

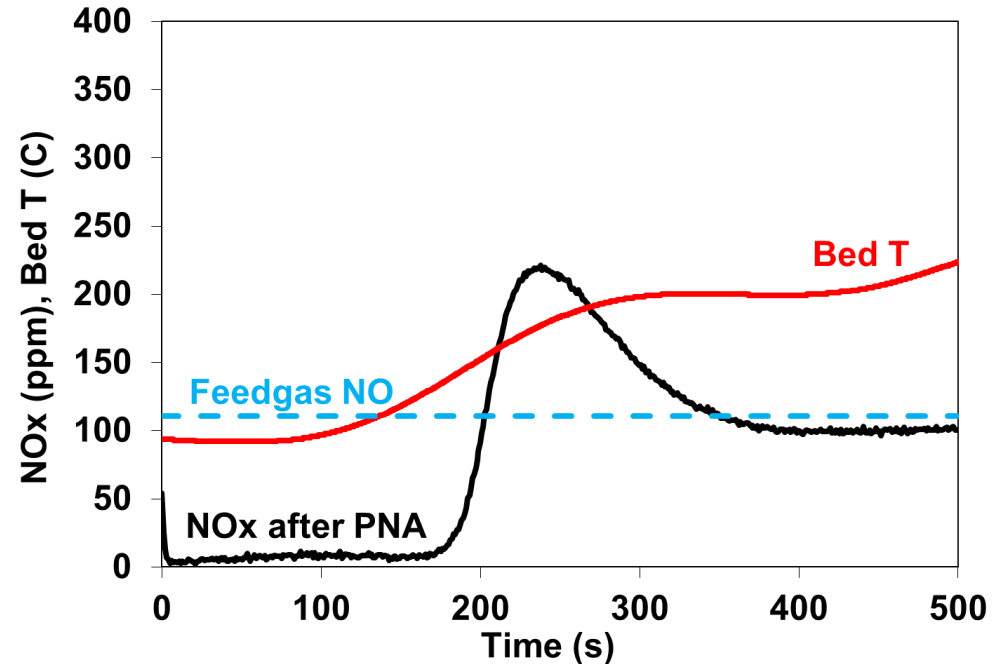
# Passive NO<sub>x</sub> Adsorbers for Diesel Applications

CLEERS Conference

April 28, 2015



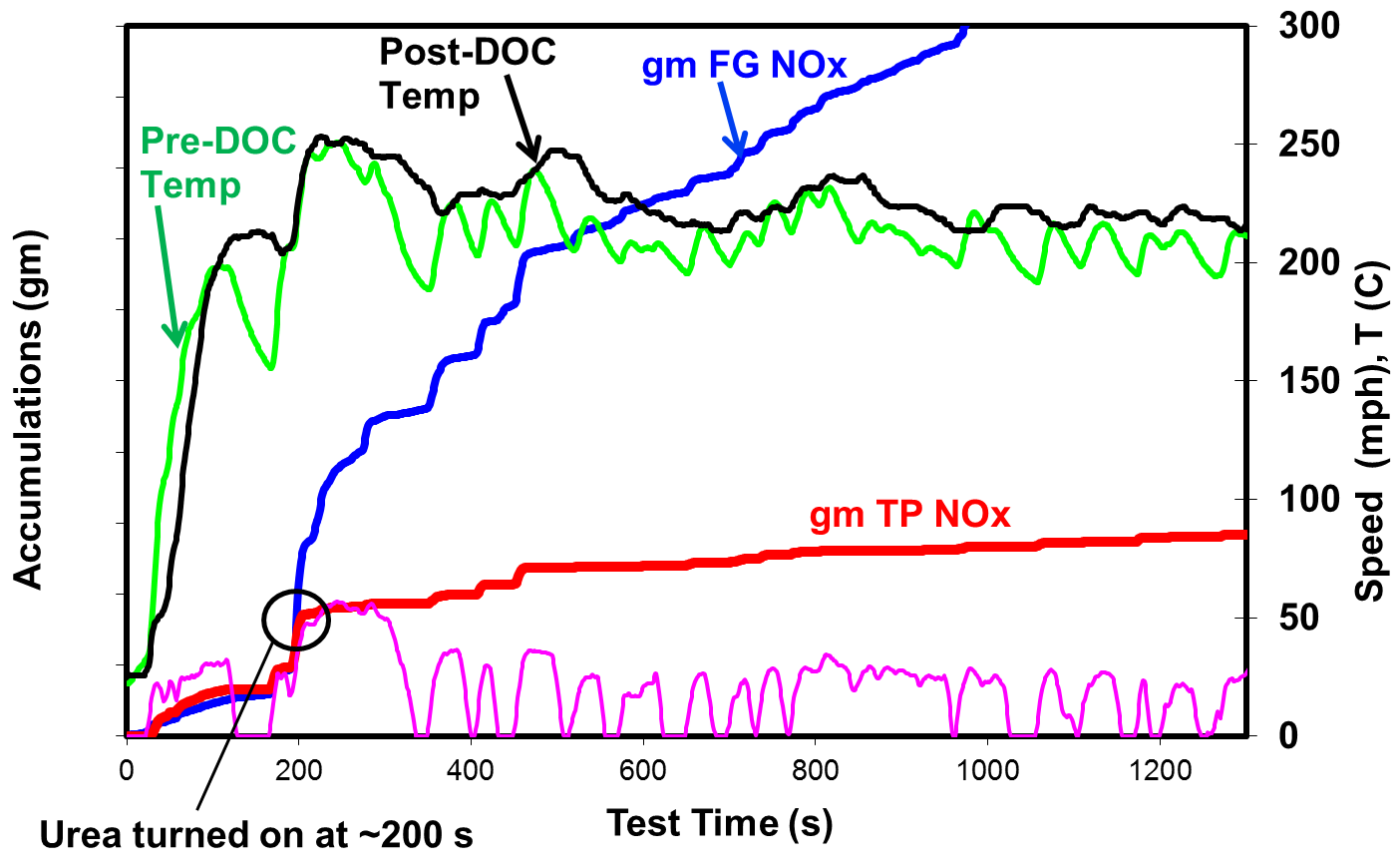
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## Background

- Urea/SCR systems effective for  $\text{NO}_x$  control above  $200^\circ\text{C}$
- Slow warm-up on diesels delays urea injection and  $\text{NO}_x$  abatement, requires extra fuel to accelerate warm-up
- PNA needed to adsorb  $\text{NO}_x$  at low T, release  $\text{NO}_x$  @ lean at higher T

