The Effect of Ceria on the Performance of Lean NOx Trap Catalysts

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May 2, 2007

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Background: Ceria in LNT Catalysis

- Role of ceria:
  - OSC for stoichiometric operation in lean-burn gasoline engines
  - water-gas shift activity for *in situ* H_2 generation:
    - » facilitates LNT regeneration at low temperatures
    - » facilitates LNT desulfation at moderate temperatures
  - NOx storage at low temperatures (<300 °C)
- Use of ceria may prove critical for low temperature applications, e.g., LD diesel (typical FTP temperatures of ~150-340 °C)
- Role of ceria largely ignored in literature LNT studies

J. Theis, J. Ura, C. Goralski Jr., H. Jen, E. Thanasiu, Y. Graves, A. Takami, H. Yamada, S. Miyoshi, SAE 2003-01-1160
T. Morita, N. Suzuki, N. Satoh, K. Wada, H. Ohno, SAE 2007-01-0239.

Objectives

- Confirm role of ceria
- Quantify effect of ceria in fresh and aged catalysts
- Study divided into two parts:

  - Powder model catalysts: Pt/Ba/Al_2O_3 with and without added Pt/CeO_2
  - Monolithic model catalysts

Part I: Powder Model Catalysts

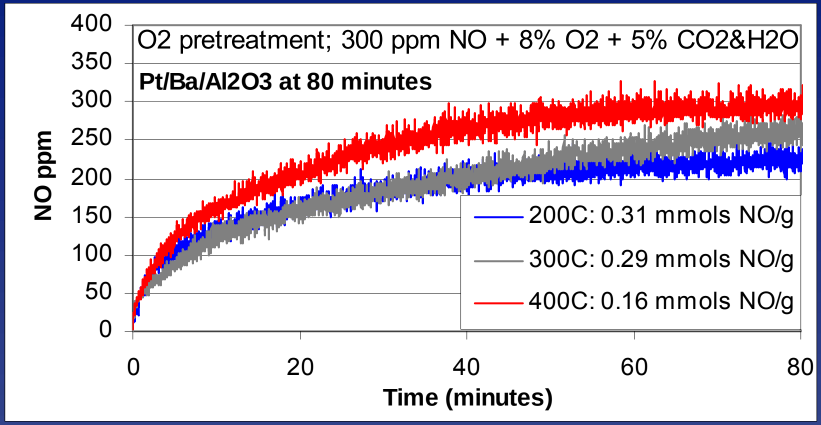
- Experiments performed in a microreactor equipped with mass spectrometer

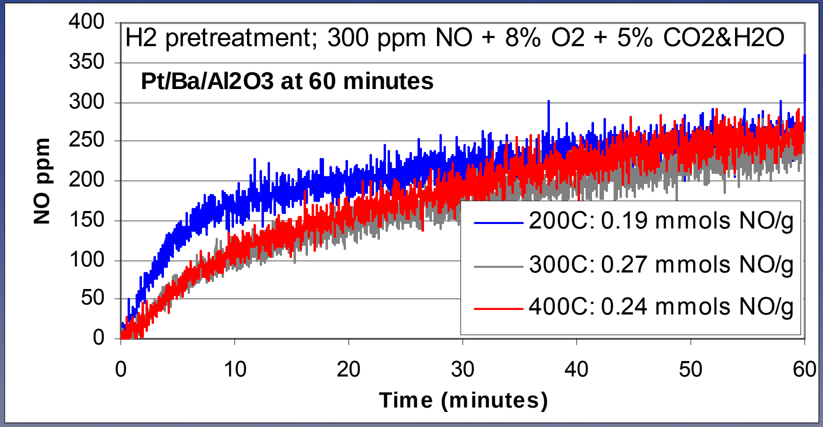
- Investigate effect of ceria on LNT functioning, including:
  - NOx storage capacity under continuous lean flow
  - Storage-regeneration behavior under long cycle conditions
  - Regeneration efficiency

- Two catalysts were prepared:
  - 1 wt% Pt/BaO/Al_2O_3 (“PBA”)
  - 1 wt% Pt/BaO/Al_2O_3 (74 wt%) + 1 wt% Pt/CeO_2 (26 wt%), physical mixture (“PBAC”)

