# Global Kinetic Modeling of a Supplier Barium and Potassium containing Lean NOx Trap

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# Acknowledgements


- Louise Olsson, Chalmers (Principal Author)
- David Monroe,  GM (Reactor experiments)
- Erik Fridell, Chalmers (Director KCK)
- Se Oh, Ed Bissett, Yongsheng He GM

# GOAL

**Extend the kinetic model and kinetic parameters for a two component, supplier LNT model**

# Outline

- **Previous model development**
- **Modifications for two component storage**
- **Experimental measurements**
- **Simulation results**
- **Summary and conclusions**

# Reactions on the precious metal

$$NO + \tfrac{1}{2} O_2 \leftrightarrow NO_2$$

(NO oxidation)

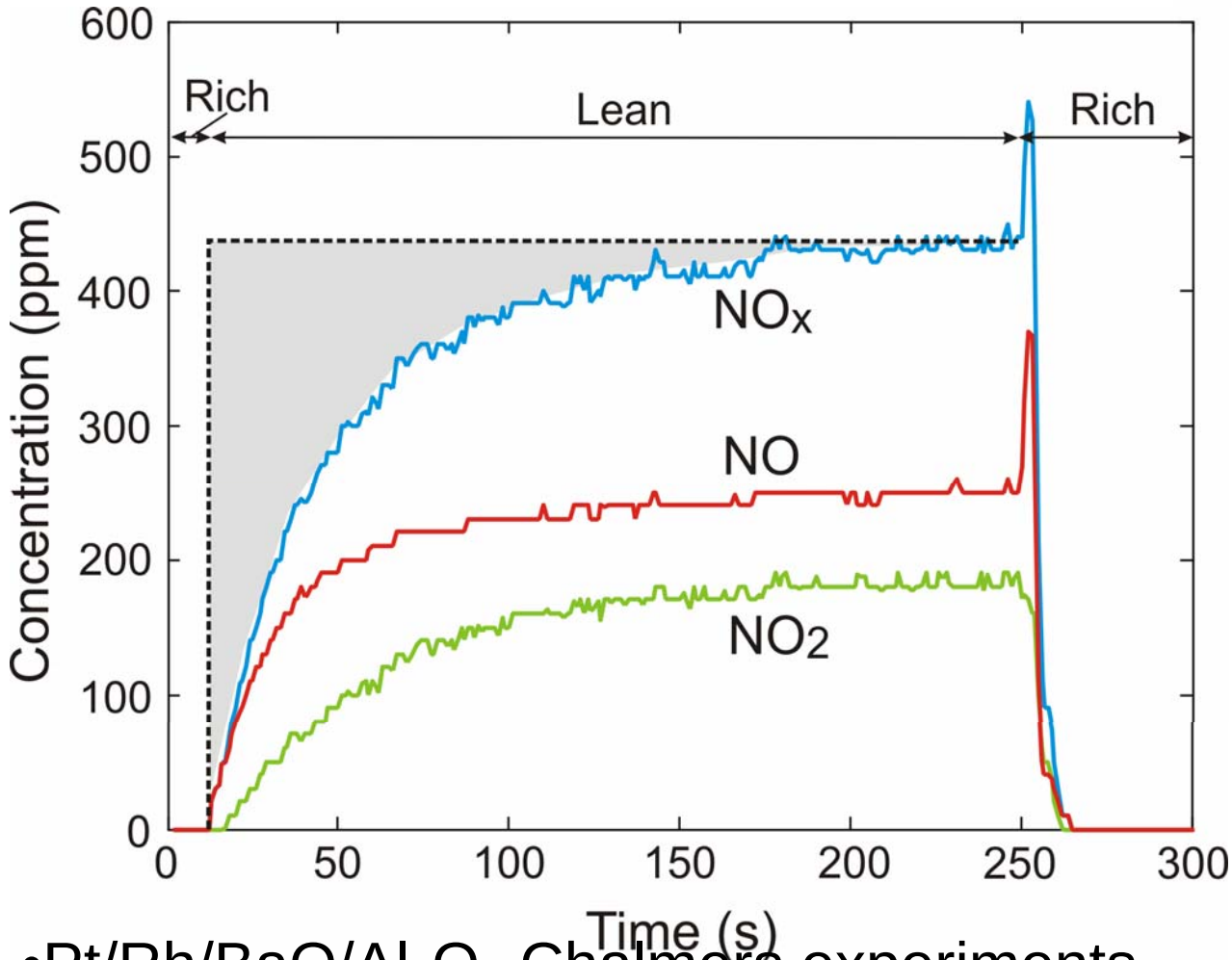
$$C_3H_6 + 9/2\ O_2 \rightarrow CO_2 + 3\ H_2O$$

