LOW TEMPERATURE LIMITERS TO CATALYST LIGHT-OFF

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CLEERS 18

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Presentation Outline

- **Background**
- **Project Objectives**
- **Catalyst Evaluated**
- **Individual Test Conditions and Results**
- **Conclusions**

This Presentation is Only a Summary

Refer to SAE Paper 2015-01-1025 for More Details, and SwRI for Further Details

Background

- **"More fuel efficient vehicles are resulting in lower exhaust temperatures. Based on exhaust temperature expectations for future engine technology, industry representatives predict light-off temperatures of ~150°C will be required to meet emission regulations for new engines used to meet vehicle fuel economy standards."**
- **"Lowering of the temperature at which catalysts become active to ~150°C is extremely difficult and forms *The 150°C Challenge*"**

USDRIVE WORKSHOP, November 29-30, 2012
Future Automotive Aftertreatment Solutions: The 150°C Challenge Workshop Report

Project Objectives

1. Identify low temperature ***limiters*** for a variety of relevant catalyst aftertreatment types

2. Postulate the ***mechanisms*** behind low temperature activity limitation

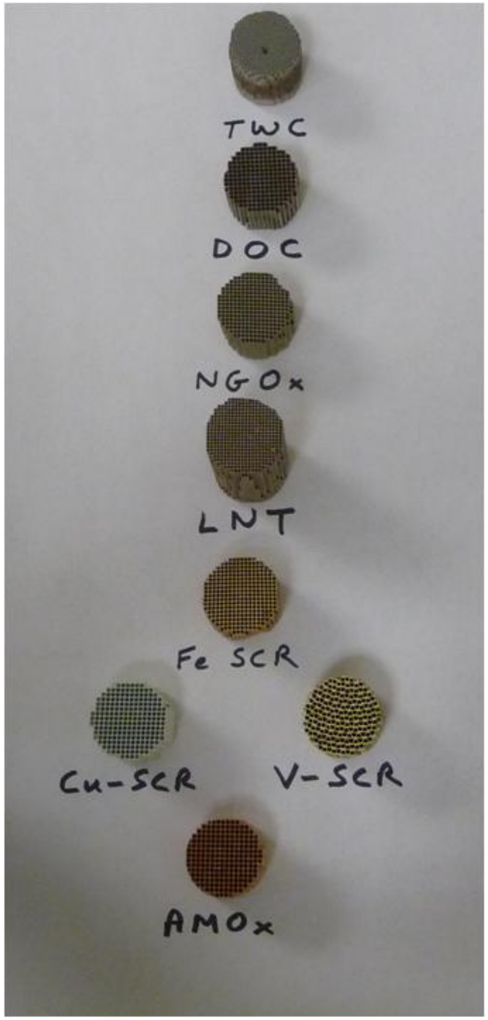
3. Consider ways in which to ***mitigate*** these limitations, facilitating low temperature activity

The objectives are listed in relative priority for the project, but all are recognized as important to the overall goal.

Seven Catalysts Investigated

- **A Wide, Shallow Dive**
  - Any one of these can be a lifetime's work

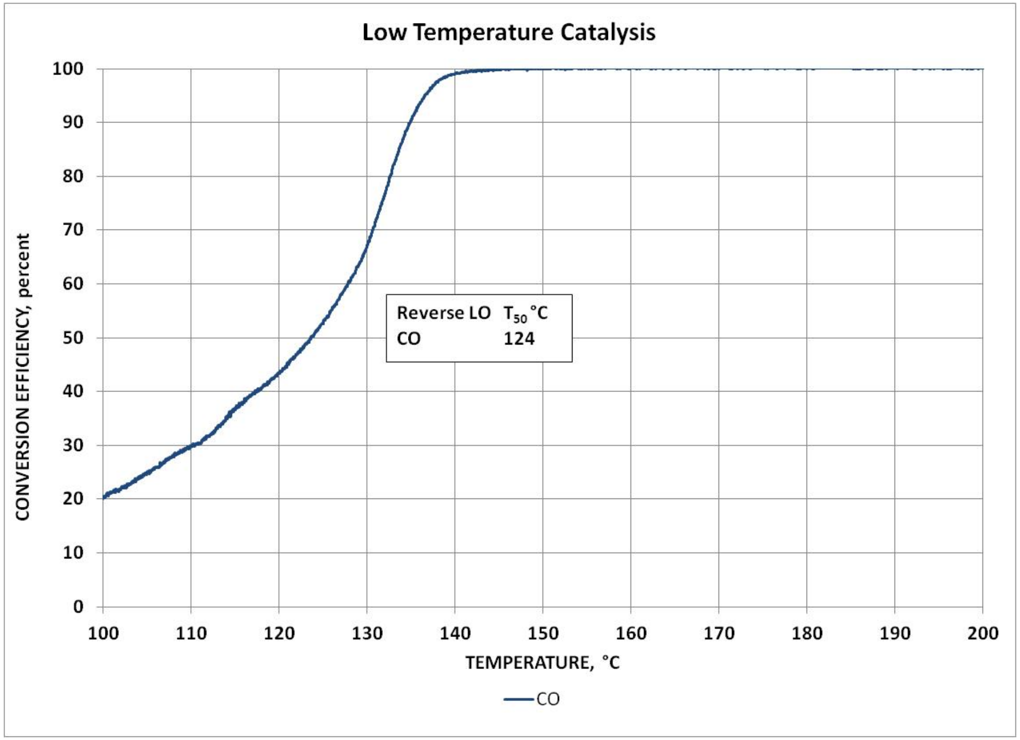
- **TWC – gasoline, stoichiometric**
- **DOC – diesel, lean**
- **NGOx – natural gas oxidation, lean**
- **LNT – gasoline, lean NO_X**
- **Fe-SCR – diesel, lean NO_X**
- **Cu-SCR – diesel, lean NO_X**
- **V-SCR – diesel, lean NO_X**
- **AMOx – diesel, lean NH_3**



Low Temperature Catalyst or Low Temperature Catalysis?

- **Considerable Efforts are Being Made to Develop Low Temperature Catalyst Formulations**

SwRI's Low Temperature Catalyst



- **100 % conversion > 150°C**
- **20% conversion at 100°C**

- **Problem Solved !**

We Cheated !!

- **The Catalyst was a Standard Three-Way Formulation**

- **The Gas Mixture was :**
  - 10 % O_2 — No H_2O
  - 100 ppm CO — No NO_x
  - 2000 ppm H_2 — No SO_2
  - Balance N_2 — No hydrocarbons

- **The Point?**

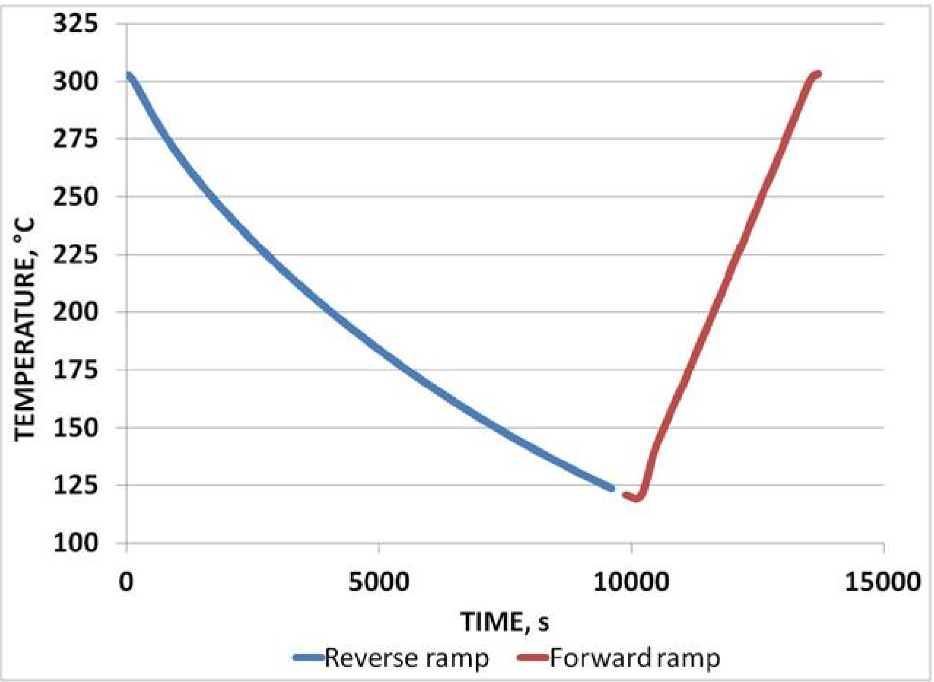
Today's catalysts are already capable of low temperature catalysis, but the environment is critical to effective low temperature catalysis

Consider Both the Catalyst and the Conditions as a *System* and Look for System Solutions

Evaluation Procedure

- **SwRI's USGR® Gas Reactor Used**
- **Reverse Light-Off → Forward Light-Off**

RLO → FLO



Three-Way Catalyst

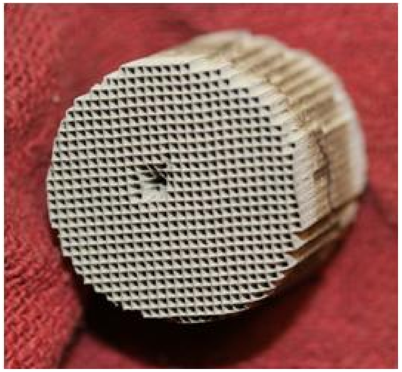
- **100,000 Mile Field Catalyst, Acid-Washed to Remove Deposits (phosphorus, zinc, calcium)**
- **Stoichiometric, Perturbated RLO → FLO**

Pt = 24 g/ft^3

Pd = 39 g/ft^3

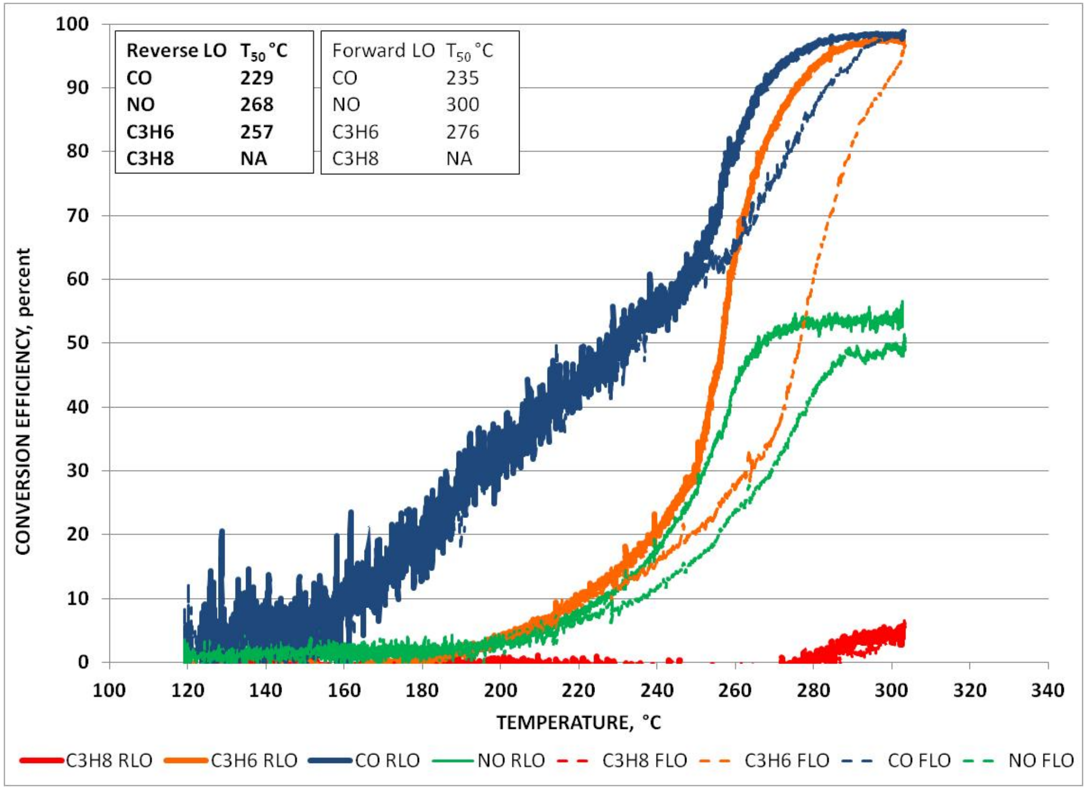
Rh = 6.5 g/ft^3

Gas	Concentration	
	Lean	**Rich**
Nitric Oxide (NO)	500 ppm	500 ppm
Propene/Propane 2:1 (C_3H_6/C_3H_8)	483 ppmC3	483 ppmC3
Carbon Monoxide (CO)	0	2000 ppm
Hydrogen (H_2)	0	667 ppm
Oxygen (O_2)	0.65 percent	0
Carbon Dioxide (CO_2)	13 percent	13 percent
Water (H_2O)	14 percent	14 percent
Nitrogen (N_2)	Balance	Balance



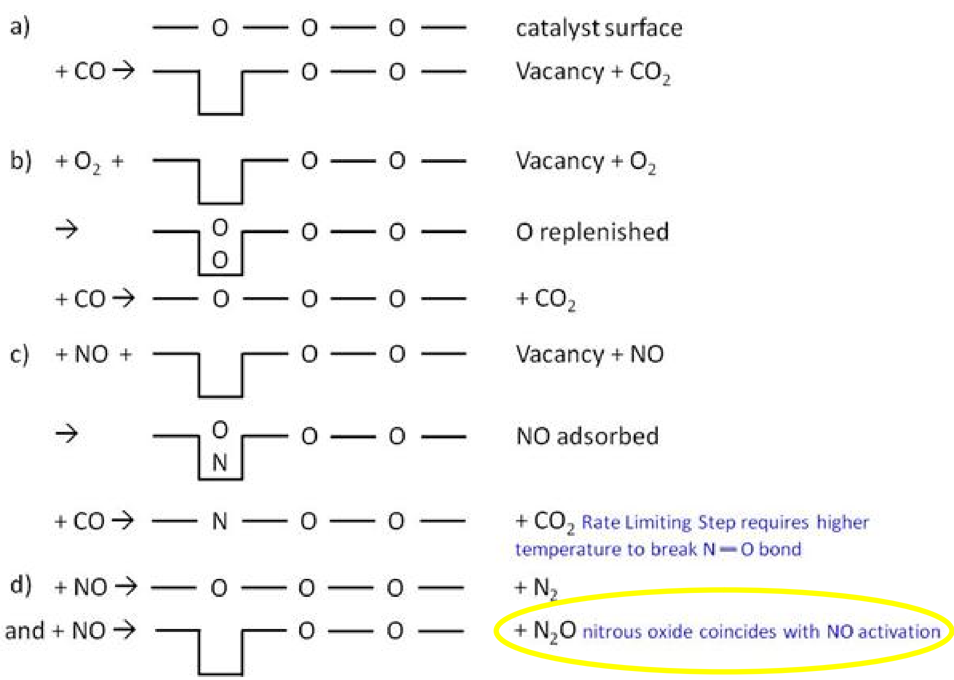
TWC – Full Gas Mix

- **CO Light-Off Initiated at 160°C, but Protracted**
- **Propene & NO Coincident**

