Development of Catalytic Materials for Non-Thermal Plasma Aftertreatment System

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August 6, 2001

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PNNL-CAT CRADA

- Program kicked off: 1999
- Materials development (PNNL & Caterpillar):1999-2000

  sol-gel Al_2O_3, metal oxide doped Al_2O_3, durability test
- Plasma reactor bench tests (PNNL): 2000
- Engine Test-1% slip stream (Caterpillar): 2001

- budget $700k/year (DOE: $350k & Caterpillar: $350k in kind)

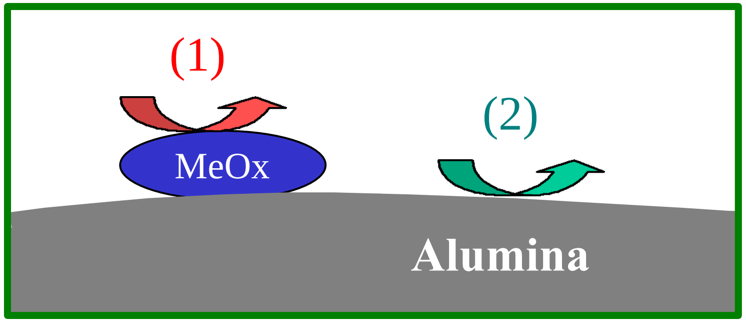
Catalyst Candidates for PAC System

Lean-NOx Catalysis Concept (Hydrocarbon reductant)

- High Temperature Lean NOx (> 450 ^{o}C): Al_2O_3, Metal Oxide/Al_2O_3
- Advantage: - very selective (low fuel penalty): inert for HC oxidation
  - thermally stable
  - inexpensive
  - moderately active (require higher temperature)
  - suitable for PAC
    - NO ---> NO_2
    - HC ---> Oxygenated hydrocarbon

  } increase activity

Proposed Dual Function Catalysis Mechanism



(1a) Hydrocarbon activation: $C_xH_y + O_2 \rightarrow C_xH_yO_z$

(1b) NOx activation: $NO \rightarrow NO_2$

(2) NOx reduction with activated hydrocarbons

$$NOx\ (NO\ or\ NO_2) + C_xH_yO_z + O_2 \rightarrow N_2 + CO_2 + H_2O$$

•Dual function mechanism: leads to new & improved catalyst formulations

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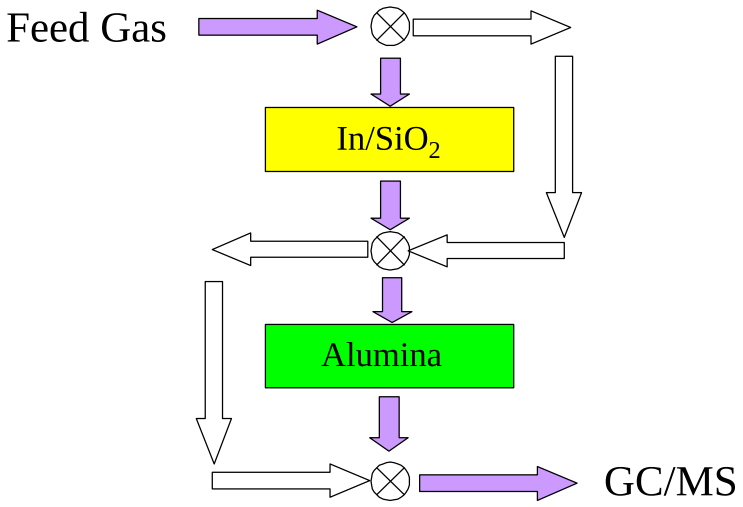
Experimental Set-Up & Conditions

Dual catalyst bed system



Reaction conditions

NO: 1000ppm

C_3H_6: 1000ppm

O_2: 9%

H_2O: 7%

sample: 0.1-0.3g

flow rate: 200cc/min

S.V.: 20,000-60,000h^{-1}

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Identification of Reaction Intermediates over In_2O_3/Al_2O_3