(hydrocarbon oxidation)

$$NO + 1/9\ C_3H_6 \rightarrow \tfrac{1}{2} N_2 + 1/3\ CO_2 + 1/3\ H_2O$$

(NO reduction)

# NO Speciated Breakthrough at 320 C




- Pt/Rh/BaO/$Al_2O_3$ Chalmers experiments

# Reactions for storage and regeneration

## Storage

$$\tfrac{1}{2}\ BaCO_3 + NO_2 + \tfrac{1}{4}\ O_2 \ \text{<->}\ \tfrac{1}{2}\ Ba(NO_3)_2 + \tfrac{1}{2}\ CO_2$$

(nitrate formation)

$$\tfrac{1}{2}\ BaCO_3 + NO_2 + \tfrac{1}{4}\ O_2 \ \text{<->}\ \tfrac{1}{2}\ Ba(NO_2)_2 + \tfrac{1}{2}\ CO_2$$

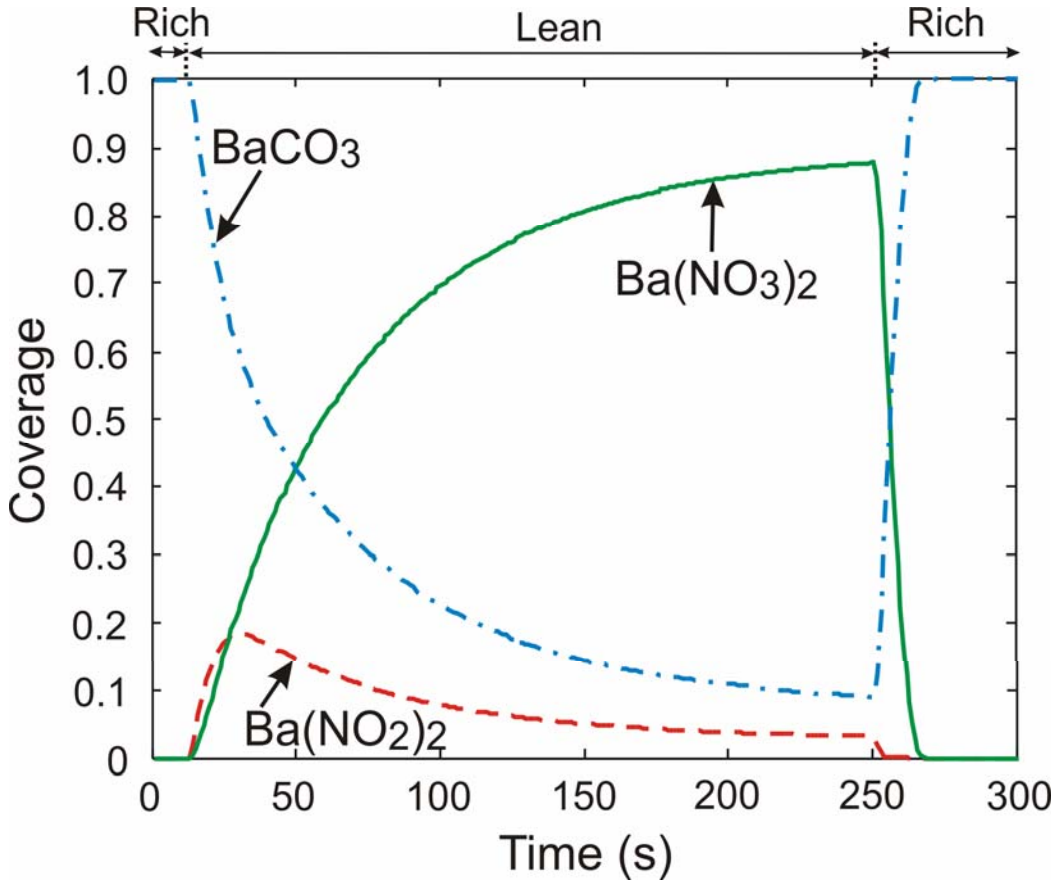
(nitrite formation)