Ford SuperDuty Diesel Temperatures & Emissions



- Pre/post-DOC Max T  $\sim 250^\circ\text{C}$
- Stab T in Bag 2  $\sim 200^\circ\text{C}$
- Urea on at  $\sim 200$  s

# Low Temperature NO<sub>x</sub> Adsorbers (LTNA)

Store NO (& NO<sub>2</sub>)  
from engine during  
cold start period

- 25 to 200°C

Release NO  
thermally under  
lean conditions  
at temperatures  
of FTP/US06

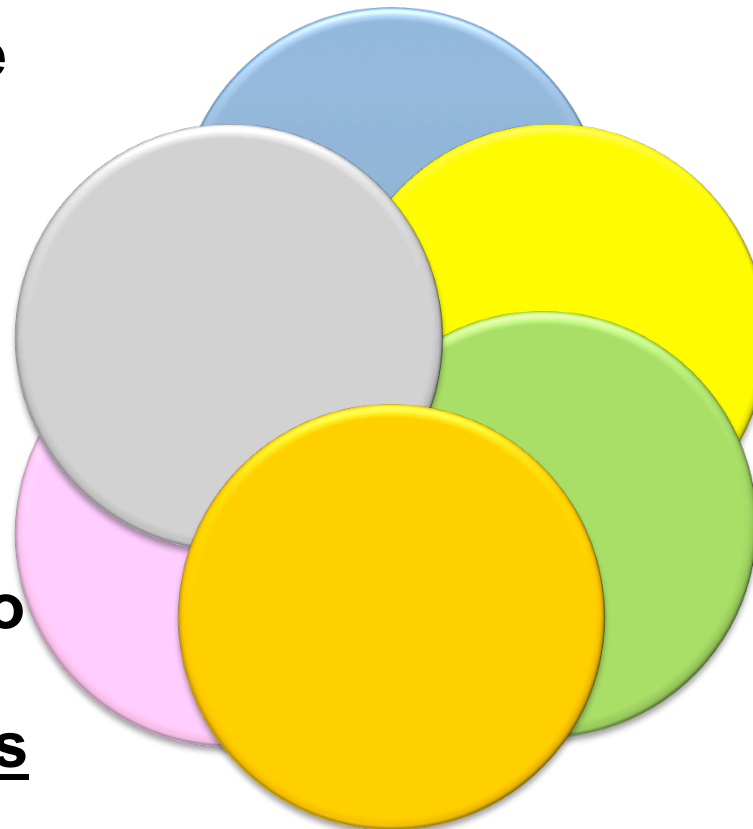
- Once urea/SCR system is operational
- 200 to 350°C

Cost Effective

- PGM loading
- PGM type
  - Pt vs Pd

Robust as  
possible to  
sulfur & able to  
deSO<sub>x</sub> under  
lean conditions