Catalyst	Product Concentration (ppm)						% Conv.		Temp (°C)
	N_2	CO	CO_2	C_3H_6	AA	Ac	C_3H_6	NO	
In_2O_3/Al_2O_3	272	469	1314	300	0	0	67	54	475
In_2O_3/SiO_2	0	96	432	824	22	16	23	0	475
Alumina	21	75	19	1040	0	0	3	4	500
In_2O_3/SiO_2 + Alumina	59	332	444	811	0	0	24	12	475 500

AA: Acetaldehyde, **Ac**: Acrolein

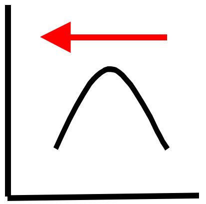
CH_3CHO $CH_2{=}CH\text{-}CHO$

- In_2O_3/Al_2O_3: excellent Lean-NOx catalyst
- In_2O_3 : converts C_3H_6 to AA & AC, no NO oxidation to NO_2
- Al_2O_3 : minor NO reduction to N_2, no oxygenated HC
- In_2O_3 + Al_2O_3: triples NO reduction, synergy effect

Catalyst Development

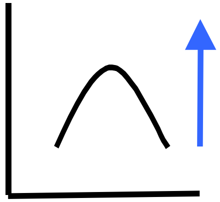
- **Activity (MeOx)**: low operation temperature

