Lean Gasoline Emissions Control: NH_3 generation over commercial Three-Way Catalysts and Lean-NOx Traps

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U.S. DEPARTMENT OF ENERGY

UNIVERSITY OF SOUTH CAROLINA

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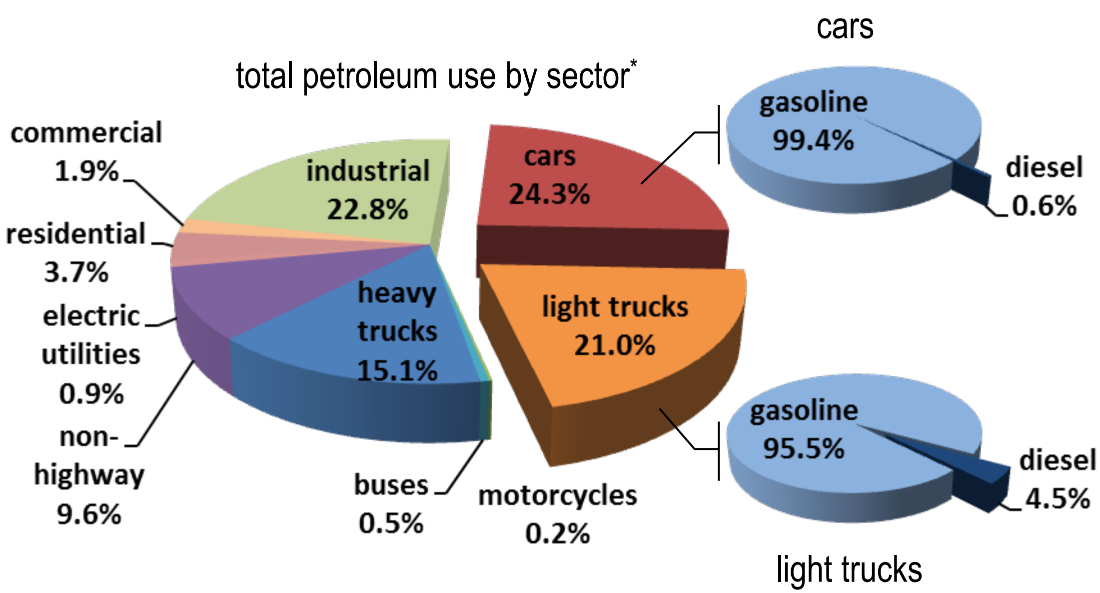
Small improvements in gasoline fuel economy <u>significantly</u> decreases fuel consumption



Lean gasoline vehicles can decrease US gasoline consumption by <u>~30 million gal/day</u>

- 132,000 million gallons of fuel used by cars and light trucks annually**
- **New car and light-truck sales dominated by gasoline engines**
- 10% fuel economy benefit † from base case of 22.6/18.1 mpg** has big impact
  - Saves >200,000,000 barrels gasoline annually
  - 5% of overall petroleum used
- HOWEVER…emissions control challenges exist

*, ** - *References: Transportation Energy Data Book, Ed. 29; *2009 data; **2008 data.*

† - *data from chassis dynamometer data at ORNL; see technical backup slides*

Why NH_3-generation on TWCs?

- Zeolite-based NH_3-SCR has been shown to have very high NOx conversions over wide temperature window

- Urea injection systems are unlikely solution in lean gasoline systems
  - Significant additional cost would deter consumers
  - Higher engine out NOx will require more urea
    - introducing urea filling infrastructure issues on this scale
  - Other NH_3 introduction methods being studied

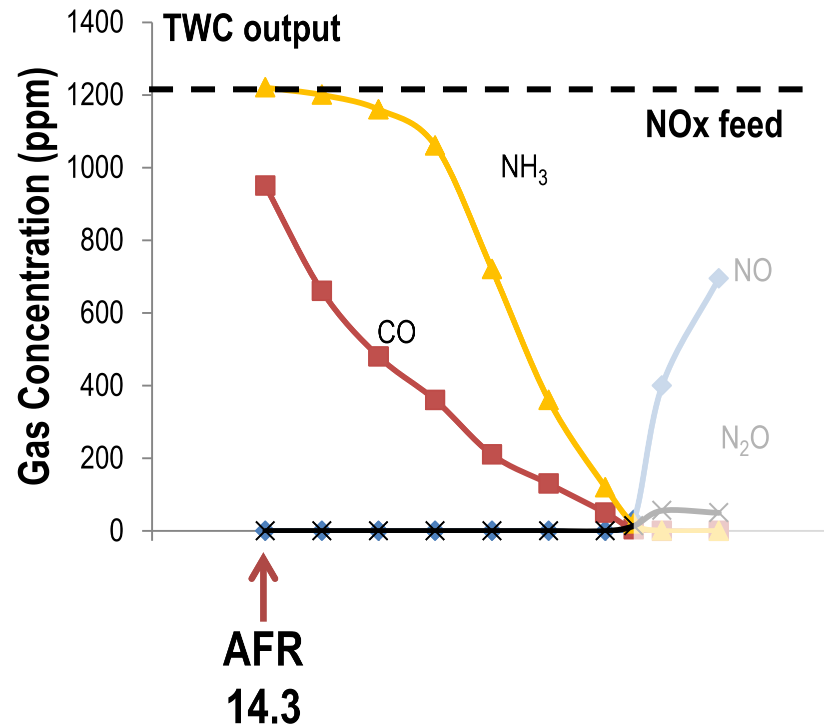
- Utilizing existing TWCs on gasoline vehicles is intriguing since they are already on the vehicle and will be needed on lean gasoline vehicles
  - NH_3 generation recently explored in "Passive SCR" approach*

- Goal is to investigate potential of using similar levels of PGM on TWC
  - while maximizing lean timing and minimizing fuel penalty

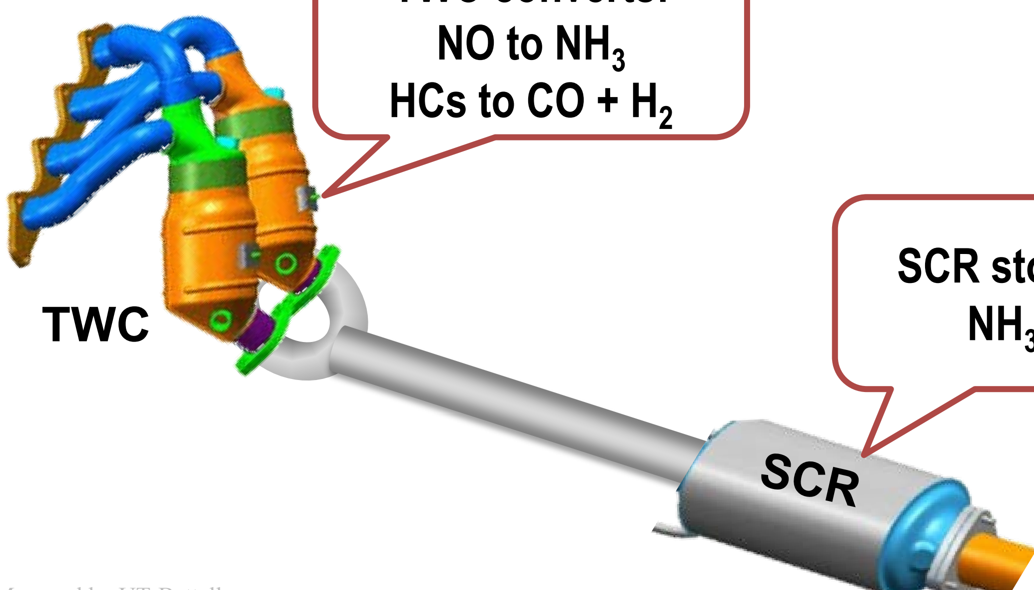
* - GM: SAE 2011-01-0306, SAE 2010-01-0366

“Passive” SCR for lean gasoline emissions control

slightly rich operation
AFR ≈ 14



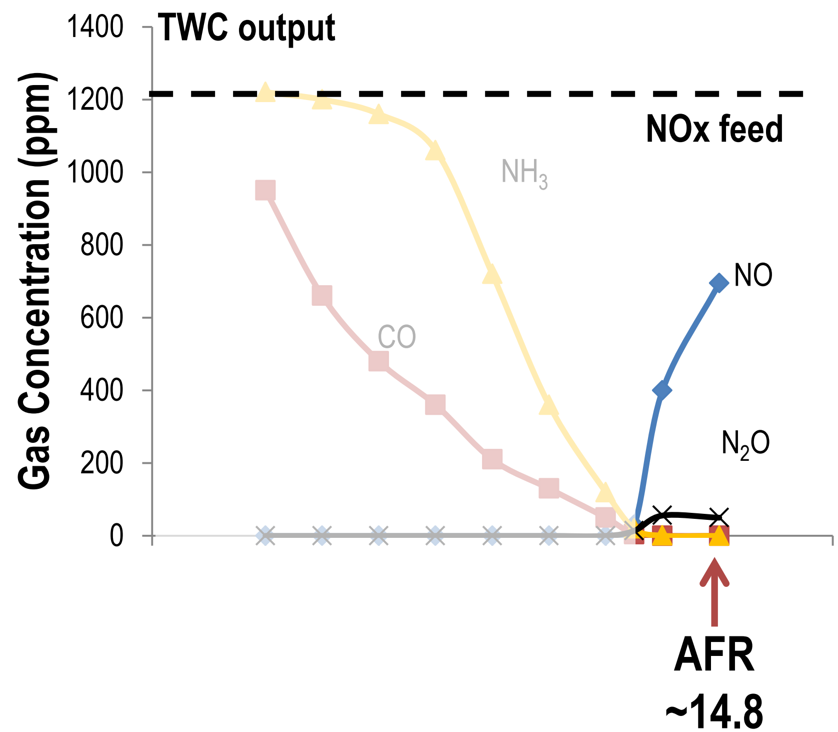
TWC converts:
NO to NH_3
HCs to CO + H_2