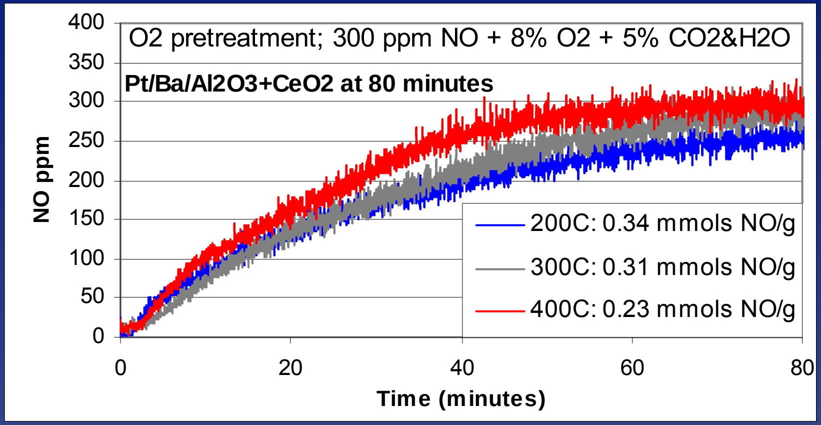
Intrinsic NOx Storage Capacity

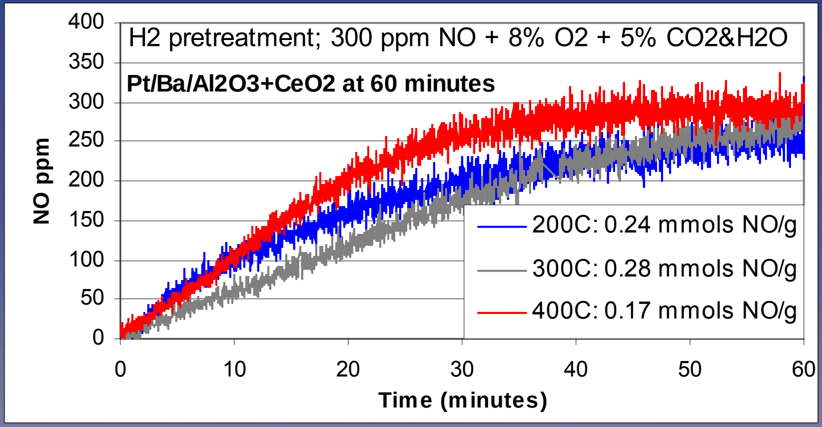
PBA





PBAC

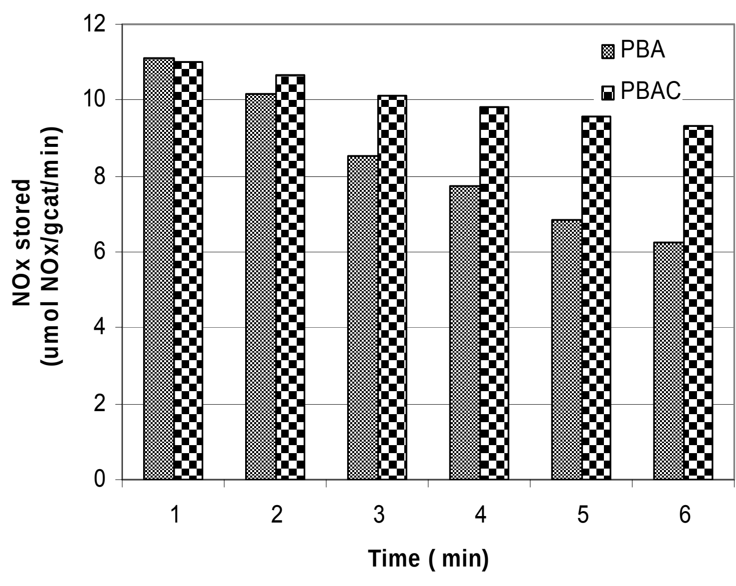




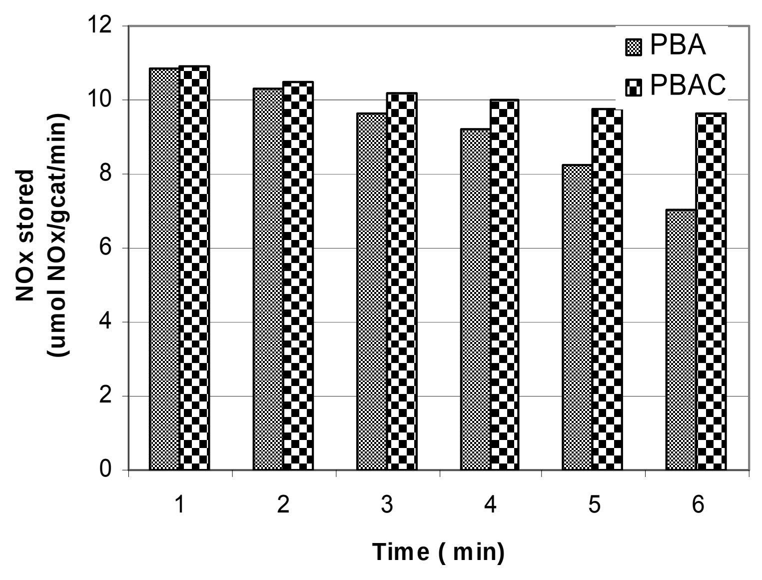
Comparison of Static NOx Storage Capacity

(after H_2 pretreatment)

T = 200 °C



T = 300 °C



Ceria-containing catalyst (PBAC) shows clear advantage at 200 and 300 °C

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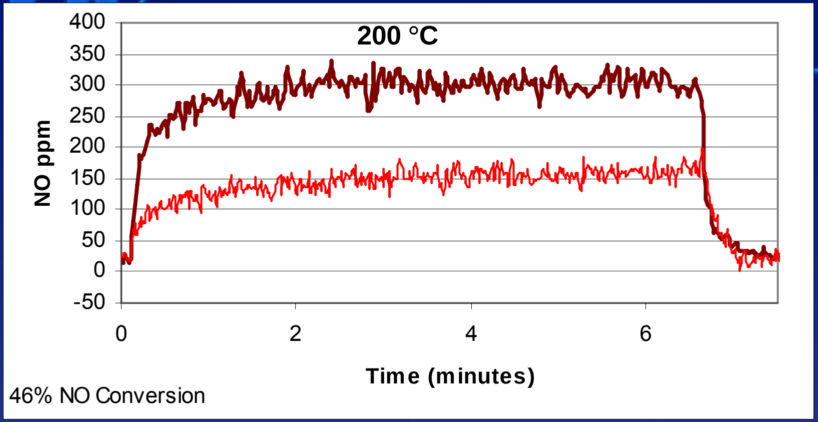
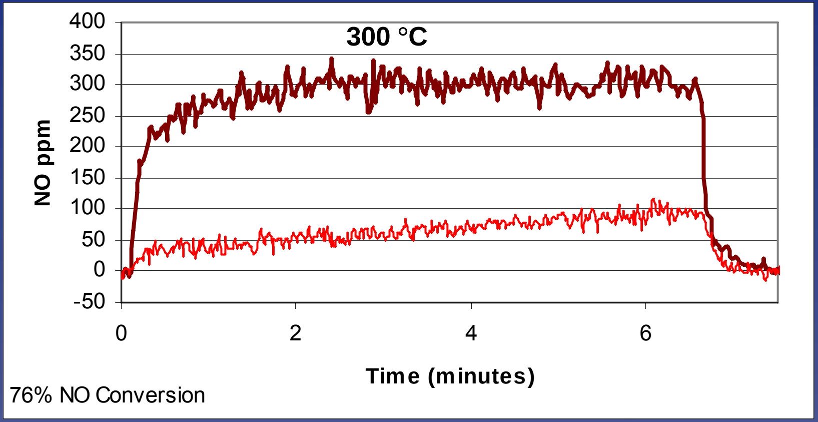
PBA – SS Cycling at 30k h^{-1}

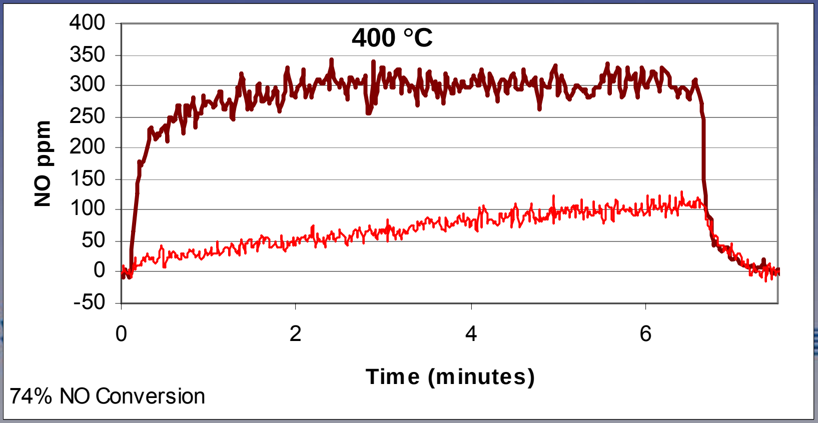
30 sec Rich – 3375 ppm H_2, 5625ppm CO, 5% H_2O and CO_2
6 minutes Lean – 300 ppm NO, 8% O_2, 5% H_2O and CO_2