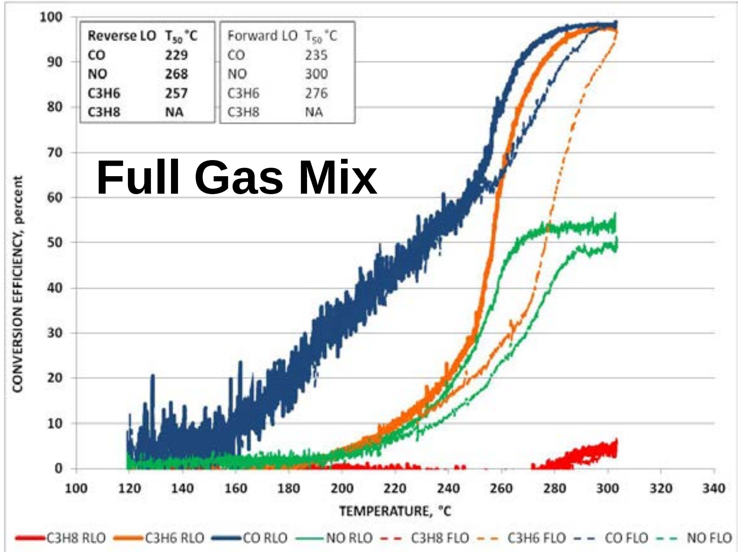


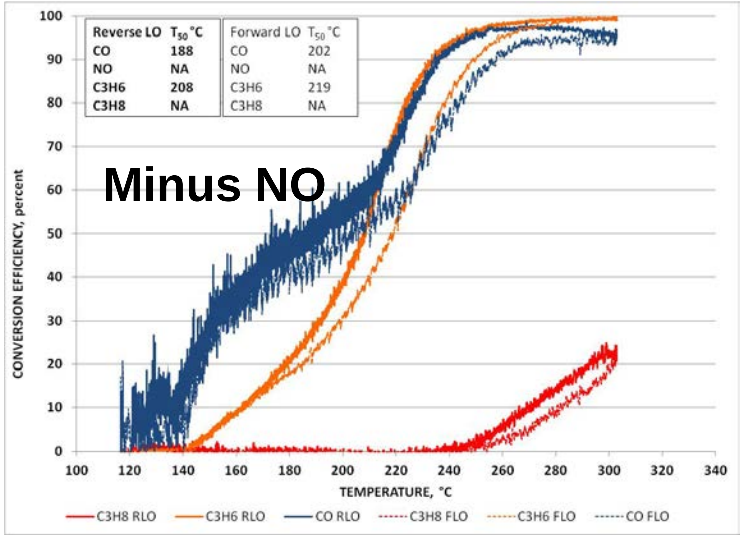
TWC – minus NO

- **Removal of NO Clearly Lowers CO and HC Light-Off Temperatures**
- **<u>NO is a Light-Off Inhibiter</u>**



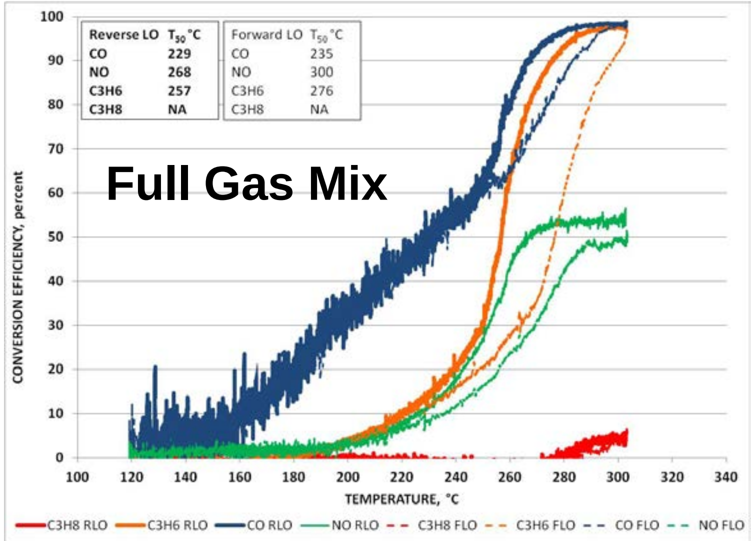
Yu Lei et al., ChemCatChem 2011, 3, 671-674

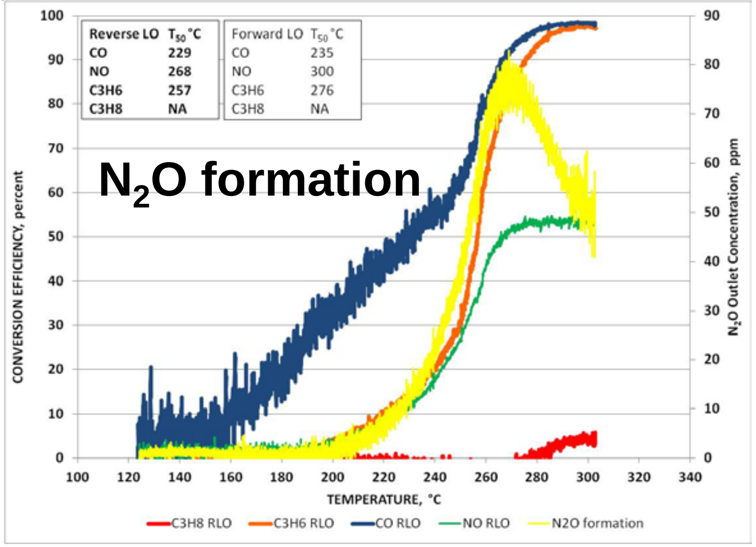




N_2O Formation

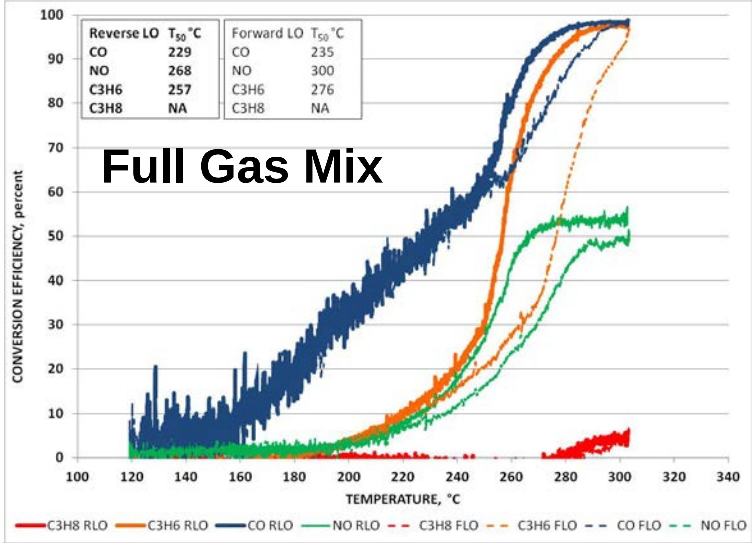
- **N_2O Formation Coincides with NO Activation**
- **NO Inhibition Mechanism Seems Plausible**
- **Use of an NO adsorber could improve low temperature activity**
  - NO_X storage typically NO → NO_2 conversion, then NO_2 storage as nitrates
  - No NO_2 formation cold, so need NO storage as nitrite

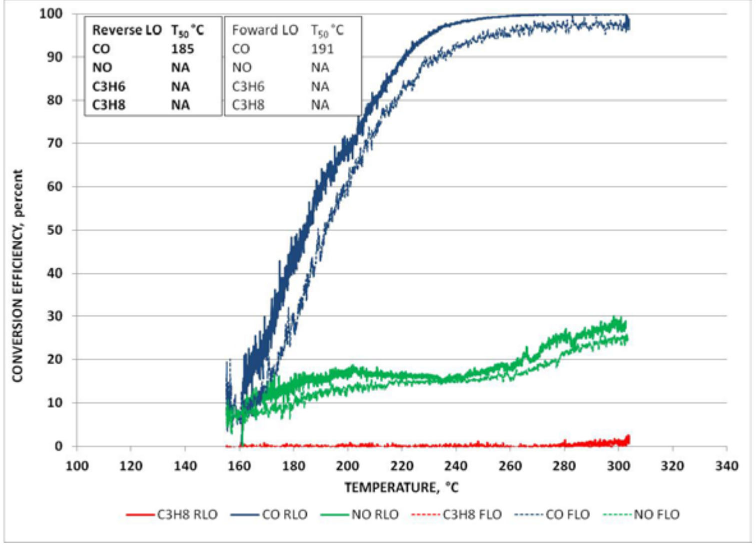




TWC – minus Propene (C_3H_6)

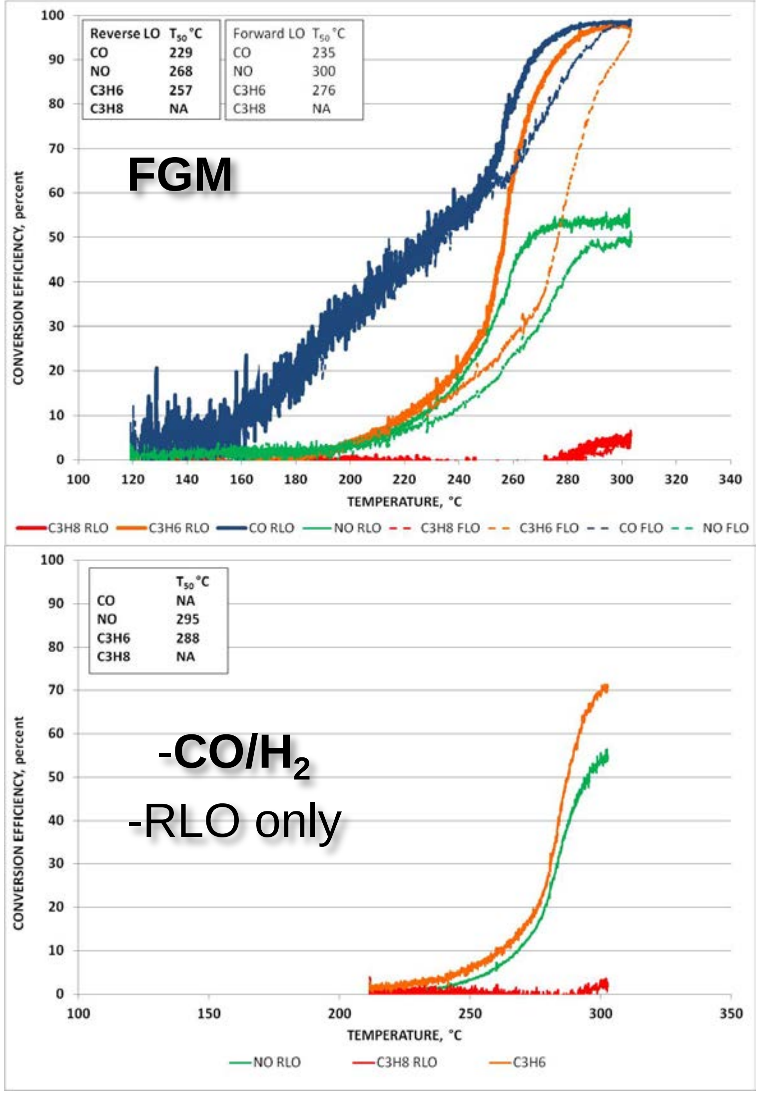
- **Removal of C_3H_6 Lowers CO Light-Off Temperatures**
- **Removal of C_3H_6 Increases NO Light-Off Temperatures**
- **<u>C_3H_6 is Both a CO Light-Off Inhibiter and a NO Light-Off Promoter</u>**





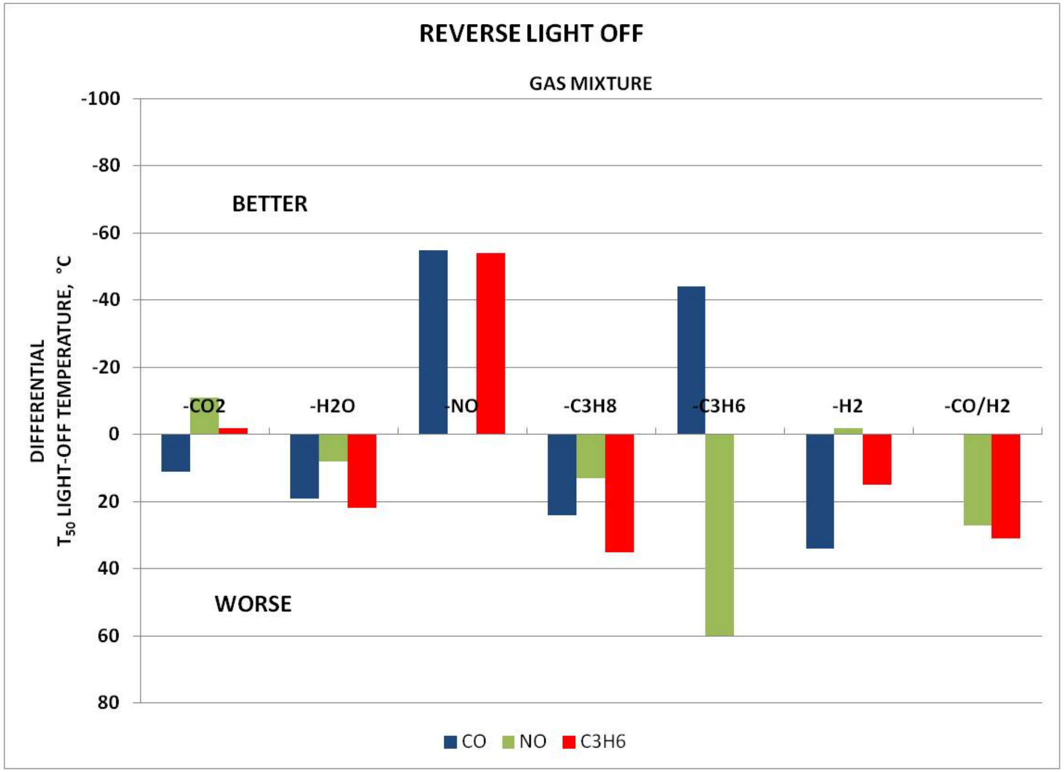
TWC – minus CO/H_2

- **Removal of CO/H_2 Increased Propene and NO Light-Off Temperatures**
- **<u>CO/H_2 is a Light-Off Promoter</u>**