SCR stores
NH_3

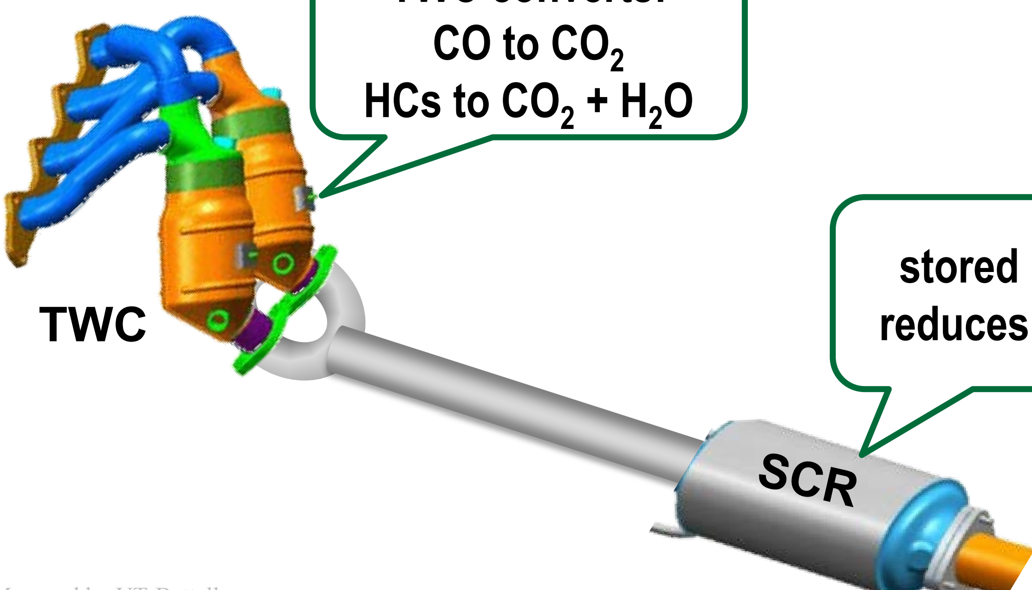
"Passive" SCR for lean gasoline emissions control

lean operation
AFR ≈ 24



TWC converts:
CO to CO_2
HCs to $CO_2 + H_2O$

stored NH_3
reduces NOx



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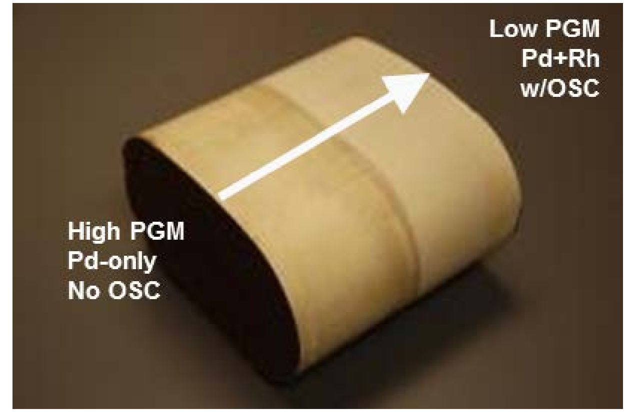
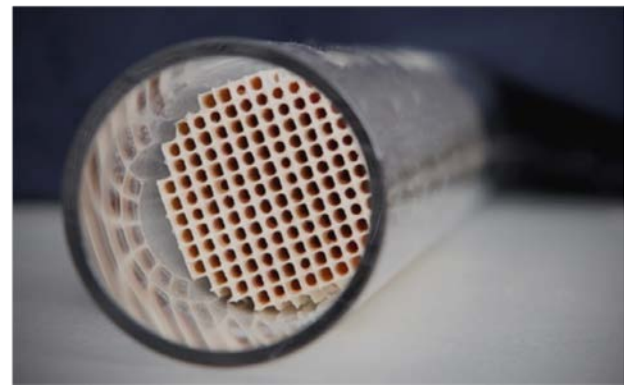
NH_3 GENERATION IN BENCH REACTORS

TWC and LNT studied in bench-core reactor with varying PGM content

- **For bench reactor, focusing on modern TWC technology**
  - **1.3L TWC is a 2 formulation combination (<u>combo</u>)**
    - Total PGM: 0/4.0/0.16 g/L Pt/Pd/Rh (118 g/ft^3 total PGM)
  - **Front 0.6L of TWC is <u>Pd-only</u> no Ce**
    - High PGM: 0/6.7/0 g/L Pt/Pd/Rh (190 g/ft^3 total PGM)
    - No ceria-based OSC, but oxygen storage measured
      - Expected to proceed via Pd-O formation
  - **Rear 0.7L of TWC is <u>Pd/Rh+Ce</u> w/ Ceria**
    - Low PGM: 0/1.1/0.3 g/L Pt/Pd/Rh (40 g/ft^3 total PGM)
  - **Investigating each portion individually and in combined form**
    - Degreened at 16h at 700C in humidified air (2.7% H_2O)





- **<u>LNT</u> is commercial formulation from lean gasoline BMW**
  - 2.6L Pt/Pd/Rh = 7/3/1, 3.3 g/L-cat (94 g/ft^3); Ba loading: 20 g/L (560 g/ft^3); Ce: 56 g/L (1600 g/ft^3)
  - Degreened at 16h at 700°C in humidified air (2.7% H_2O)

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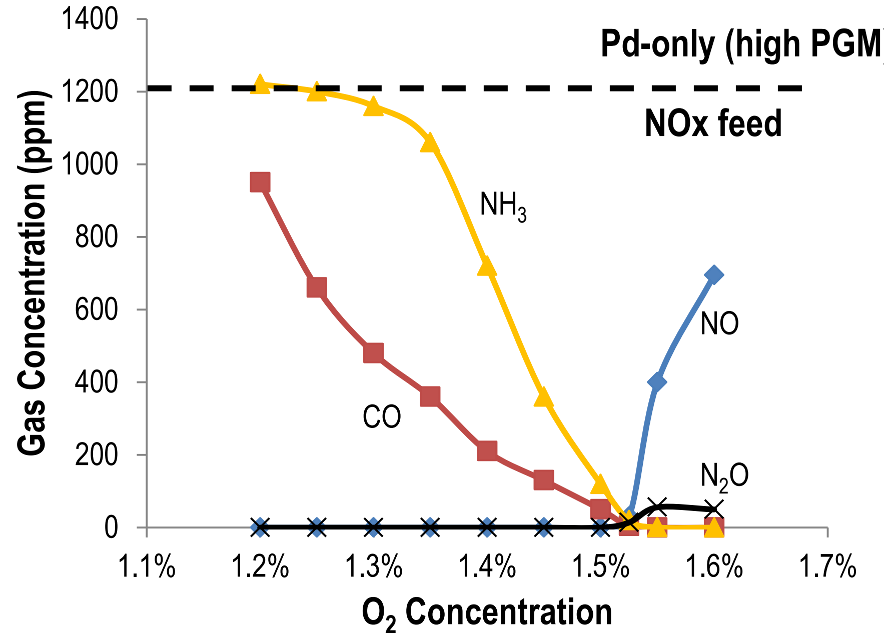
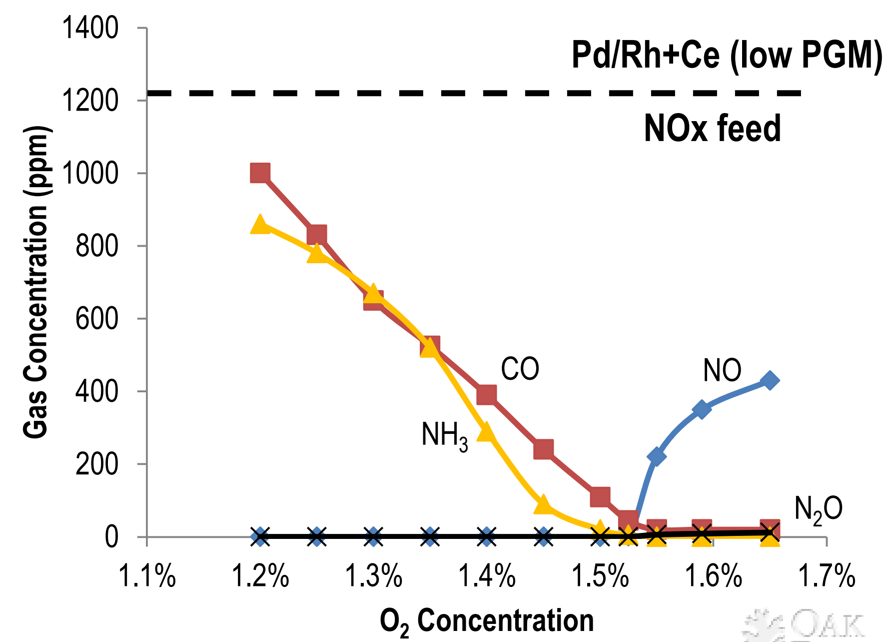
TWC is effective and tunable NH_3 generator

- **Example feed conditions:**

~AFR	O_2	NO	CO	H_2	C_3H_6
14.6	**1.59%**	0.12%	1.80%	0.60%	0.10%
14.4	**1.34%**	0.12%	1.80%	0.60%	0.10%
14.2	**1.06%**	0.12%	1.80%	0.60%	0.10%

- **NH_3 readily generated; varies with PGM**
  - For Pd-only TWC with high PGM:
    - All NO fed converted to NH_3 when very rich
  - For Pd/Rh+Ce (low PGM) TWC:
    - NH_3 production is still significant but reduced
- **At all conditions, >95% CO conversion**
  - C_3H_6 not observed in effluent
- **N_2O formation observed under lean conditions and varies with PGM content**
  - Up to 56 ppm with high PGM (Pd-only) TWC
  - Less than 10 ppm with low PGM (Pd+Rh) TWC