46% NO Conversion



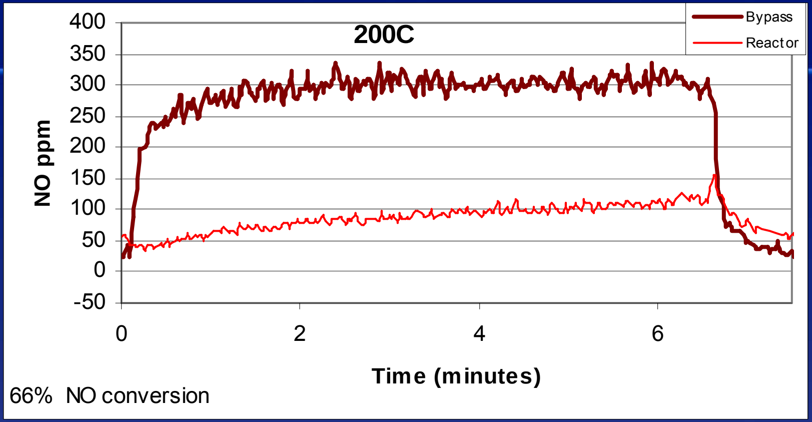
76% NO Conversion



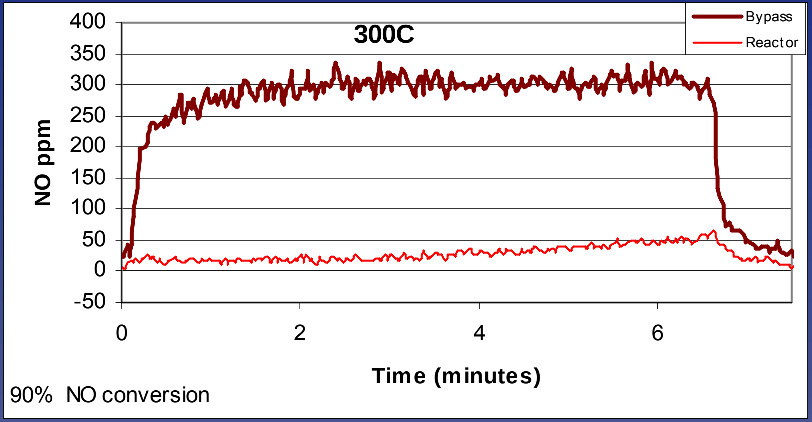
74% NO Conversion

PBAC – SS Cycling at 30k h^{-1}

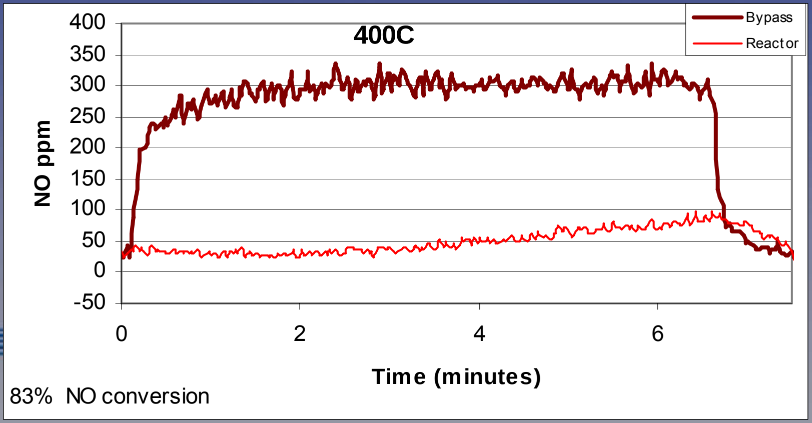
30 sec Rich – 3375 ppm H_2, 5625ppm CO, 5% H_2O and CO_2
6 minutes Lean – 300 ppm NO, 8% O_2, 5% H_2O and CO_2



66% NO conversion



90% NO conversion



83% NO conversion

Comparison of NOx storage, release and reduction during lean/rich cycling

Catalyst	Temp (°C)	NOx stored (μmol/g)	NOx rel.[a] (μmol/g)	NOx conv. (μmol/g)			NOx conv.[b] (%)	N_2 sel.[c] (%)
				Total	NOx→N_2	NOx→NH_3 + N_2O		
PBA	200	29.9	1.6	28.3	23.3	5.0	45.9	82.3
	300	47.4	0.5	46.9	32.4	14.5	75.9	69.1
	400	46.4	0.9	45.5	35.5	10.0	73.8	78.0
PBAC	200	42.8	1.7	41.1	37.8	3.2	66.6	92.2
	300	56.0	0.5	55.5	42.0	13.5	90.0	75.7
	400	51.8	1.1	50.7	44.4	6.3	82.1	87.6

[a]: the amount of NOx released after the switch from lean to rich phase; [b]: NOx conversion = ((NOx stored during lean phase – NOx released during switch)/total inlet NO) x 100; [c]: N_2 selectivity = (NOx converted to N_2/total NOx converted during rich period) x 100.

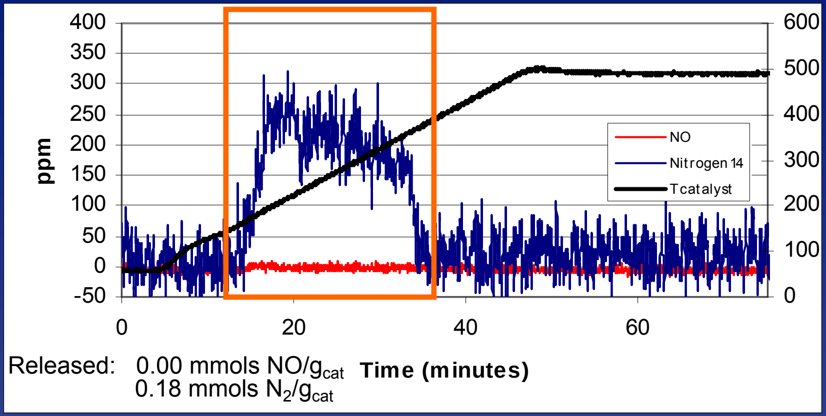
LNT Regeneration Studies

- Method:
  - Microreactor equipped with mass spectrometer during temperature-programmed reduction with H_2 or CO reductant

- Procedure:
  - Pre-treat catalyst in H_2 at 450 ° C (30 min)
  - Store NOx at 300 °C (300 ppm NO and 8% O_2 in Ar)
  - Cool to RT in Ar
  - Start TPR in rich feed gas with a ramp of 5 °C/min; evolved species monitored by MS