TWC - Summary

- **NO Inhibits CO and HC**
- **C_3H_6 Inhibits CO, but Promotes NO**
- **CO/H_2 is a Light-Off Promoter**



Solutions may include:

cold start NO adsorber

run slightly rich to increase CO, H_2 and alkenes, and reduce NO (supplemental O_2 may be needed)

Diesel Oxidation Catalyst

- **Degreened Catalyst from 2007 MY Class 8 Truck**
- **Lean RLO → FLO**

Pt = 0.838 wt%

Pd = 0.155 wt%

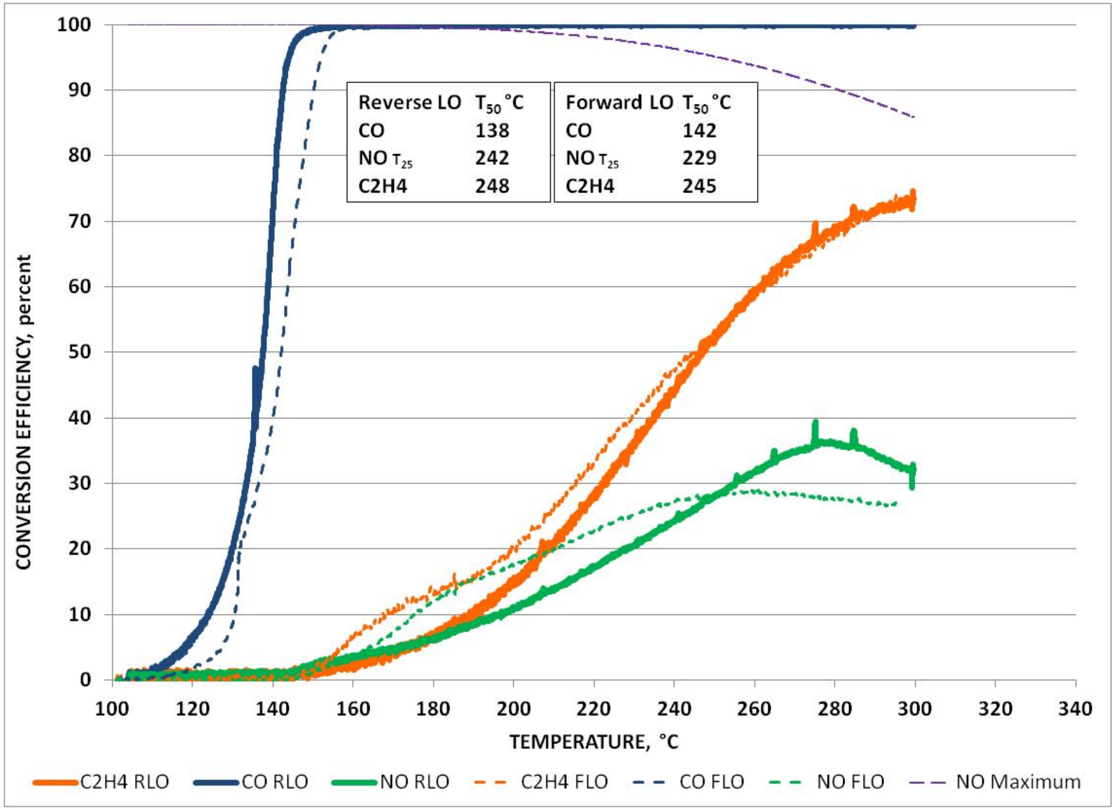
Gas	Concentration
Nitric Oxide (NO)	600 ppm
Ethene (C_2H_4)	75 ppmC2
Carbon Monoxide (CO)	300 ppm
Hydrogen (H_2)	100 ppm
Oxygen (O_2)	10 percent
Carbon Dioxide (CO_2)	5.6 percent
Water (H_2O)	6.0 percent
Nitrogen (N_2)	Balance

DOC – Full Gas Mix

- **CO T_{50} Light-Off at $140^{o}C$**
- **C_2H_4 T_{50} Light-Off at $246^{o}C$**
- **Forward Light-Off Temperatures of C_2H_4 & NO are Lower Than Reverse Light-Off Temperatures**

Inverse Hysteresis*

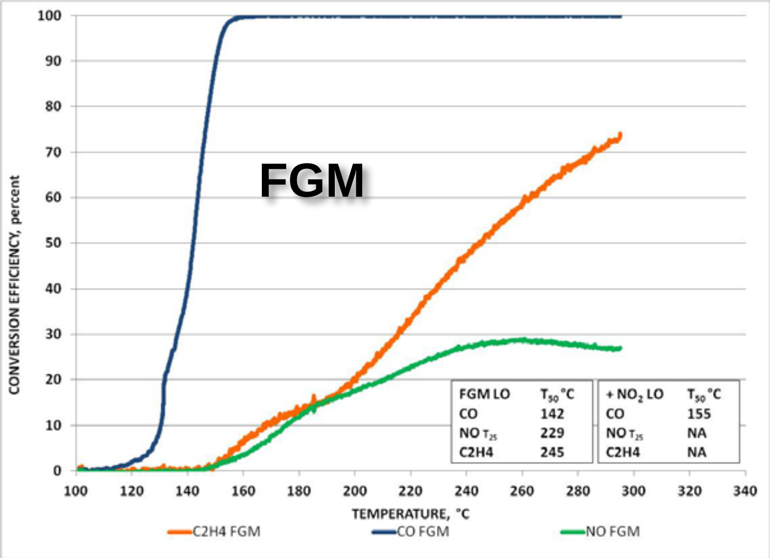
- **A Product of Reactions Inhibits Reverse Light-Off – NO_2 …?**

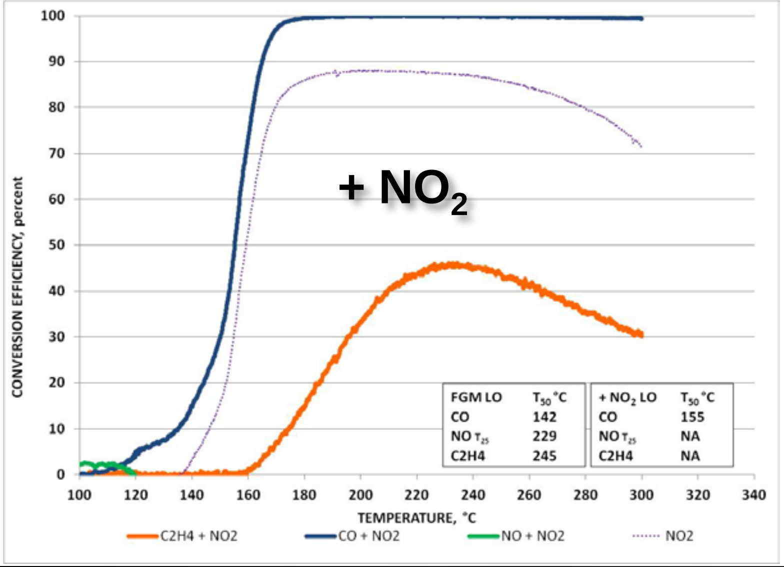


* Martin Votsmeier – CLEERS 2014

NO_2 Effect on Forward Light-Off

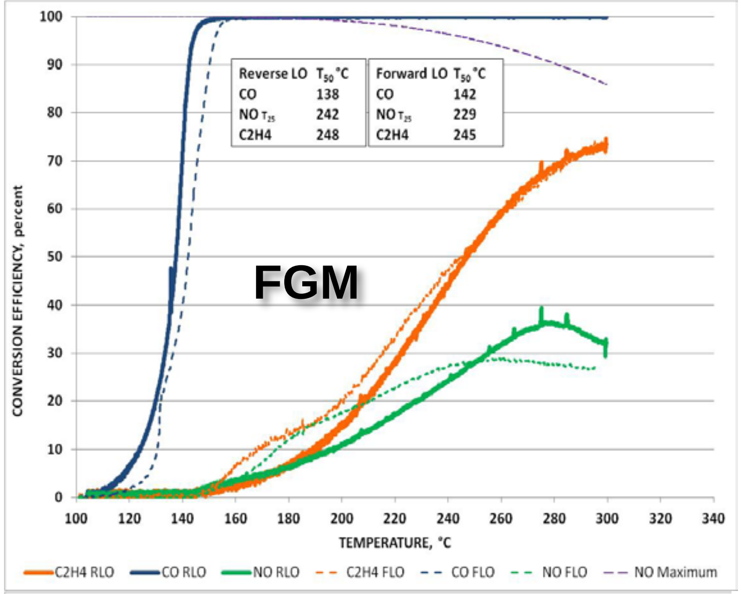
- **50:50 NO:NO_2 Mixture**
- **NO_2 Inhibits CO & Promotes Low Temperature C_2H_4, but Inhibits Higher Temperature C_2H_4**

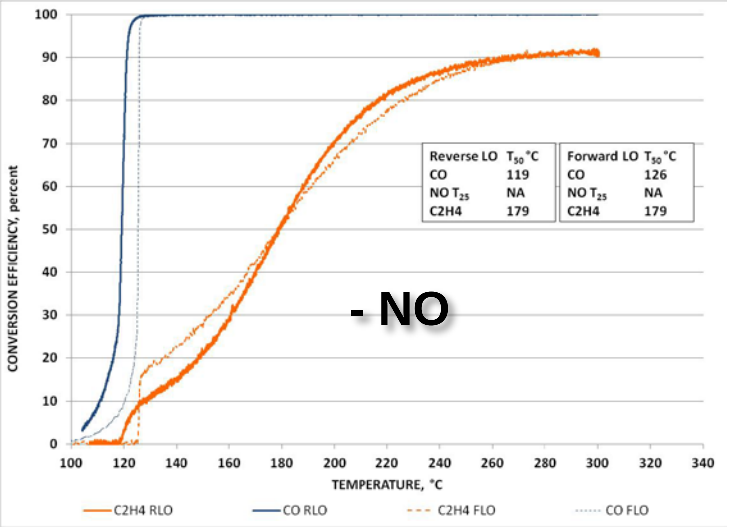




DOC – minus NO_X

- **Removal of NO_X Clearly Lowers CO and HC Light-Off Temperatures**
- **<u>NO_X is a Light-Off Inhibiter</u>**
- **NO Inhibition Mechanism Like TWC…?**

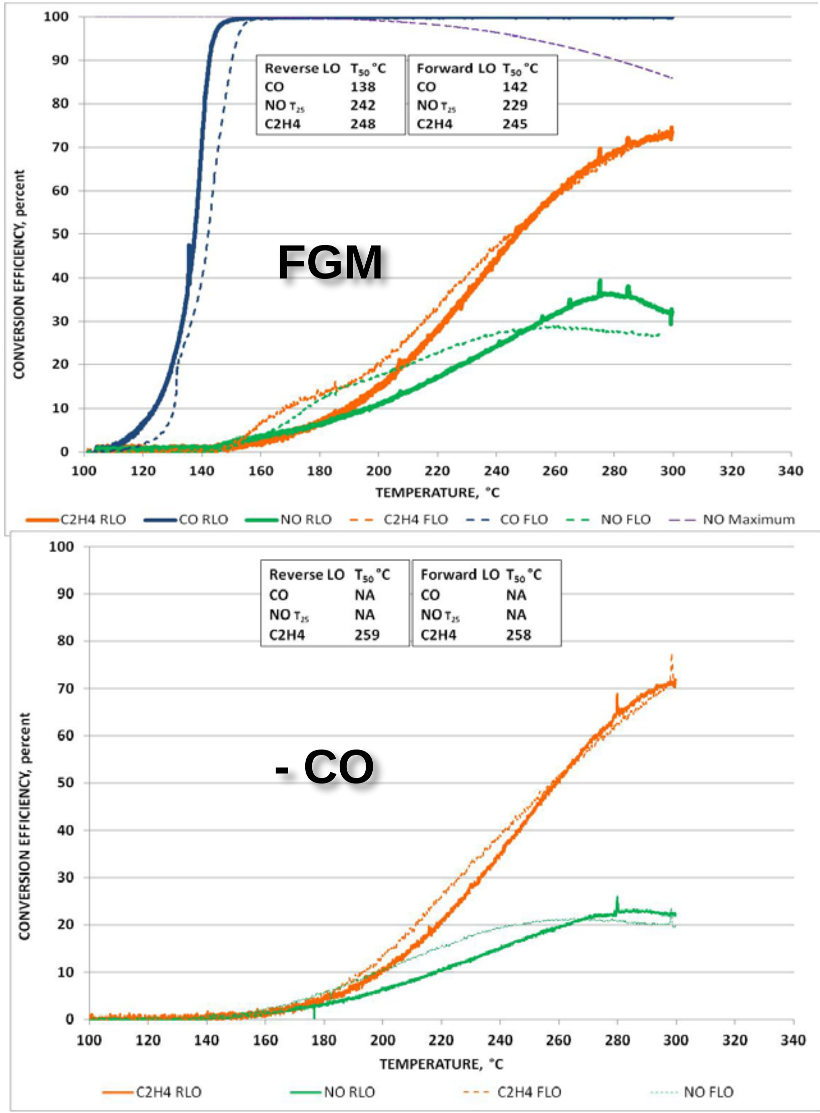




DOC – minus CO

- **Removal of CO Raised C_2H_4 and NO Light-Off Temperatures**

- **<u>CO is a Promoter of Low Temperature HC Light-Off</u>**



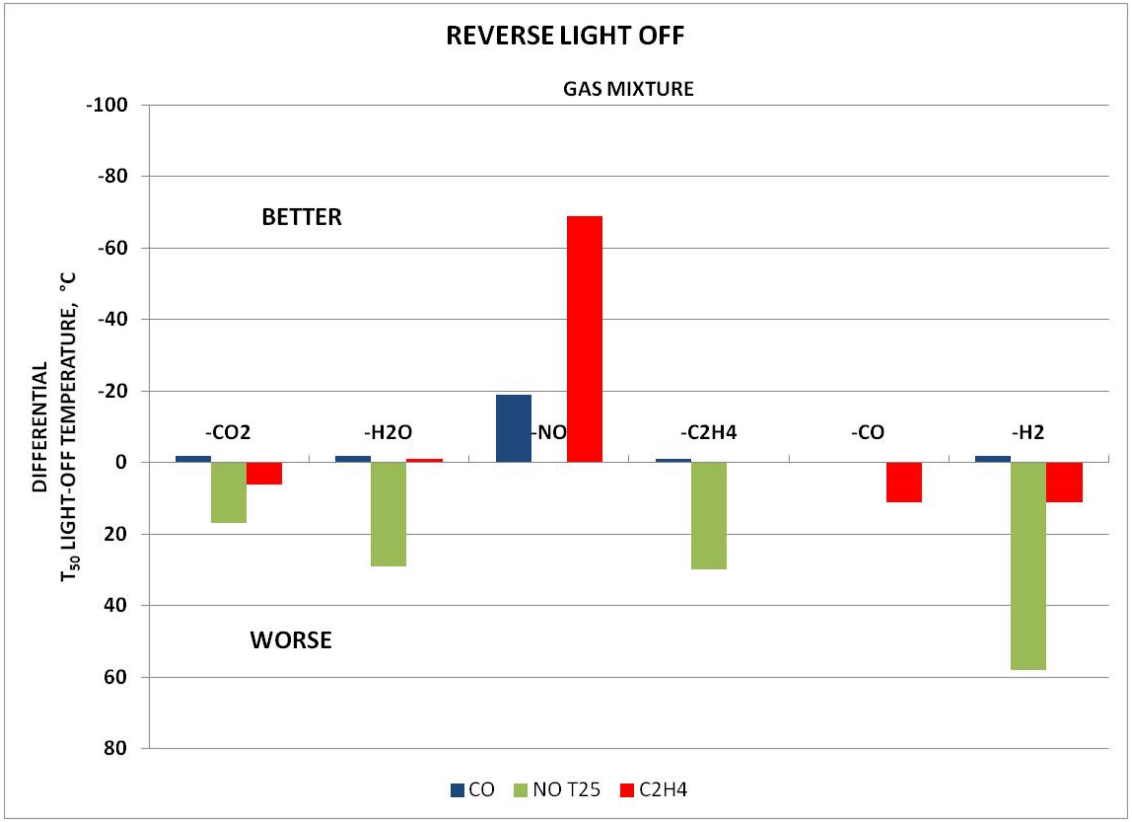
DOC - Summary

- <u>**NO Inhibits CO and C_2H_4**</u>
- <u>**CO Promotes C_2H_4**</u>
- <u>**C_2H_4 Promotes NO**</u>
  - Lean NO_X catalysis
- **Also, H_2, CO_2 and H_2O Promote NO Light-Off**
  - Competative adsorption ?