  HC • oxygenated HC



- **Selectivity (Al_2O_3)**: high NOx reduction

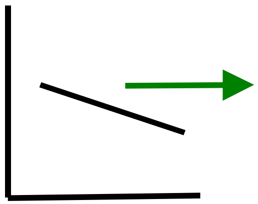
  NO • NO_2 oxidation



- **Durability**: hydrothermal & sulfur tolerance

  compositional variation

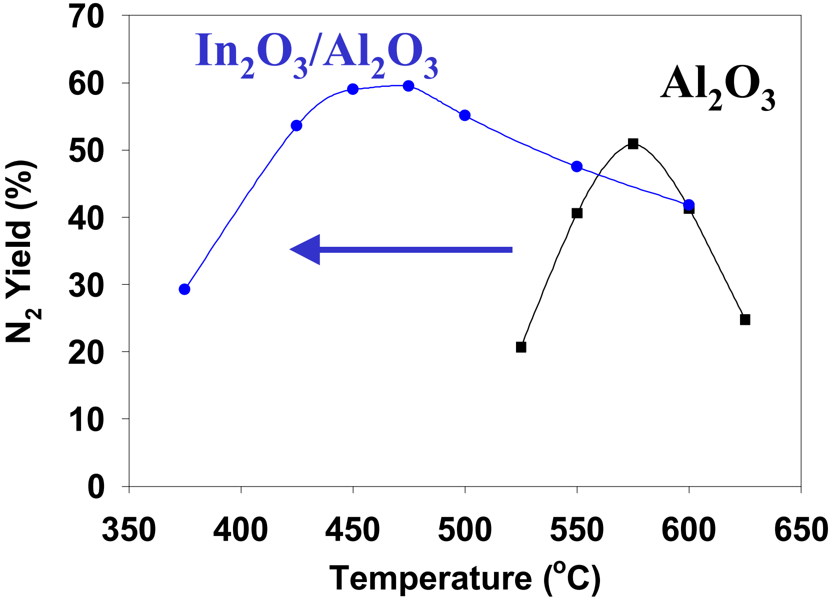
  reactant conditioning



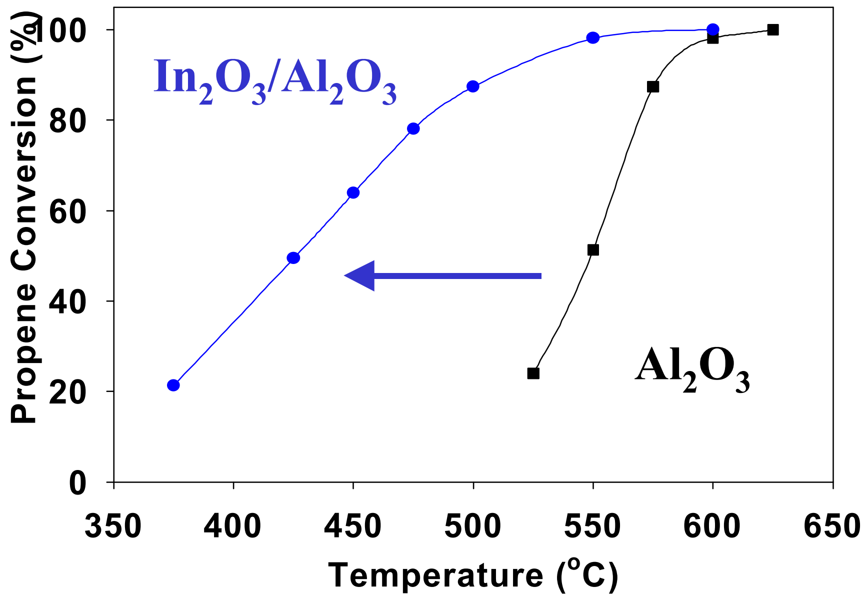
•Non thermal plasma reduces required catalyst functions and increases catalyst options.

Catalytic Activity Improvement

NO Reduction



Propene Conversion

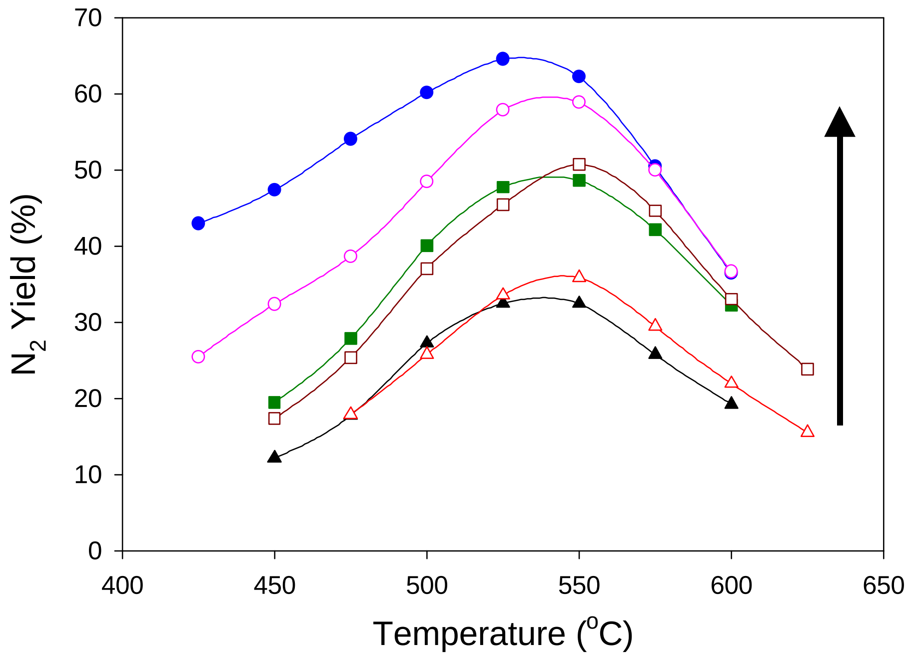


- Metal Oxide additive: improves activity
- Hydrocarbon Reforming: propene • acrolein, acetaldehyde

Catalytic Selectivity Improvement

(Alumina physical & chemical properties)

NO_2 reduction over various aluminas



Characterization of various aluminas

Surface Area (m^2/g)	Pore Volume (cc/g)	Pore Size (nm)	Impurity (%)		
			Na_2O	SO_4	additive
230	**1.1**	**14**	**0.0**	**0.0**	**-**
240	**0.28**	**4**	**0.0**	**0.0**	**-**
260	**0.84**	**9**	**0.1**	**0.2**	**-**
270	**0.70**	**8**	**0.1**	**0.3**	**-**
280	**0.92**	**10**	**0.2**	**0.7**	**SiO_2**
280	**0.45**	**5**	**0.1**	**0.0**	**La_2O_3**