## Regeneration

$$\tfrac{1}{2}\ Ba(NO_3)_2 + 1/6\ C_3H_6 \rightarrow \tfrac{1}{2}\ BaCO_3 + NO + \tfrac{1}{2}\ H_2O$$

$$\tfrac{1}{2}\ Ba(NO_2)_2 + 1/18\ C_3H_6 + 1/3\ CO_2 \rightarrow \tfrac{1}{2}\ BaCO_3 + NO + 1/6\ H_2O$$

# Coverage for NOx Storage




- Nitrides are found only in the initial parts of the storage
- Pt/Rh/BaO/Al2O3 Chalmers experiments

# Storage Reactions for Two Component Model

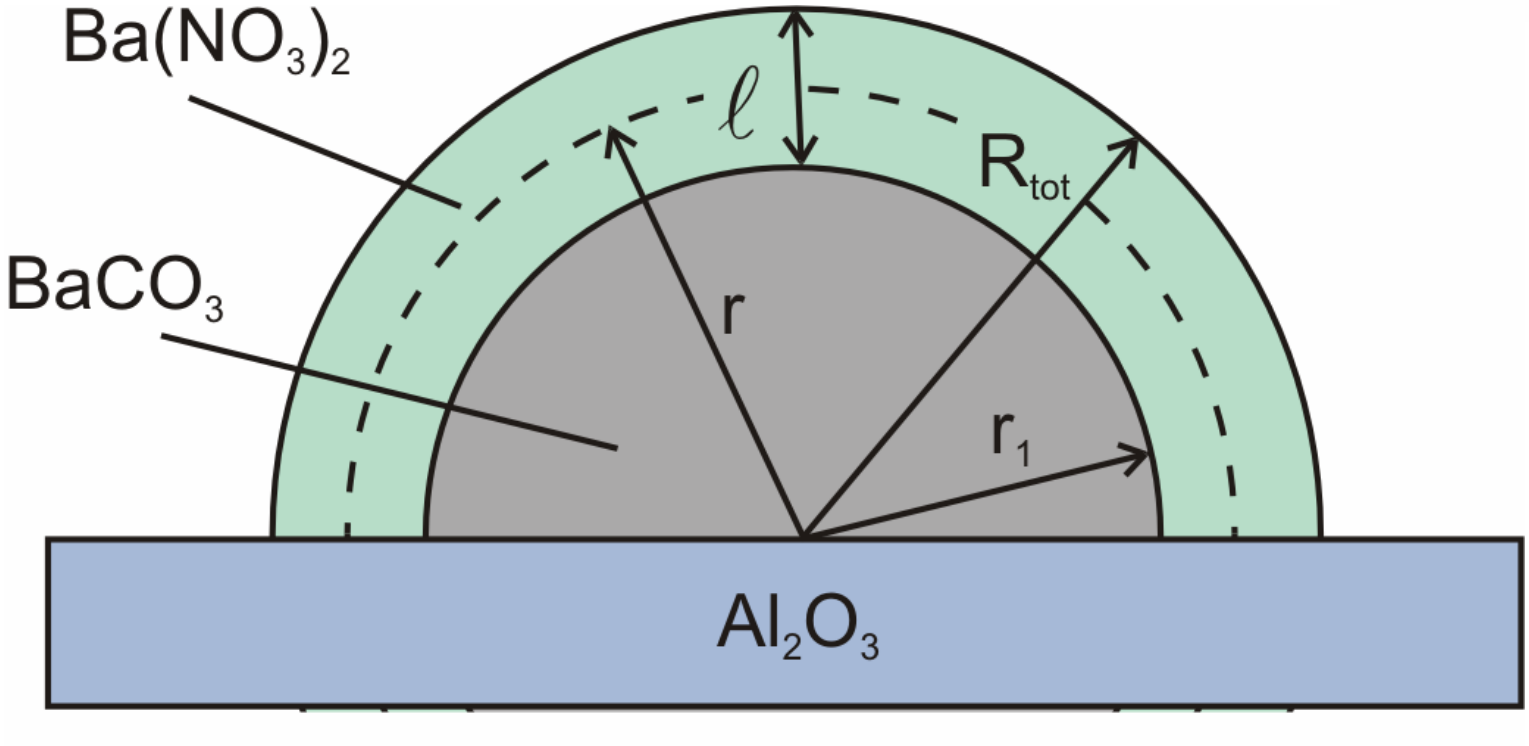
$$1/2\ BaCO_3 + NO + 3/4\ O_2 \Leftrightarrow 1/2\ Ba(NO_3)_2 + 1/2\ CO_2$$

