REINHOLD ENVIRONMENTAL Ltd.

# 2017 NOx-Combustion-CCR Round Table Presentation

February 27 & 28, 2017, in Cleveland, OH / Hosted by FirstEnergy

# Reinhold Environmental Conference
# Cleveland, Ohio

## February 27, 2017

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HALDOR TOPSOE

# Agenda

- Introduction of Haldor Topsoe, Inc.
- DNX catalyst basics – importance of catalyst pore structure
- GTC – 802 dual function catalyst basics
- Review of operating history at Exelon, Wolf Hollow Plant
- GTC – 802 operating characteristics
- Value added & what the future CCGT might look like

# Haldor Topsoe
## In brief

- Established in 1940 by Dr. Haldor Topsøe.
- Private 100% family-owned company.
- Market leader in heterogeneous catalysis and surface science for more than 75 years.
- 2,600 employees in 10 countries.
- Headquarters in Copenhagen, Denmark.
- Production in Frederikssund, Denmark, Houston, USA, and Tianjin, China.
- Spends around 10% of revenue on R&D.

2015 revenue
DKK 5,785m
(~USD 850m)

2015 operating profit DKK 502m
(~USD 75m)

# Headquartered in Denmark,
## our 2,600 employees work with customers all over the globe

**Locations:**
Bahrain
Beijing
Buenos Aires
Copenhagen
Dalian
Edmonton
Houston
Joinville
Kuala Lumpur
Los Angeles
Moscow
New Delhi
Rio de Janeiro

- H Headquarters
- P Production
- E Engineering
- S Sales & Service
- R Research & Development

With over **150** different **catalysts**, and the capability to design and manufacture **custom** catalysts and **equipment** for specific tasks, each process is guaranteed to **perform optimally.**

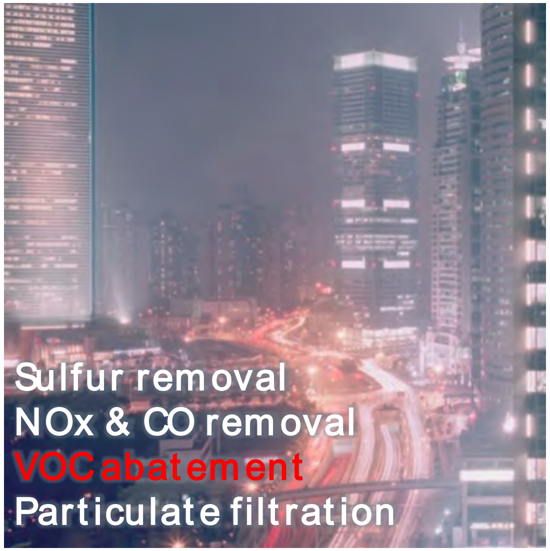
# **We supply a range of more than 150 different catalysts and have the** capability to design and manufacture custom catalysts for specific tasks

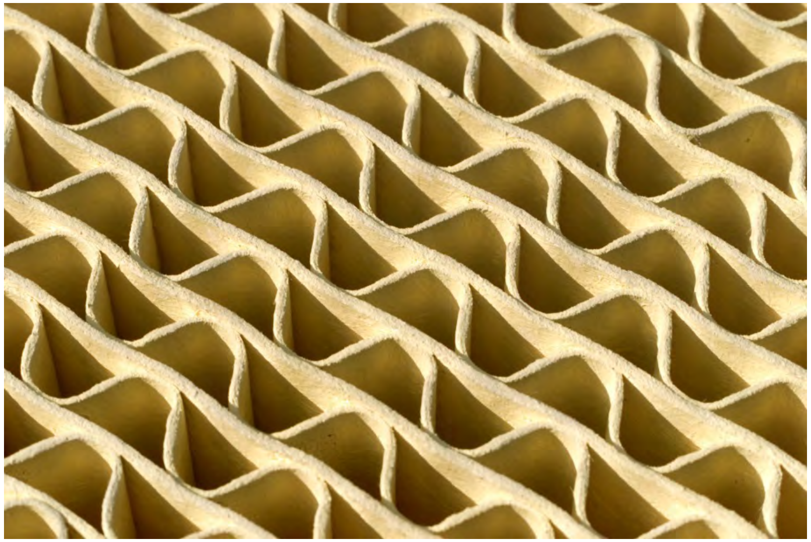
# We design, engineer, and license a broad range of processes for chemical processing, hydroprocessing, and emissions management

## Chemical Processing


## Hydroprocessing


## Emissions Management





# The DNX® Catalyst Basics

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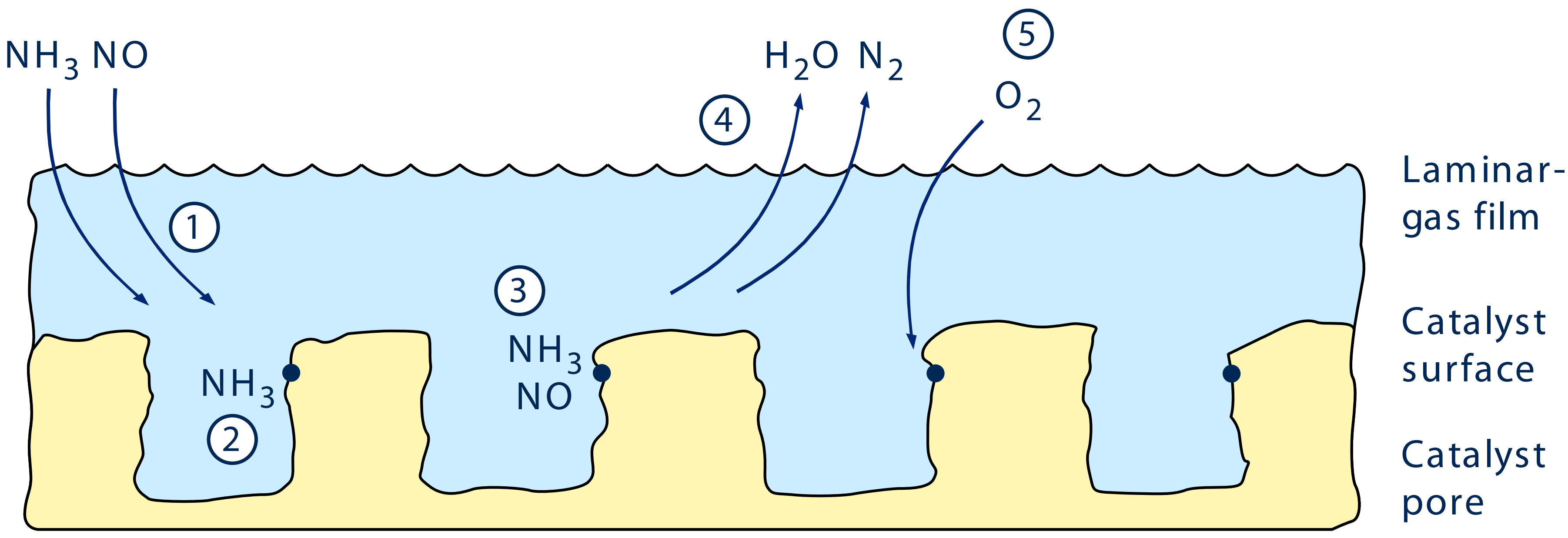
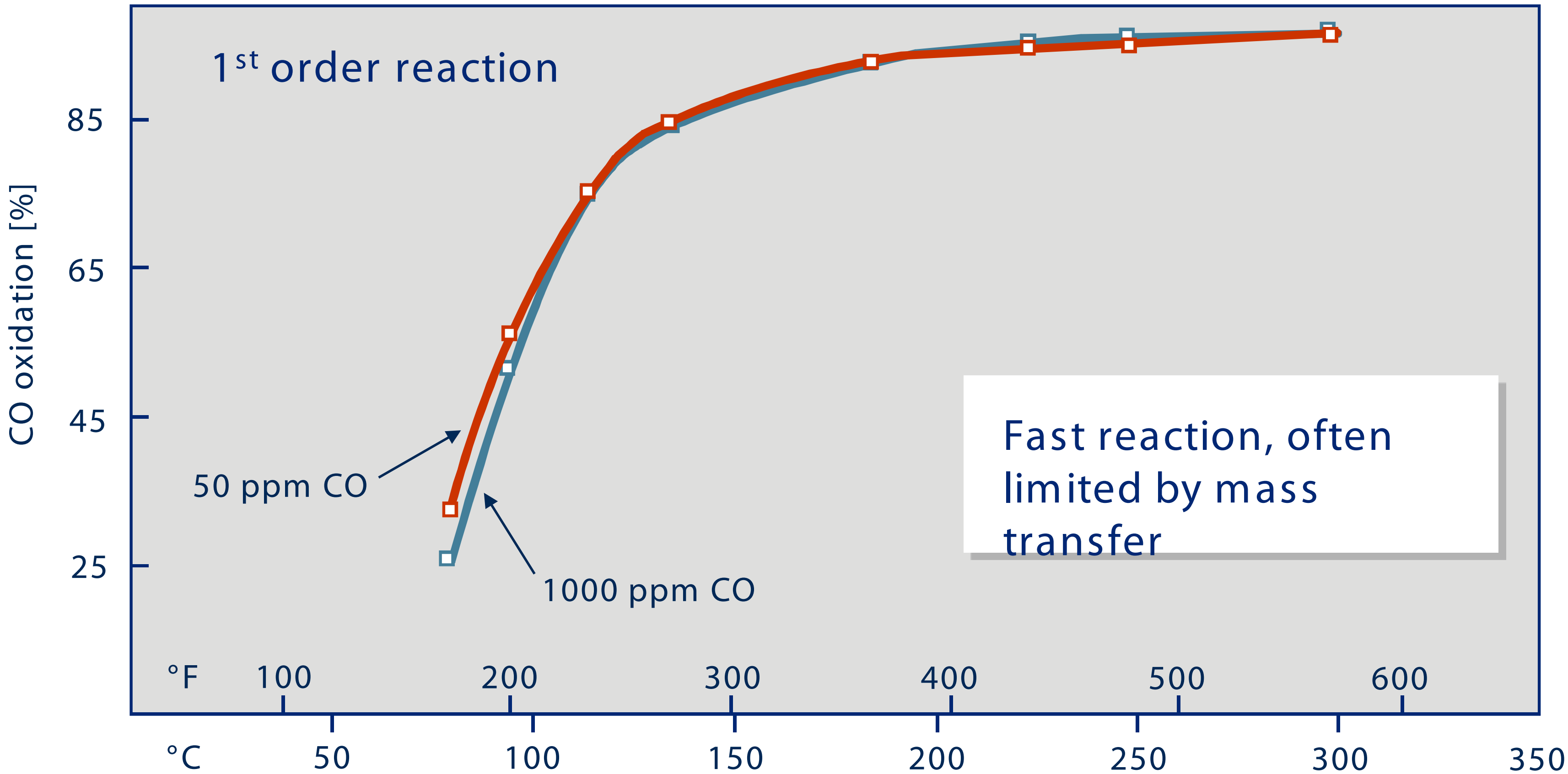
# Basic SCR Reactions