Midbed Temperatures: 460-500°C

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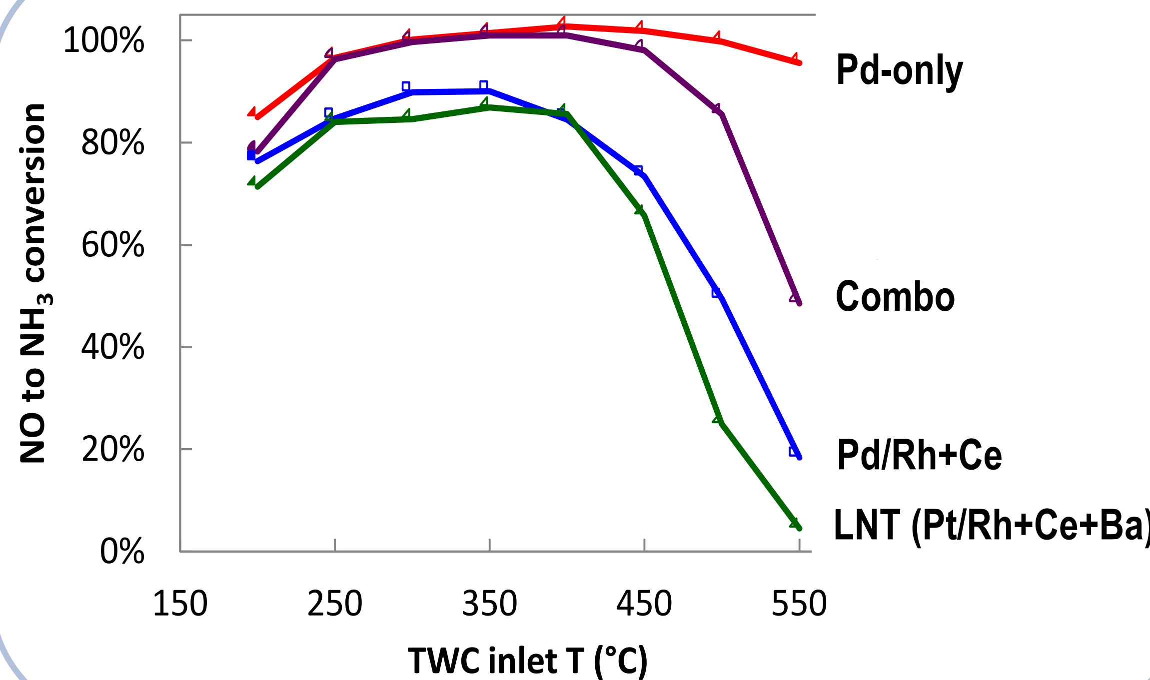
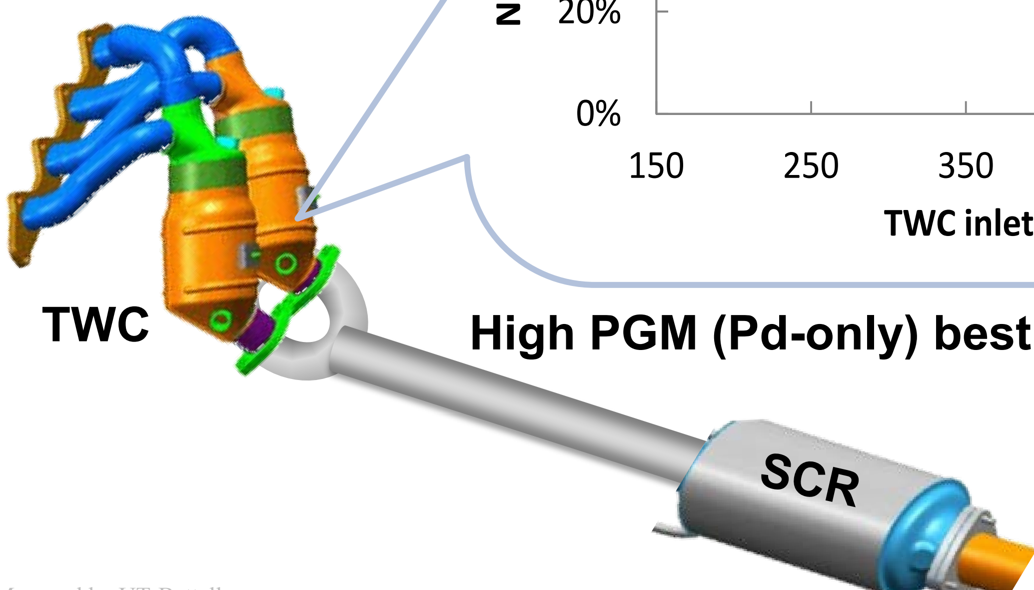
PGM content and Pt/Pd/Rh ratios impact NH_3 production

Evaluated multiple upstream catalyst formulations for NH_3 generation





High PGM (Pd-only) best for NH_3 generation

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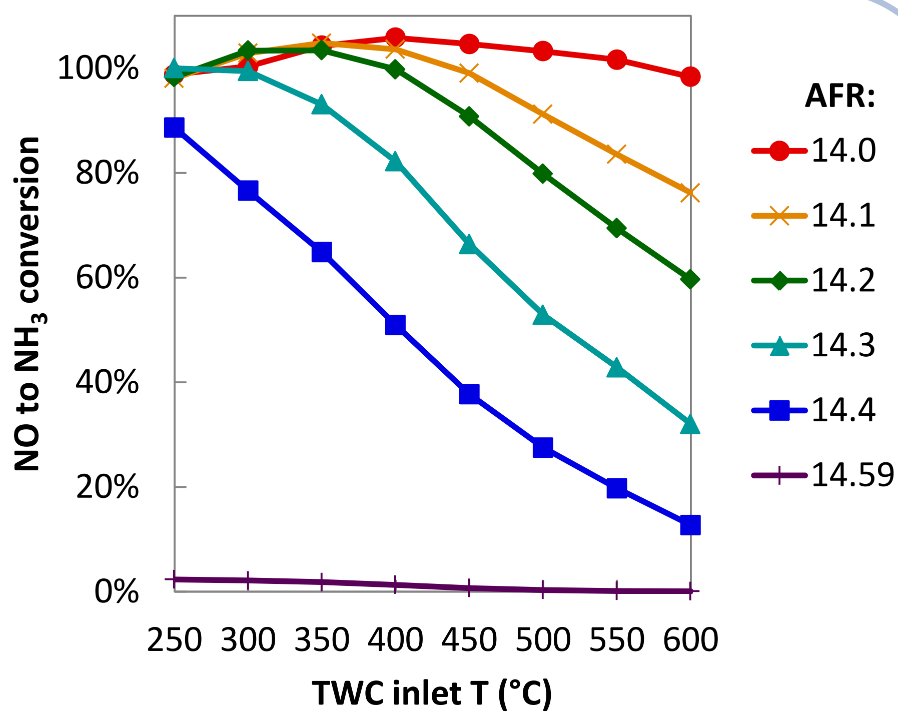
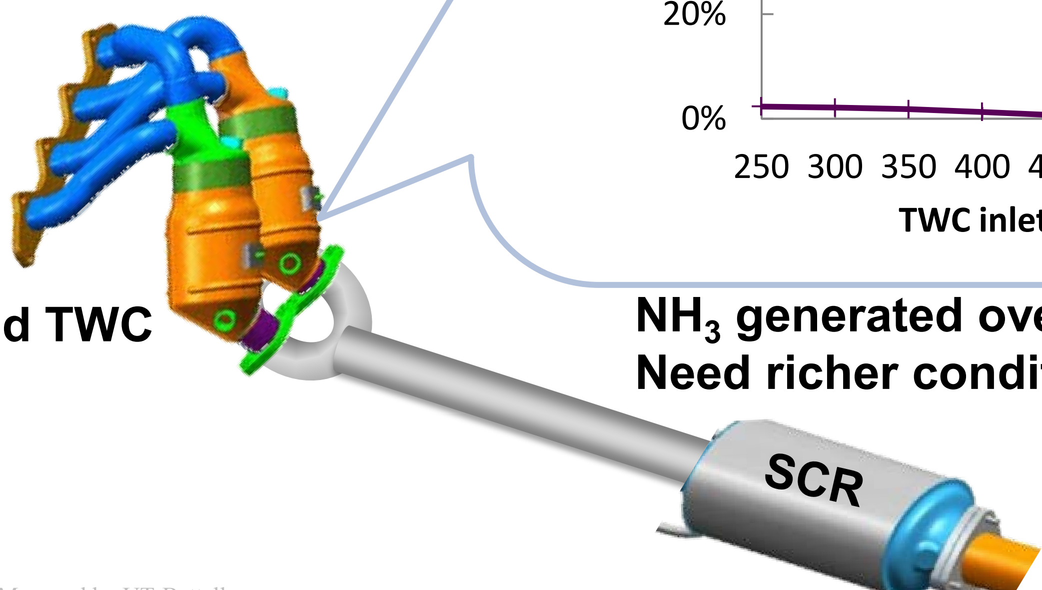
AFR and temperature dictate NH_3 production

Quantified NH_3 generation over Pd only TWC





Pd TWC

NH_3 generated over wide T window
Need richer conditions at higher T

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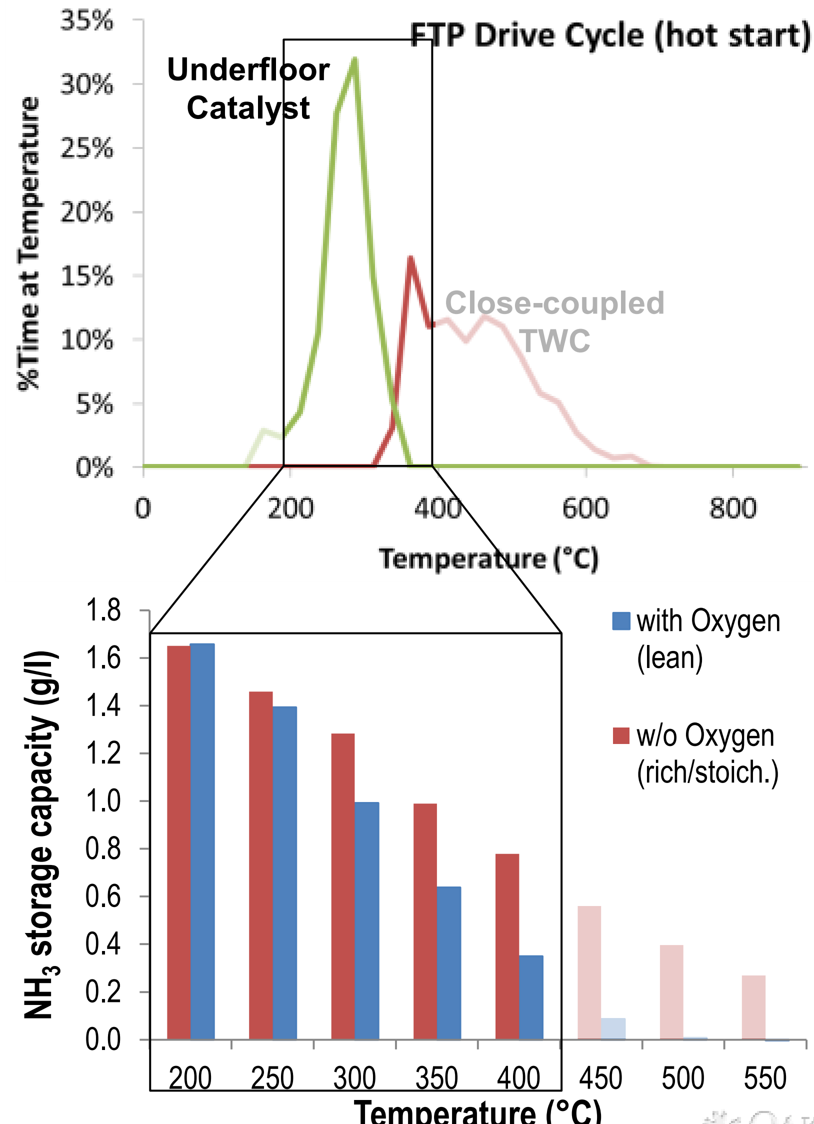
NH_3 production over LNT and TWC occurs at temperatures relevant to vehicle operation and NH_3 storage on SCR