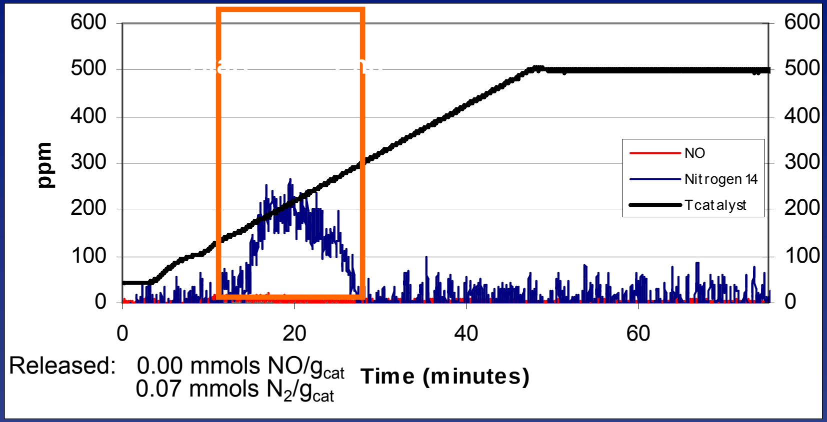
TPR under 2000 ppm H_2

PBA

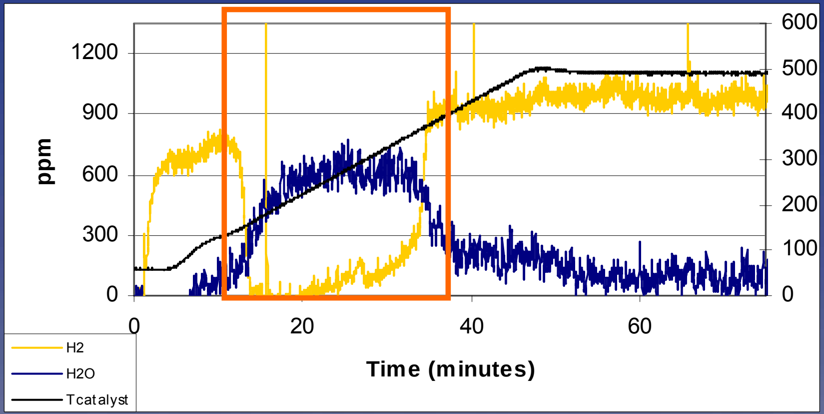


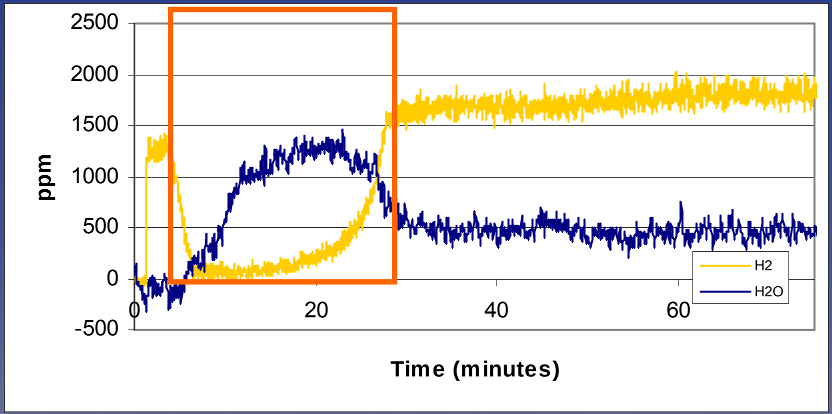
Released: 0.00 mmols NO/g_{cat}
0.18 mmols N_2/g_{cat}

PBAC



Released: 0.00 mmols NO/g_{cat}
0.07 mmols N_2/g_{cat}

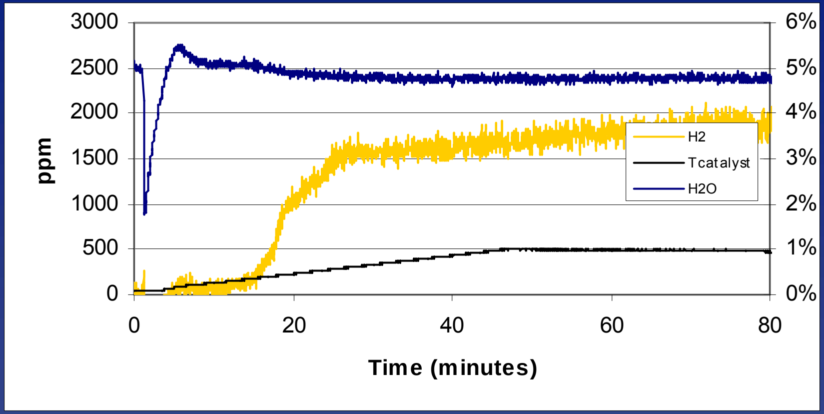


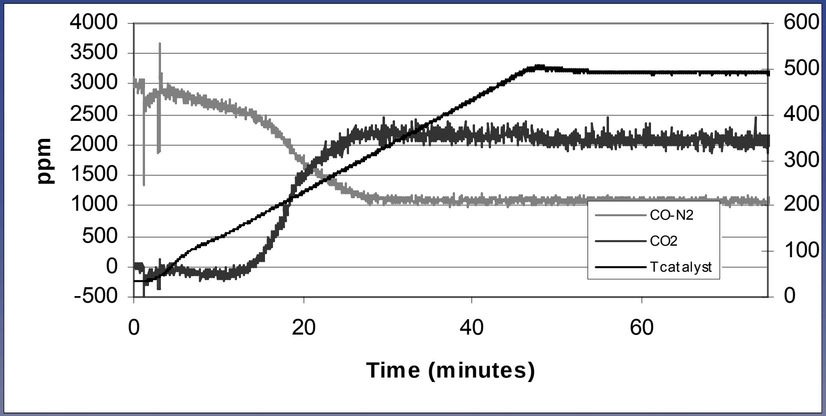


- H_2 consumption over PBAC commenced at a lower temperature than PBA
- N2 evolution complete at