- $4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O$
- $NO + NO_2 + 2\ NH_3 \rightarrow 2\ N_2 + 3\ H_2O$
- $2\ NO_2 + 4\ NH_3 + O_2 \rightarrow 3\ N_2 + 6\ H_2O$



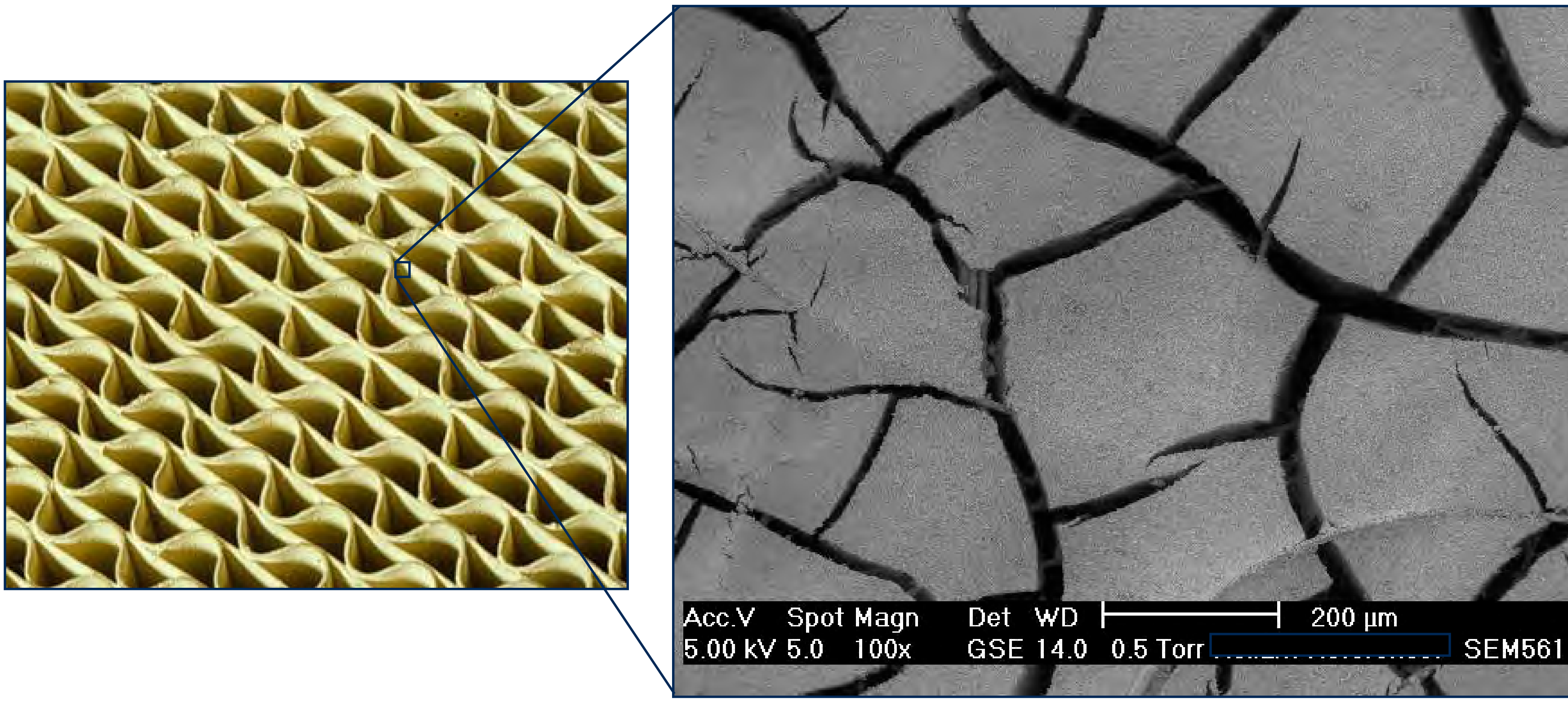
# Basic CO Oxidation

- $CO + ½ O_2 \rightarrow CO_2$



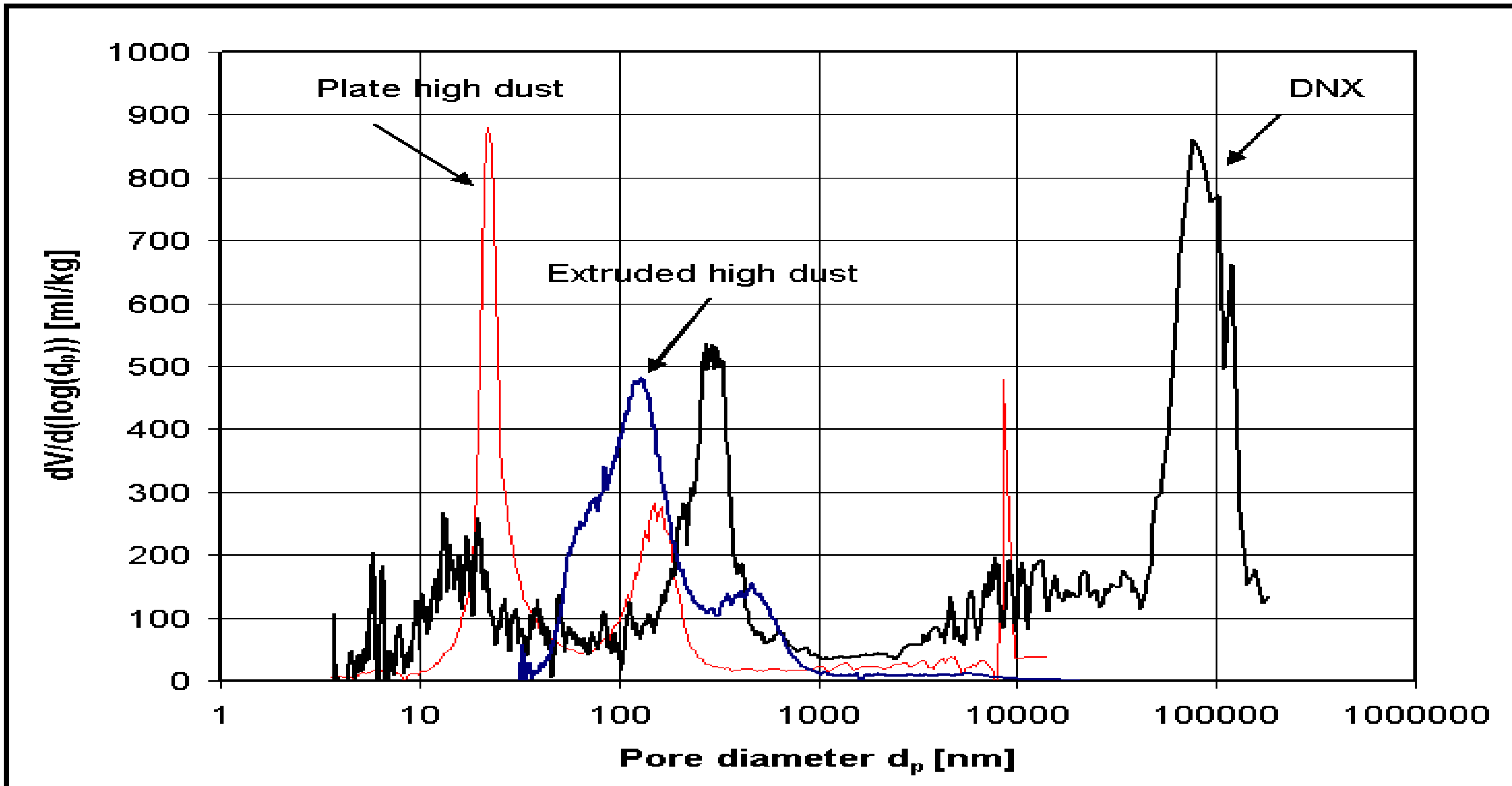
# Advantages of DNX Catalyst – Surface Area

## DeNOx reaction is "Diffusion Limited"
## more highways = higher diffusion rate = higher activity
## Tri-modal pore structure



# Advantages of DNX Catalyst – Pore Volume

- Topsoe tri-modal pore volume compared to plate and extruded catalyst



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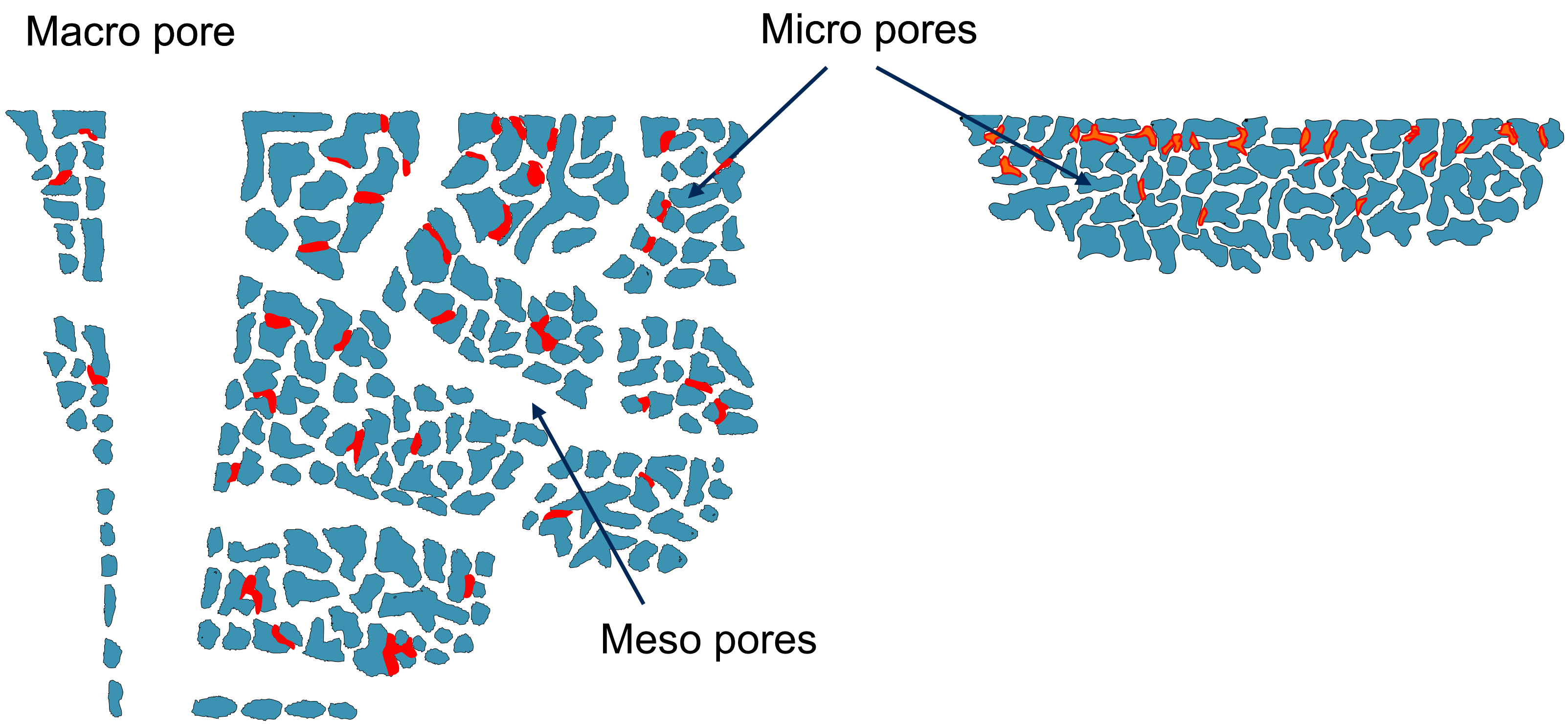
# Pore structures