- 650 to 750°C
- DPF regens



Minimal N<sub>2</sub>O

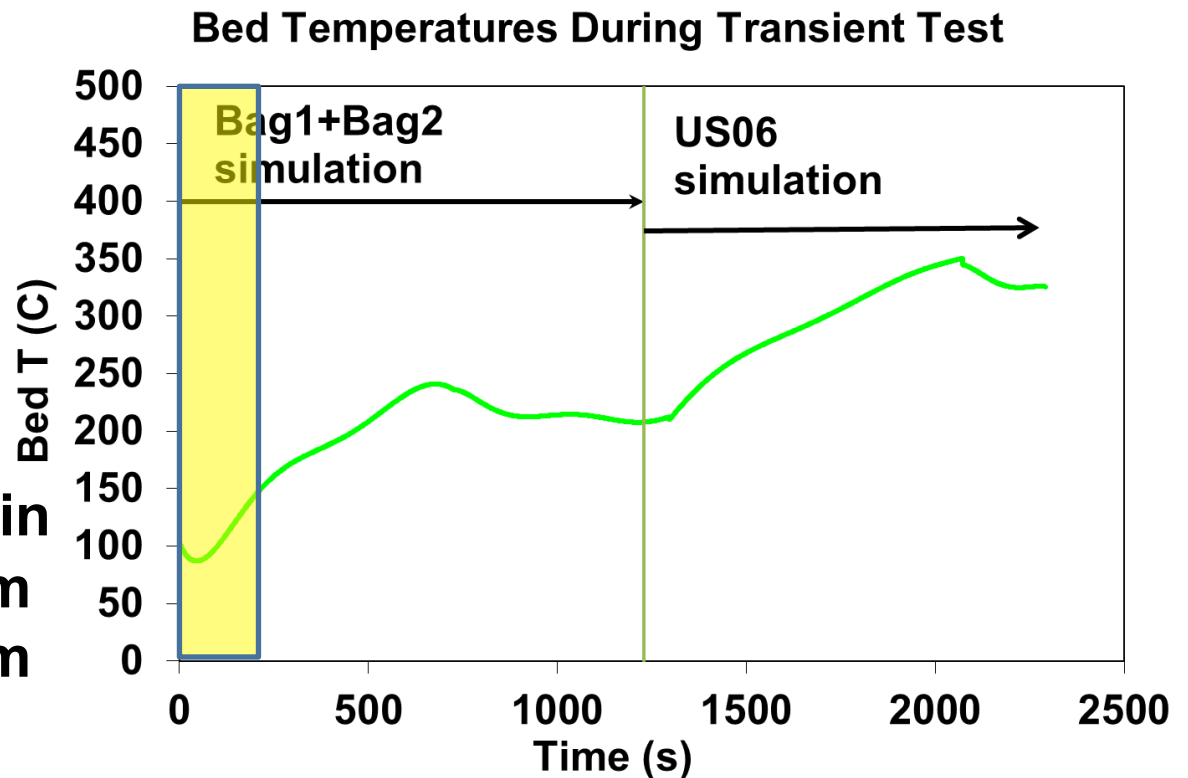
- GHG Regulations

High temperature  
durability

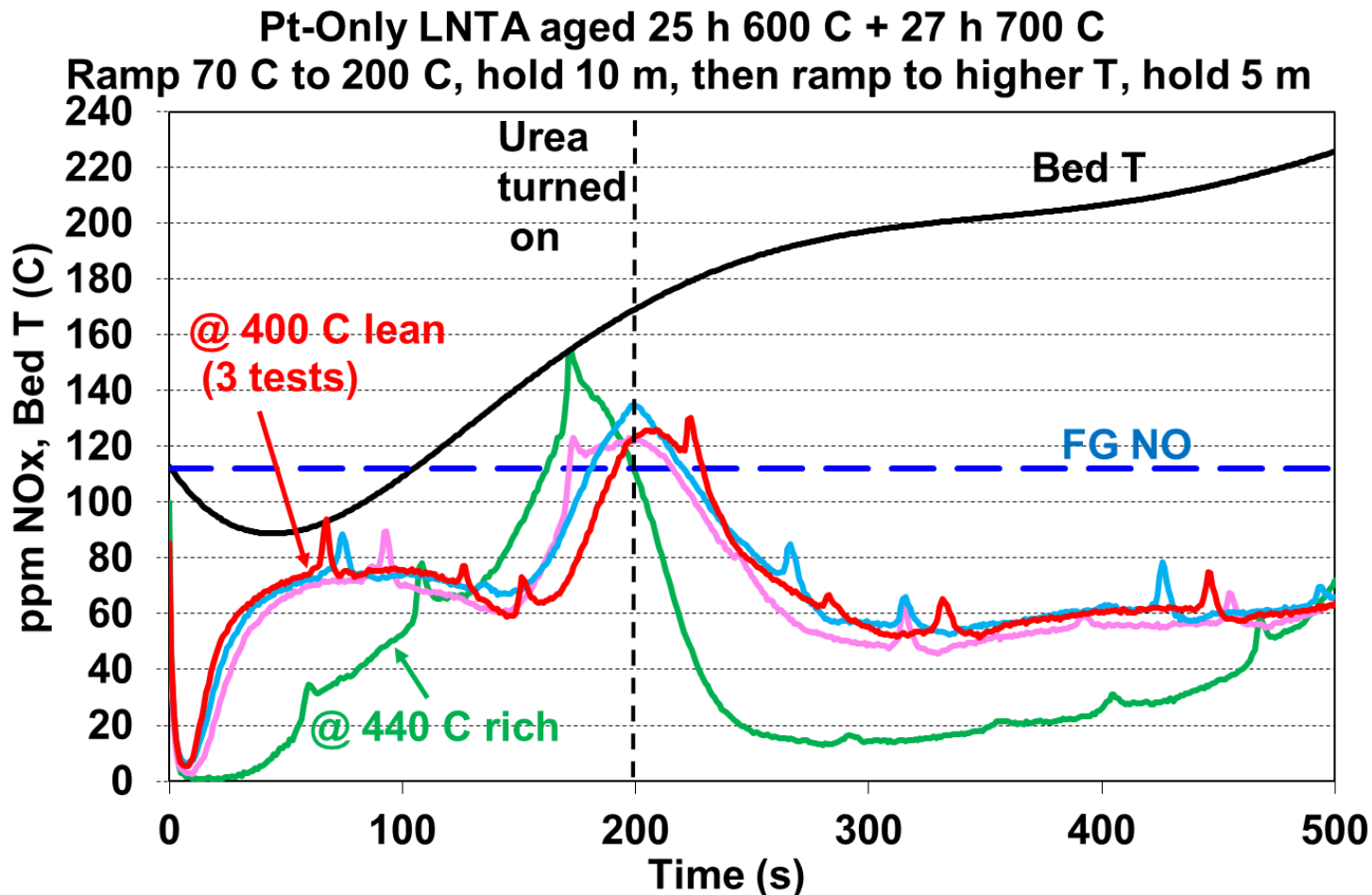
- 800 to 850°C under lean conditions (e.g., high loads)

# Transient Test on Lab Reactor

- **Goal: simulate Bags 1 & 2 of FTP + US06 on SuperDuty Diesel**
  - 250°C max during Bag 1, 200°C at end of Bag 2
- **In FG mode, stabilize**
  - 100-110 ppm NO
  - 500 ppm HC (C1)
  - 5% H<sub>2</sub>O/CO<sub>2</sub>
  - 10% O<sub>2</sub>
- **In sample mode,**
  - Ramp rate: 10°C/min
  - 70-175°C, hold 10 m
  - 175-300°C, hold 5 m
- **Focus: Ave NO<sub>x</sub> storage efficiency over first 200 s**



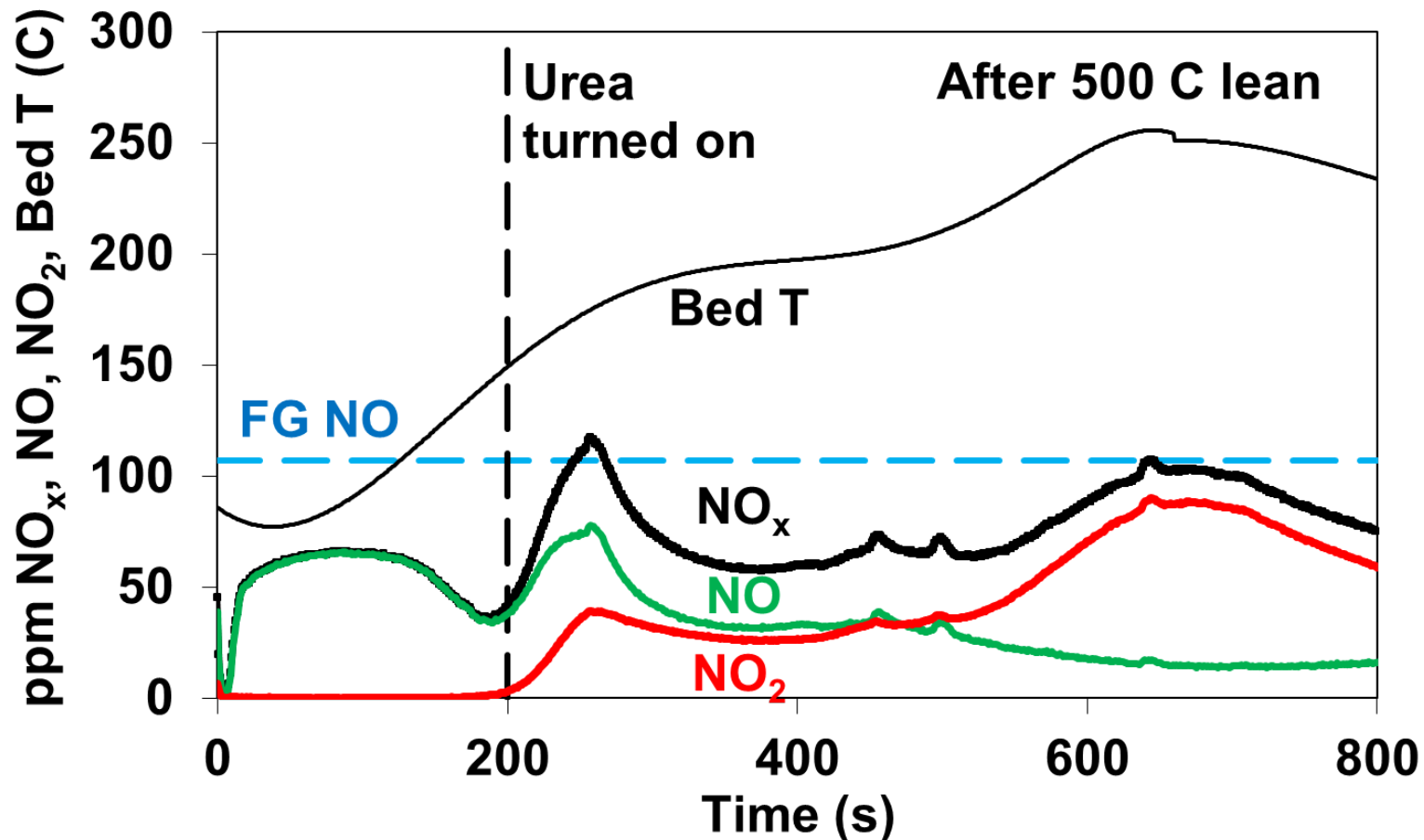
# Transient Test on 180 gpcf Pt-Only LTNA