- **Histogram of catalyst temperatures during drive cycle with BMW 120i**
  - FTP (hot start)
  - 200-350°C for underfloor catalyst
  - 350-600°C for close-coupled (cc) TWC
- **TWC: tunable NH_3 production 250-600°C**



- **NH_3 production temperatures over cc-TWC mesh well with NH_3 storage temperatures on underfloor SCR**
  - More NH_3 storage occurs under rich/stoichiometric conditions
  - However switching from rich to lean will result in NH_3 release if over-saturated

PASSIVE SCR APPROACH IN BENCH REACTOR

Fully-automated two furnace bench reactor employed with TWC and SCR

Lean

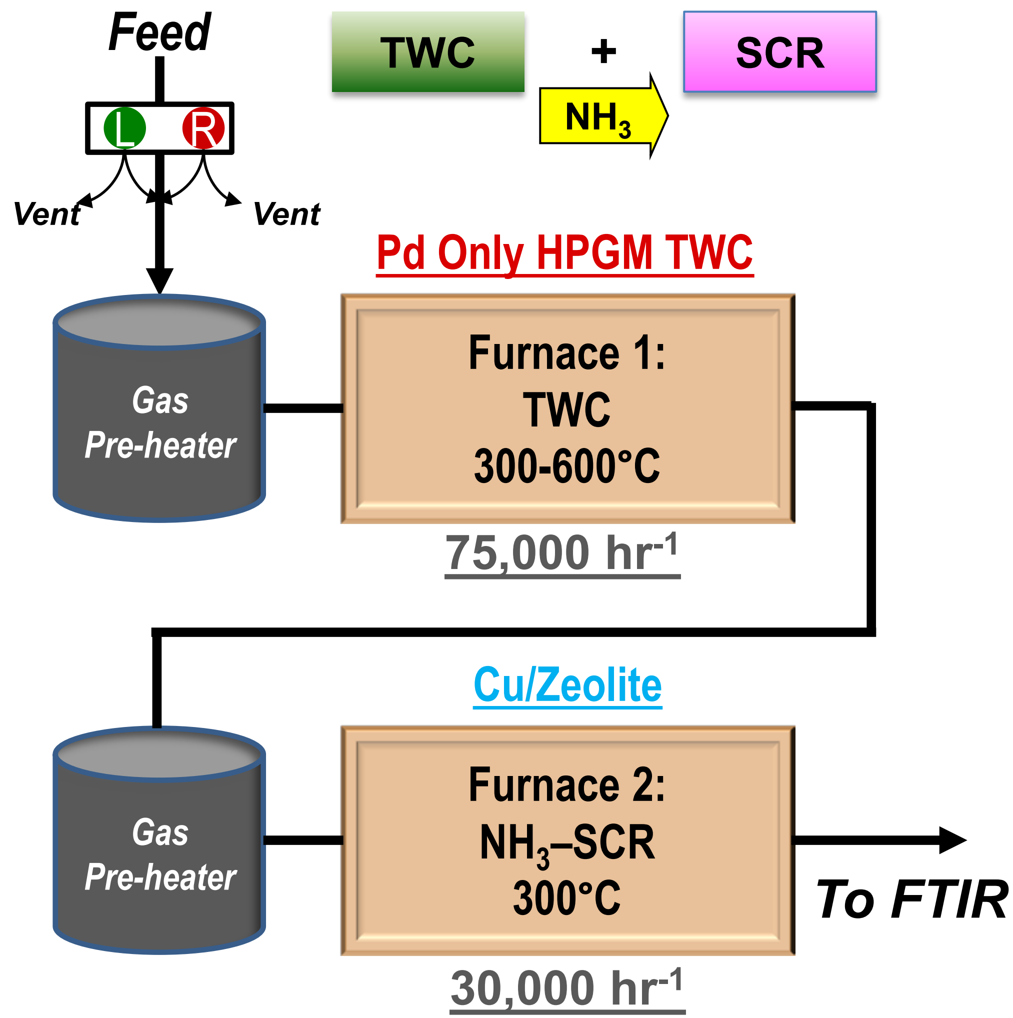
600 ppm NO_X
8% O_2
5% H_2O, 5% CO_2, Bal. N_2

- Switches from lean to rich when FTIR reads 20 ppm NOx

Rich

1200 ppm NO_X
1.8% CO
0.6% H_2
0.1% C_3H_6
0.79%, 0.98%, 1.06%, 1.20% :O_2
14.0 14.1 14.2 14.3 :AFR
5% H_2O, 5% CO_2, Bal. N_2

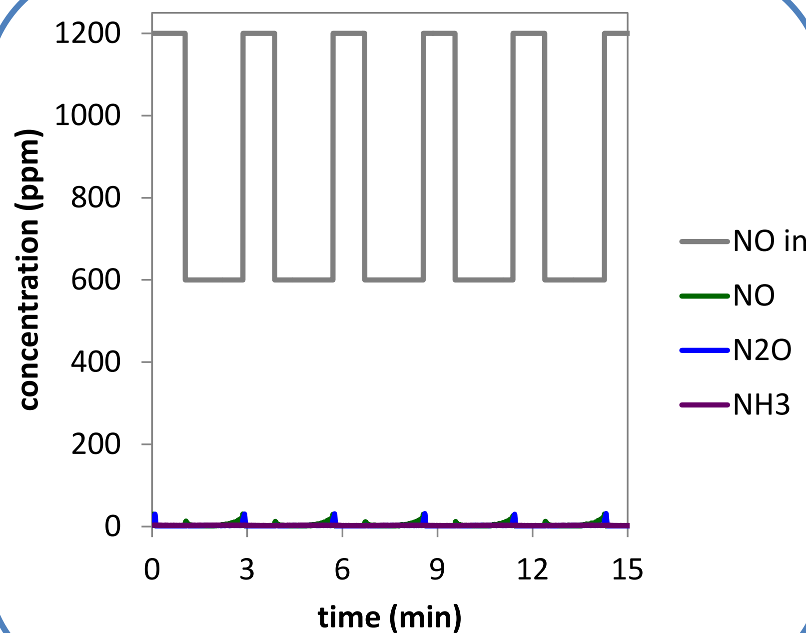
- Rich to lean when predicted NH_3 storage is half filled



Manual optimization of cycling illustrates the potential of this approach

TWC inlet	450 °C
SCR inlet	300 °C
rich time	60 s (AFR≈14)
lean time	110 s (AFR≈24)
NOx conv.	99.5%
CO conv.	93.9%

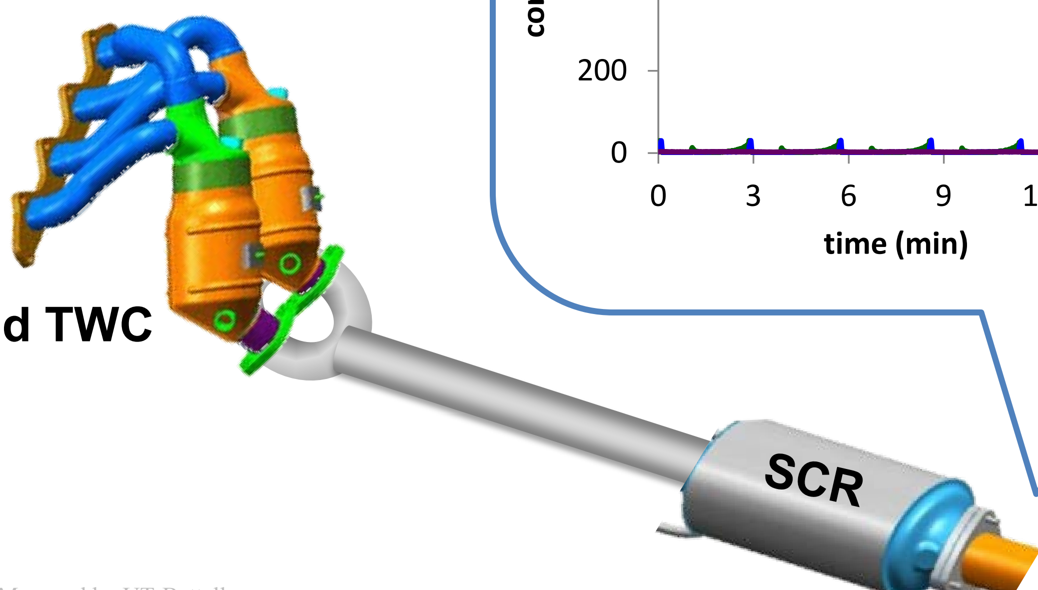
Flow reactor proof of concept: TWC+SCR under cyclic operation