- Topsøe DNX type catalyst
  - Trimodal pore structure
- Extruded & plate type catalyst
  - Homogenous micro pore structure



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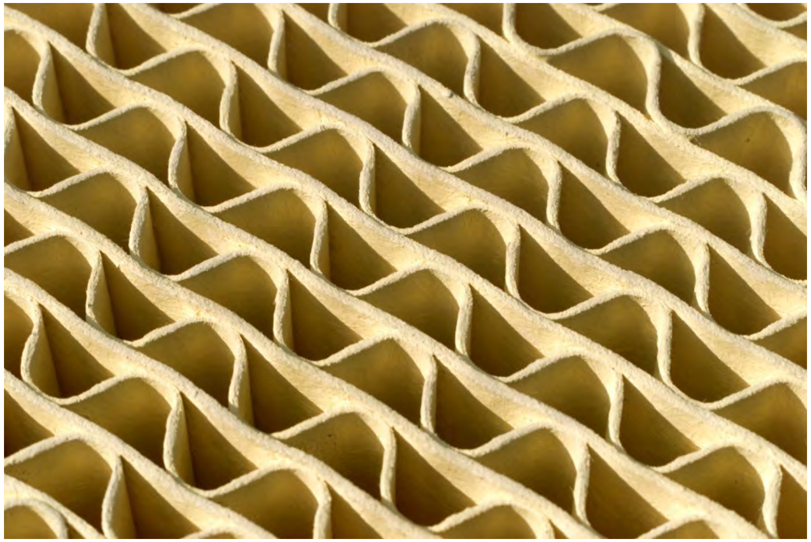

# The DNX® GTC-802 Catalyst Basics

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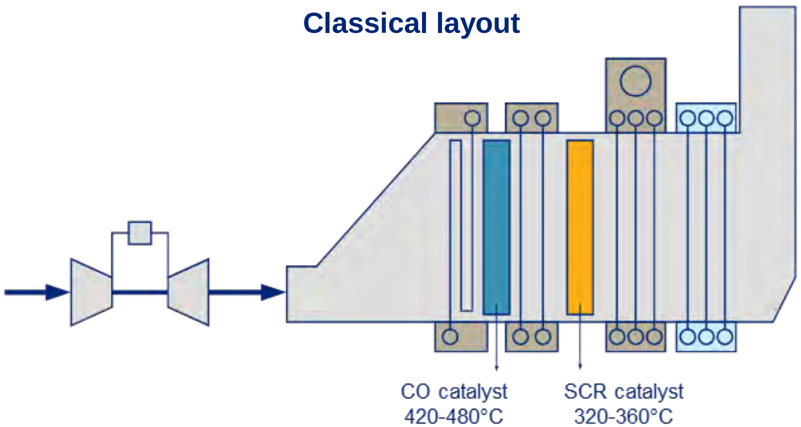
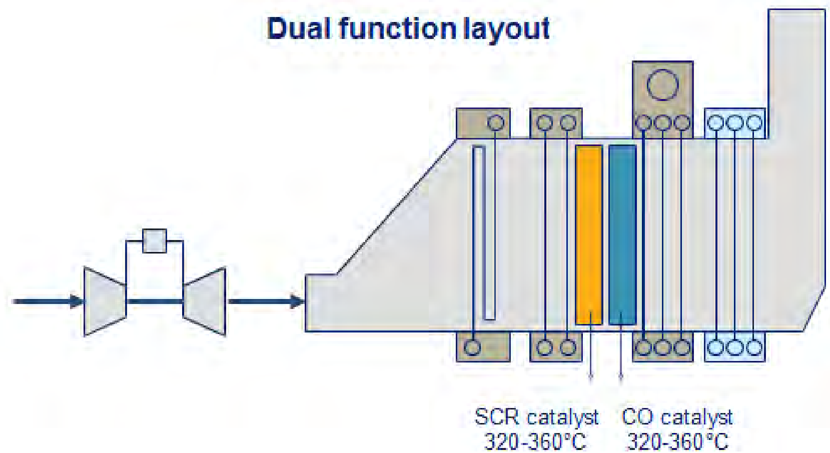
# Comparison – About the Position of the CO Catalyst




| Classical Layout | Dual Function Layout |
|---|---|
| Lower CO-catalyst volumes | Lower specific pressure drop |
| Higher HC oxidation | Lower $SO_2$ oxidation |
| Can't be exposed to $NH_3$ | Not impacted by $SO_2$ |
| Very high $SO_2$ oxidation | Easier installation |
| CO catalyst impacted by $SO_2$ | Liquid ammonia injection |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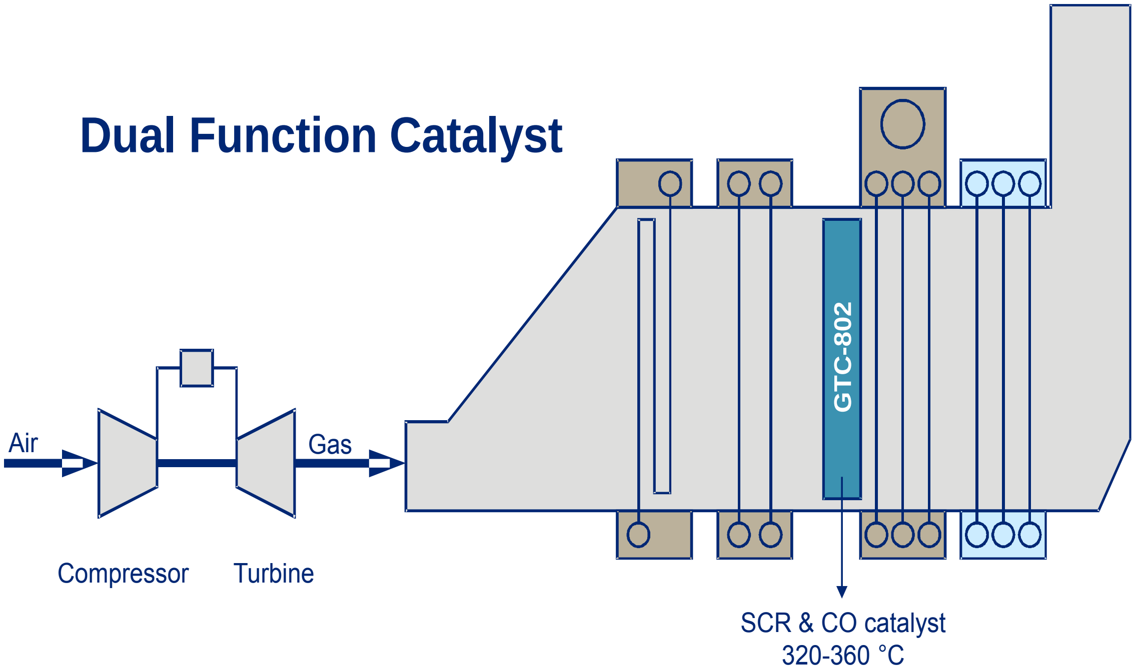
# Performance
# Comparison of the CO Catalyst Locations

## Optimized

### Dual Function Arrangement

- Lowest specific system pressure drop
- Lowest $SO_2$ oxidation
- Lowest NO oxidation
- Easiest installation
- Lower $NH_3$ slip
- Can utilize frameless module design
- Liquid ammonia injection

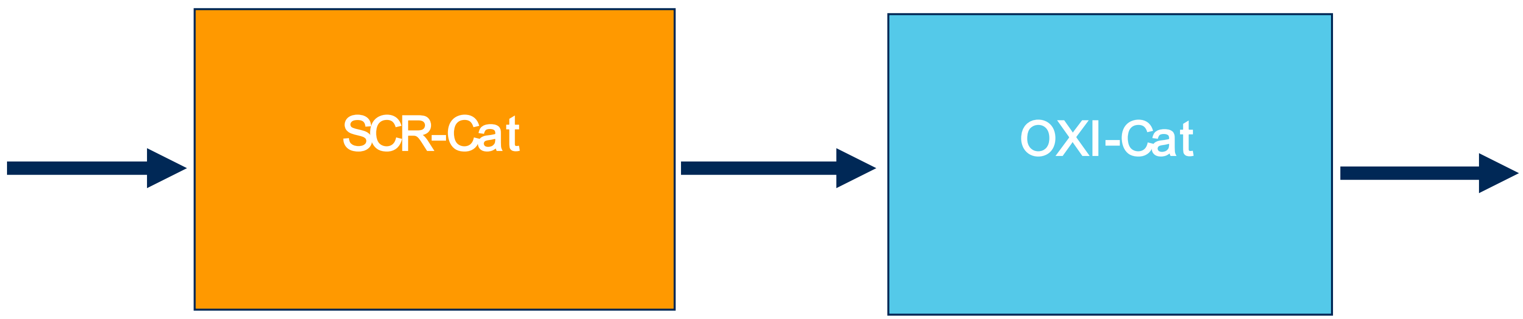
## Dual Function Catalyst



# The Dual Function Position – Reactions

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

$$CO + ½\ O_2 \rightarrow CO_2$$




CO = 100 ppm

NOx = 50 ppm

$NH_3$ = 50 ppm

CO = 100 ppm

NOx < 5 ppm

$NH_3$ < 5 ppm

CO < 5 ppm

NOx < 5 ppm

$NH_3$ < 5 ppm



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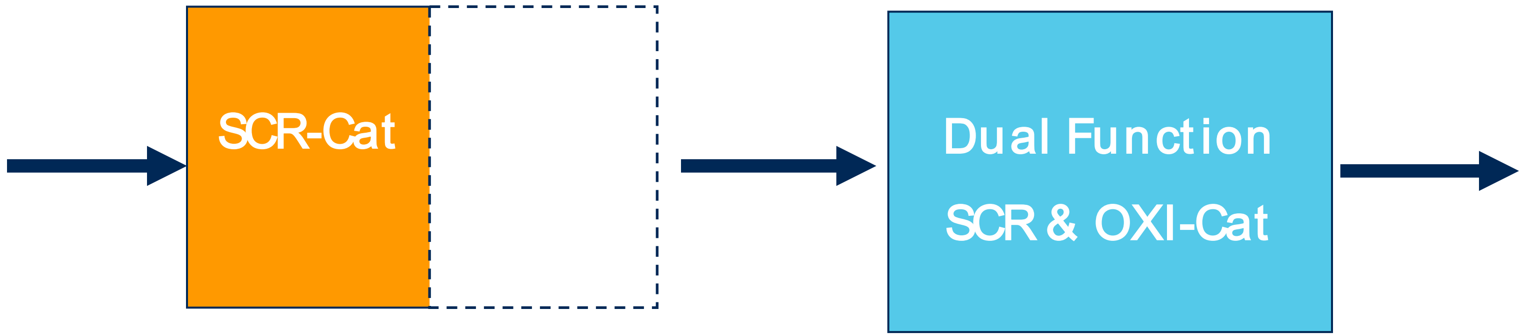
# The Dual Function Catalyst – Basic Principle