$$r_{NOx-Ba} = k^{bulk,*}_{NOx-Ba,f}\, C_{NO}\, C^{1/4}_{O2}\, \theta_{BaCO3} - k^{bulk,*}_{NOx-Ba,b}\, C^{1/2}_{CO2}\, \theta_{Ba(NO3)2}$$

$$1/2\ K_2CO_3 + NO + 3/4\ O_2 \Leftrightarrow 1/2\ KNO_3 + 1/2\ CO_2$$

$$r_{NO-K} = k^{bulk,*}_{NO-K,f}\, C_{NO}\, C^{1/4}_{O2}\, \theta_{K2CO3} - k^{bulk,*}_{NO-K,b}\, C^{1/2}_{CO2}\, \theta_{KNO3}$$

# Mass Transport Described using the Shrinking Core Model

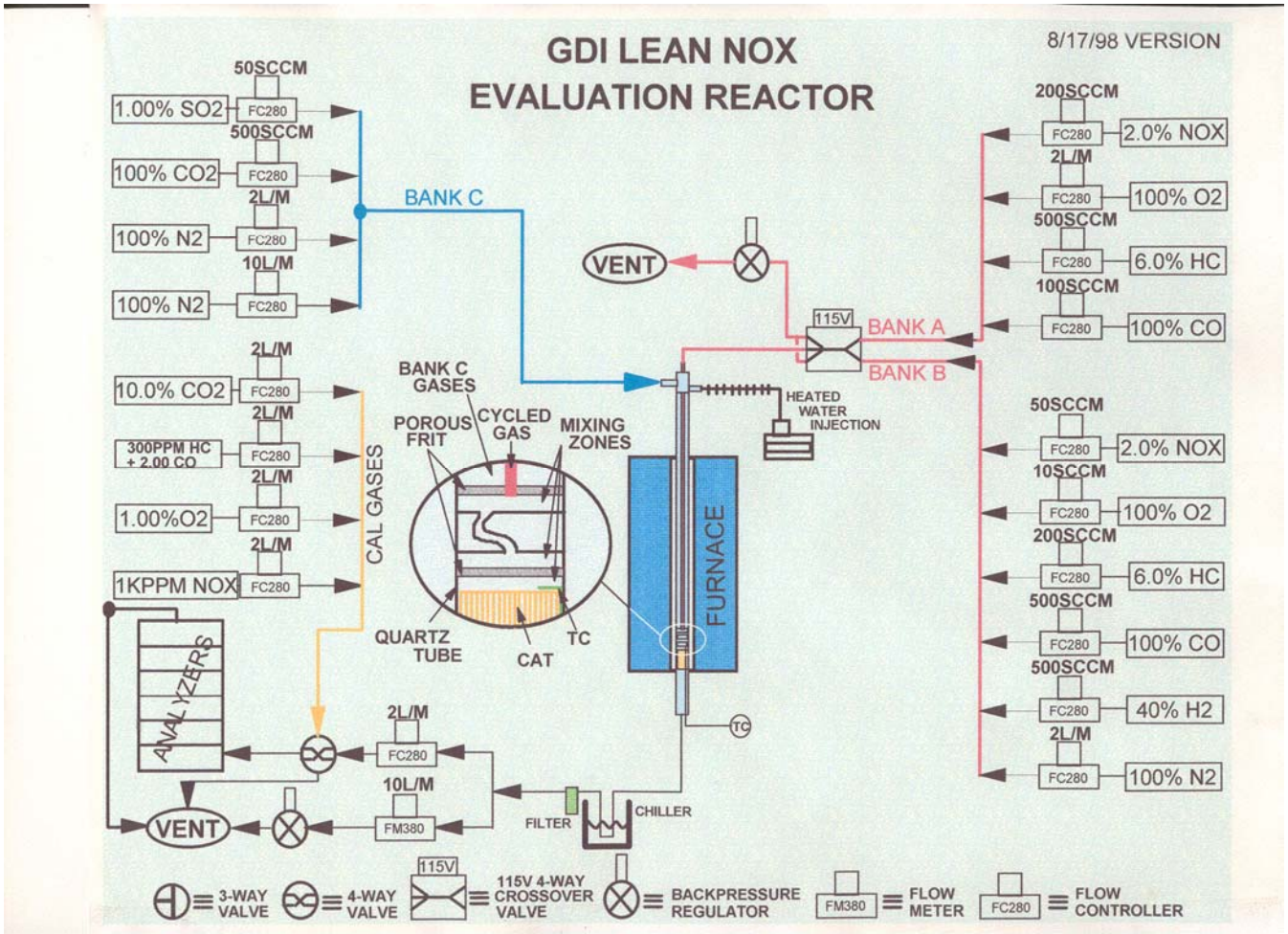