- NO<sub>x</sub> slip high @ 400°C lean purges – poor NO oxidation, poor NO storage efficiency
- NO<sub>x</sub> slip better after 440°C rich due to good purging, improved NO oxidation activity

# Transient Test on 120 gpcf BM (2.4/1 Pt/Pd) LTNA

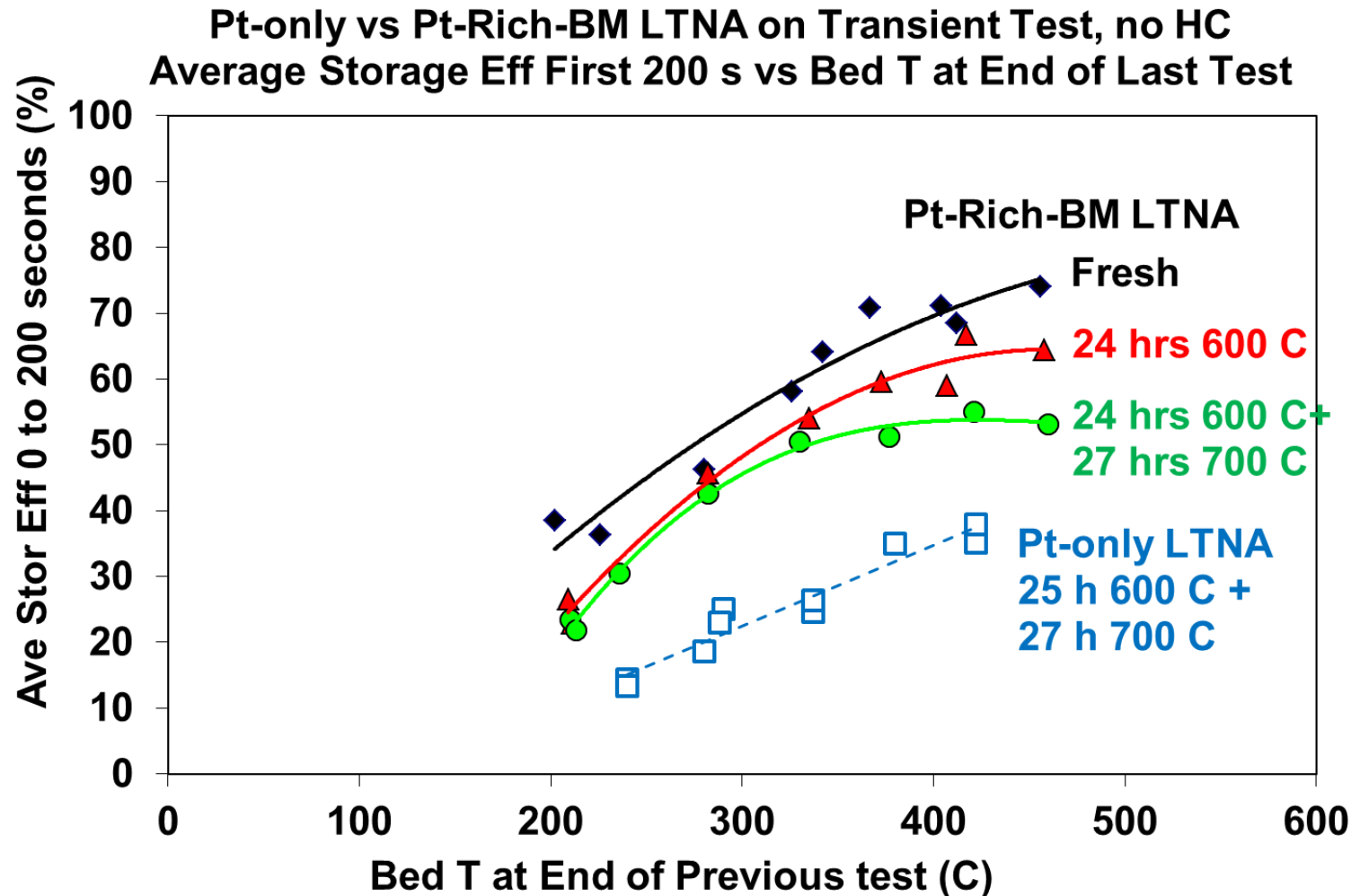
Pt-Rich-BM LTNA aged 24 h 600°C + 25 h 700°C, no HC  
Ramp 70 to 175°C, hold 10 m, ramp to Higher T, hold 5 m



**NO<sub>x</sub> slip high during 200 second window**

- Low NO oxidation + low NO storage efficiency
- NO<sub>x</sub> released as both NO and NO<sub>2</sub>