- **Primary parameters : impurity, pore volume, additives**
- **2nd parameters : surface area**

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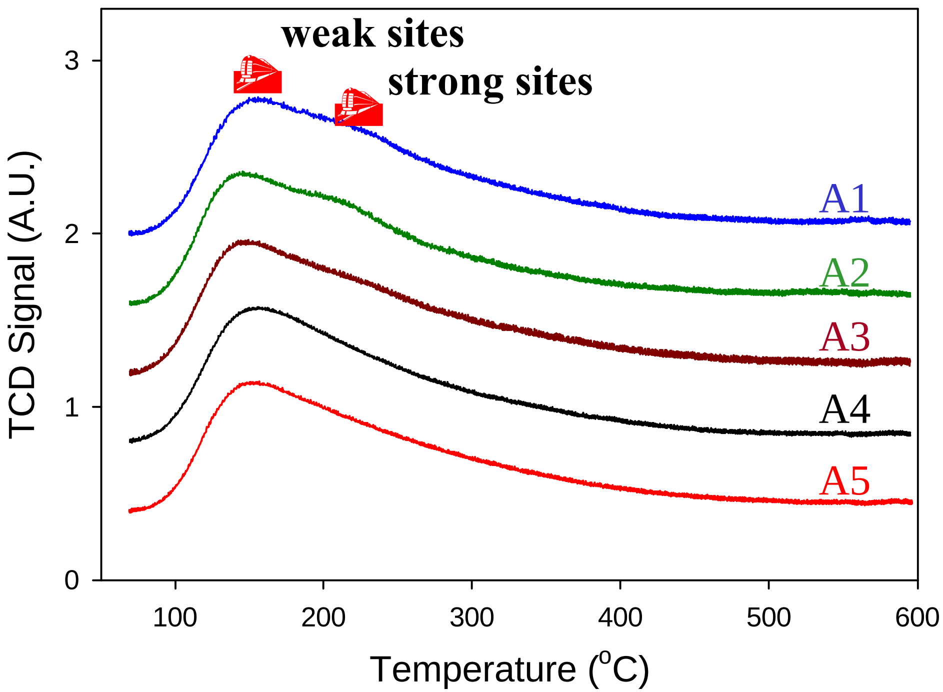
The Role of Surface Acidity

NH_3-TPD Spectra of Various Aluminas



NO_2 reduction at 500°C (%)	Total NH_3 Desorption (cc/m^2)
60%	0.045
40%	0.043
37%	0.045
27%	0.044
26%	0.043

- **Primary parameter may be acid site distribution (pyridine).**
- **Secondary parameter may be total acid sites (NH_3).**