Solutions may include:

cold start NO adsorber

increase CO, H_2 & reduce NO in exhaust



Natural Gas Oxidation Catalyst

- **Used a TWC from an ISX-12G, Preconditioned with 150 Engine Hours (no NGOx available)**
- **Lean RLO → FLO**

Pt = 1.3 g/ft^3

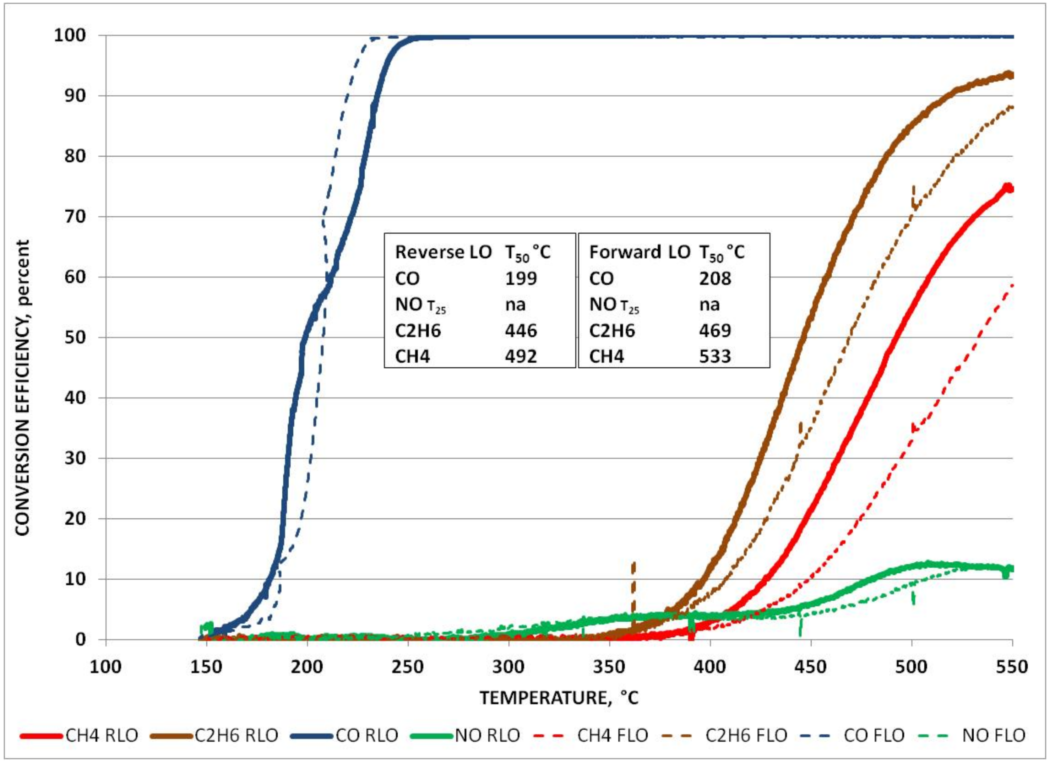
Pd = 57 g/ft^3

Rh = 1.1 g/ft^3

Gas	Concentration
Nitric Oxide (NO)	500 ppm
Methane (CH_4)	1500 ppm
Ethane (C_2H_6)	150 ppm
Carbon Monoxide (CO)	1200 ppm
Hydrogen (H_2)	280 ppm
Oxygen (O_2)	10 percent
Carbon Dioxide (CO_2)	7.5 percent
Water (H_2O)	8.0 percent
Nitrogen (N_2)	Balance

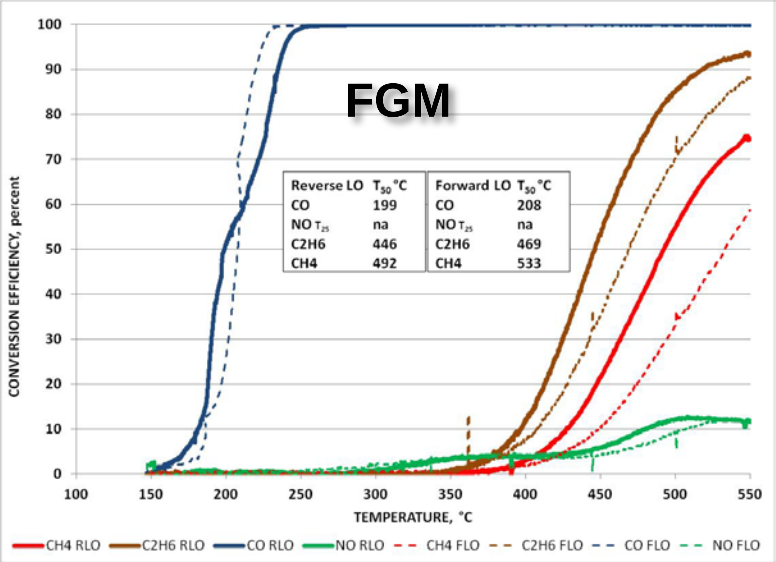
NGOx – Full Gas Mix

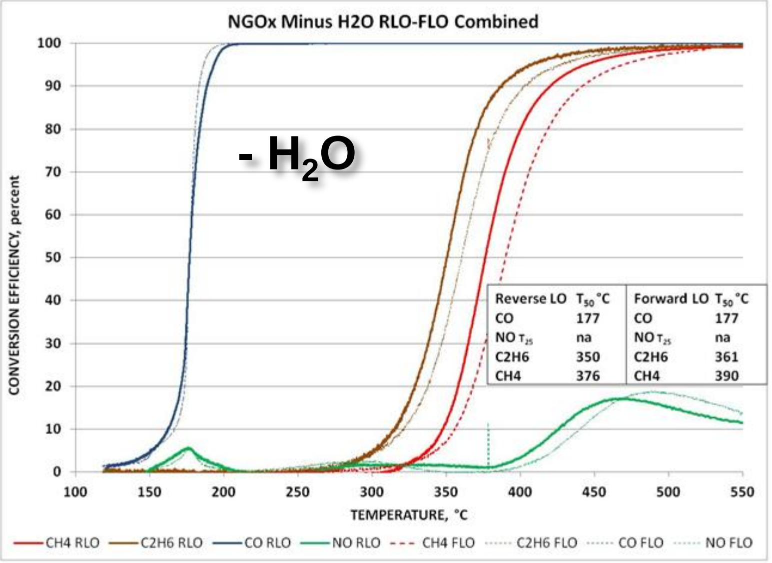
- **CH_4 Oxidation was Primary Goal**
- **CH_4 T_{50} Light-Offs Around 500°C**
- **Clearly Not an Ideal Catalyst, but Trends Should Still be Valid**



NGOx – minus H_2O

- **Removal of H_2O Clearly Lowers CO and HC Light-Off Temperatures**
  - CH_4 light-off lowered by 116 – 143^{o}C
- **<u>H_2O is a Strong Light-Off Inhibiter</u>**



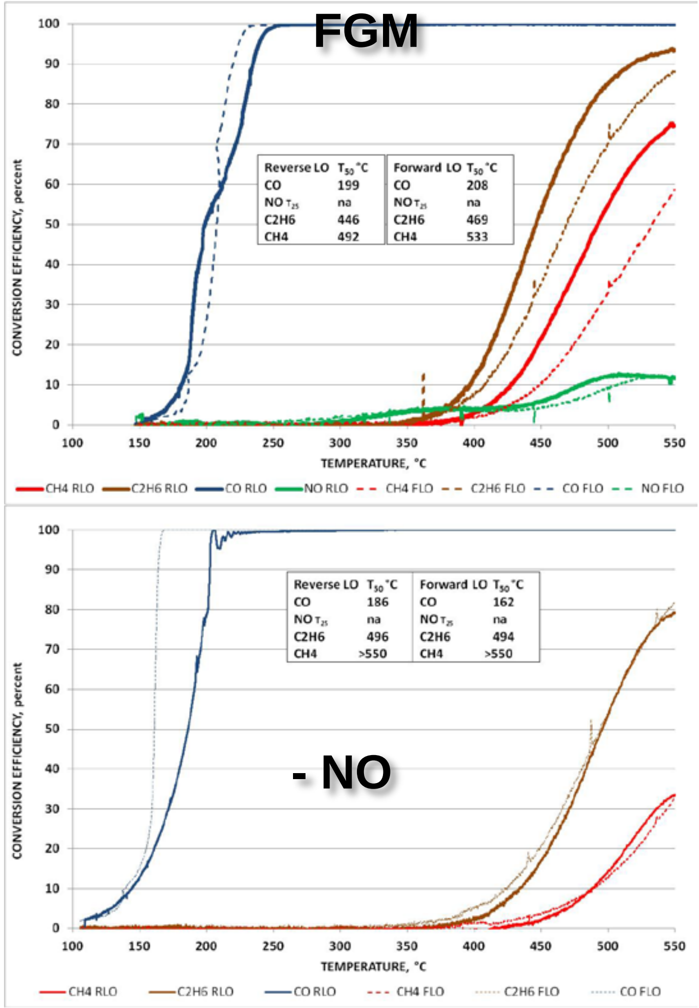


NGOx – minus NO

- **NO Inhibits CO Forward Light-Off,**

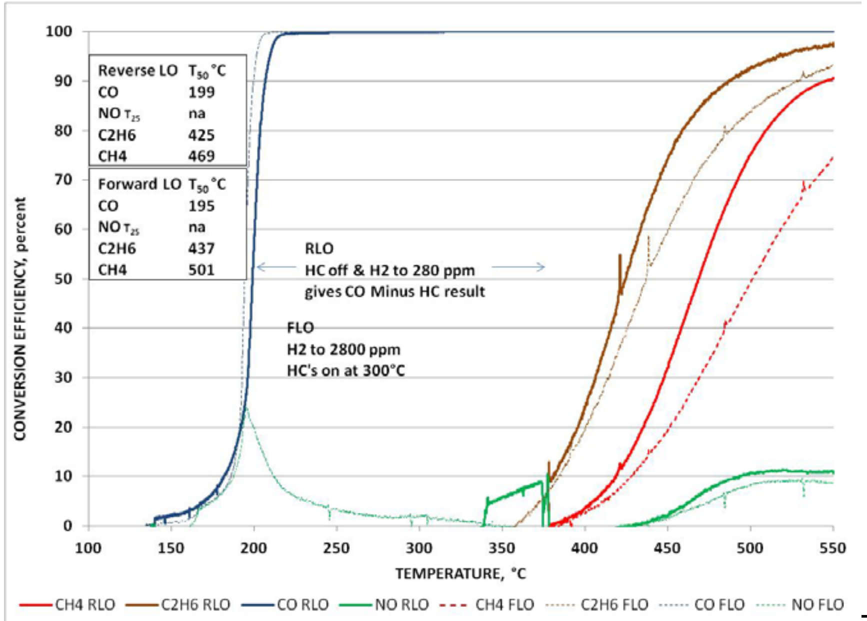
  but

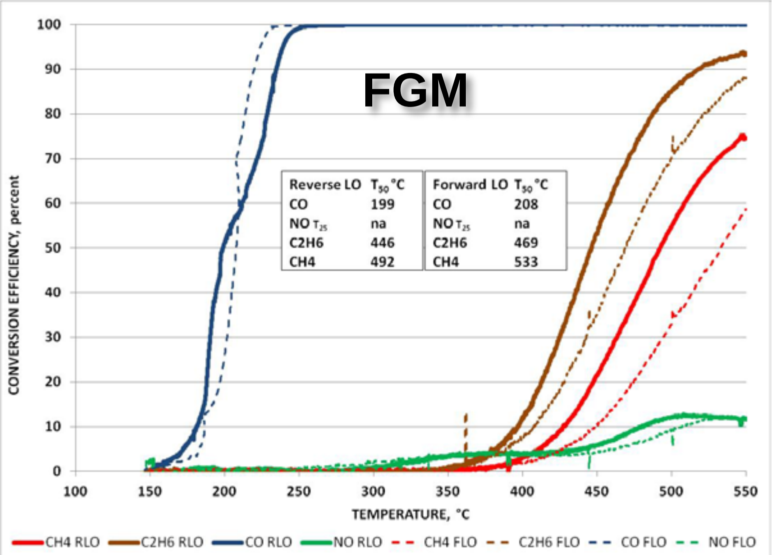
- **NO Promotes HC Light-Off**
  - Lean NO_X catalysis
- **<u>NO is a Promoter for CH_4 Oxidation</u>**