	avg (ppm)	max (ppm)
NO	4	31
N_2O	2	32
NH_3	3	4
CO	1200	3900

Estimated fuel economy gain: 5-6%

Pd TWC



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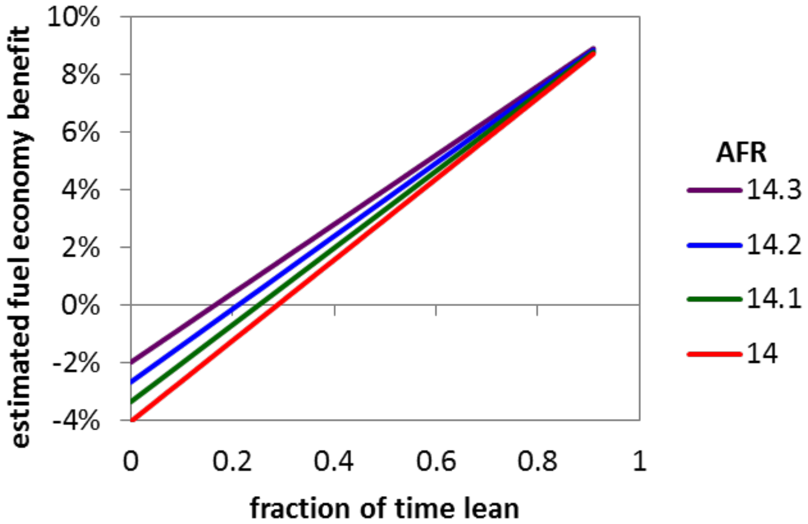
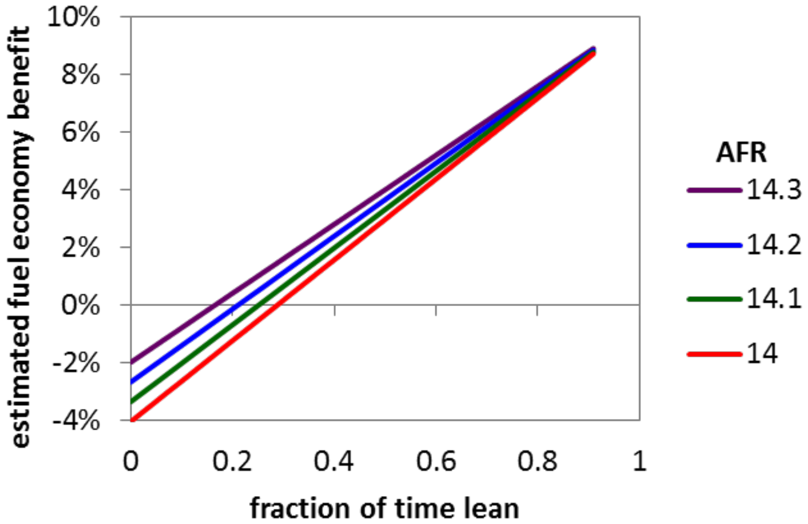
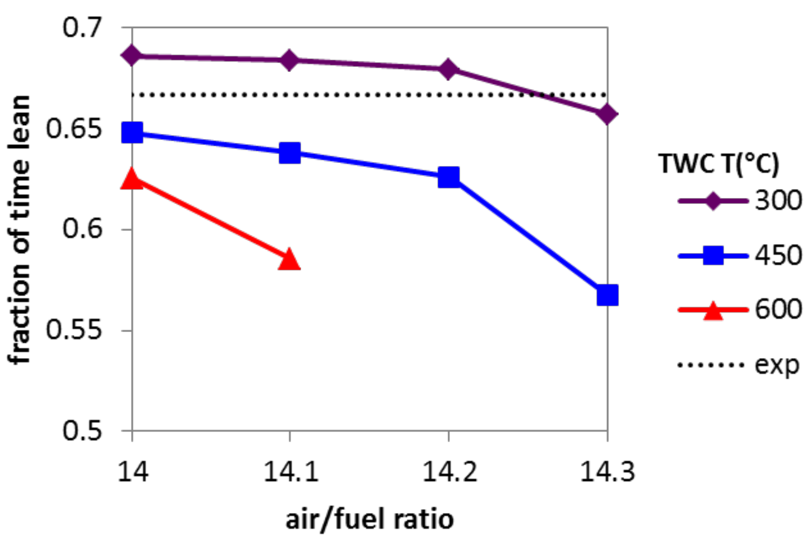
Fuel economy impacts of NOx emissions compliance with passive SCR



- Rich excursions to generate NH_3 increase fuel consumption due to:
  - temporary loss of lean operation fuel economy boost (assumed 10%)
  - injection of excess fuel
- Overall impact on fuel economy depends on:
  - how long the engine can run lean
  - how rich it must go to generate NH_3

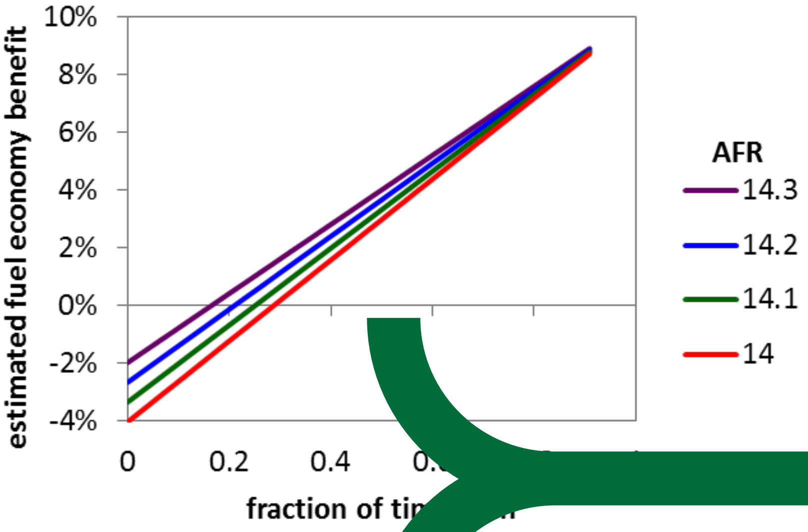
Fuel economy impacts of NOx emissions compliance with passive SCR

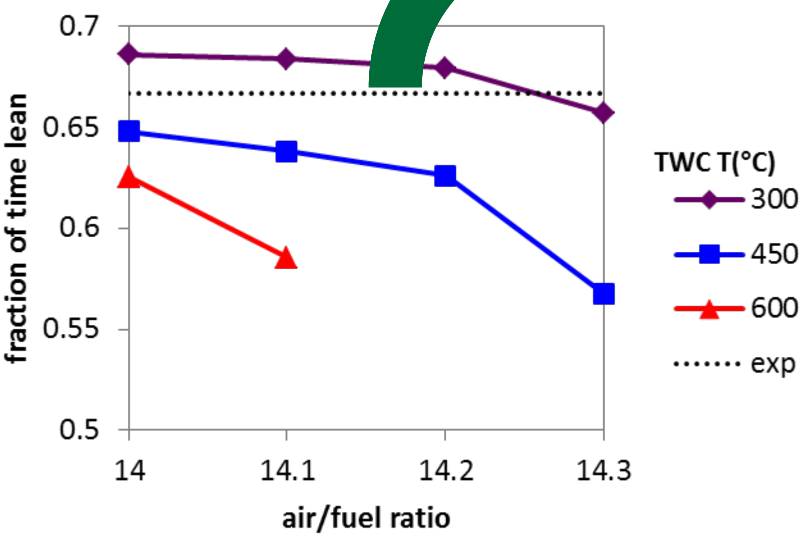




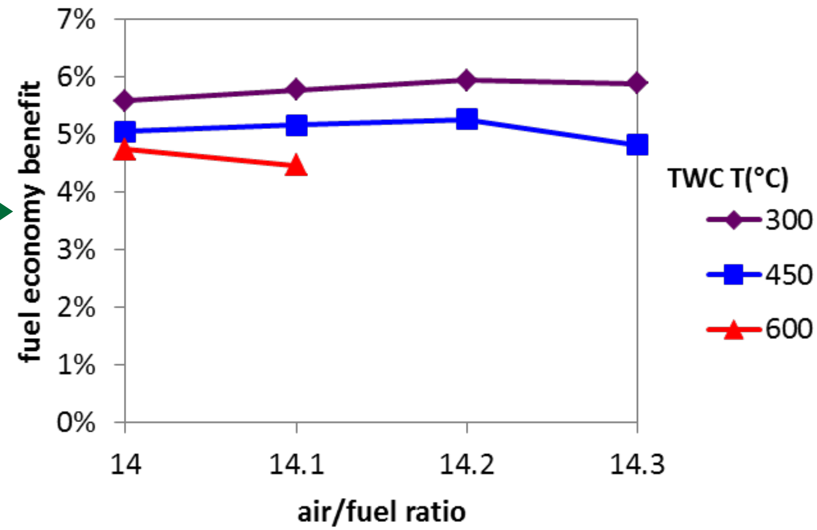
- Fraction of time lean depends on:
  - NH_3 yield during rich operation
    - decreases with TWC T and AFR
  - relative NOx flux (concentration and flow rate) during rich vs. lean
    - rich NOx = 2 x lean NOx here
- Exploiting flow changes during transient driving could increase lean operation time
- Higher than expected lean time at 300°C due to NOx storage over TWC during lean operation
  - possible formulation strategy
- For all conditions shown NOx conversion is > 99%

Fuel economy impacts of NOx emissions compliance with passive SCR





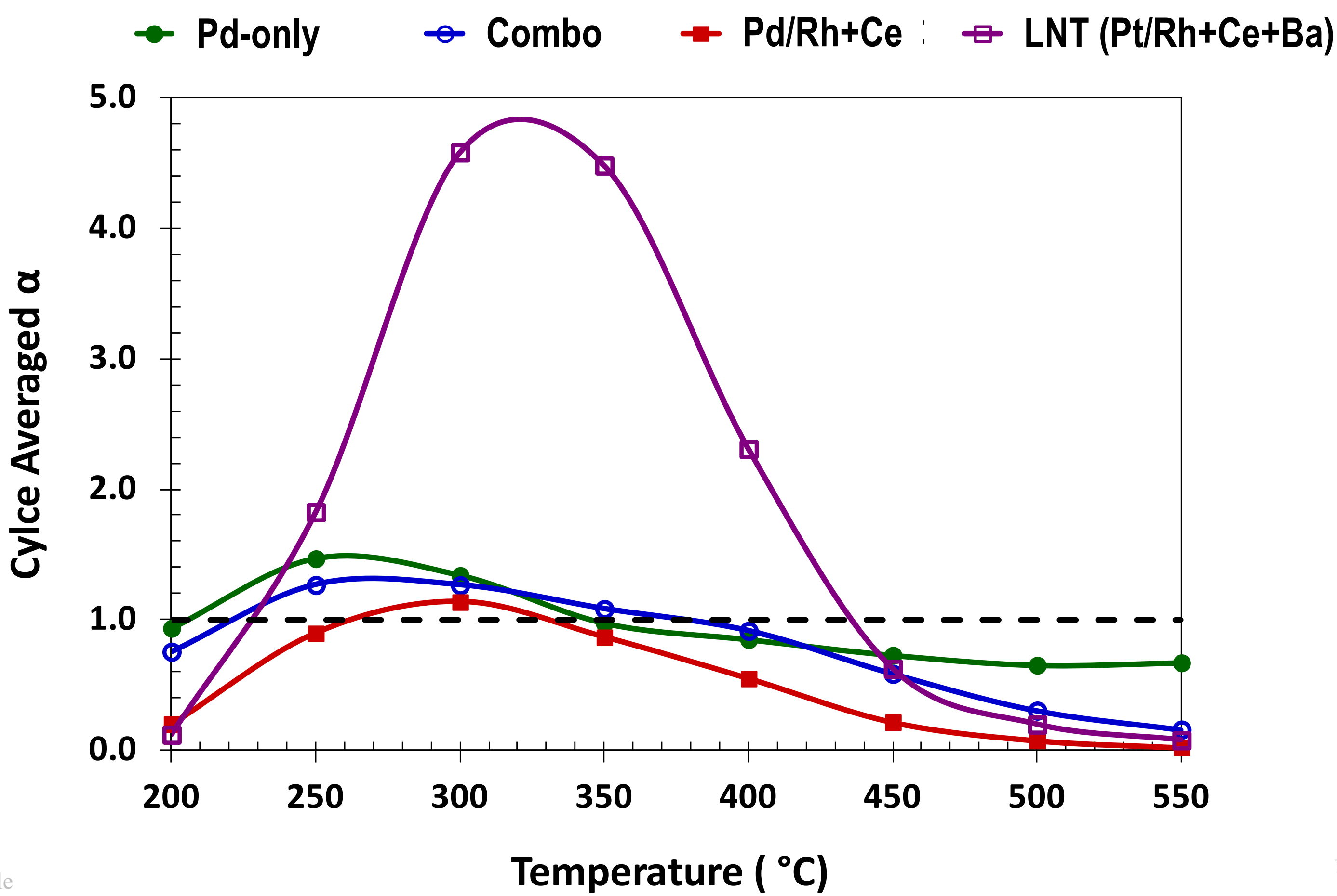
- **Current implementation of passive SCR generates a net fuel economy benefit of 5-6% over a comparable stoich. engine**
- **Optimal AFR depends on TWC T**



