates to increase performance at high space velocity.

5. Need to examine whether alcohols may be blended and pulled out of fuel for on-board SCR agents.

6. Additional engine testing including transient cycles.

7. Additional mechanistic investigations.
   - -Optimum dopant levels in active lean-NOx vs plasma-facilitated SCR
   - -Determination of surface intermediates
   - -Continue to look at alternate SCR agents