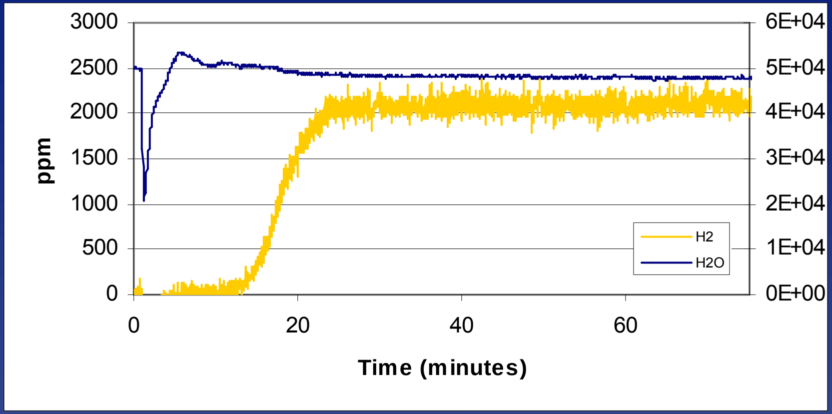
TPSR under CO + H_2O

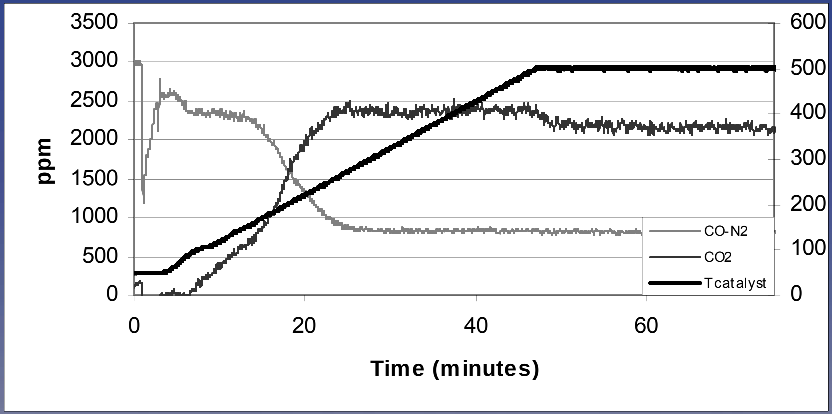
PBA - 3000 ppm CO + 5% H_2O no NO stored





PBAC - 3000 ppm CO + 5% H_2O no NO stored





- Water-gas shift reaction took place on both catalysts
- PBAC exhibited higher H_2 production than PBA at low temperatures (<275 °C)

Summary of TPR Study

Catalyst	TPR	H_2 consumption		N_2 release	
		T_{start} (^{o}C)	T_{end} (^{o}C)	T_{start} (^{o}C)	T_{end} (^{o}C)
PBA	H_2	150	385	150	384
	H_2 (w/ H_2O)	110	340	125	353
	CO	---	---	195	500
	CO (w/ H_2O)	---	---	175	399
PBAC	H_2	81	305	130	307
	H_2 (w/ H_2O)	35	345	127	342
	CO	---	---	193	431
	CO (w/ H_2O)	---	---	118	371

Summary of Powder Model Catalyst Studies

- PBAC shows superior NOx storage capacity to PBA at T $\leq$ 300 °C (for H_2 and O_2 pretreatments)
- In lean/rich cycling, PBAC shows superior *effective* NOx storage capacity to PBA at 200 °C, 300 °C and 400 °C
- Rich phase NOx slip during cycling is similar for PBA and PBAC, hence overall NOx conversion is significantly higher for PBAC during L/R cycling
- Reduction of stored NOx reaches completion at lower temperatures on PBAC than on PBA (H_2 TPR)

Part II: Monolithic Catalysts

- To examine effect of ceria on performance of monolithic catalysts under realistic cycling conditions

- Catalyst preparation:

  - Focus on LNTs for diesel applications

  - Employ model catalysts which are representative of 2nd generation LNT formulations (⇒ use of ceria; also of relevance for lean-burn gasoline LNTs)

  - Monolithic catalysts with systematic variation of ceria concentration

Monolithic Catalyst Compositions

Component	Loading			
	30-0	30-50	30-100	30-100Z
Pt, g/L (g/cuft)	3.53 (100)	3.53 (100)	3.53 (100)	3.53 (100)
Rh, g/L (g/cuft)	0.71 (20)	0.71 (20)	0.71 (20)	0.71 (20)
BaO, g/L	30	30	30	30
CeO_2, g/L	0	50	100	-
CeO_2-ZrO_2, g/L	-	-	-	100
Al_2O_3, g/L	Balance	Balance	Balance	Balance

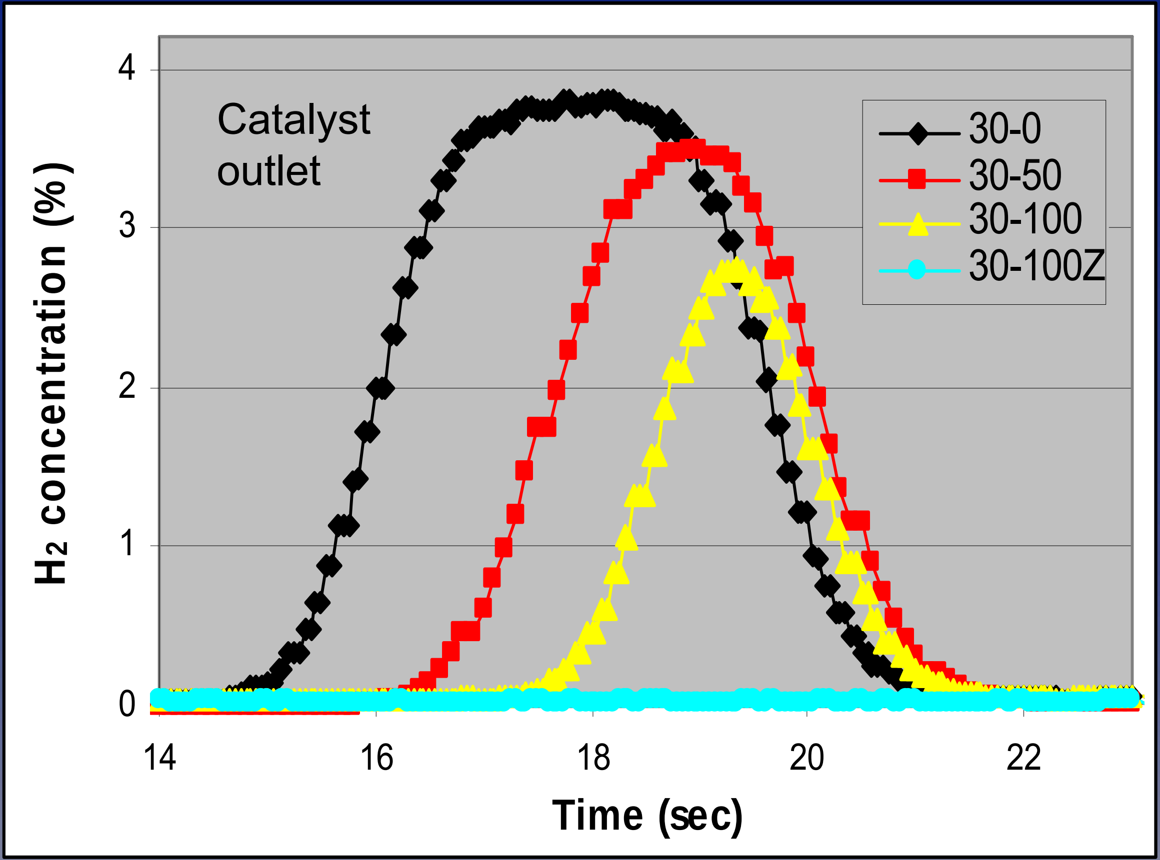
Total washcoat loading = 260 g/L

Baseline Catalyst Testing

- Bench (core) reactor
- Testing procedure:
  - De-green catalyst at 500 °C under lean-rich cycling for 5 h
  - Measure oxygen storage capacity at 350 °C under lean-rich cycling
  - Lean-rich cycling with NO at 350 °C.
  - Fully regenerate catalyst at 500 °C in H_2/Ar flow (with 5% CO_2 & 5% H_2O) prior to testing at next temperature