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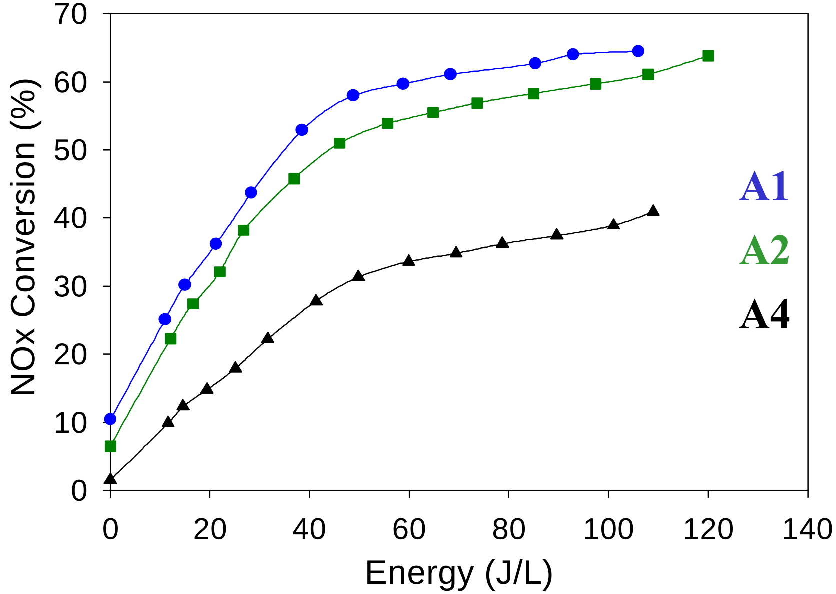
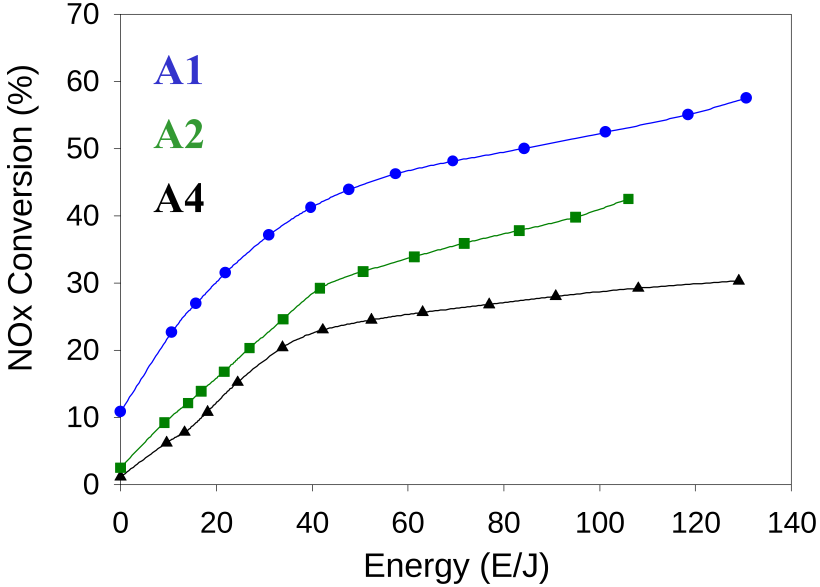
NOx Reduction over Aluminas + Plasma Reactor System

Fresh Aluminas (350 °C)



Reaction condition: 500ppm NO, 0/20ppm SO_2 9% O_2, 300ppm CO, 2000ppm C_3H_6, 8% CO_2, 15,000-25,000 h^{-1}

Aged Aluminas (350 °C)



Aging condition: 520°C, 250hr, 30ppm SO_2, 7% H_2O, 5L/min air

•Plasma increases activity & selectivity of NOx Performance over fresh & aged Aluminas