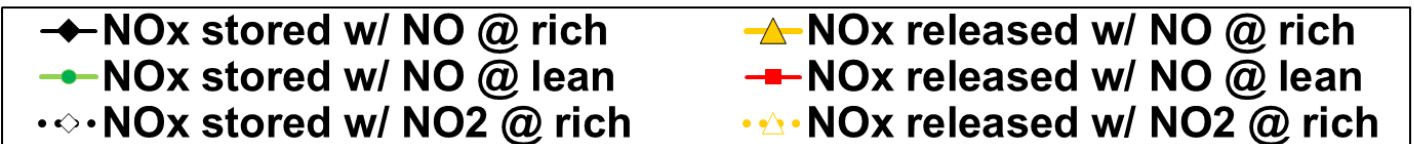
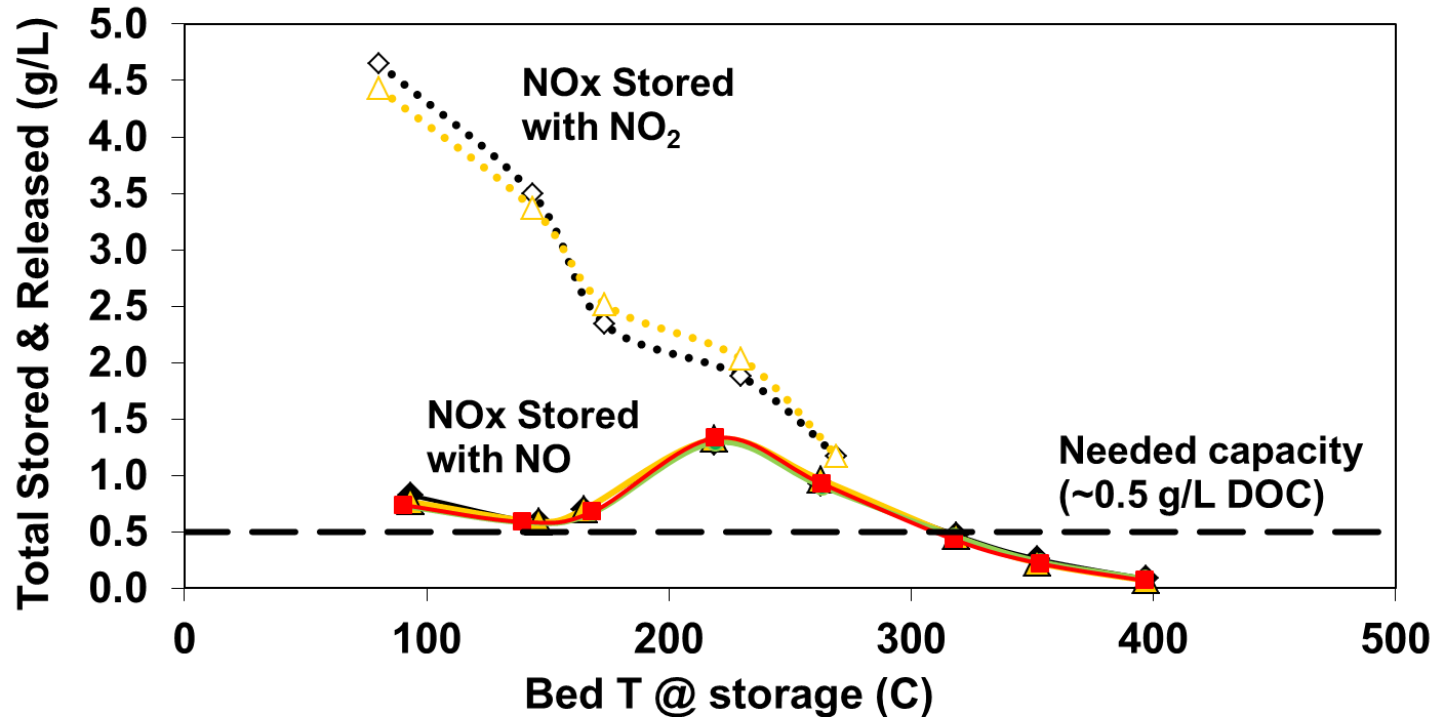
# 200 s NO<sub>x</sub> Storage Efficiency vs Previous Max T



- Ave NO<sub>x</sub> storage efficiency of Pt-Rich-BM LTNA decreased with aging
- Pt-rich-BM LNTA outperforms Pt-only LTNA after similar aging

# NO<sub>x</sub> Capacity of Fresh Pt-Rich BM LTNA with NO and NO<sub>2</sub>

Fresh Pt-Rich-BM LTNA, After Rich or Lean treatment at 440 C  
Store with either NO or NO<sub>2</sub>