Oxygen Storage Capacity

Lean (60 s) : 10%O_2, 5%CO_2 and 5%H_2O; Rich (5 s) : 4.2%H_2, 5%CO_2 and 5%H_2O, with N_2 as balance (GHSV = 30,000 h^{-1} , T= 350 °C)



Catalyst	Ave.OSC (mmol/L)
30-0	10.8
30-50	19.1
30-100	28.0
30-100Z	36.6

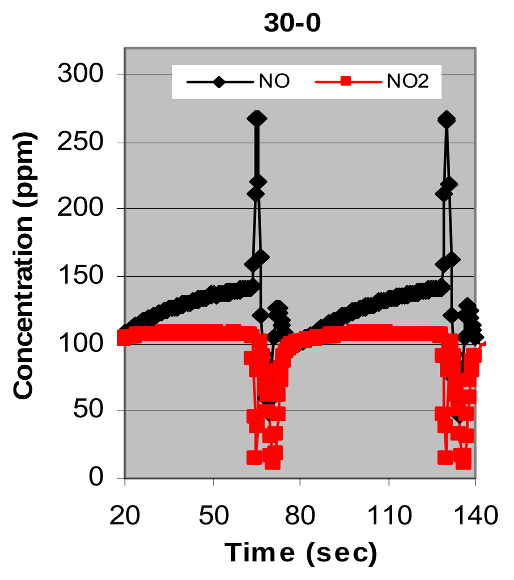
OSC increases with ceria loading and Ce-Zr mixed oxide shows a much higher OSC than ceria

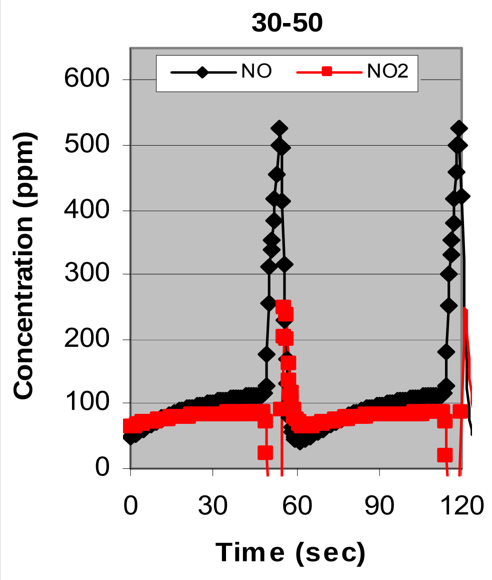
Test conditions

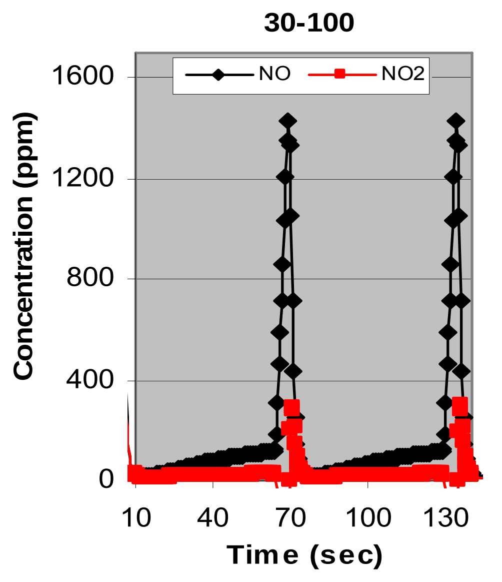
Component	Lean phase	Rich phase
NO (vppm)	300	300
CO (%)	0	2.625
H_2 (%)	0	1.575
O_2 (%)	10	0
CO_2 (%)	5	5
H_2O (%)	5	5
N_2	Balance	Balance
GHSV (h^{-1})	30,000	30,000
T (°C)	150, 250, 350, 450	150, 250, 350, 450
Duration (s)	60	5

NOx storage and release

T = 150 ºC



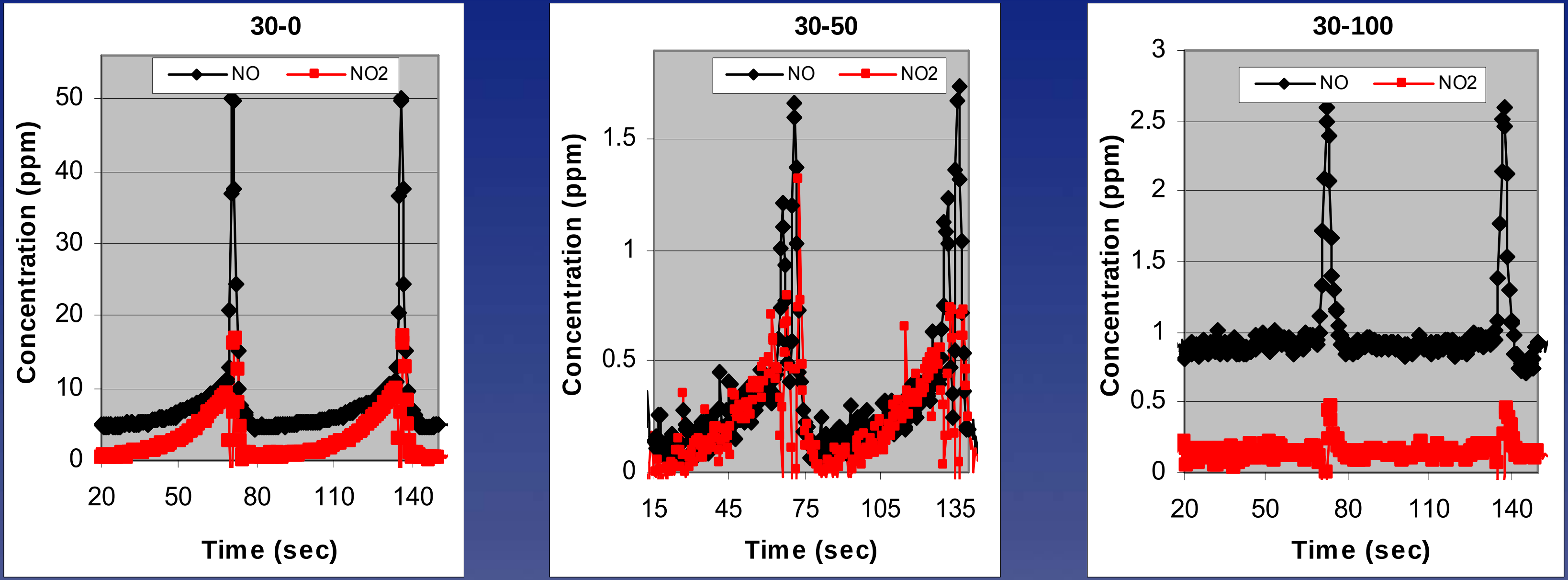




- Enhanced NOx storage capacity with increasing ceria loading
- Rich phase NOx release also increases with ceria loading
  → inbalance between NOx reduction rate and NOx release rate