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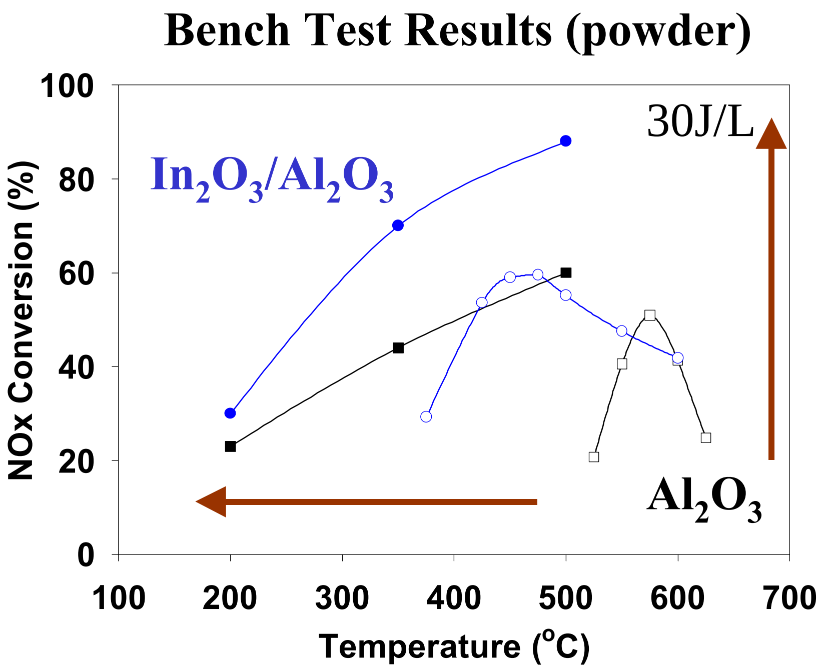
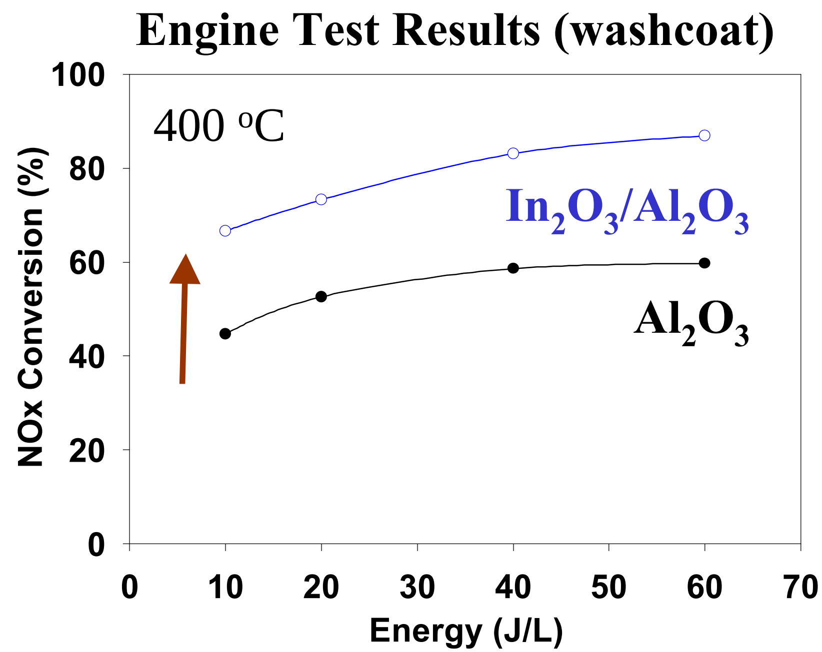
Catalytic Activity & Selectivity Improvement