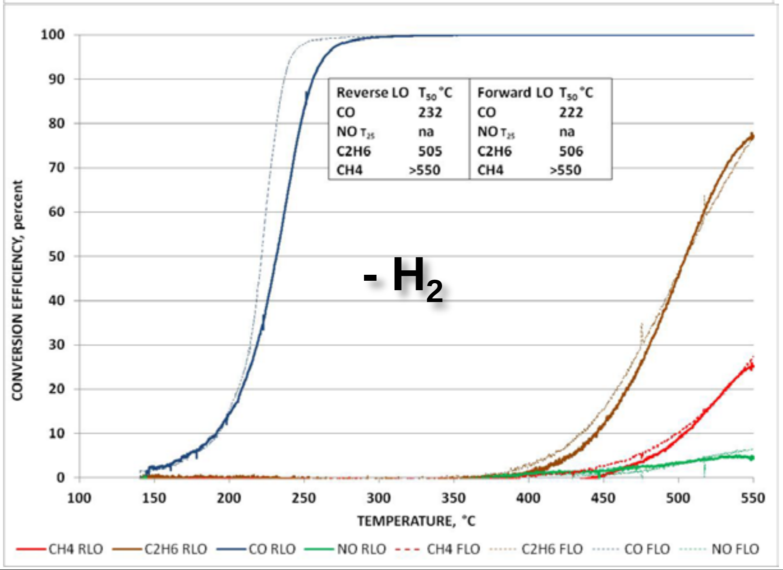


NGOx – H_2 Effect

- **<u>H_2 Promotes CO and HC Light-Off</u>**
- **Increasing H_2 10x Further Improves CH_4 Oxidation Light-Off**
  - FLO 533°C → 501°C
  - RLO 492°C → 469°C







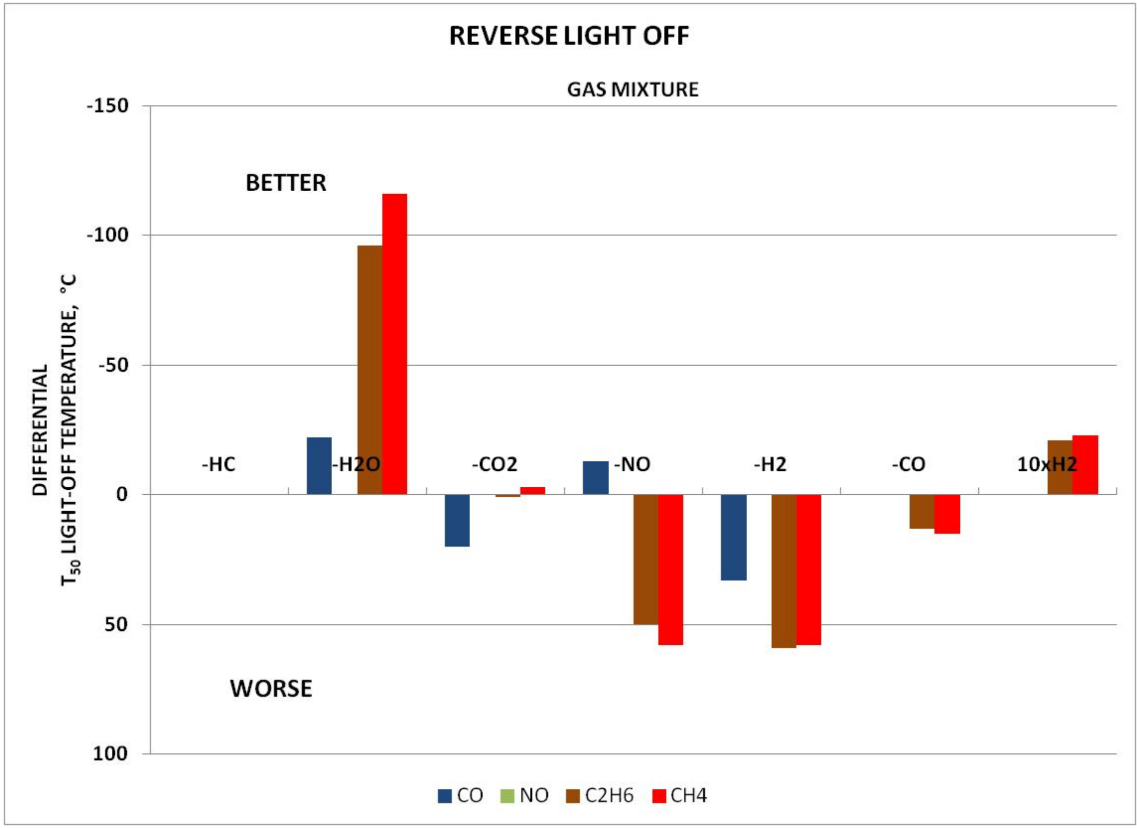
NGOx - Summary

- **H_2O Strongly Inhibits CH_4 Oxidation**
- **NO and H_2 Promote CH_4 Oxidation**

Solutions for Lower Temperature CH_4 Oxidation may Include:

hydrophobic catalyst support

increase NO, H_2 & reduce H_2O in exhaust



Lean NO_X Trap

- **Fresh OEM LNT for 2011 VW Jetta 2.0L TDI**
- **RLO → FLO**
  - lean/rich cycling 200s/50s
    - Intentionally extended to create NO and NH_3 breakthroughs

Gas	Concentration	
	Lean	**Rich**
AFR/λ	15.88/1.088	14.46/0.990
Nitric Oxide (NO)	30 ppm	30 ppm
Propene/Propane 2:1 (C_3H_6/C_3H_8)	67 ppmC3	67 ppmC3
Carbon Monoxide (CO)	0	750 ppm
Hydrogen (H_2)	0	250 ppm
Oxygen (O_2)	1 percent	0
Carbon Dioxide (CO_2)	7.4 percent	7.4 percent
Water (H_2O)	8 percent	8 percent
Nitrogen (N_2)	Balance	Balance

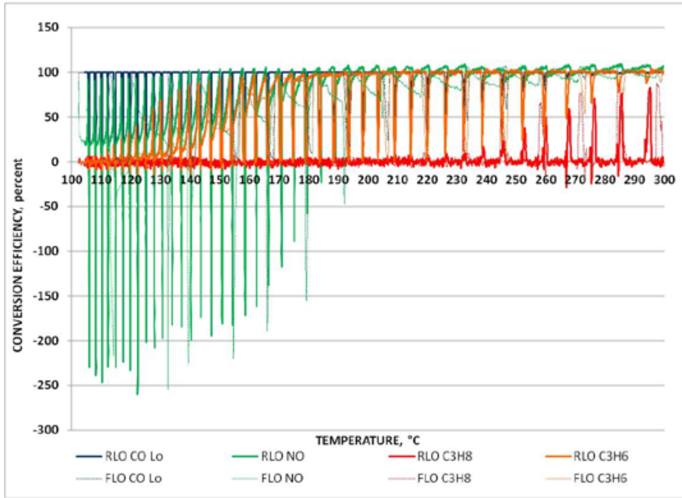
Pt = 78 g/ft^3

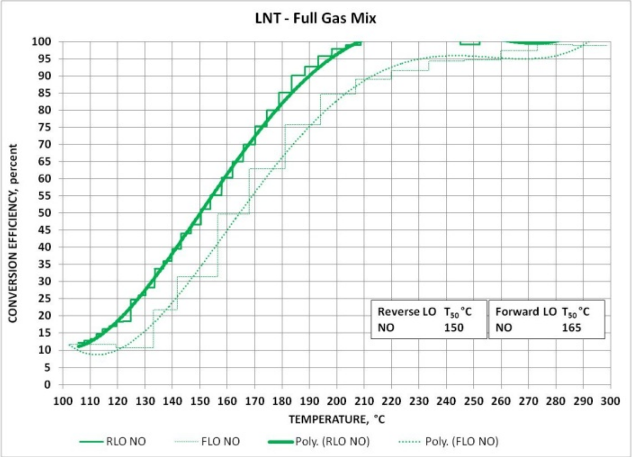
Pd = 13 g/ft^3

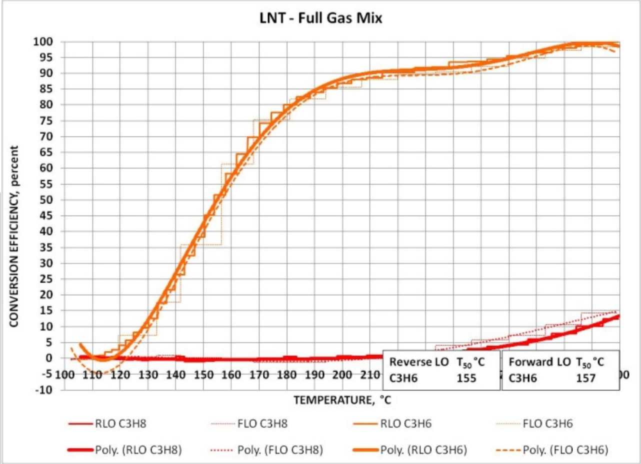
Rh = 7.7 g/ft^3

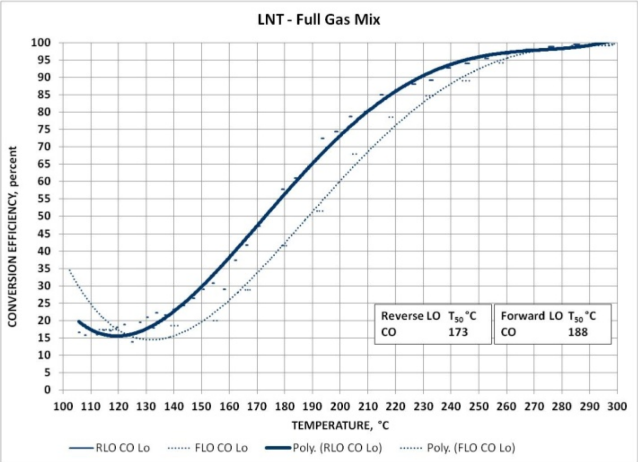
LNT – Cycle Averaging

- **Complex 1 Hertz Data Simplified to Cycle Average Conversion Efficiency**









LNT – Differential Light-Off Behavior

- **H_2O Inhibits NO Light-Off**
- **CO Inhibits NO Light-Off**
- **HCs Inhibit NO Light-Off**

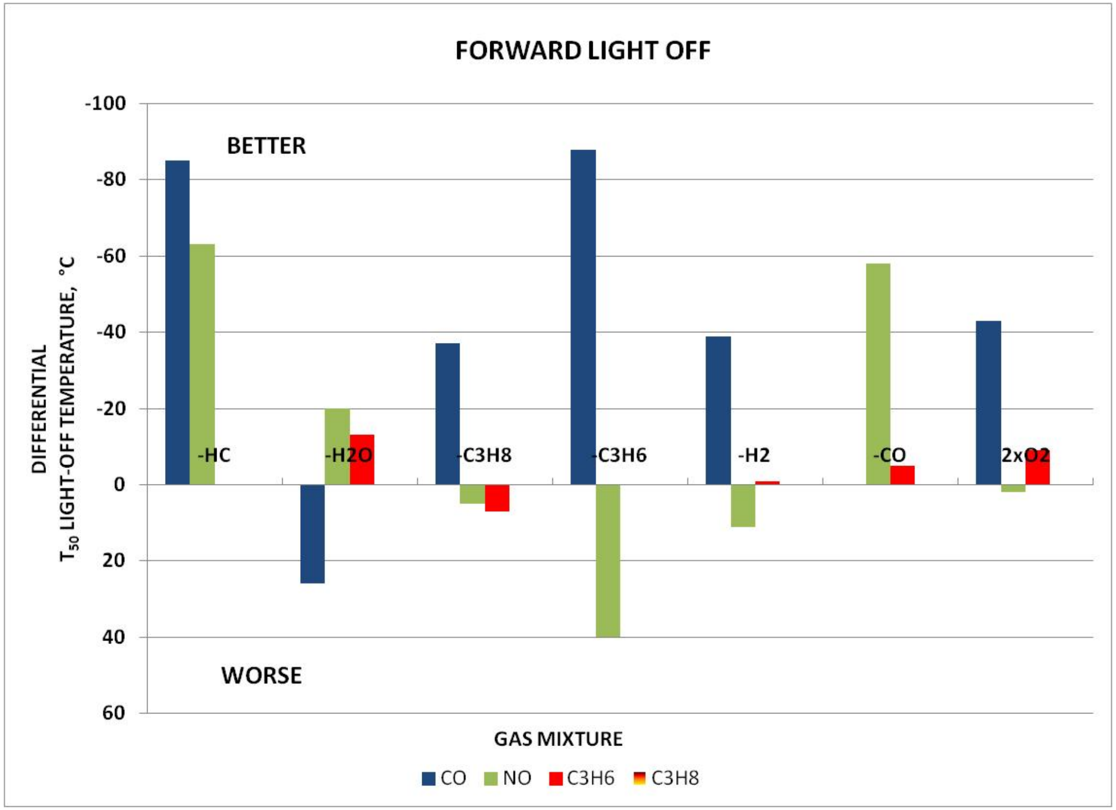
But

- **C_3H_6 Promotes NO Light-Off**

Solutions may include:

cold start HC absorber

decrease cold start CO

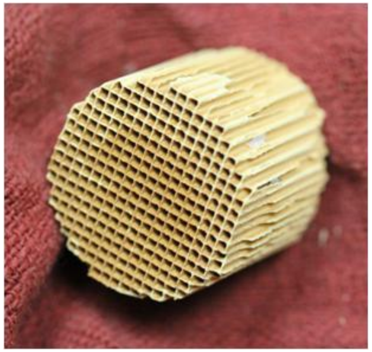


Fe-Zeolite SCR Catalyst

- **Field-Aged, Moderate Mileage, Excellent Condition**
- **RLO only**
  - Forward light-off problems with NH_3 storage and NH_4NO_3 formation
- **Fast Reaction Mixture**