NOx storage and release

T = 350 ºC



- All catalysts show high NOx storage capacity and low rich phase NOx release

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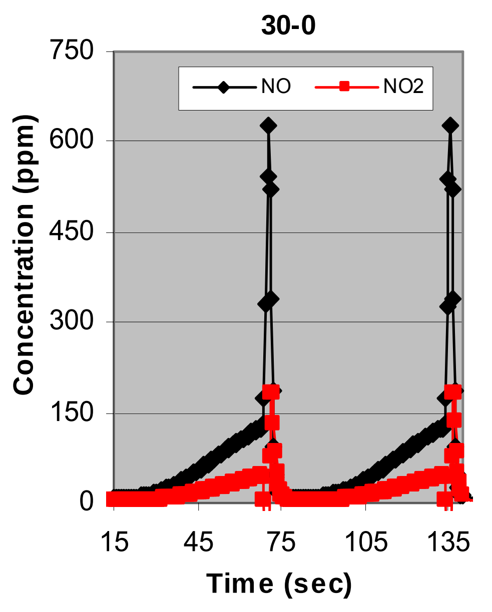
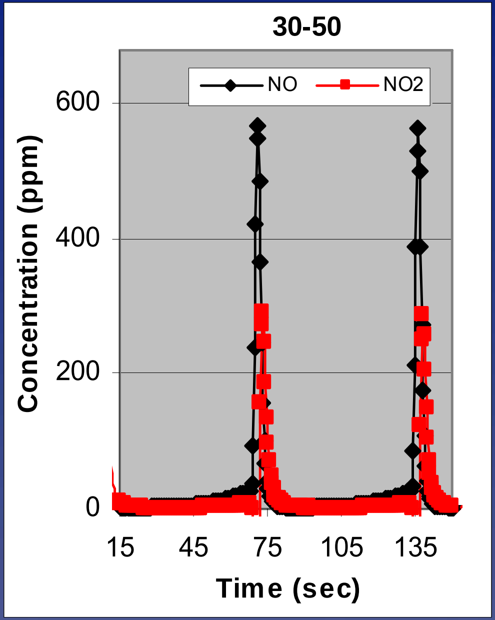
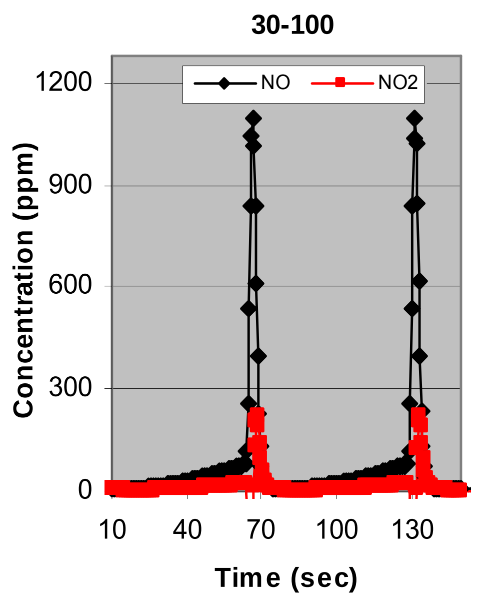
NOx storage and release

T = 450 °C



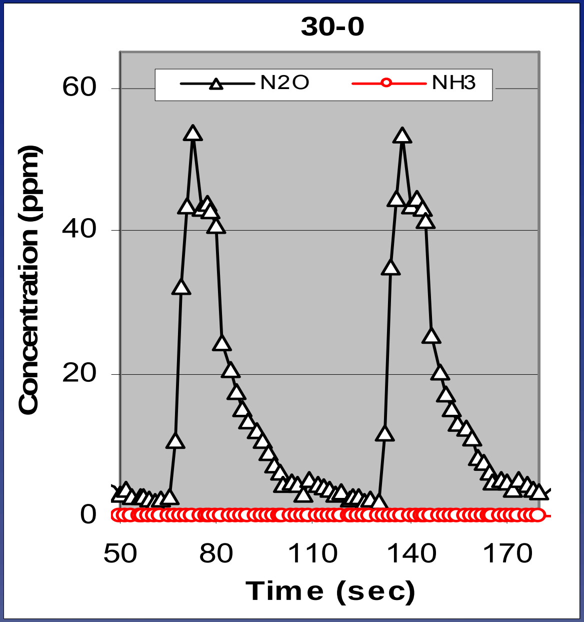


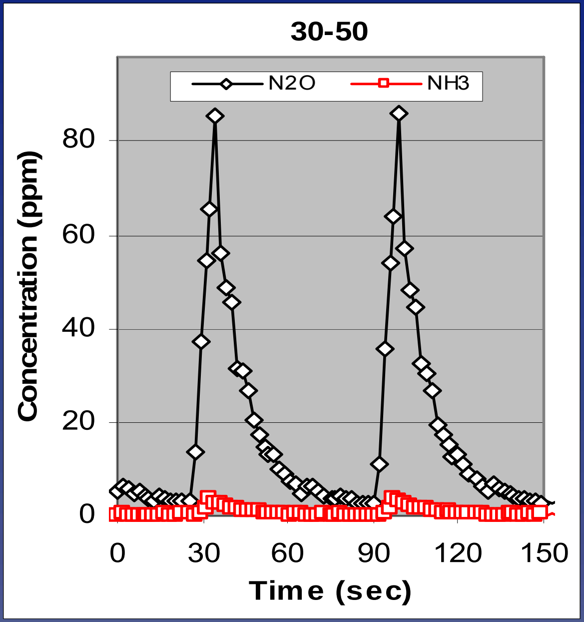


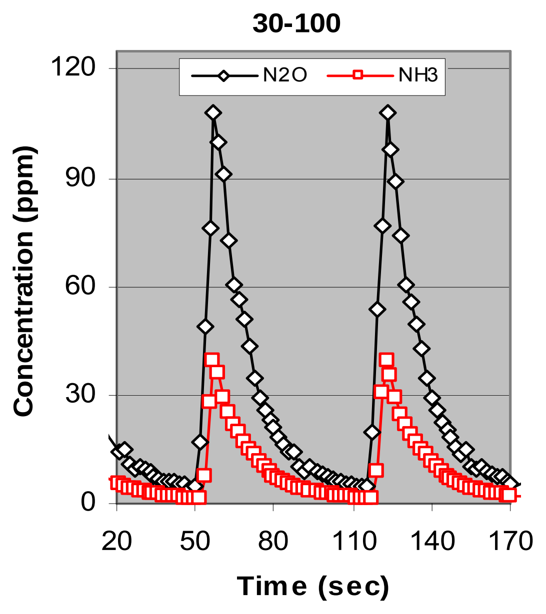
- Significant rich phase NOx release resulting from thermal instability of stored NOx
- Benefit of ceria addition is no longer obvious