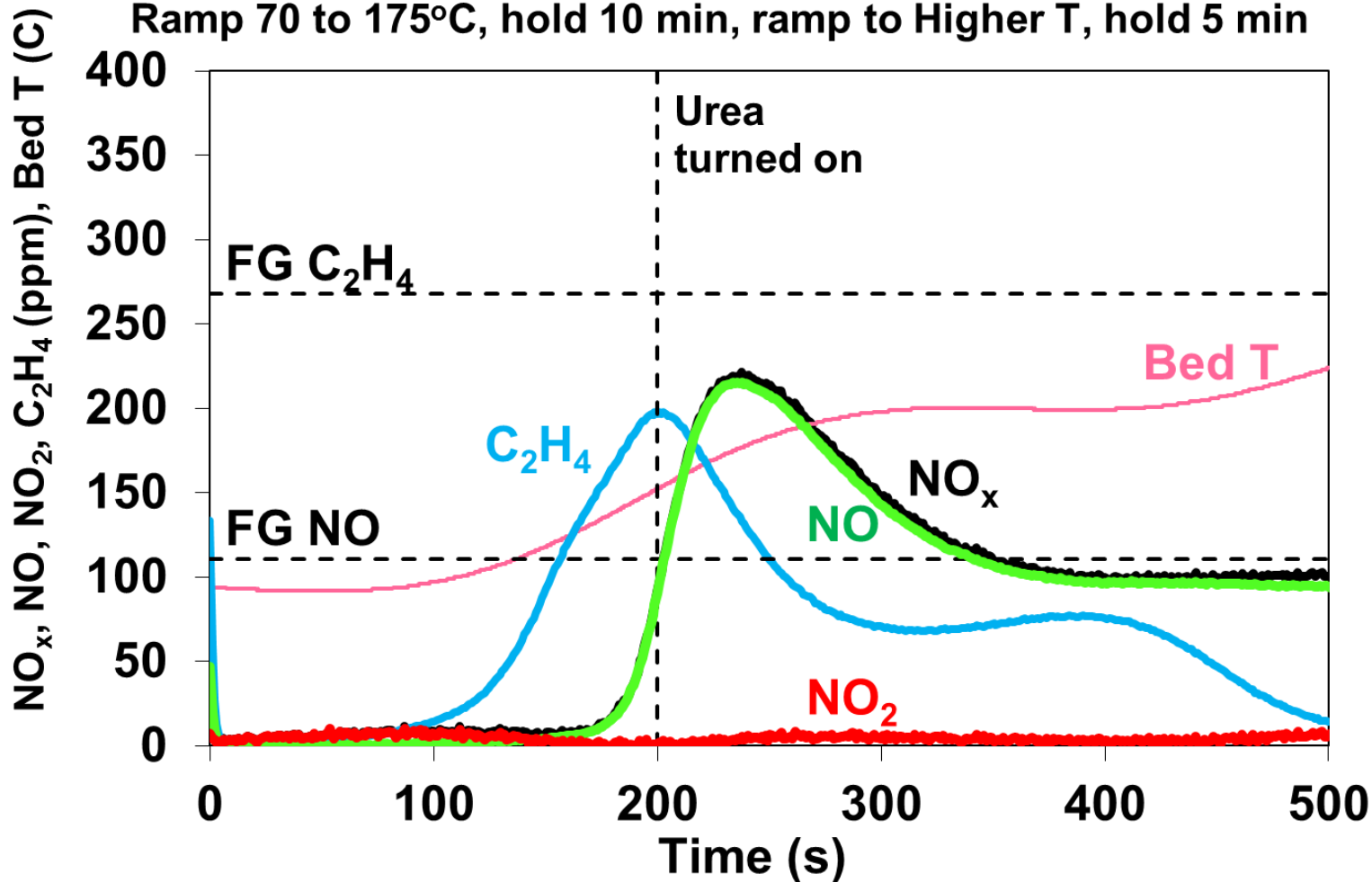


➤ Storage of NO below 250°C limited by NO oxidation



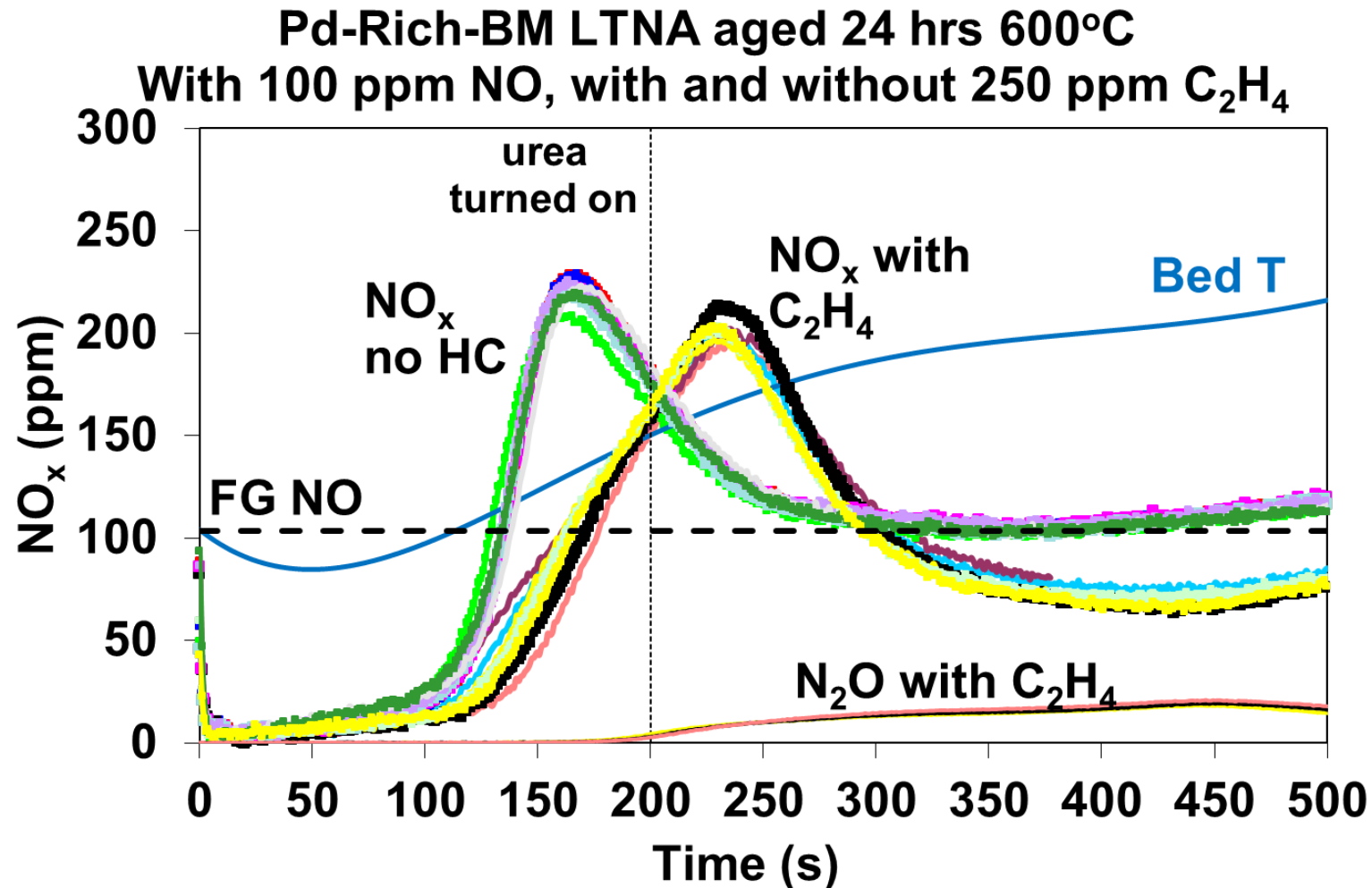
# Transient Test on 118 gpcf BM (1/3.7 Pt/Pd) LTNA

Pd-Rich-BM LTNA aged 15h700°C + 17h740°C, 270 ppm C<sub>2</sub>H<sub>4</sub>  
Ramp 70 to 175°C, hold 10 min, ramp to Higher T, hold 5 min