- Noble metal based
  - Pd
- Supported on a DeNOx catalyst
  - V,W on Titania




CO = 100 ppm
NOx = 50 ppm
$NH_3$ = 50 ppm

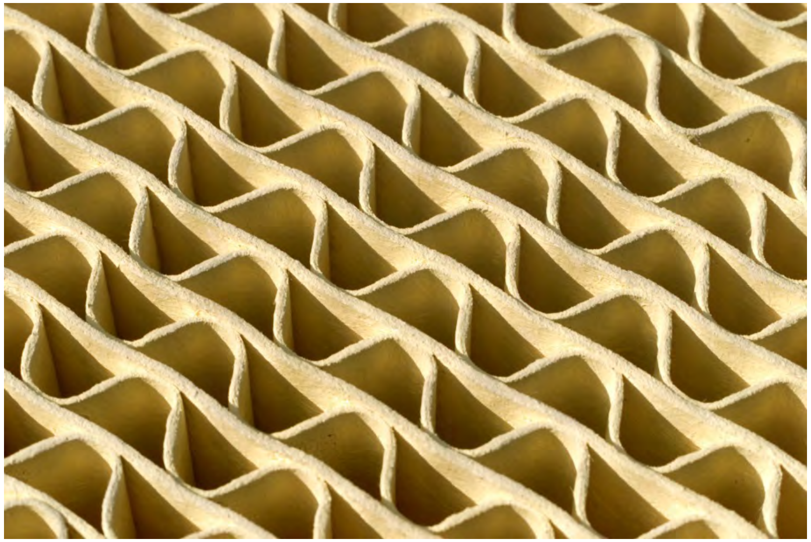
CO = 100 ppm

CO < 5 ppm
NOx < 5 ppm
$NH_3$ < 5 ppm

# Operating Performance – GT/GTC Catalyst Comparison – New Catalyst

| | Catalyst | DeNOx, % | DeCO, % | $NH_3$ slip, ppmv |
|---|---|---|---|---|
| SCR only | GT-201 | 93.5 | 0 | 5.7 |
| Dual function (SCR and CO oxidation) | GTC-802 | 92.9 | 97.8 | 4.4 |

Test conditions: Gas inlet composition: 50 ppmv NOx, 55 ppmv $NH_3$, 100 ppmv CO, 15%vol $O_2$, 10 % vol $H_2O$, $N_2$ balance. Temperature: 350°C / 662°F



# The DNX® GTC-802 Catalyst Performance Results: Exelon, Wolf Hollow, Units 1&2

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# THE STORY
# Exelon Wolf Hollow Units 1&2
# 16 months of operation

# Reference List Dual Function Catalyst: North America

| No. of Units | Location | User Type | | Status |
|---|---|---|---|---|
| 1 | USA | Diesel Engine | | Running |
| 4 | ECUADOR | HRSG | | Unknown |
| 1 | USA | Ethanol | | Running |
| 1 | USA | HRSG (GE LM6000) | | Running |
| 2 | USA | HRSG (Taurus 70) | | Running |
| 7 | USA | Large NG Engine | | Running |
| 3 | USA | Large NG Engine | | Running |
| 2 | USA | Large NG Engine | | Running |
| 3 | USA | Large NG Engine | | Running |
| 2 | USA | HRSG (MHI 501G) | | Running |
| 1 | USA | Boiler | | Running |
| 2 | USA | Auxiliary boilers | | Running |
| 1 | USA | Refinery FCC unit (High Dust) | | Running |
| 1 | USA | Cement Plant (After bag house) | | Running |
| 1 | USA | Carbon Black - Thermal Oxidizer | | Running |
| 1 | USA | Auxiliary boiler | | Running |
| 2 | USA | HRSG (GE 7F.05) | | On Order |
| 1 | USA | Auxiliary boiler | | On Order |
| 2 | USA | Refinery Heater | | On Order |
| 3 | USA | Large NG Engine | | On Order |
| 1 | USA | Large steam methane reformer | | On Order |

# Story: Exelon, Wolf Hollow Plant

Left to Right:

Exelon Generation,

Wolf Hollow Unit 2 & 1

725 MWe

# Story: DNX® GTC Installation, Wolf Hollow Unit 2

DNX® GTC-802

Prior to installation in Unit 2 at Wolf Hollow



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# Story: GTC Catalyst Installation Wolf Hollow Unit 2

# Operating Performance - Wolf Hollow
# INITIAL START-UP

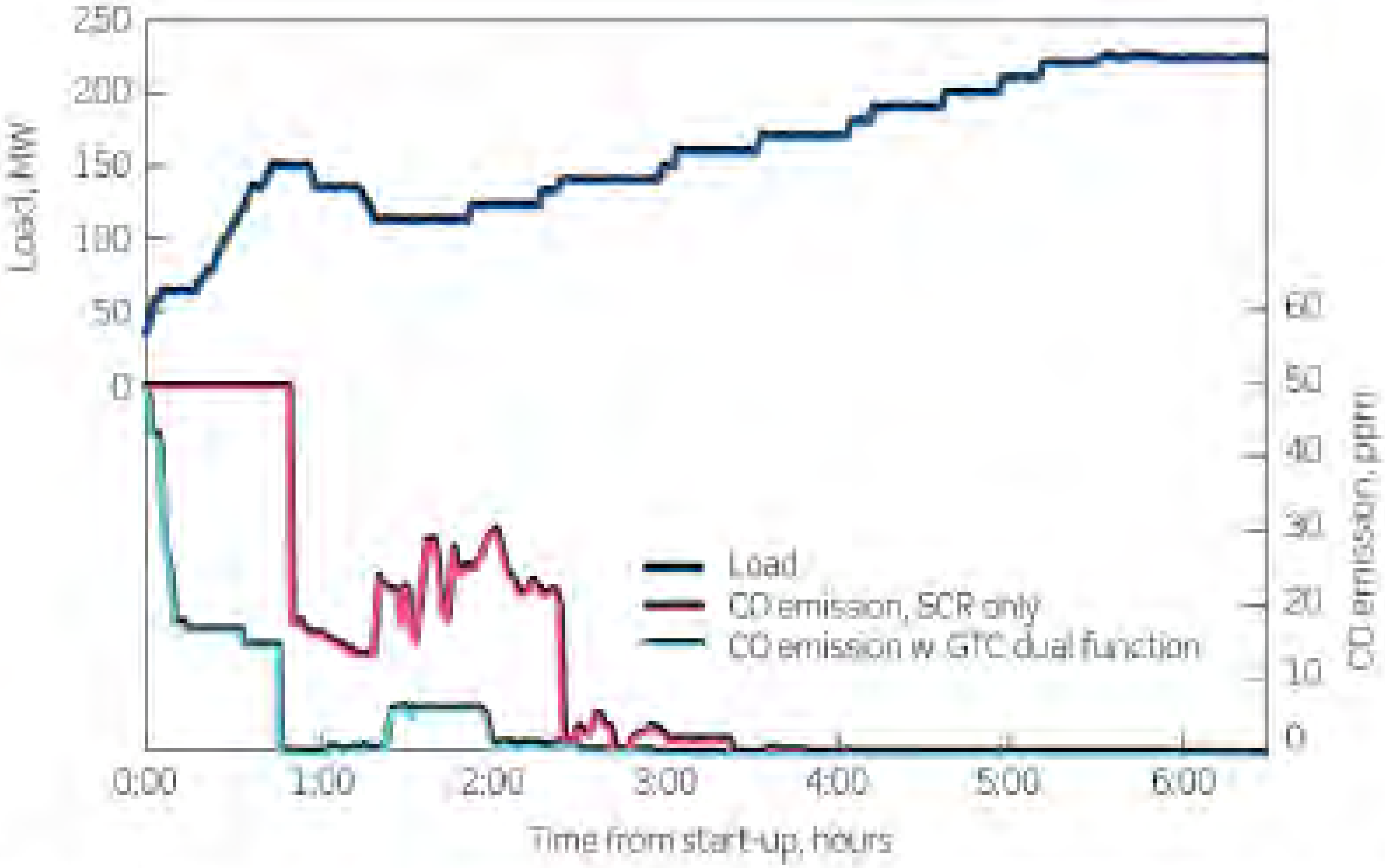



Figure 10 Comparison of performance between DNX® GTC-802 and DNX-929 SCR-only catalysts

# Results

- Wolf Hollow: Overall performance – January 15, 2015

| Condition No | I | II | III | IV |
|---|---|---|---|---|
| Load | 90 | 130 | Maximum | Max. with duct burners I/S |
| NOx removal, % | 77.0 | 78.2 | 86.7 | 87.3 |
| CO oxidation, % | 96.1 | 96.4 | ~100 | ~100 |
| NOx as NO2, % | 3.1 | ~0 | ~0 | ~0 |
| Ammonia slip, ppmvd @ 15% O2 | N/A | 1.9 | 4.9 | 5.3 |

# Operating Performance – SOR until March 2016

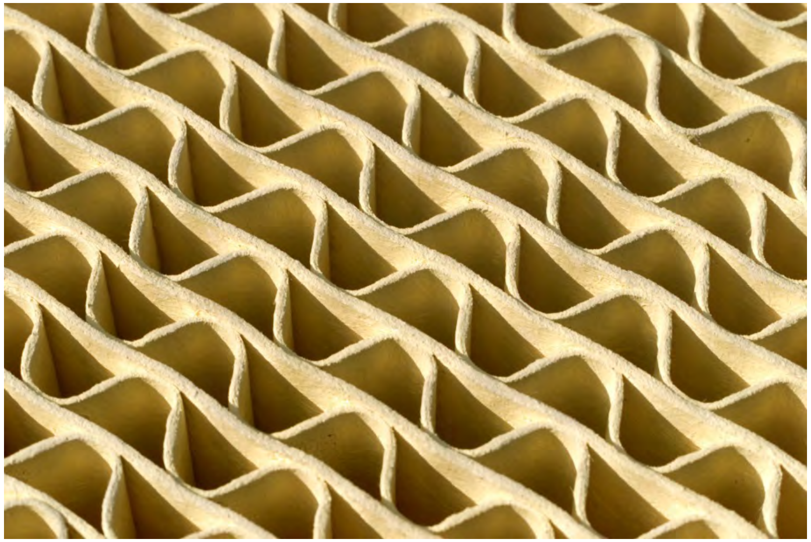
- DeNOx Performance @ 662F / 350C & 0ppm CO
- GTC-802

| Sample Tested | Hours | Sample Length | Gas velocity Nm/s | NH3/NOx ratio | K NOx Nm/hr |
|---|---|---|---|---|---|
| | | | | | |
| SOR, Oct. 2014 | 0 | 250mm | 2.5 | 1.2 | 89 |
| April 2015 | 4,000 | 500mm | 2.5 | 1.2 | 89 |
| March 2016 | 11,000 | 500mm | 2.5 | 1.2 | 89 |
| | | | | | |