$$1/2\ BaCO_3 + NO_2 + 1/4\ O_2 \Leftrightarrow 1/2\ Ba(NO_3)_2 + 1/2\ CO_2$$

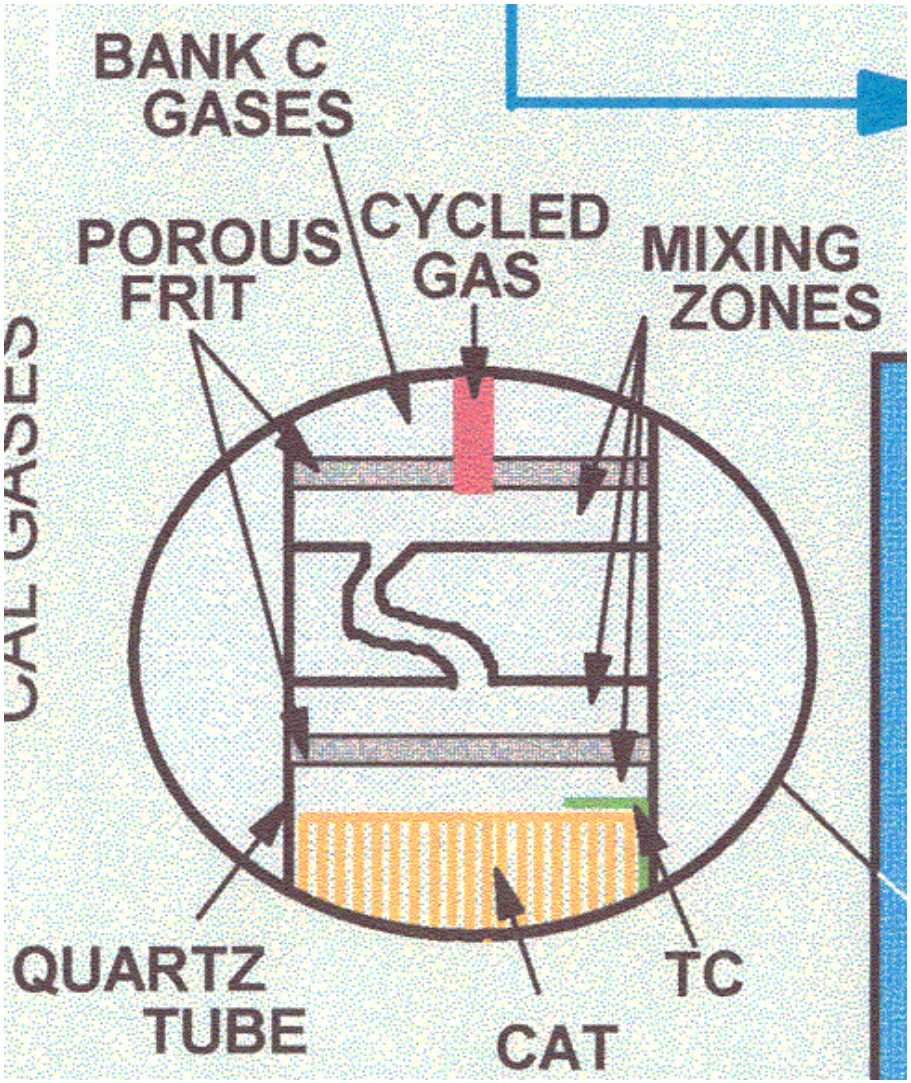
Hepburn, et al, SAE 982596

# Experimental Measurements on Supplier Catalyst

- Aged in air with 10 % water and 10% CO2 at 700°C for 16 hours
- Total feed flow rate was 6 l/min, yielding a space velocity of 50 000 $h^{-1}$
- Cycling
  - Lean: 10% O2, 5% CO2, 5 % H2O, and 100 ppm (,200 or 300) NO
  - Rich: 3% CO, 5% CO2, 5 % H2O, and 100, 200 and 300 ppm NO
  - 660s lean/240s rich