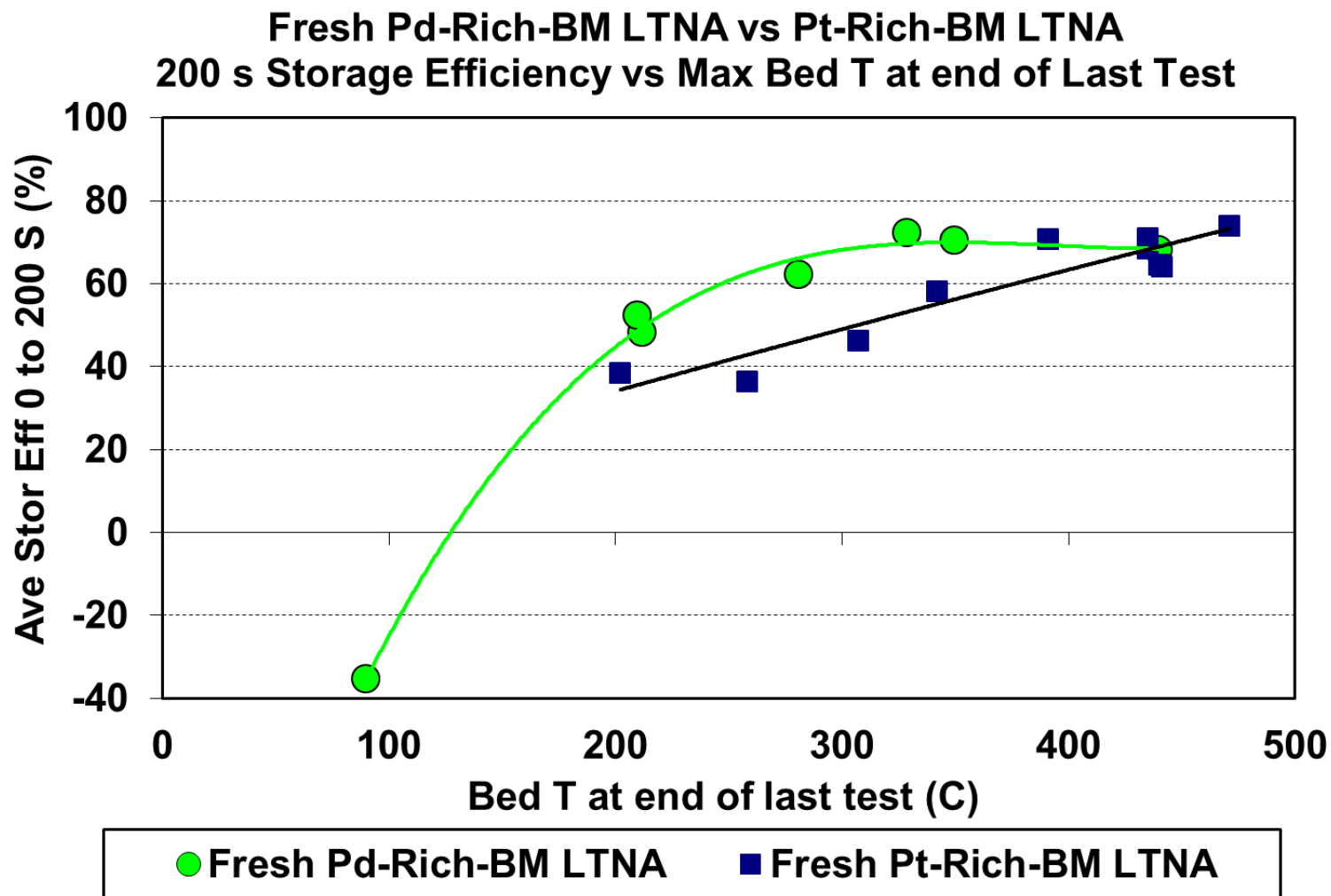
- Pd-rich-BM LTNA stored NO and C<sub>2</sub>H<sub>4</sub> very efficiently at low T
- Stored NO<sub>x</sub> released as NO → NO is stored directly at low T
- C<sub>2</sub>H<sub>4</sub> never exceeds FG level, so stored C<sub>2</sub>H<sub>4</sub> is converted

# Ethylene Improves $\text{NO}_x$ Storage Efficiency of Pd-Rich-BM



- Peak release of  $\text{NO}_x$  is delayed in presence of  $\text{C}_2\text{H}_4$ 
  - NO and HC interaction below 160°C, delays  $\text{NO}_x$  release
  - HC-SCR above 160°C (i.e., beyond 200 s) as indicated by  $\text{N}_2\text{O}$  formation

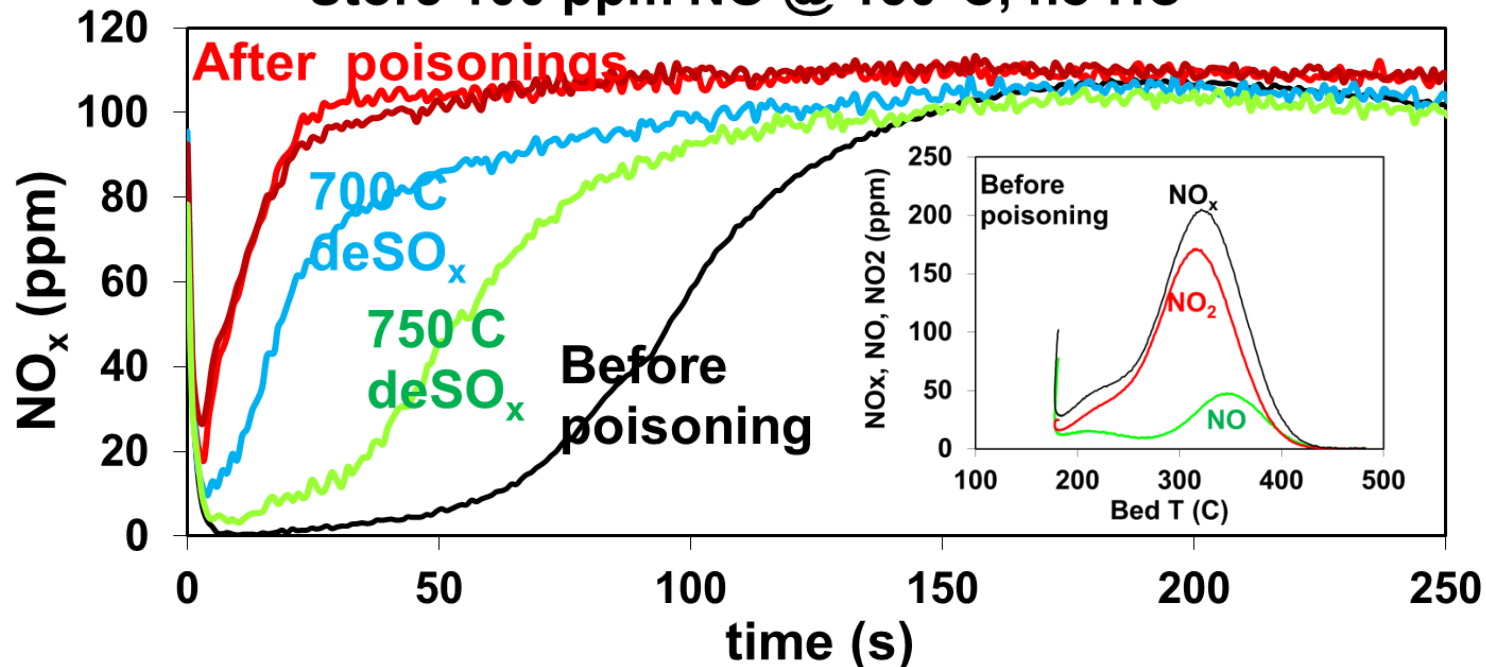
# Fresh 200 s storage efficiency of Pt-Rich-BM and Pd-Rich-BM LTNAs vs Prev Max T