# Operating Performance – SOR until March 2016

- CO Oxidation Performance, with ammonia injection
- GTC-802

| Sample Tested | Hours | Sample Length | Gas Temperature F/ C | Gas velocity Nm/s | NH3/NOx ratio | CO Oxidation % |
|---|---|---|---|---|---|---|
| | | | | | | |
| SOR, Oct. 2014 | 0 | 500mm | 700 / 371 | 3.2 | 1.0 | 98.7 |
| April 2015 | 4,000 | 500mm | 700 / 371 | 2.7 | 1.0 | 99.2 |
| March 2016 | 11,000 | 500mm | 700 / 371 | 2.7 | 1.0 | 99.6 |
| | | | | | | |



# The DNX® GTC-802 Catalyst Performance Characteristics

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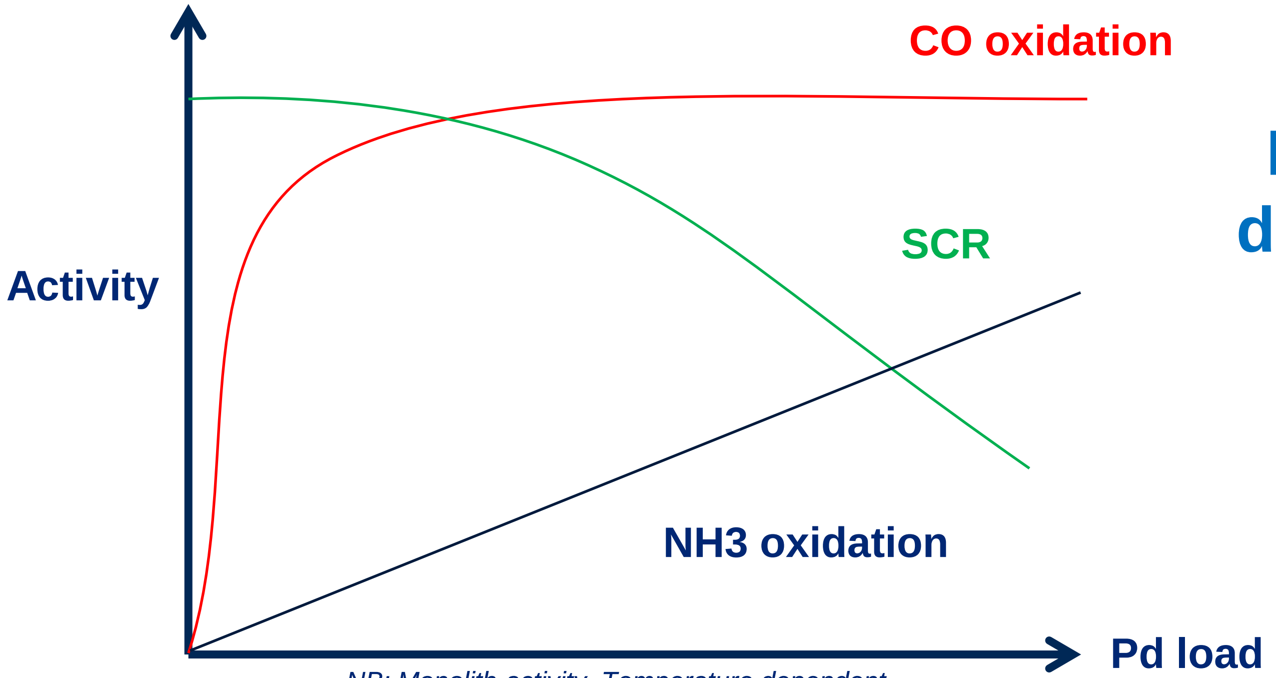
# Development of a Dual Function Catalyst

- Pd loading
  - Optimal Pd-load to be found
    - CO oxidation vs. $NH_3$ oxidation
    - Cost