- **Possibilities for reducing fuel penalty:**
  - **higher NOx flux ratios during transient operation on vehicle**
  - **addition of a NOx storage material**

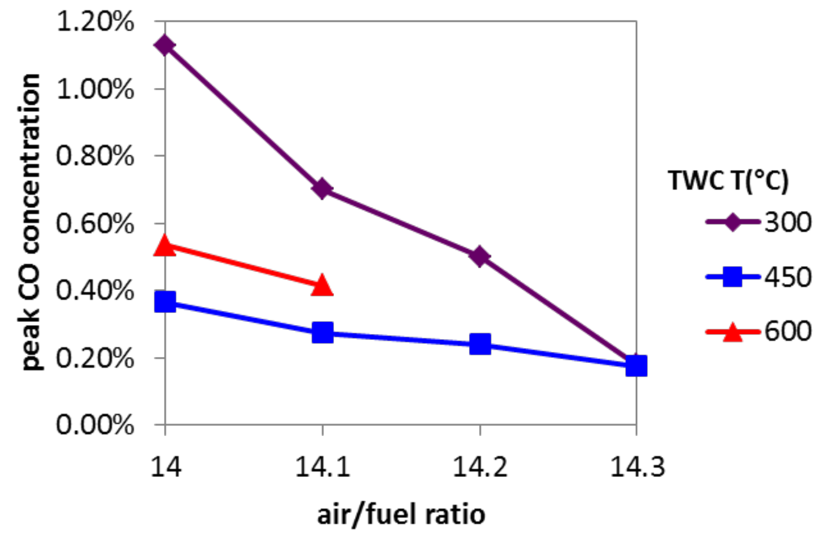
For a fixed cycle, addition of NOx storage significantly increases NH_3 formation

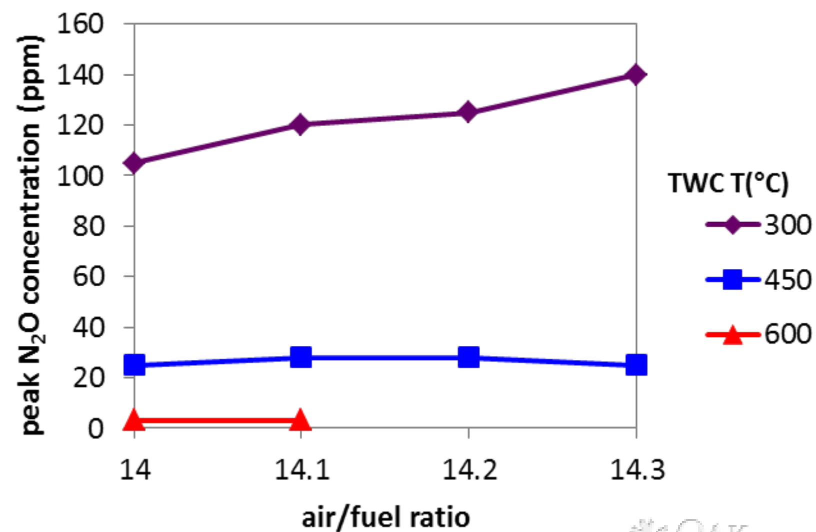
- Cycle Averaged Alpha is 3+ times higher than best TWC formulation
  - Alpha: NH_3 produced / NOx in effluent



Emissions other than NOx still present potential challenges

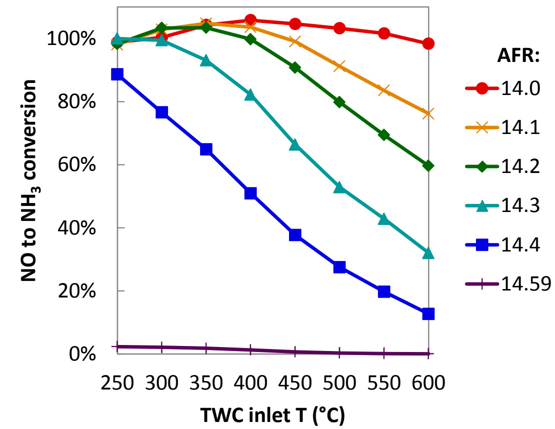
- Current operating strategies optimized for NOx reduction
- Minimal HCs observed with 0.1% C_3H_6 in feed
  - Consumed by reactions with NOx, O_2, or steam reforming
- Significant CO slips during rich operation
  - higher AFRs reduce but do not eliminate
  - CO slip a complicated function of TWC temperature due to water-gas shift kinetics and thermodynamics
  - downstream cleanup catalyst and secondary air may be required
- N_2O may be problematic at low TWC temperatures
  - potential for mitigation by changes in formulation or operating strategy



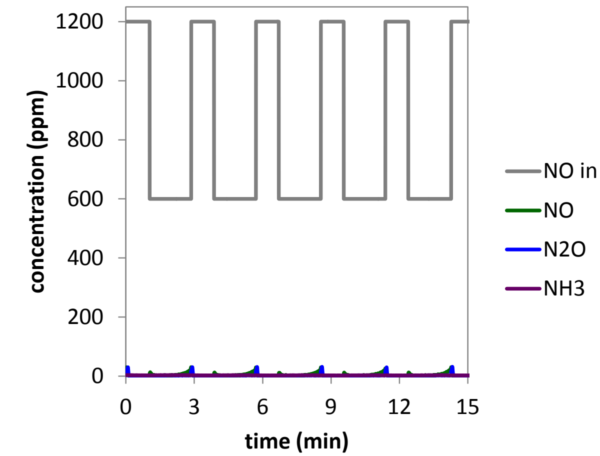


Summary

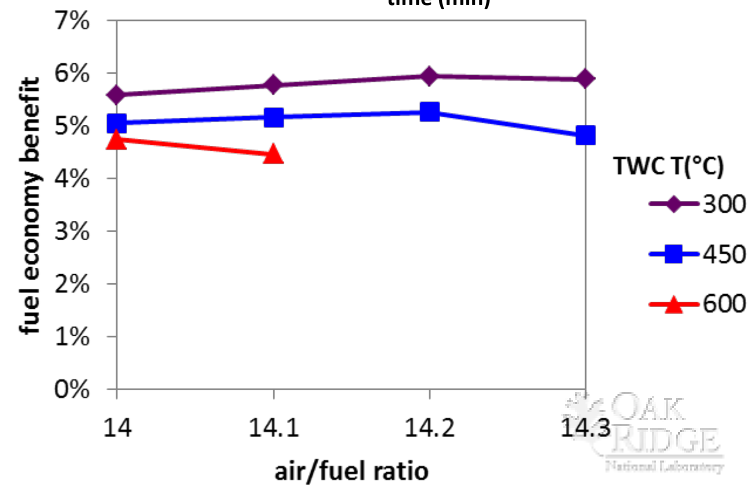
- TWCs shown to be able to produce NH_3 over a broad temperature window
  - Key variables are PGM content, temperature and AFR



- Greater than 99% NOx conversion observed in passive approach
  - Lean-only conversion is >98%
  - CO slip is a concern and will need to be accounted for



- Significant fuel economy gain realized which could be improved with NOx storage on TWC
  - Future efforts exploring addition of NOx storage component on Pt-free TWC



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- University of Wisconsin
  - Modeling (not discussed here) and Monthly teleconferences
  - Chris Rutland and Jian Gong

ADDITIONAL SLIDES

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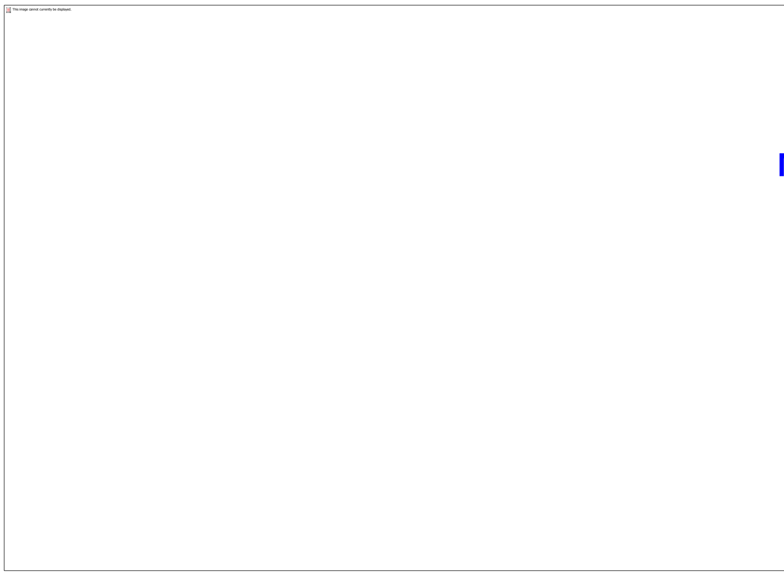
Reaction Conditions

Lambda	AFR	O_2	NO	CO	H_2	C_3H_6
1.000	**14.59**	**1.59%**	0.12%	1.80%	0.60%	0.10%
0.996	**14.54**	**1.525%**	0.12%	1.80%	0.60%	0.10%
0.995	**14.52**	**1.51%**	0.12%	1.80%	0.60%	0.10%
0.987	**14.40**	**1.34%**	0.12%	1.80%	0.60%	0.10%
0.973	**14.20**	**1.06%**	0.12%	1.80%	0.60%	0.10%
0.960	**14.00**	**0.79%**	0.12%	1.80%	0.60%	0.10%