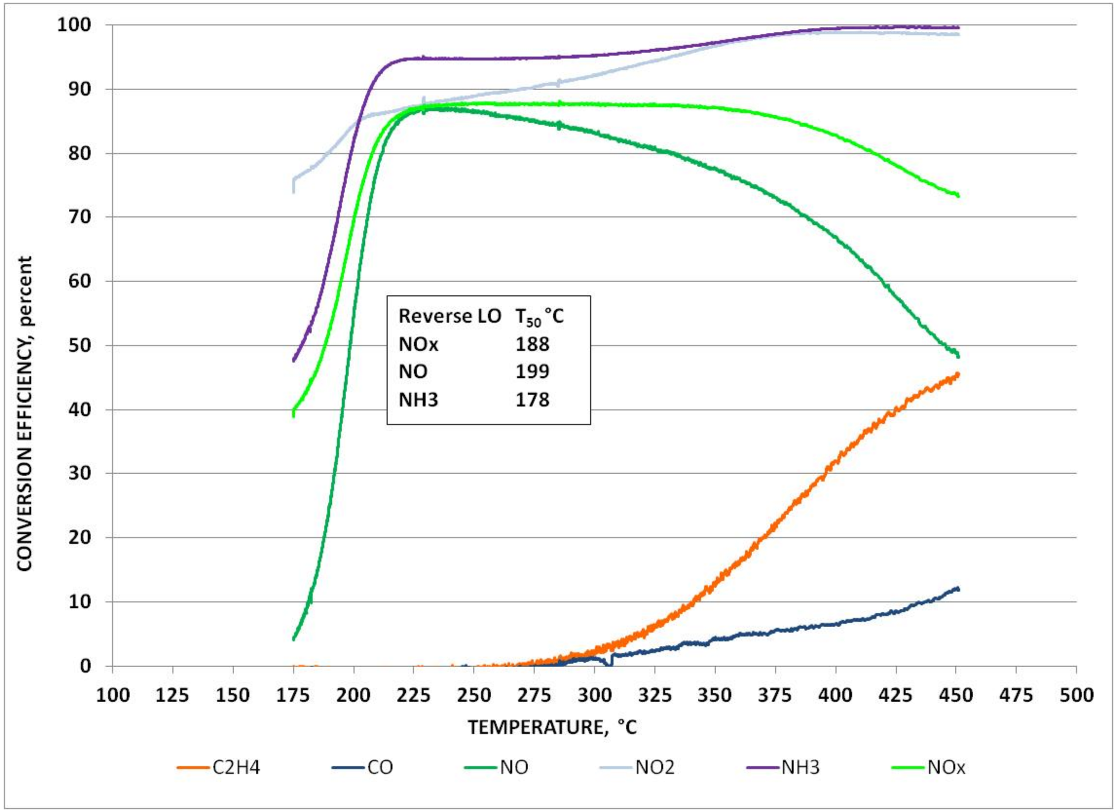
$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$$

Gas	Concentration
	Lean
Nitric Oxide (NO)	300 ppm
Nitrogen Dioxide (NO_2)	300 ppm
Ethylene (C_2H_4)	75 ppmC2
Carbon Monoxide (CO)	300 ppm
Hydrogen (H_2)	100 ppm
Oxygen (O_2)	10 percent
Ammonia (NH_3)	600 ppm
Water (H_2O)	6 percent
Nitrogen (N_2)	Balance



Fe-Zeolite – Full Gas Mix

- **Good NO_X Light-Off Just Above Urea Injection Minimum Temperature**
- **C_2H_4 & CO Light-Offs Coincide with Downturn in NO_X Efficiency**
  - concurrent oxidation of NH_3



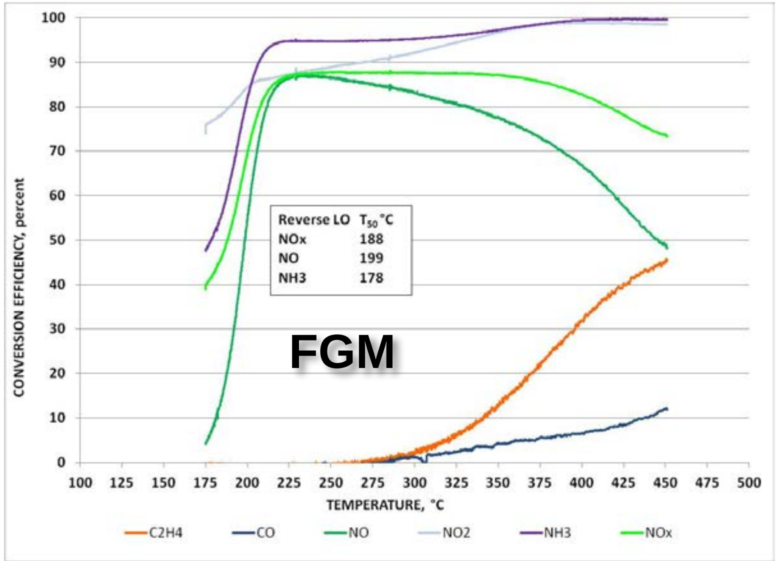
Fe-Zeolite – NO_X Reactions

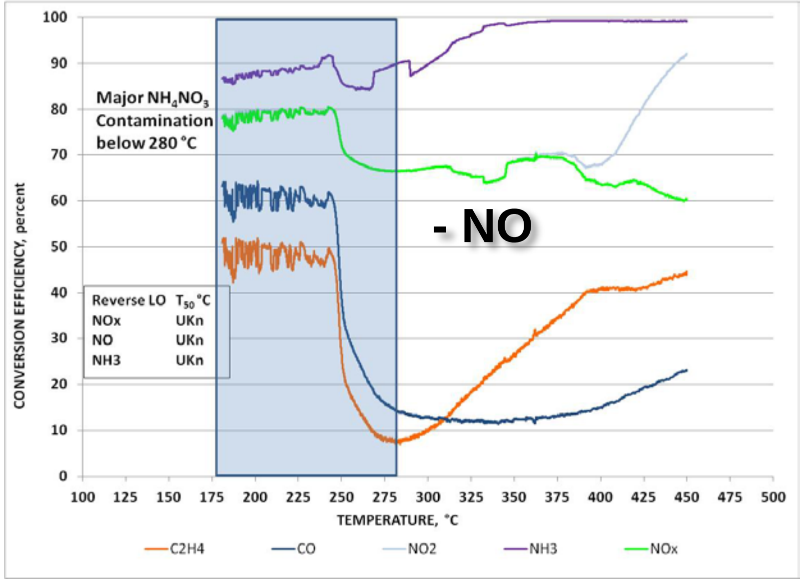
- **Removal of NO_2 (all NO) Switches to Standard Reaction with Higher Light-Offs**

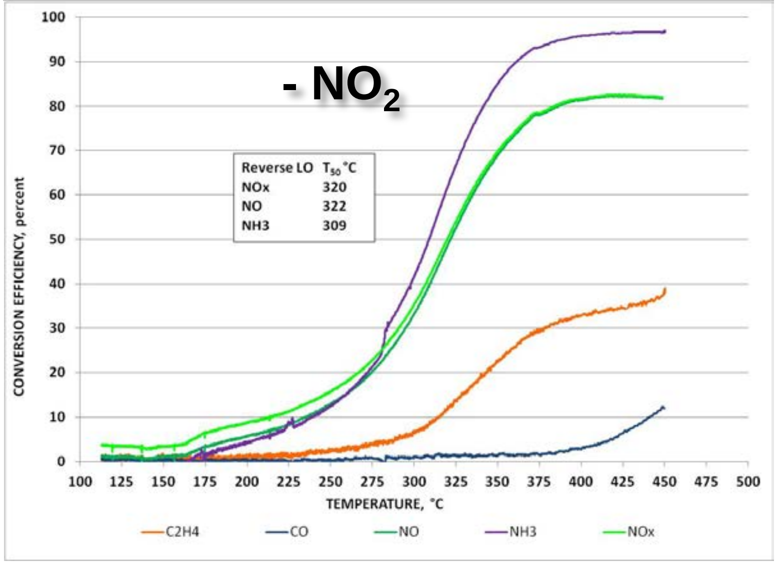
$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$

- **Removal of NO (all NO_2) Results in Low Temperature NH_4NO_3 Formation**

$2NO_2 + 2NH_3 \rightarrow N_2 + NH_4NO_3 + H_2O$

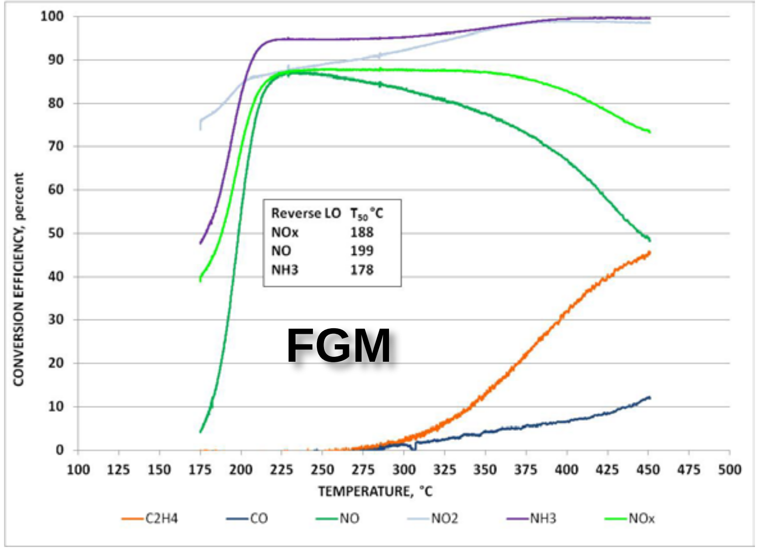


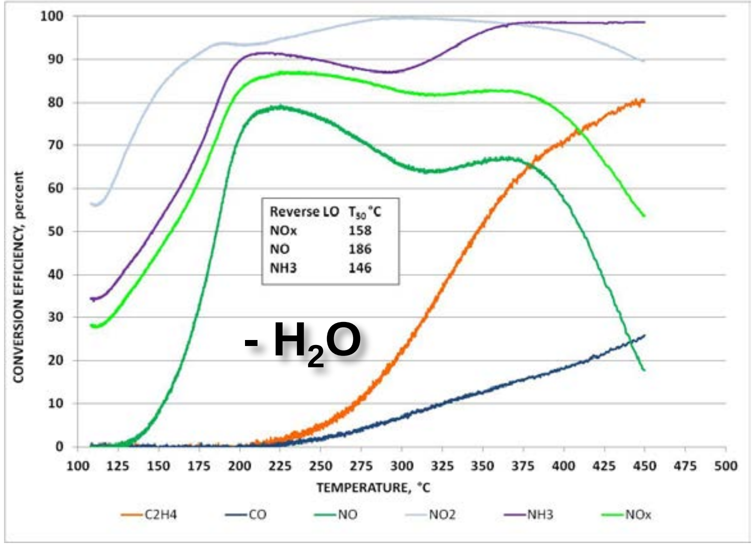




Fe-Zeolite – minus H_2O

- **Removal of H_2O Lowered NO_X, HC and CO Light-Offs**
- **<u>H_2O is an Inhibiter</u>**



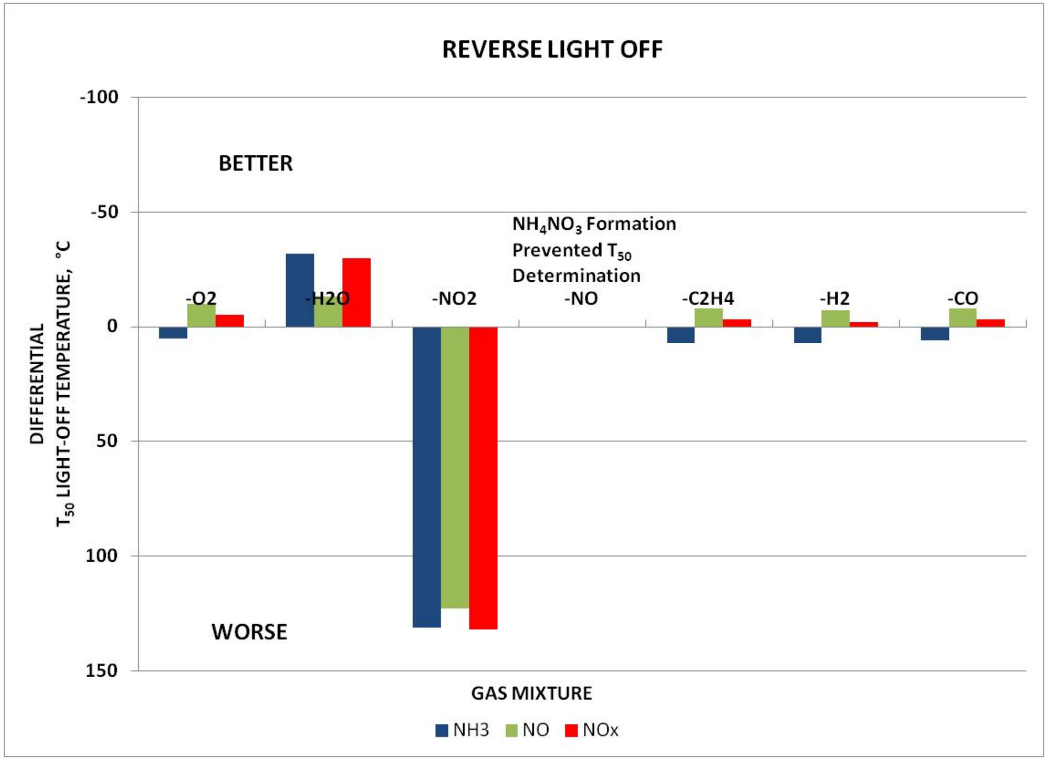


Fe-Zeolite - Summary

- **Normal NO_X Reaction Behaviors**
- **H_2O Inhibits NO_X Light-Off**

Solutions for lower temperature NO_X light-off may include:

Use of a different reductant than urea e.g. H_2



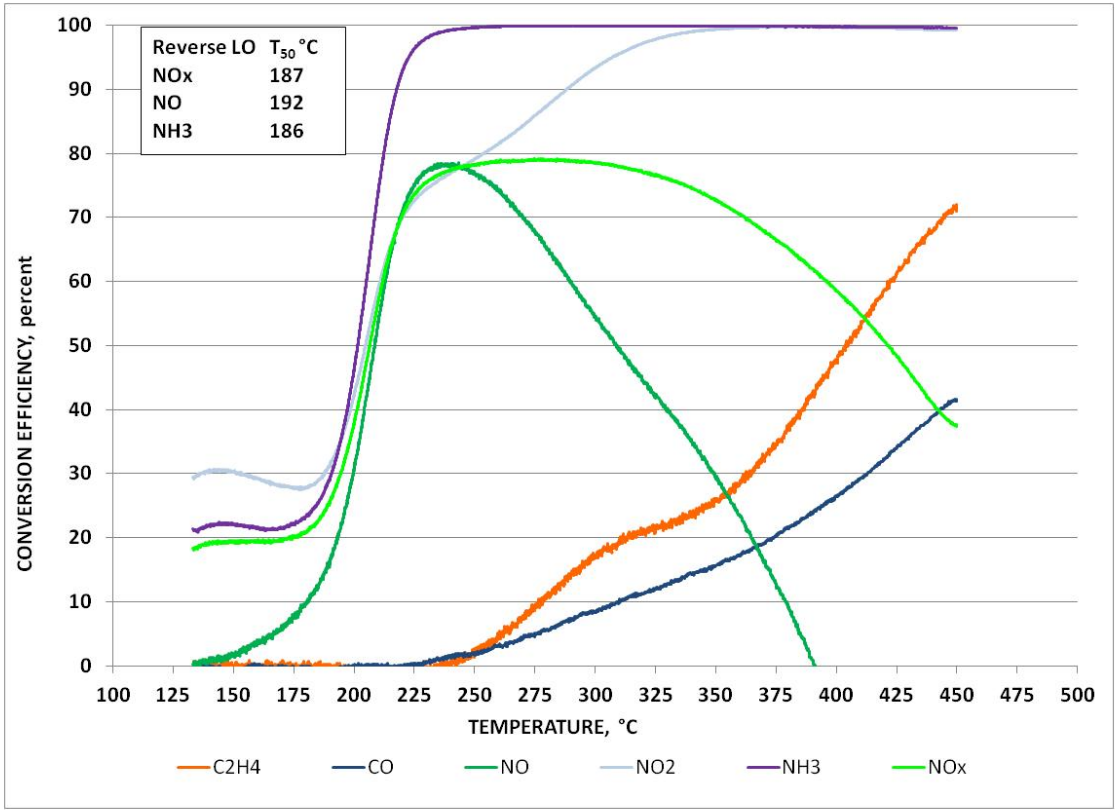
Cu-Zeolite SCR Catalyst

- **USGR-aged, 16 hrs, 775^{o}C, 14% O_2, 5% CO_2, 6% H_2O, bal N_2**
- **RLO only**
- **Same Gas Mix as for Fe-zeolite**