*NB: Monolith activity. Temperature dependent.*

**Pd load and distribution is the key**

# Development of a Dual Function Catalyst

## Performance Characteristics

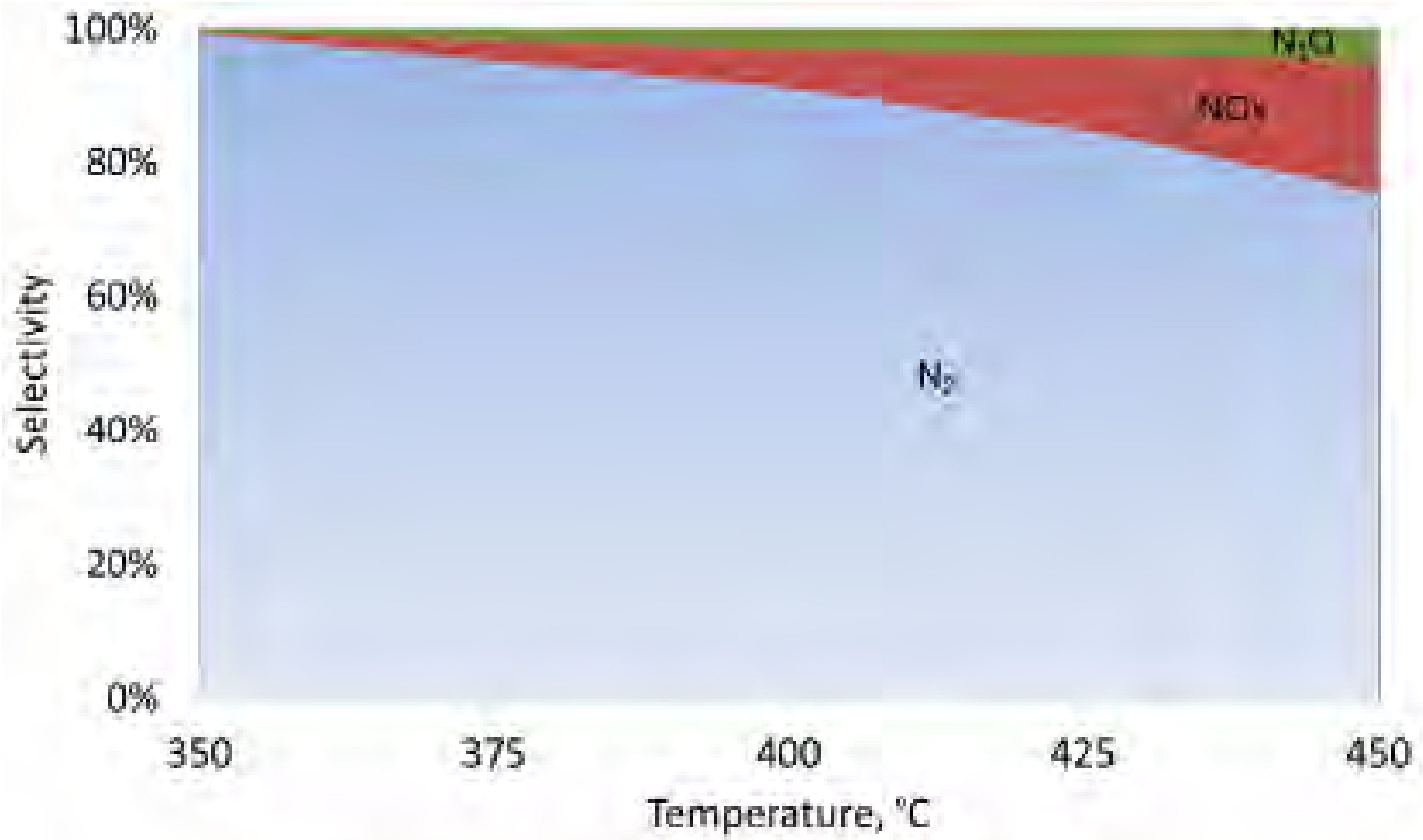



Figure 6 $NH_3$ oxidation selectivity on DNX® GTC-802

# Development of a Dual Function Catalyst

## Performance Characteristics

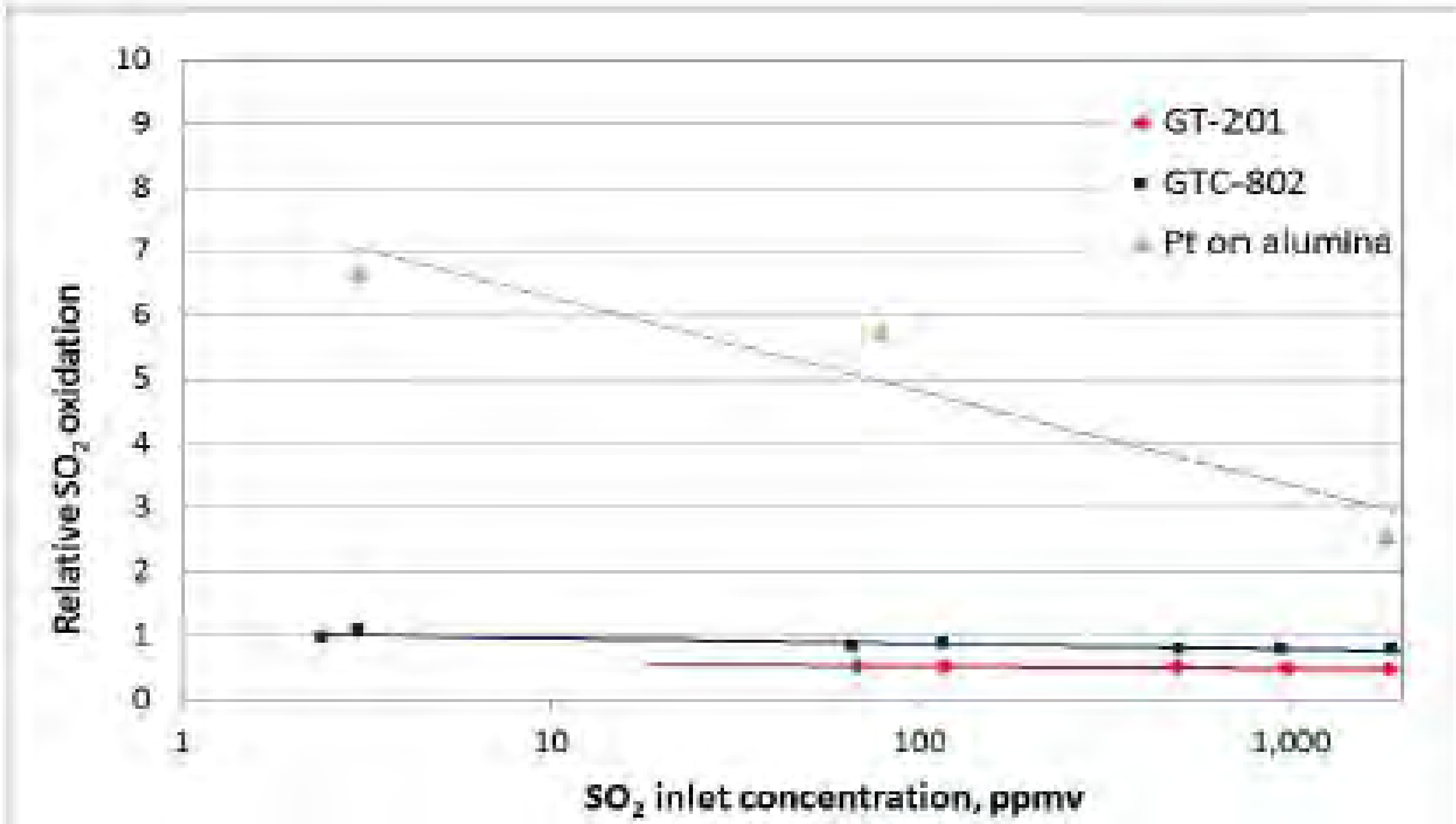
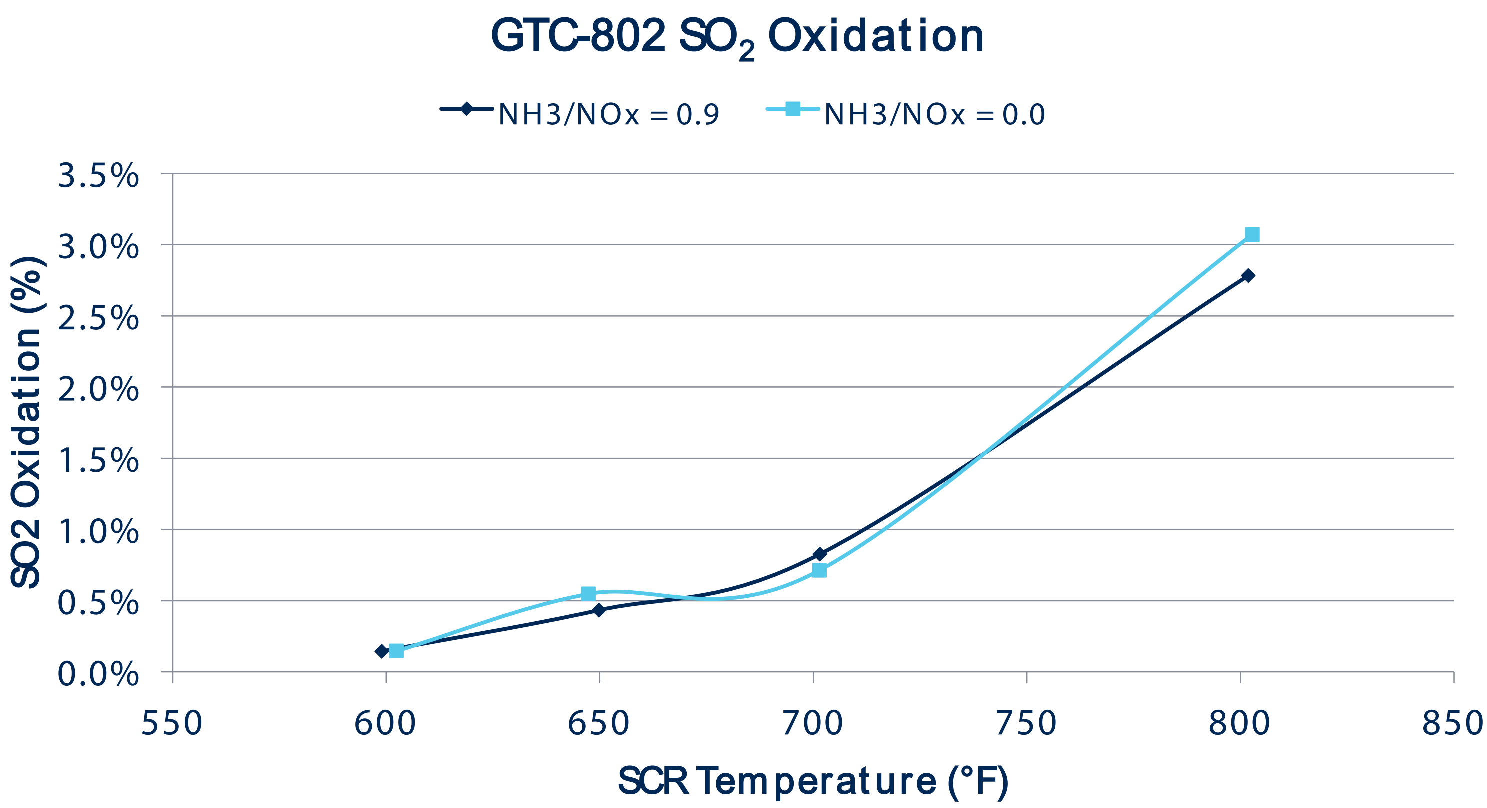


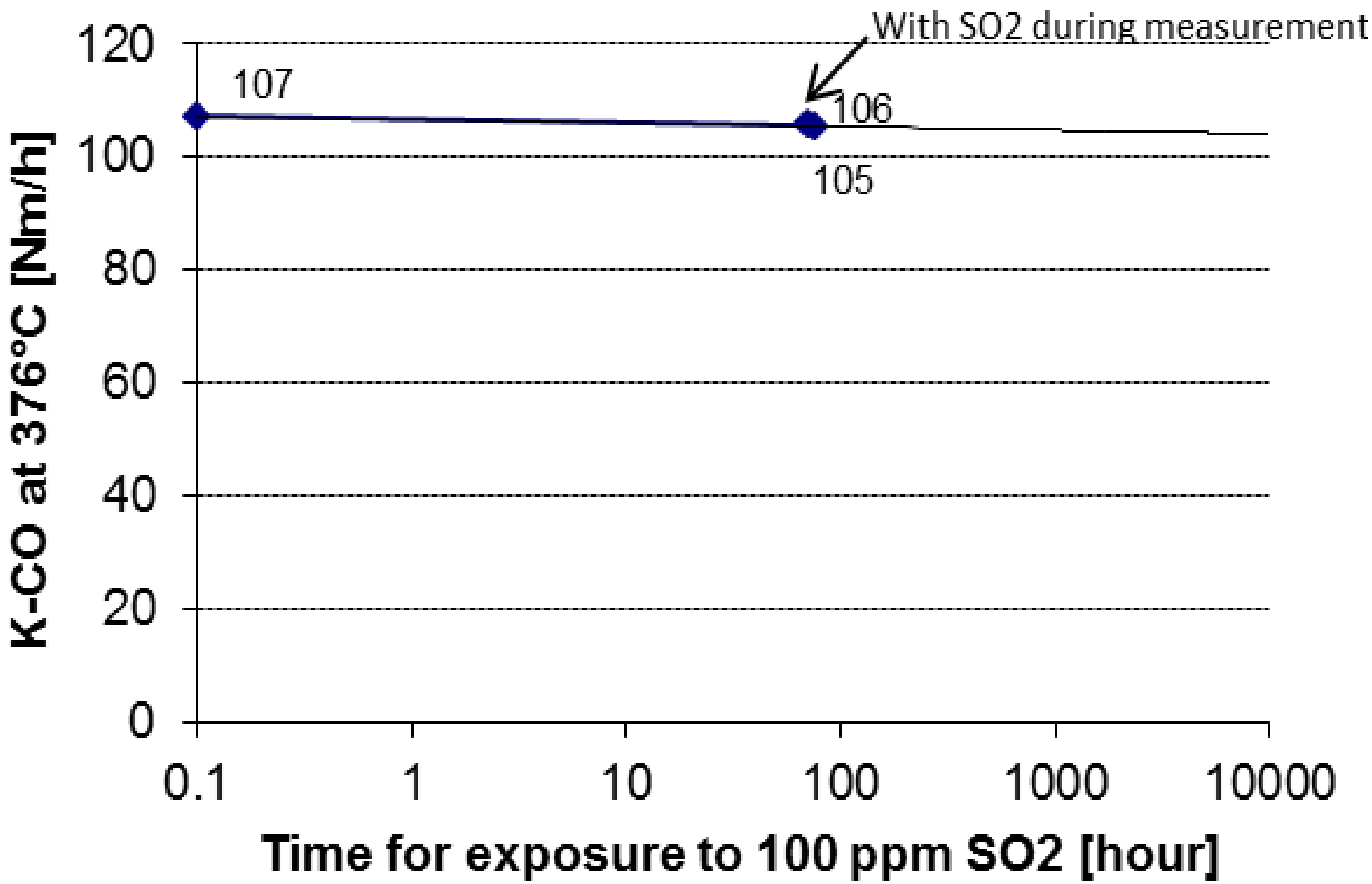

Figure 8 $SO_2$ oxidation of GTC-802 dual function catalyst compared to GT-201 SCR only catalyst and a conventional Pt based CO oxidation catalyst