- MeOx additive & Plasma: improve activity & selectivity

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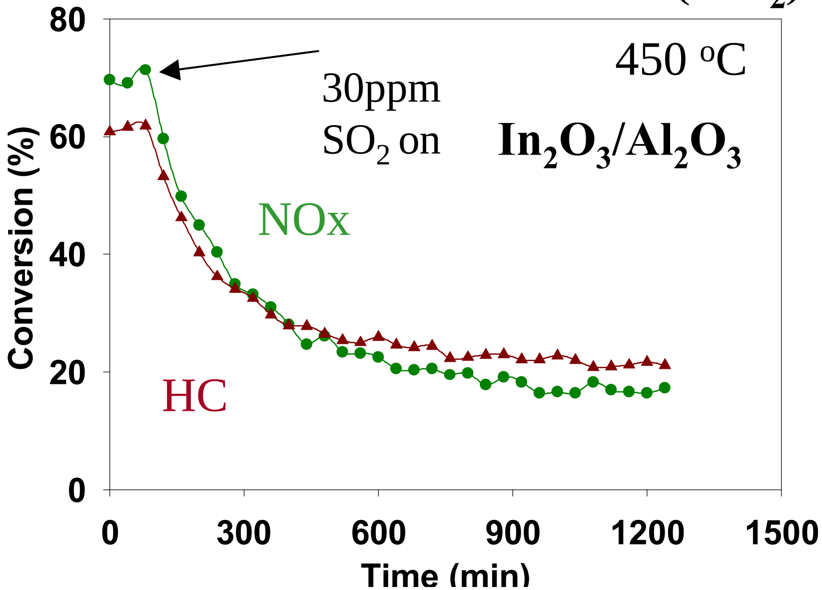
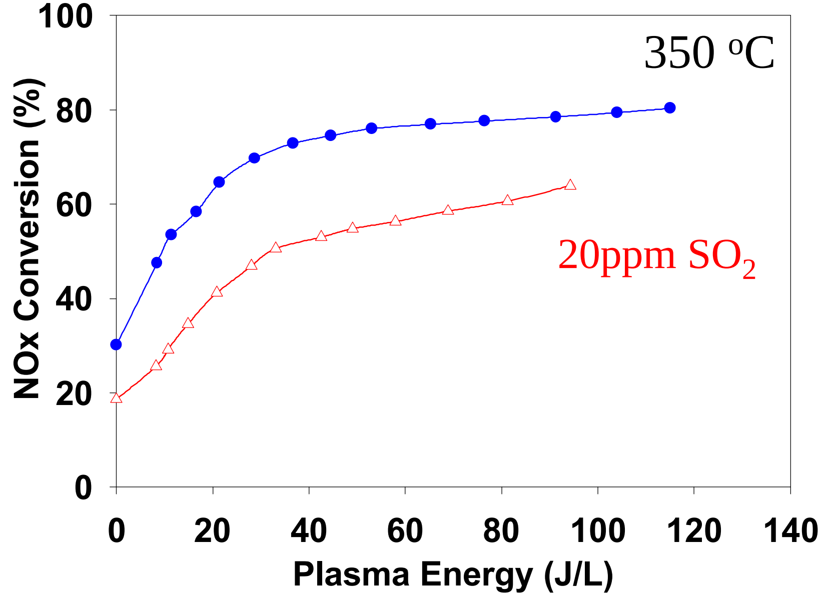
Catalyst Durability Improvement with Plasma

Powder test bench result (NO_2)



- 70% loss after 10 hr
- sulfur adsorbs primary to MeOx site

Plasma test bench result



- Plasma enhanced catalyst durability
  - Oxygenated Hydrocarbon
  - NO • NO_2
  - compete adsorption against SO_2

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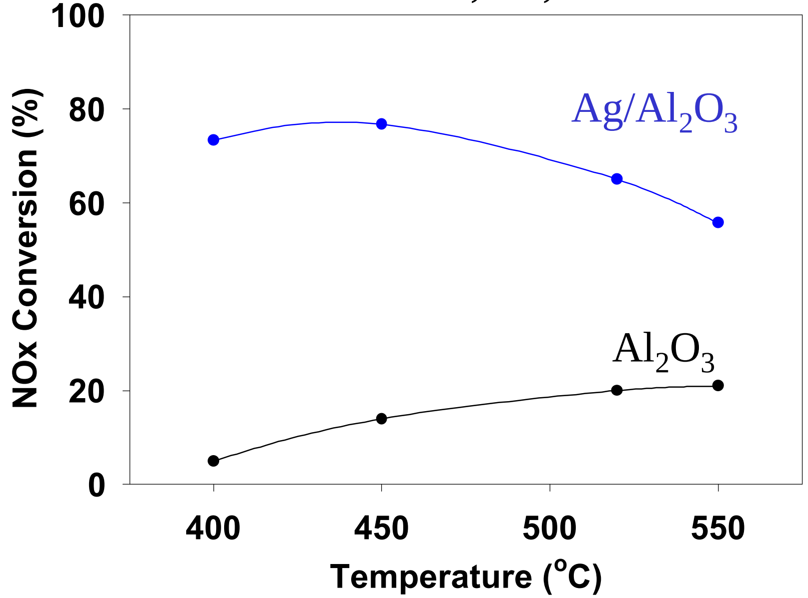
Catalyst Activity, Selectivity and Durability Improvement