Gas	Concentration Lean
Nitric Oxide (NO)	300 ppm
Nitrogen Dioxide (NO_2)	300 ppm
Ethylene (C_2H_4)	75 ppmC2
Carbon Monoxide (CO)	300 ppm
Hydrogen (H_2)	100 ppm
Oxygen (O_2)	10 percent
Ammonia (NH_3)	600 ppm
Water (H_2O)	6 percent
Nitrogen (N_2)	Balance

Cu-Zeolite – Full Gas Mix

- **Good NO_X Light-Off Just Above Urea Injection Minimum Temperature**
- **C_2H_4 & CO Light-Offs Coincide with Downturn in NO_X Efficiency**
  - concurrent oxidation of NH_3

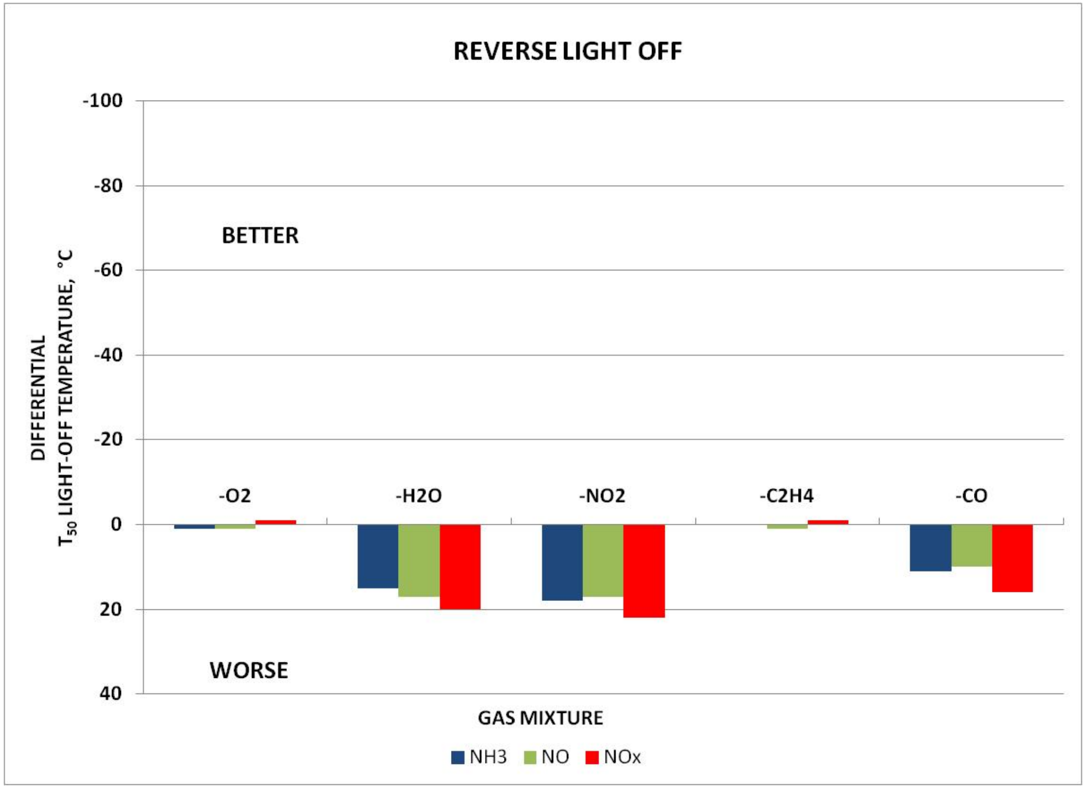


Cu-Zeolite - Summary

- **No Inhibiters Identified**
- **<u>H_2O, NO_2 & CO all Mild Promoters</u>**

Solutions for lower temperature NO_X light-off may include:

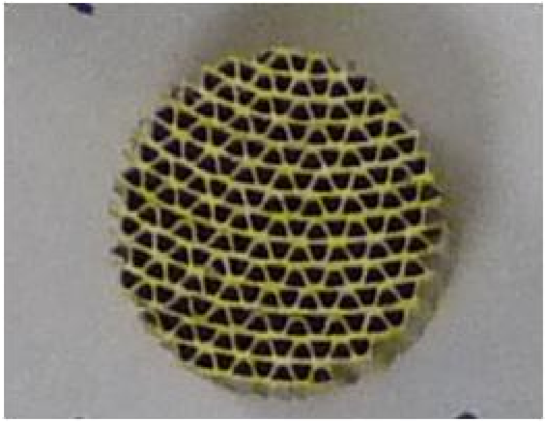
Use of a different reductant than urea e.g. H_2



V-SCR Catalyst

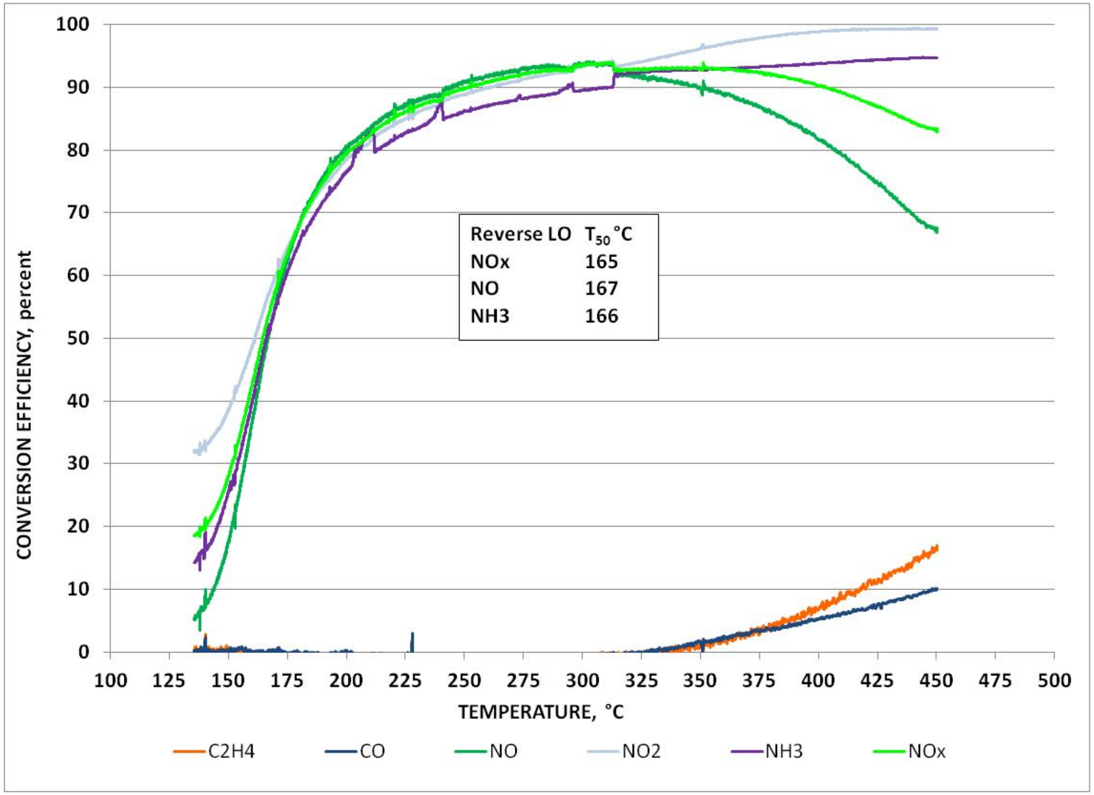
- **Engine-Preconditioned, 24 hrs DAAAC Cycle Using 2004 Caterpillar C15**
- **RLO only**
- **Same Gas Mix as for Fe-Zeolite**

Gas	Concentration
	Lean
Nitric Oxide (NO)	300 ppm
Nitrogen Dioxide (NO_2)	300 ppm
Ethylene (C_2H_4)	75 ppmC2
Carbon Monoxide (CO)	300 ppm
Hydrogen (H_2)	100 ppm
Oxygen (O_2)	10 percent
Ammonia (NH_3)	600 ppm
Water (H_2O)	6 percent
Nitrogen (N_2)	Balance



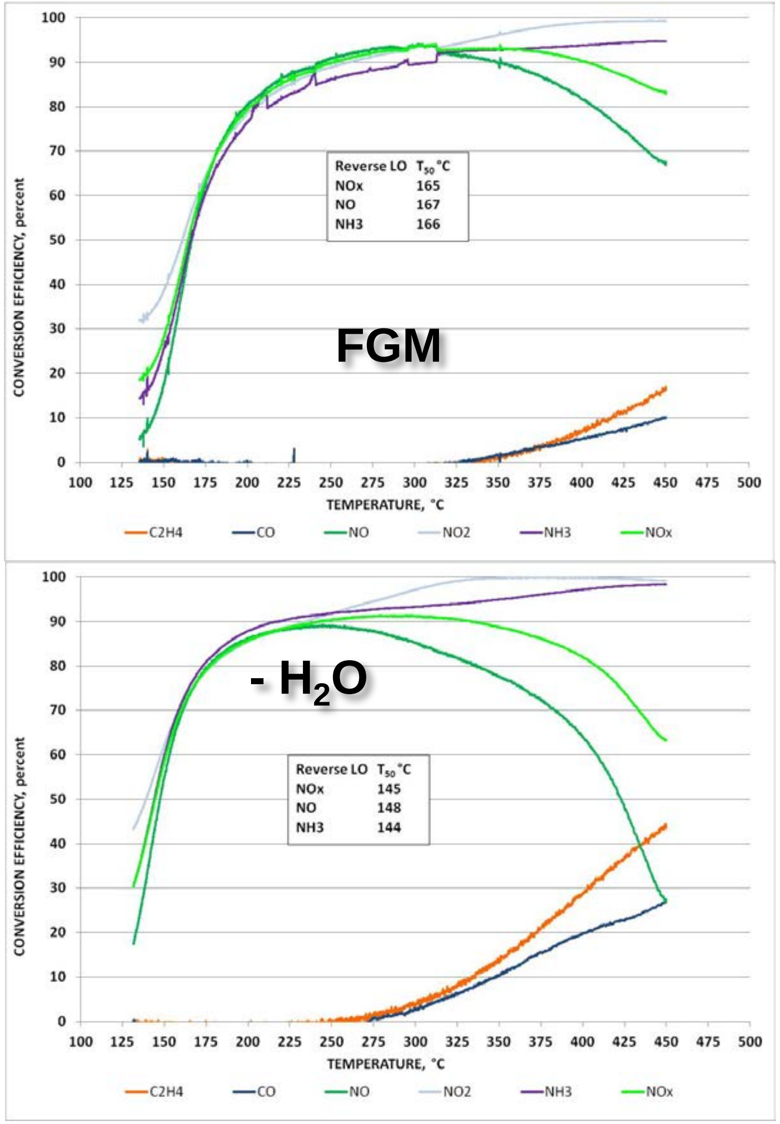
V-SCR – Full Gas Mix

- **Excellent NO_X Light-Off *Below* Urea Injection Minimum Temperature**
- **C_2H_4 & CO Light-Offs Coincide with Downturn in NO_X Efficiency**
  - concurrent oxidation of NH_3



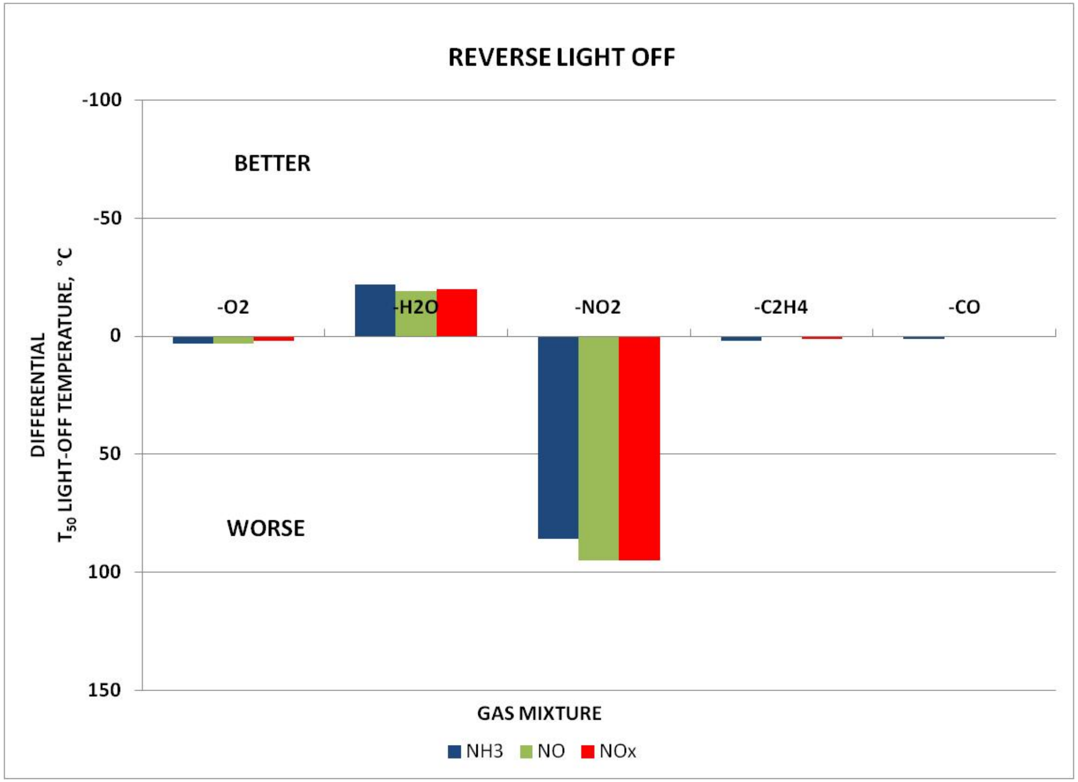
V-SCR – minus H_2O

- **Removal of H_2O Lowered NO_X, HC and CO Light-Offs**
- **<u>H_2O is an Inhibiter</u>**
- **NO_X T_{50} Light-Off at 145°C !**
  - well below urea minimum temperature