# SO2 to SO3 Oxidation Rate

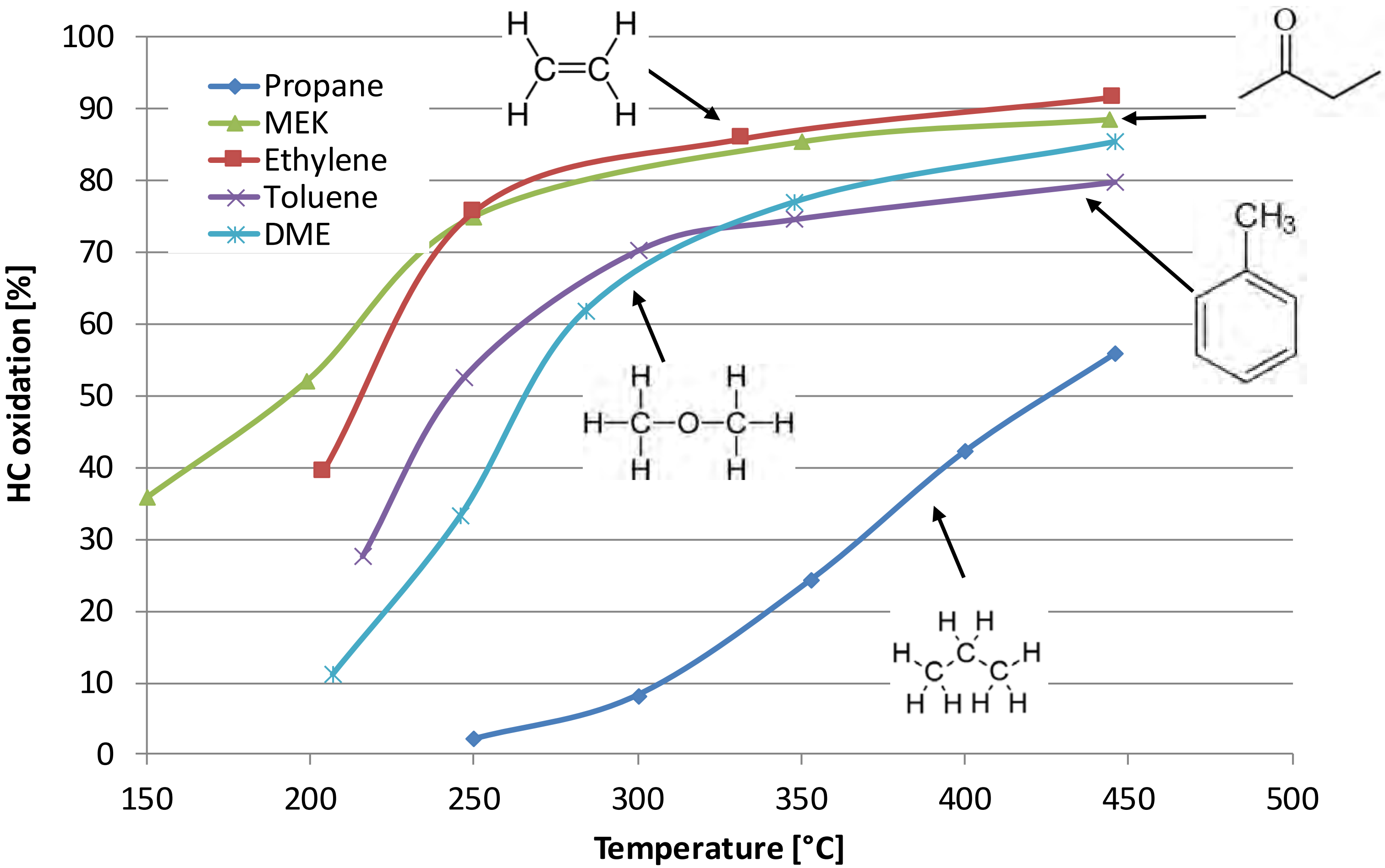


# Performance CO activity GTC catalyst – $SO_2$ tolerance

- T=376°C/709°F, 100 ppm CO,100 ppm $SO_2$,

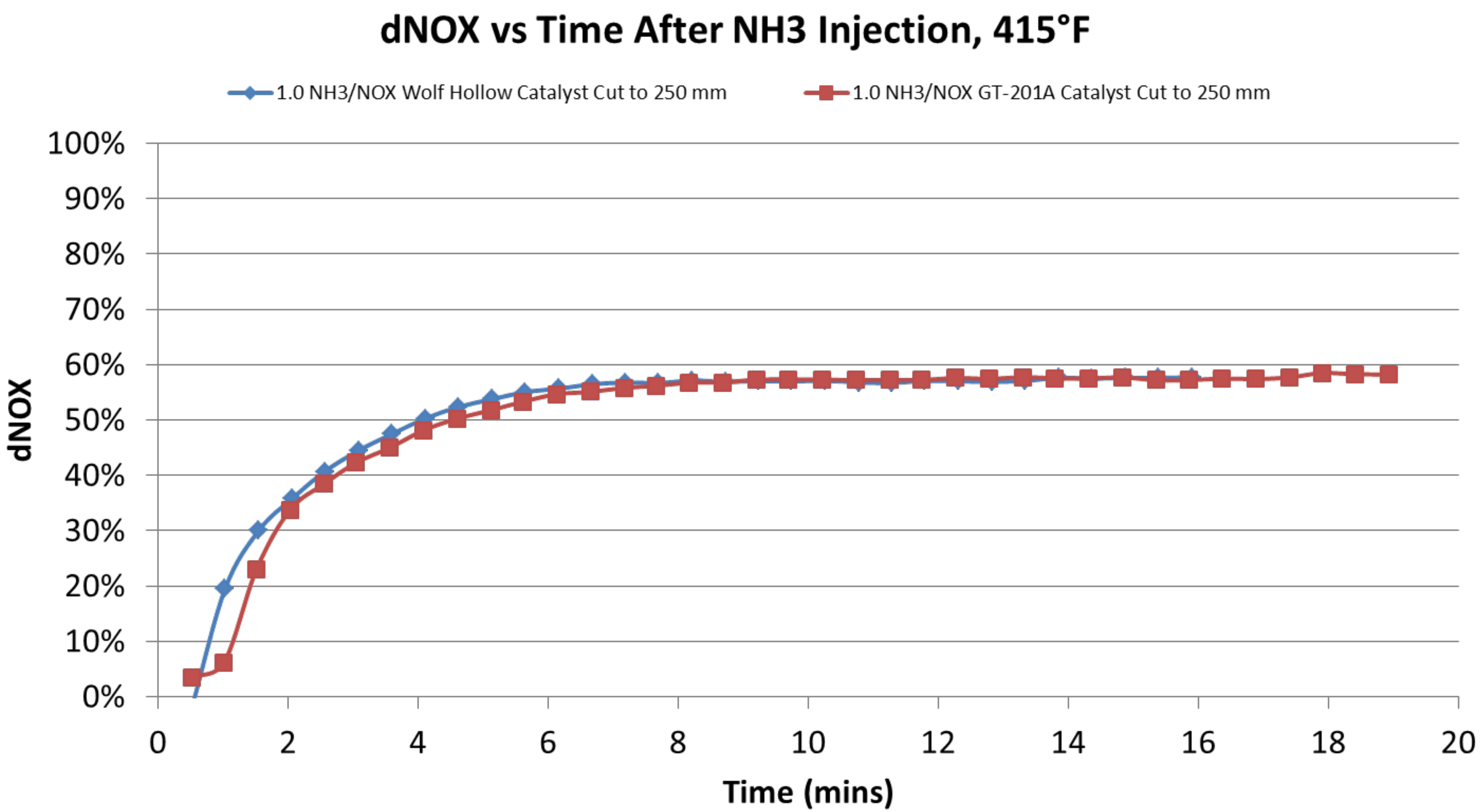


# Performance VOC Activity



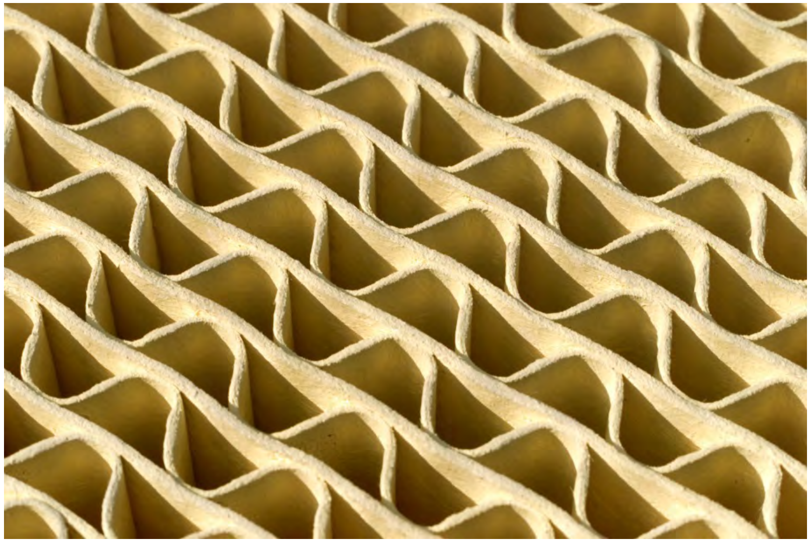
# Response Comparison GT vs GTC Catalyst

- 250 mm catalyst length



# Summary
## GTC Catalyst - Characteristics

- Optimal Pd loading insures high CO oxidation, high DeNOx and low oxidation of undesirables
- Very tolerant to $SO_2$ in the flue gas
- High selectivity to $N_2$
  - Selectivity decreases with increased temperature
- Near ”zero” NO to $NO_2$ oxidation rate
- Over 10 times lower $SO_2$ oxidation compared to Pt catalyst
- Up to 2 inches wc reduction in system pressure drop
- Effectively oxidizes other VOC’s
- GT & GTC catalysts respond very quickly at 415F / 212C
- Can utilize HTI’s frameless module support system
- Can implement “liquid ammonia/urea injection”



# The DNX® GTC-802 Catalyst: Value Added and What the Future Might Look Like

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# GTC – 802 Dual Function Catalyst

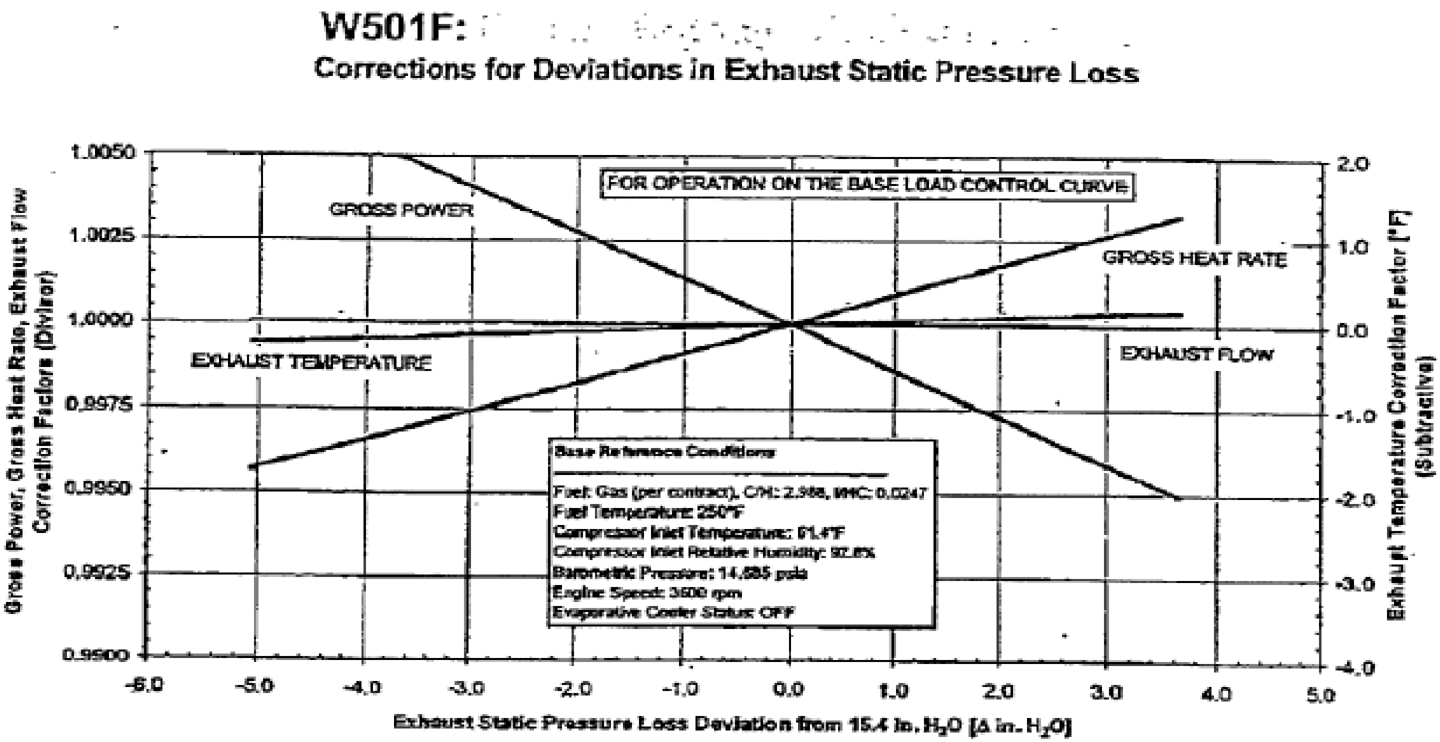
- Much more than just a replacement for traditional oxidation catalyst