NOx reduction

T = 150 ^{o}C



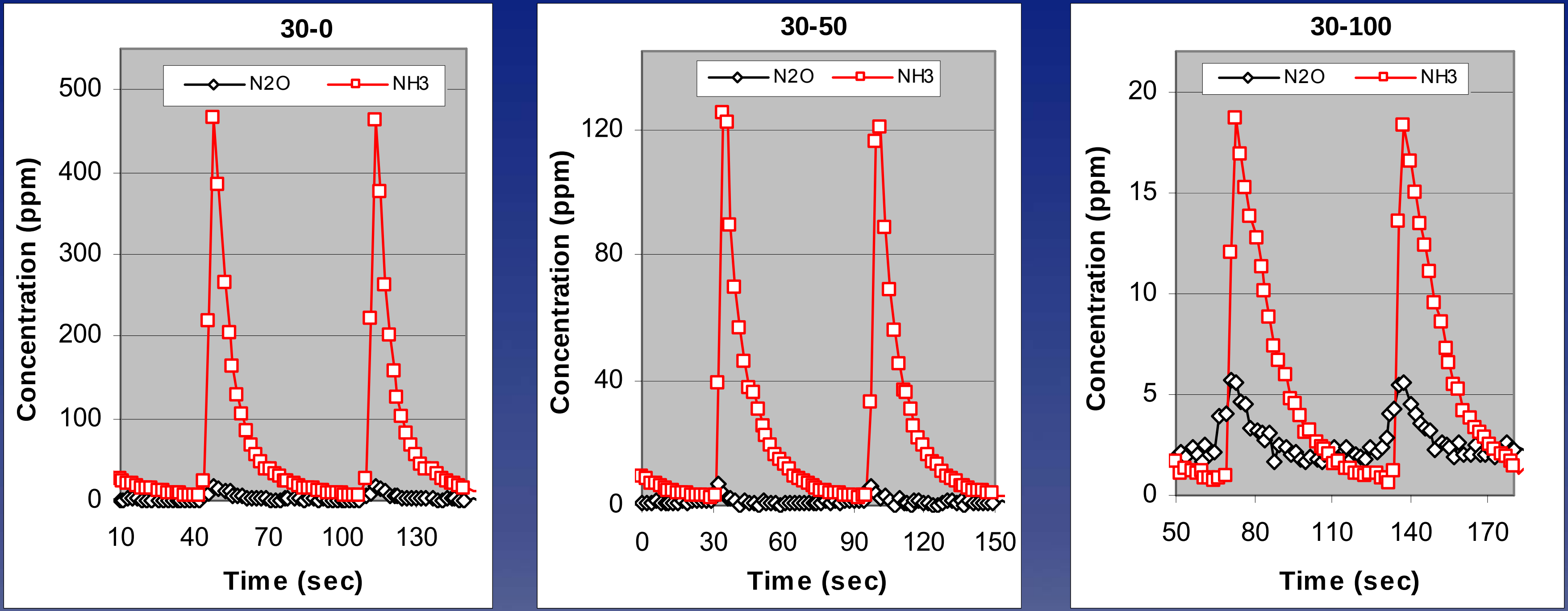




- NH_3 and N_2O formation increased with increasing ceria loading

NOx reduction

$T = 350\ ^{o}\mathrm{C}$



- Significant NH_3 formation for 30-0; NH_3 make follows the order: 30-0 > 30-50 > 30-100

Baseline Catalyst Testing: Summary

Catalyst	Temp (°C)	NOx conv. (%)	N_2 sel. (%)
30-0	150	14.1	18.0
	250	94.0	31.5
	350	95.9	66.4
	450	67.3	66.7
30-50	150	25.1	37.5
	250	99.6	73.0
	350	99.8	89.6
	450	85.5	91.3
30-100	150	34.6	20.9
	250	98.6	76.8
	350	98.6	95.8
	450	64.1	94.7
30-100Z	150	21.6	38.2
	250	96.5	79.3
	350	97.4	97.0
	450	67.8	96.6

Baseline Catalyst Testing: Summary (1)

- All catalysts show high activity (NOx conversions of > 95%) in the range 250 - 350 °C
- High selectivity to N_2O found at 150 °C for all catalysts, decreases with temperature
- In general, ceria-containing catalysts showed much higher N_2 selectivity than ceria-free catalyst. N_2 selectivity increases in the order : 30-0 < 30-50 < 30-100 < 30-100Z, in line with their OSC:
  → low OSC results in higher effective concentration of reductant, leading to "over-reduction" of stored NOx to NH_3?
  → reaction of NH_3 with oxygen stored in rear of catalyst ?

Baseline Catalyst Testing: Summary (2)

- Presence of ceria increases *effective* low temperature NOx storage capacity (much lower NO_2 slip for 30-100 at 150 °C relative to 30-0)
- NOx conversion at 150 °C for 30-100 mainly limited by kinetics of NOx reduction (imbalance in rates of NOx release and reduction results in high rich phase NOx slip)
- NO oxidation does not appear to be limiting at 150 °C, except for catalyst 30-100

Summary of Main Findings to Date

- Powder and core tests on the fresh catalysts have identified significant effects associated with the presence of ceria:

  - increased NOx storage, particularly at low temperatures
  - increased water-gas shift activity at low temperatures
  - lowering of reduction temperatures for stored NOx
  - improved selectivity to N_2 during reduction of stored NOx (versus NH_3)
  - significantly higher NOx conversion levels at $T \leq 250\ ^{\circ}C$
  - sizeable exotherms during rich operation

Outstanding Issues

- Does the ability of Pt/CeO_2 to store NOx result in decreased formation of bulk $Ba(NO_3)_2$ (and hence improve ease of regeneration of Ba phase)?

- Does Pt/CeO_2 play a role in sulfur storage, thereby lessening $BaSO_4$ formation (and hence improve ease of desulfation of Ba phase)?

➢ *In situ* XRD studies required to quantify extent of bulk $Ba(NO_3)_2$ and $BaSO_4$ formation in PBA and PBAC catalysts

- Effect of aging on performance of ceria-rich catalysts

Acknowledgements

Catalyst preparation:

DCL Int.: Mojghan Naseri
Shazam Williams

Umicore: Owen Bailey

Funding:

Department of Energy