V-SCR - Summary

- H_2O Inhibits NO_X Light-Off
- No Other Inhibiters Outside of Normal SCR Behavior



Solutions for lower temperature NO_X light-off may include:

Use of a different reductant than urea e.g. H_2

AMOx Catalyst

- **State-Of-The-Art Formulation (zeolite over Pt), Hydrothermally Aged 72 hrs at 620^{o}C**
- **RLO-FLO**

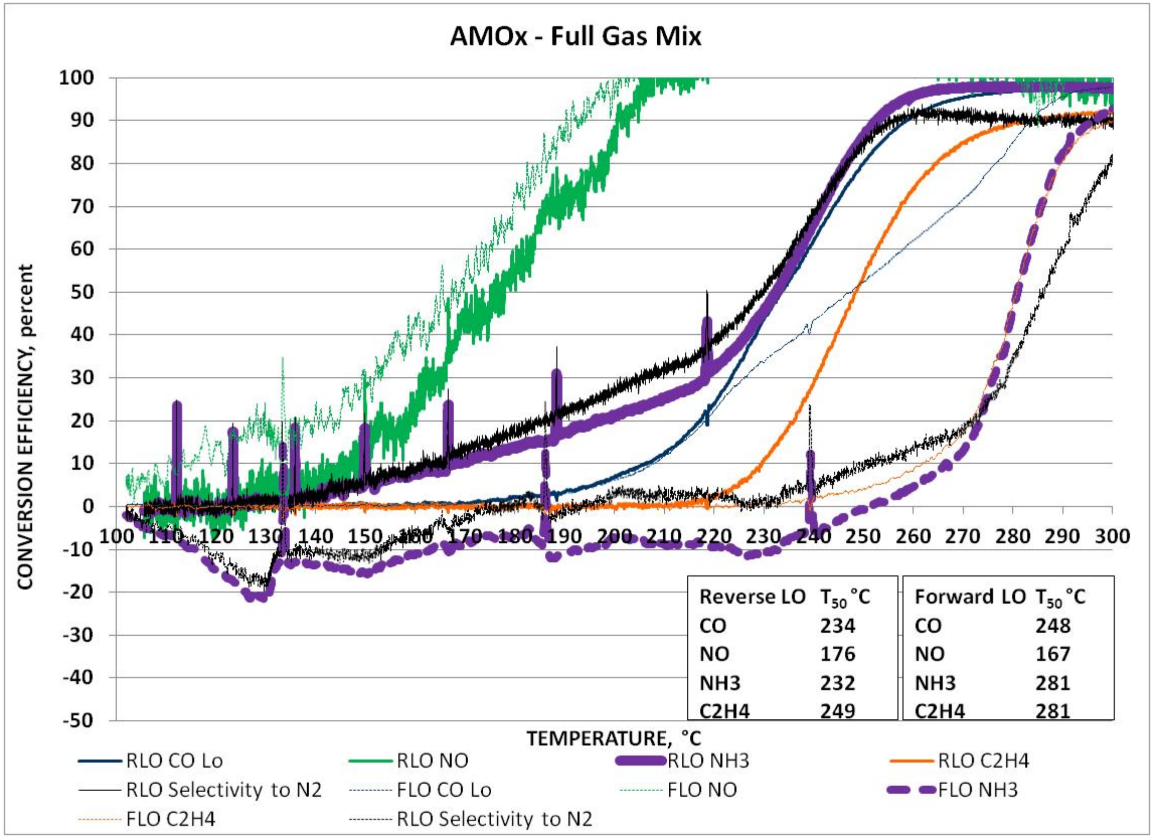
Pt = 0.012 wt%

Cu = 0.469 wt%

Gas	Concentration
	Lean
Nitric Oxide (NO)	15 ppm
Ammonia (NH_3)	100 ppm
Ethylene (C_2H_4)	75 ppmC2
Carbon Monoxide (CO)	300 ppm
Hydrogen (H_2)	100 ppm
Oxygen (O_2)	10 percent
Carbon Dioxide (CO_2)	5.6 percent
Water (H_2O)	6 percent
Nitrogen (N_2)	Balance

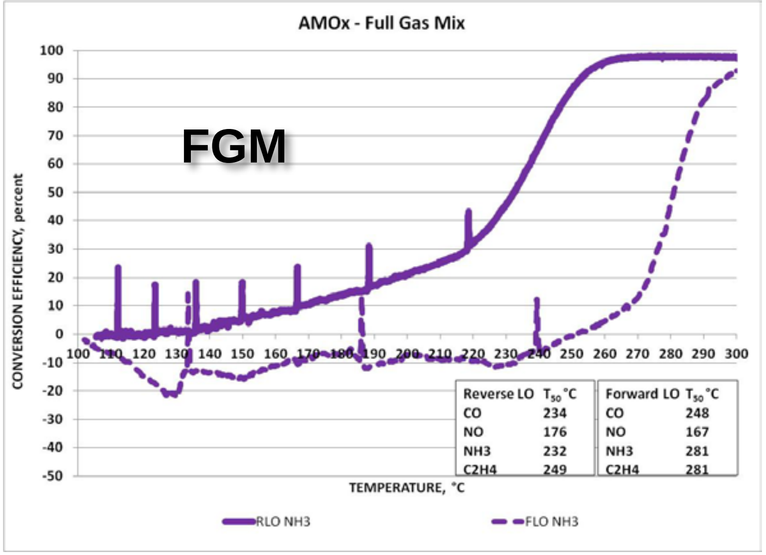
AMOx – Full Gas Mix

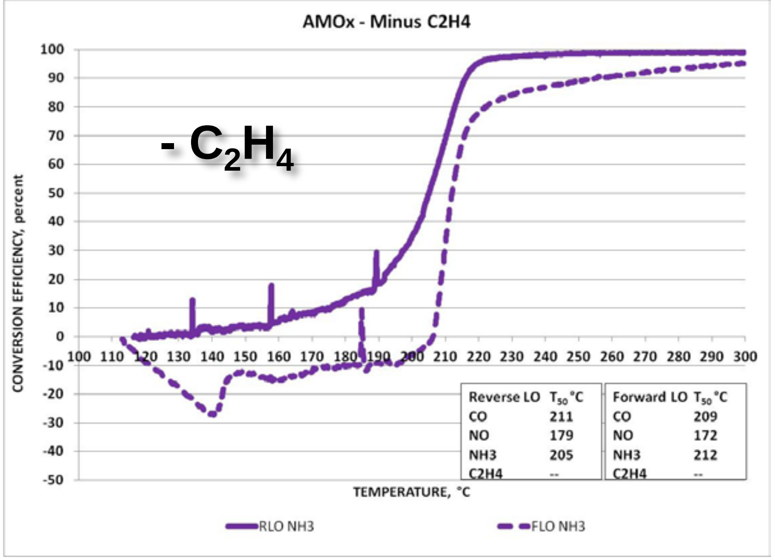
- **RLO NH_3 T_{50} at 232°C**
- **FLO NH_3 Desorption (Negative Conversion Efficiency) and Elevated Light-Off at T_{50} = 281°C**



AMOx – minus ethene (C_2H_4)

- **Removal of C_2H_4 Lowered NH_3 Light-Off by 27 – 69°C**
- **<u>C_2H_4 is an Inhibiter</u>**
- **If AMOx is Downstream of DOC/DPF/SCR, HCs May be Very Low Already**
- **If AMOx is Downstream of SCR Only, HCs Could Cause Issues**



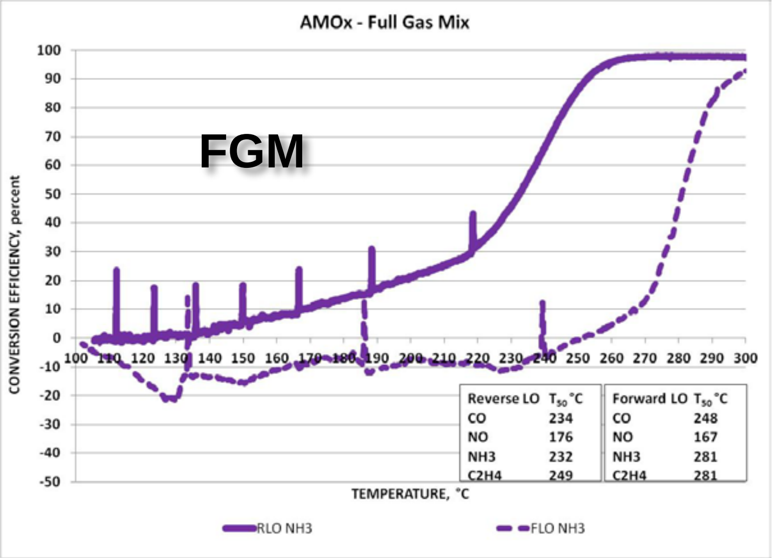


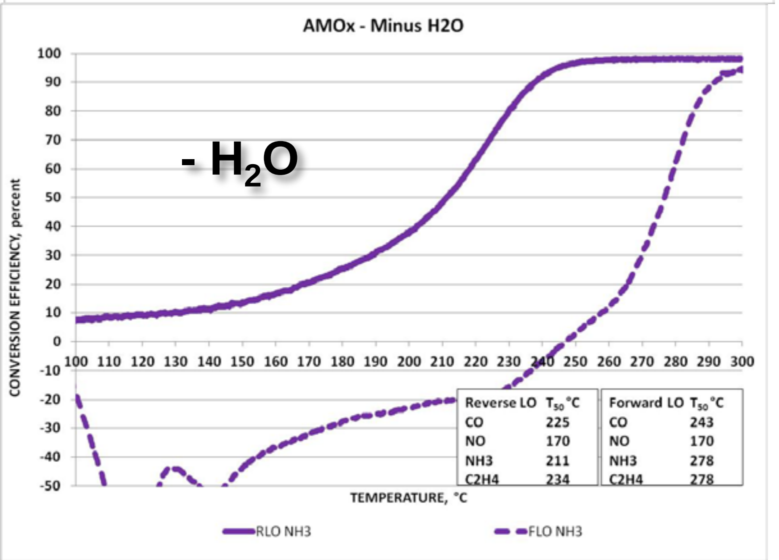
AMOx – minus H_2O

- **Reverse Light-Off Temperature Slightly Lower**
- **Forward Light-Off Temperature Unaffected**
- **<u>H_2O is a Mild Inhibiter</u>**

but

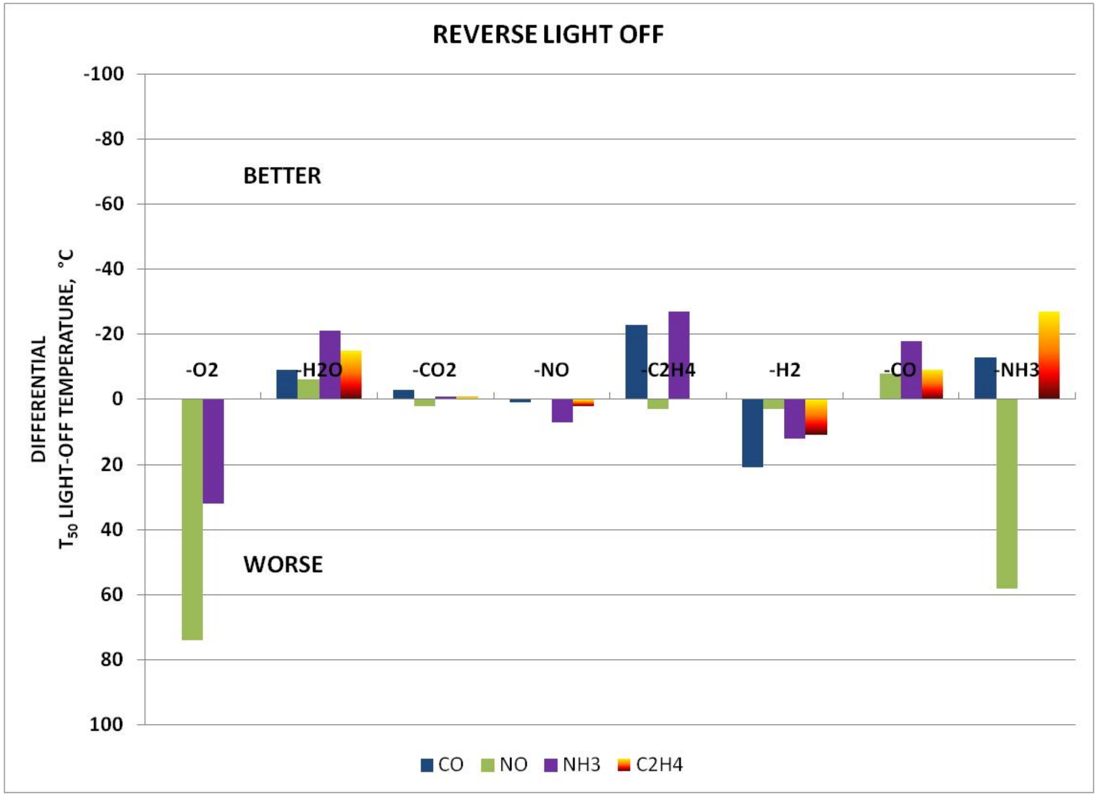
- **Significantly More NH_3 Desorption at Cold Start**
  - Stored H_2O reduces stored NH_3
- **If AMOx is Downstream of SCR Only, HCs Could Cause Issues**
- **If AMOx is Downstream of DOC/DPF/SCR, HCs May be Very Low Already**





AMOx - Summary

- H_2O, C_2H_4 & CO are Inhibiters to NH_3 Light-Off
- O_2 is a Promoter for NH_3 Light-Off



Solutions for lower temperature NH_3 light-off may include:

Upstream DOC/DPF

HC absorber to remove unsaturated HCs

Conclusions

- **The Inhibiters and Promoters are Summarized in the Table**

Catalyst Type	Limiters	Promoters
TWC	NO, C_3H_6	H_2
DOC	NO, C_2H_4, NO_2	CO
SCR – Fe-Z	H_2O	NO_2
SCR – Cu-Z		H_2O, NO_2, CO
SCR – V/W/TiO_2	H_2O	NO_2
LNT	H_2O, C_3H_8+C_3H_6	C_3H_6
AMOx	C_2H_4, CO	H_2
NGOx	H_2O	NO, H_2

THANK YOU