# Consider Future Design Challenges - Discussion

- >93% DeNOx, 2 - 5 ppm $NH_3$ slip & >90% CO oxidation
  - **< 10% RMS ammonia to NOx maldistribution**; AIG system design, liquid injection
  - **Near "zero" flue gas bypass; liner bypass?**
  - Impact of duct burner firing on NOx profile – dual AIG's?
  - Ammonia feed control loop design and tuning
  - Multi point CEMS stack probes

- Earlier need to start controlling NOx emissions
  - Controlling ammonia slip at very low loads, controls and time lag

# Correction Curves, Exhaust Static Pressure Loss




**Gross Power:**

$y = -4.25015E{-}06x^2 - 1.37103E{-}03x + 1.00000E{+}00$

**Exhaust Flow:**

$y = -1.27637E{-}08x^2 - 1.04935E{-}05x + 1.00000E{+}00$

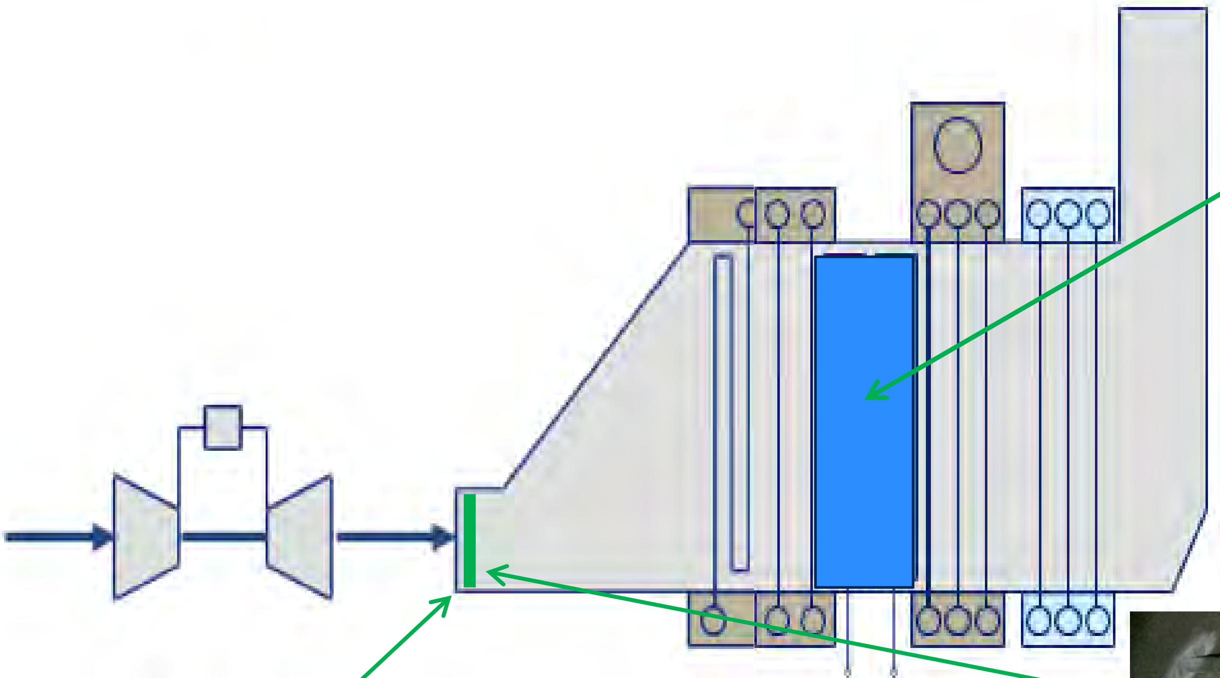
**Gross Heat Rate:**

$y = 3.90318E{-}06x^2 + 6.72123E{-}04x + 1.00000E{+}00$

**Exhaust Temperature:**

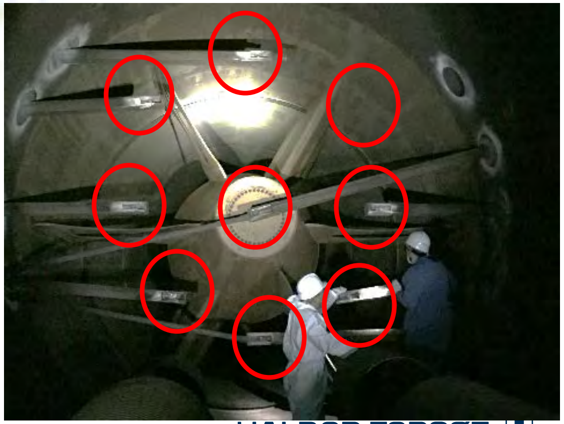
$y = 7.46294E{-}05x^2 + 4.39450E{-}02x$

# Direct Injection/Dual Function Catalyst



Dual Function or a combination of SCR and Dual Function Catalyst

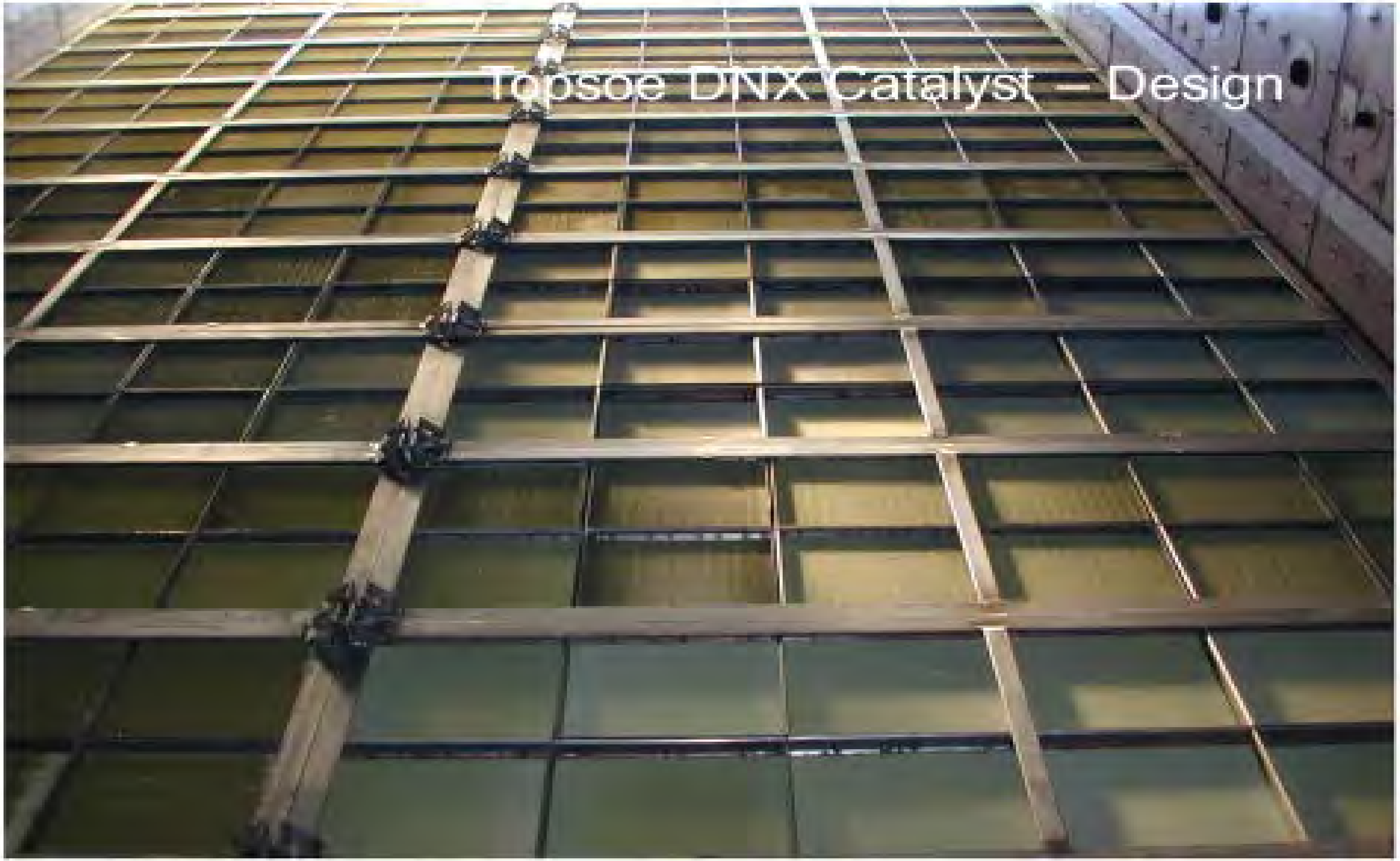
NOx and CO Removal



Direct Injection of Aqueous Ammonia or Urea

# Frameless Design – No Module Support Frame

# Frameless Design – No Module Support Frame



# GT-802 Catalyst: The CCGT of the Future

- Lowest possible system pressure drop using dual function catalyst, additional reduction with use of frameless module design
- Elimination of AIG, dilution air fans, ammonia skid, interconnecting piping by using direct liquid ammonia/urea injection
- Reduce HRSG by 10 – 12 feet in length
- Lowest $SO_2$ oxidation rate, reduced backend deposition and corrosion
- Elimination of $NO_2$ concerns with dual function catalyst
- Elimination of traditional support frame for CO catalyst
- Significantly improved ammonia to NOx distribution required to meet >92% DeNOx and very low ammonia slip
- Installation of permanent sample grid after catalyst
- Substantial reduction in both Capex and future O&M costs