- Fresh Pd-rich LTNA achieved max performance after 330-350°C (US06)
  - Significantly lower than fresh Pt-rich LTNA (nitrates more stable)

# SO<sub>2</sub> Effects on Pd-Rich-BM LTNA at 150°C SS

Pd-Rich-BM LTNA aged 24 h 600°C Lean  
 Pois w/ 5 ppm SO<sub>2</sub>, DeSO<sub>x</sub>ed lean at 700°C and 750°C  
 Store 100 ppm NO @ 150°C, no HC



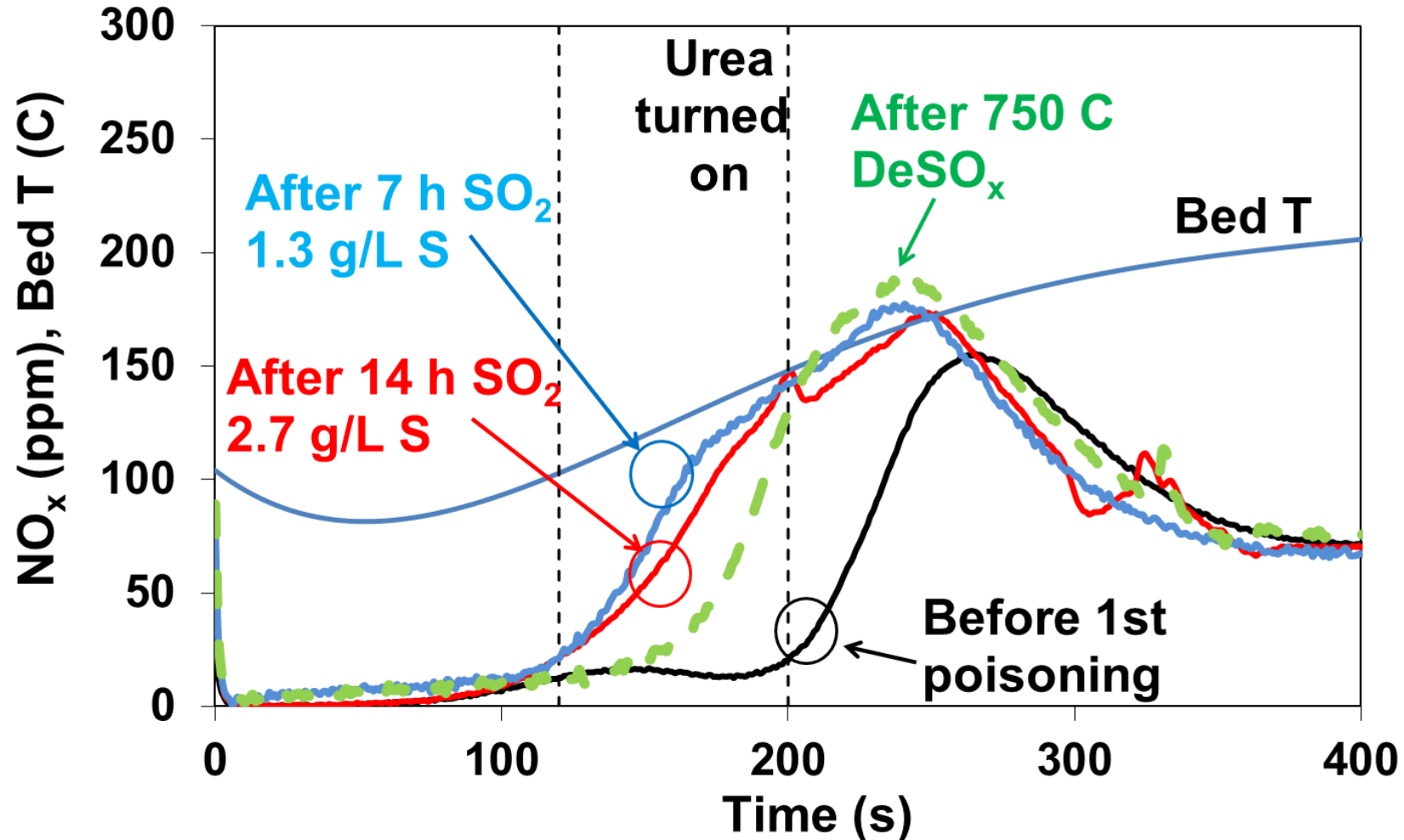
—before poisons  
 —after 14 hrs SO<sub>2</sub> (2.7 g/L S)  
 —after dSO<sub>x</sub> at 700 C  
 —after 7 hrs SO<sub>2</sub> (1.3 g/L S)  
 —after dSO<sub>x</sub> at 750 C

- NO<sub>x</sub> storage at 150°C was degraded significantly by the SO<sub>2</sub>
  - Some recovery after 700°C lean deSO<sub>x</sub>, more after 750°C lean
- NO<sub>x</sub> stored at 150°C released mostly as NO<sub>2</sub> → nitrate formation
  - Storage of NO<sub>2</sub> as nitrates is degraded by SO<sub>2</sub> poisoning

# SO<sub>2</sub> Effects on Pd-Rich-BM LTNA during Transient Test

Pd-Rich-BM LTNA aged 24 hrs 600°C

SO<sub>2</sub> Effects on NO<sub>x</sub> Adsorption during Low T Transient Test



- However, NO still stored w/ high efficiency at low T for 120 s > NO storage as nitrites on Pd-Rich-BM LTNA more robust to SO<sub>2</sub>