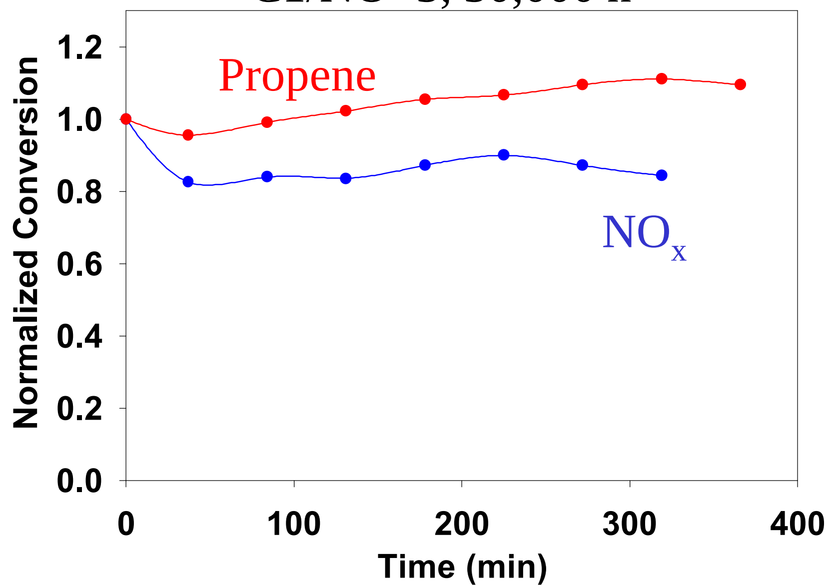
NOx Reduction(EtOH)

C1/NO=4.3, 50,000 h^{-1}



Durability Test (30ppm SO_2)

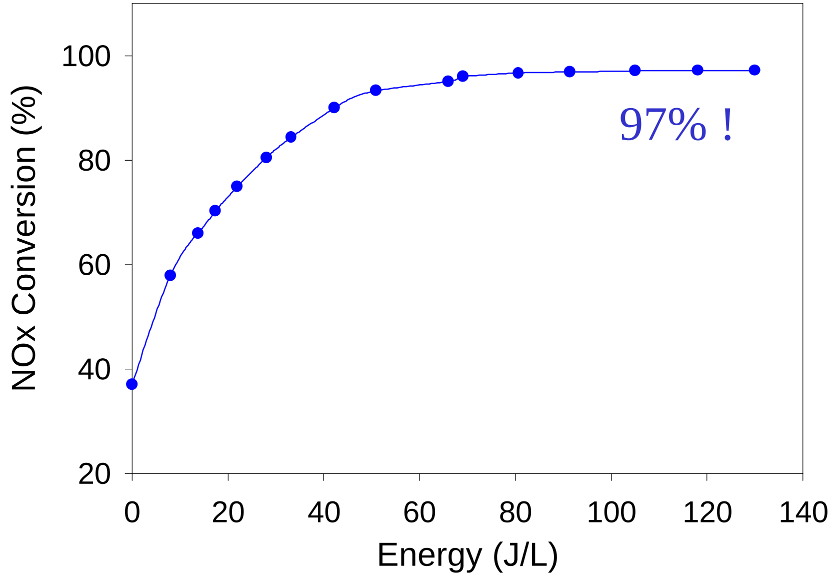
C1/NO=3, 30,000 h^{-1}



- Improve Activity & Selectivity: right reductant + right catalyst
- Resistance to SO_2 poisoning

NOx Reduction of Ag/Al_2O_3 + Plasma Reactor System

NOx conversion at 350 °C with propene reductant



- Plasma provides right reductant to the catalyst (oxygenates)
- Engine test will follow.

Conclusions

- $MeOx/Al_2O_3$ is a suitable catalyst for PAC.
  - dual functional system
    - plasma: NOx & HC activation
    - catalyst: HC activation & NOx reduction

- Catalytic *activity*, *selectivity* and *durability* can be improved significantly through a catalyst formulation specifically designed for PAC system.
  - metal oxide selection & optimum dispersion
  - alumina material
  - hydrocarbon reductant

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Acknowledgement

CRADA: Caterpillar & PNNL

DOE: OHVT office

Gurpreet Singh

Dr. Sidney Diamond

Dr. D. Ray Johnson