BMW lean GDI LNT benchmarking against CLEERS reference

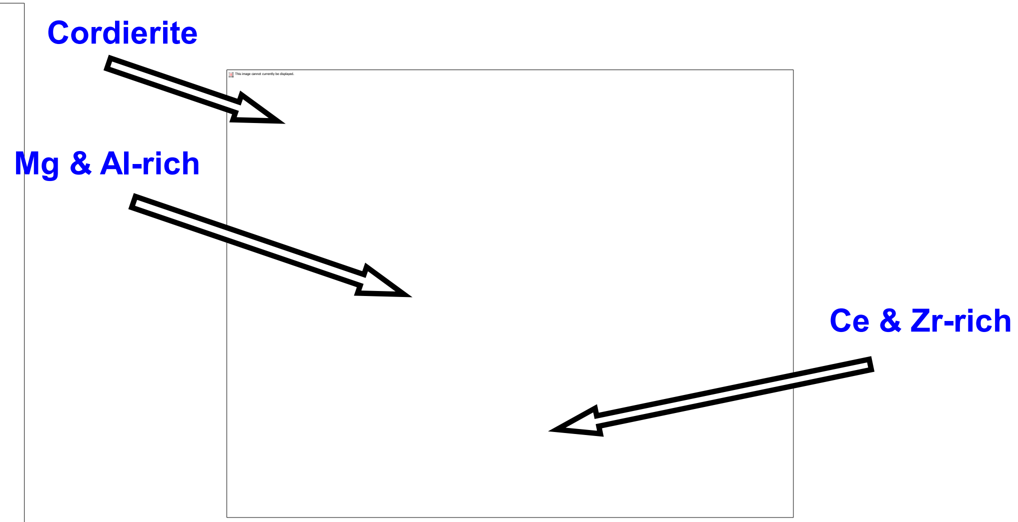
CLEERS reference

Lean GDI, 2004, provided by Umicore



New LNT

Lean GDI, 2009, from BMW 120i vehicle



	CLEERS reference	New LNT
Cell density (cpsi)	625	413
Ba loading (g/ft^3)	442	565
PGM loading (g/ft^3)	103	94
Pt/Pd/Rh ratio	8/3/1	7/3/1

- **Responsive to FY10 review comments**
- **Initial characterization indicates similar basic components in both LNTs**
  - **Reactor evaluation planned**
  - **Catalyst used in an ORNL lean gasoline engine-based project** (see ACE033 talk)

Detailed elemental analysis of different LNT technologies on hand

New LNT

Lean GDI, 2009, from BMW 120i vehicle

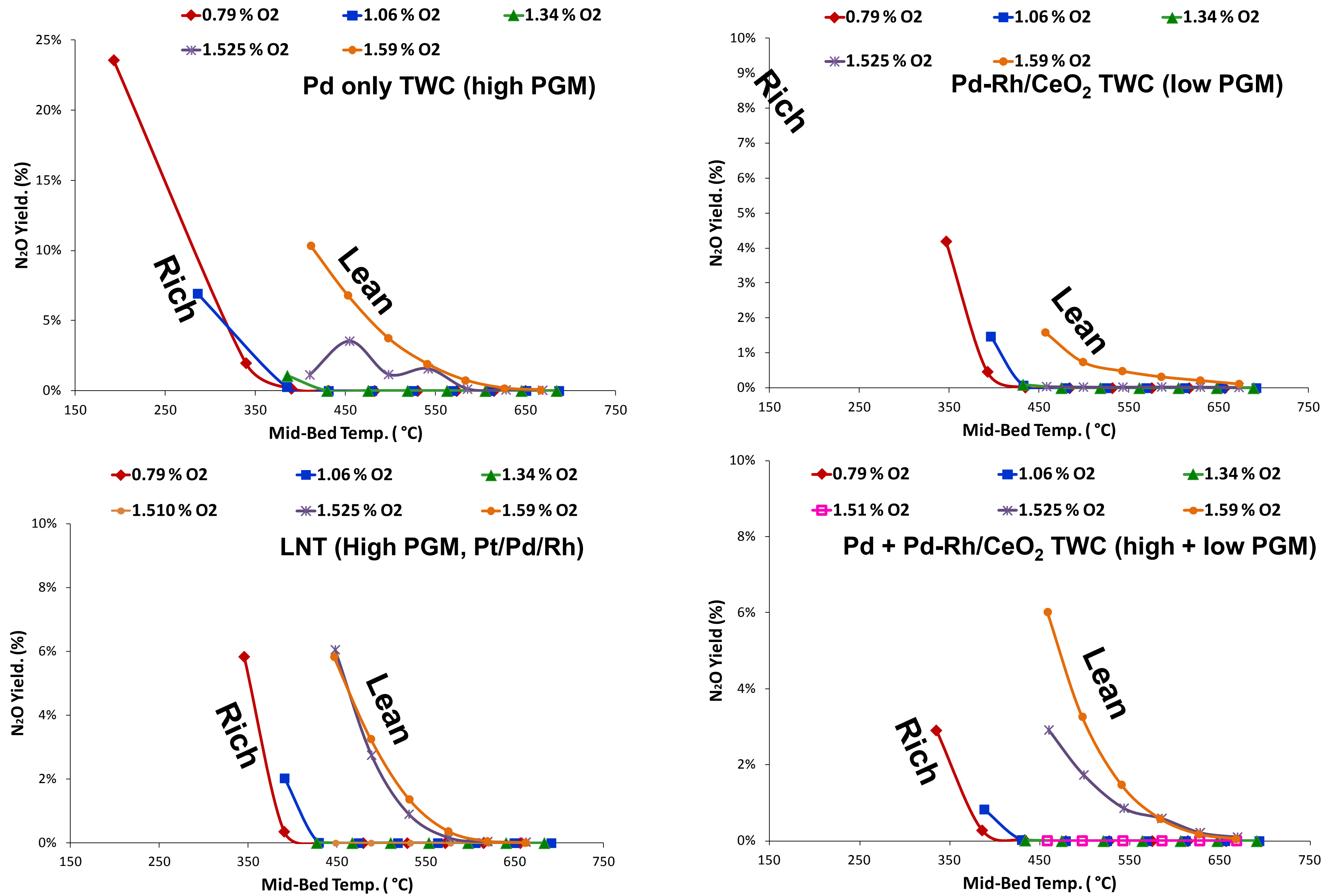
BMW LNT					
Element	Loading (g/ft3)	Loading (g/in3)	Loading (g/L)		
Ba	565	0.33	19.9		
Ce	1572	0.91	55.5		
Zr	122	0.07	4.3		
La	69	0.04	2.5		PGM ratio
Pt	62	0.04	2.2		7
Pd	24	0.01	0.8		3
Rh	8	0.00	0.3		1
PGM loading	94	0.05	3.3		

CLEERS reference

Lean GDI, 2004, provided by Umicore

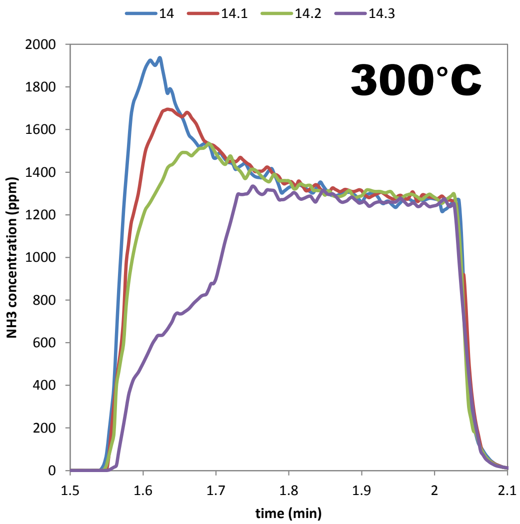
cf. CLEERS Umicore LNT					
Element	Loading (g/ft3)	Loading (g/in3)	Loading (g/L)		
Ba	442	0.256	15.6		
Ce	1978	1.145	69.9		
					PGM ratio
Pt	72	0.042	2.5		8
Pd	23	0.013	0.8		3
Rh	9	0.005	0.3		1
PGM loading	103	0.06	3.6		

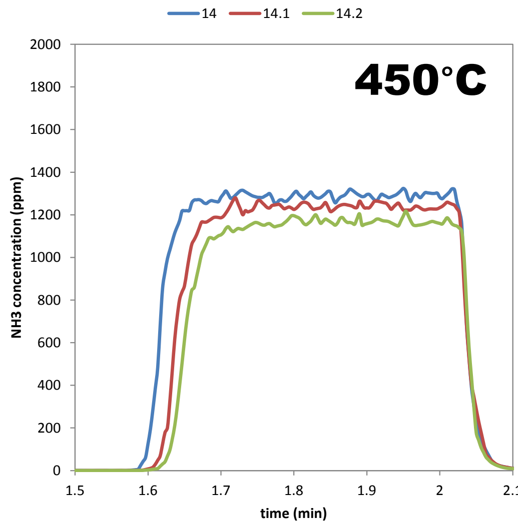
N_2O formation can be significant on all catalysts and under lean or rich operation

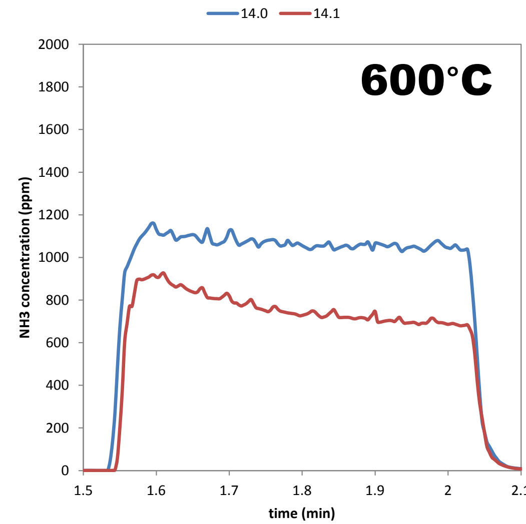


TWC (high PGM Pd-only) transients

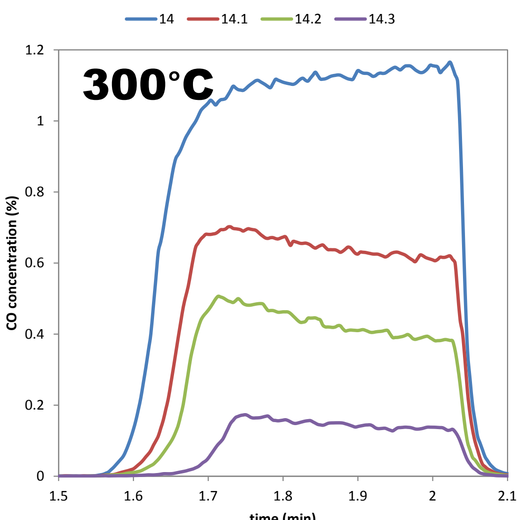
- NH_3 profiles during lean to rich transitions:

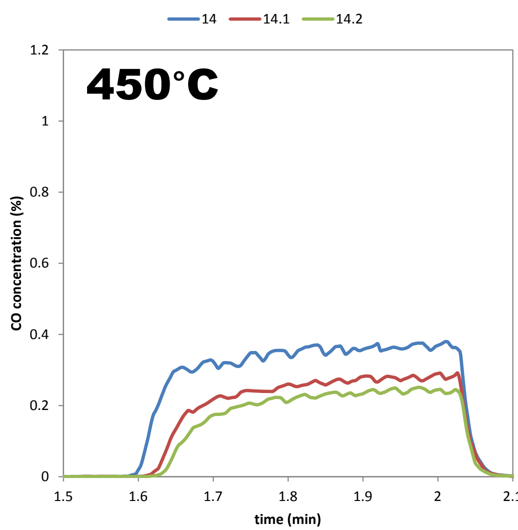


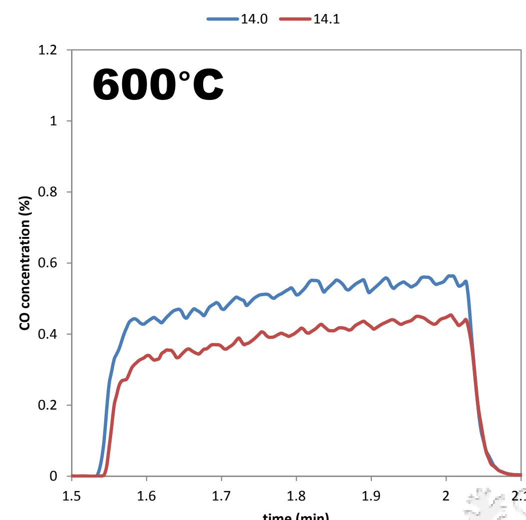




- CO profiles during lean to rich transitions:

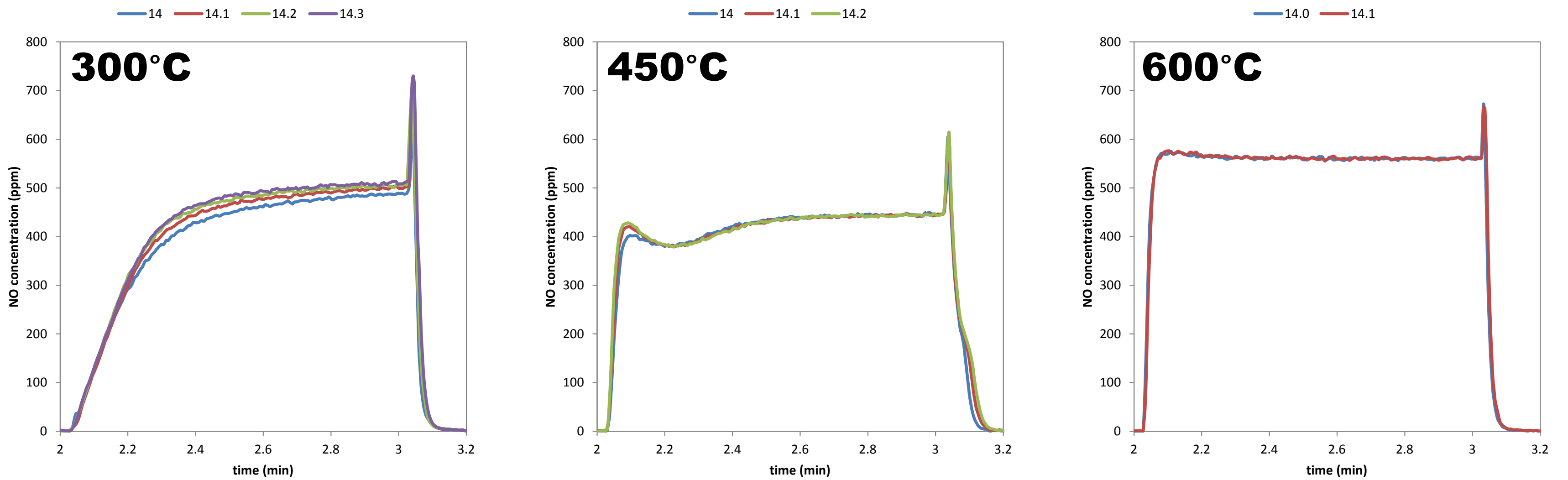




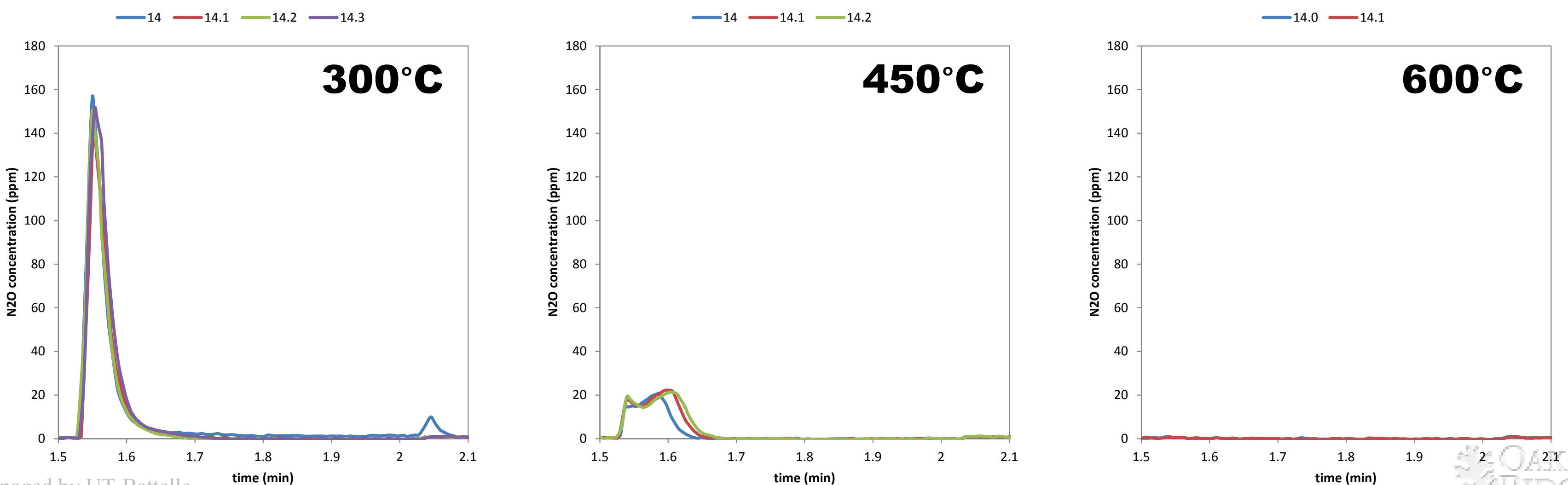


TWC (high PGM Pd-only) transients

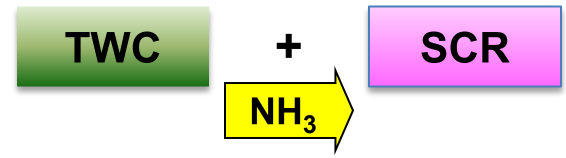
- NO profiles during lean to rich transition illustrate some storage at low temperature:



- N_2O profiles during lean to rich transitions:



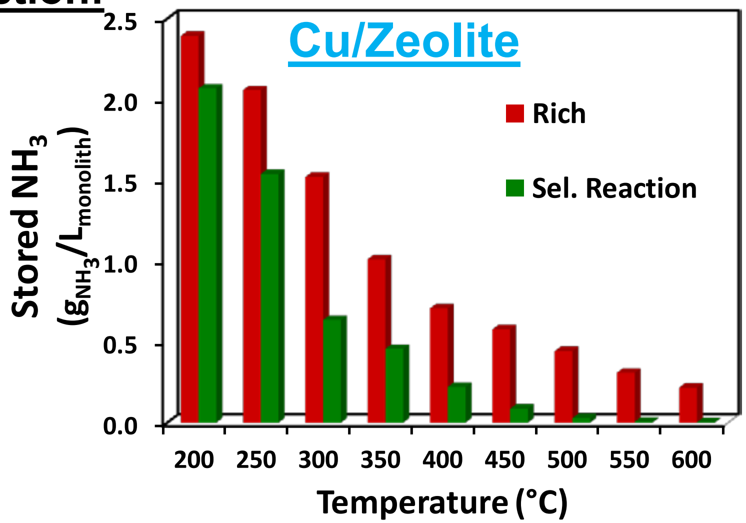
SCR Screening:

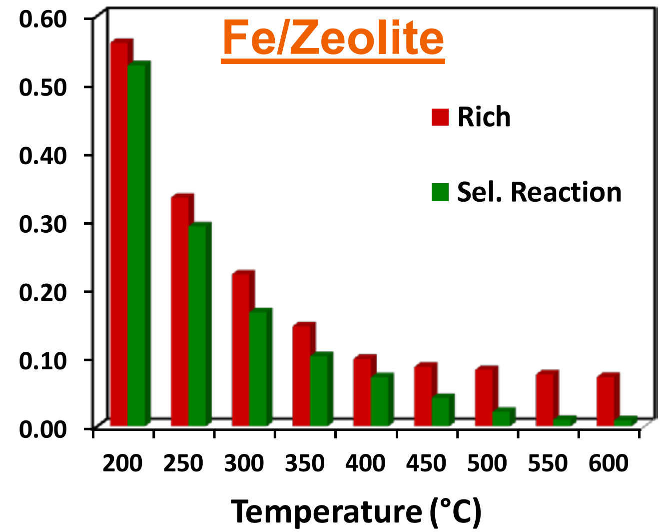


NH$_3$–SCR Storage/Reaction:
SV = 30,000 hr^{-1}

Storage:
500 ppm NH$_3$
5% H$_2$O, bal. N$_2$

Reaction:
500 ppm NO
10% O$_2$
5%H$_2$O, bal. N$_2$





Steady-State NH$_3$–SCR:
SV = 30,000 hr^{-1}

500 ppm NO
500 ppm NH$_3$
10% O$_2$
5% H$_2$O