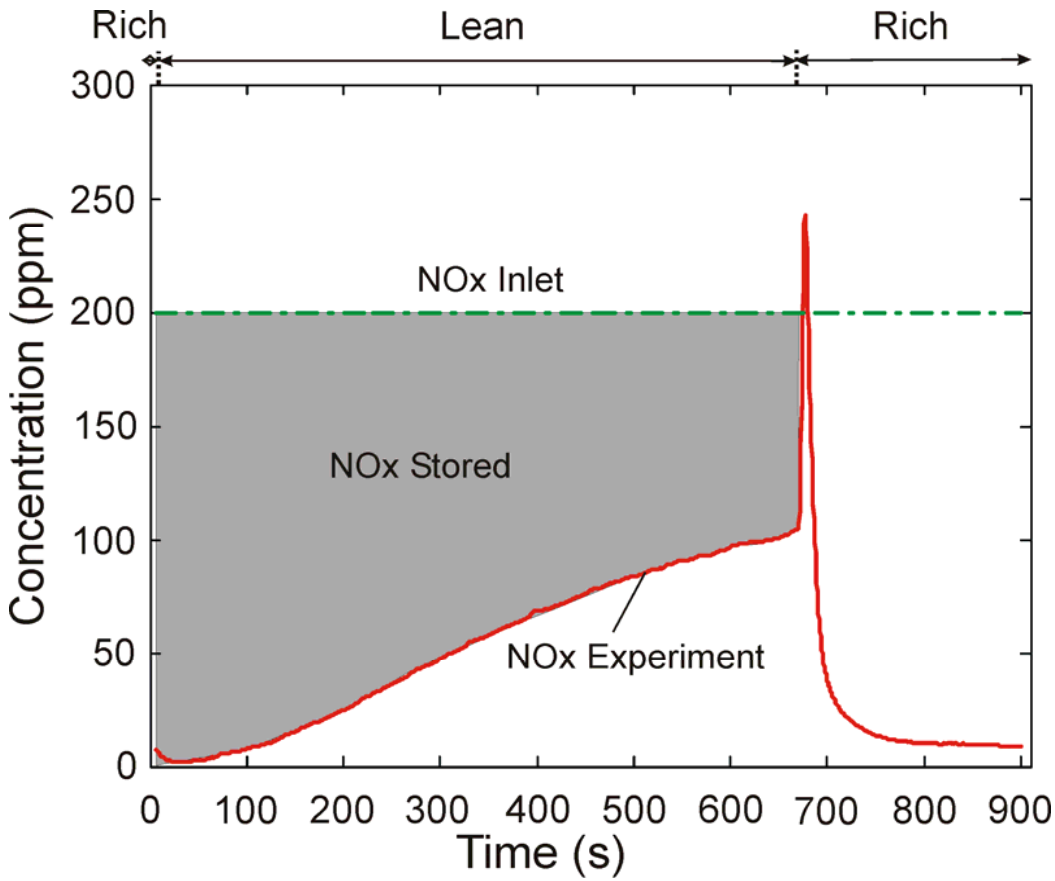


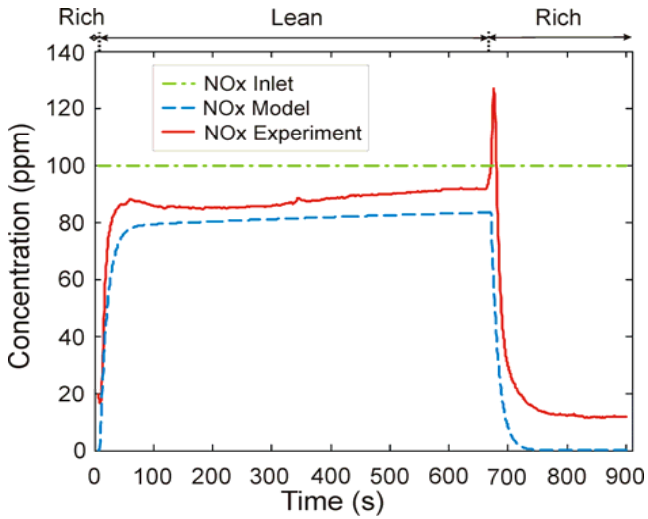

•Designed by David Monroe



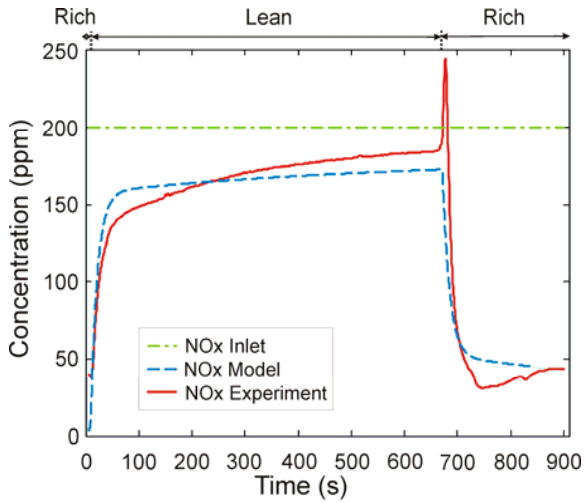

- Bank A and B gases alternated through capillary
- Mixing accomplished by the glass frit
- Mixing estimated to be on the order of 100 ms.

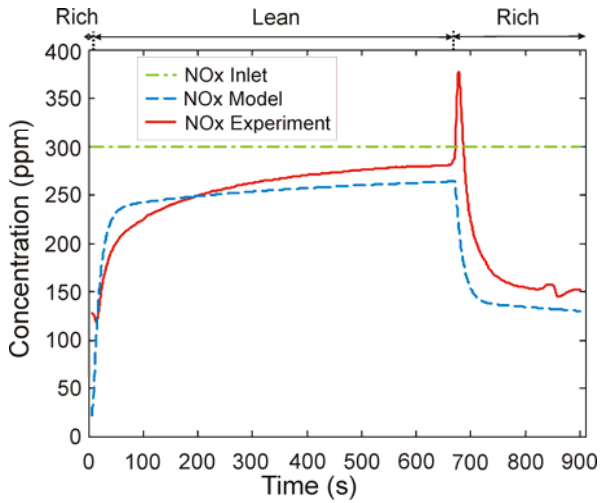
# Experimental Measurement of NOx Stored at 400 C

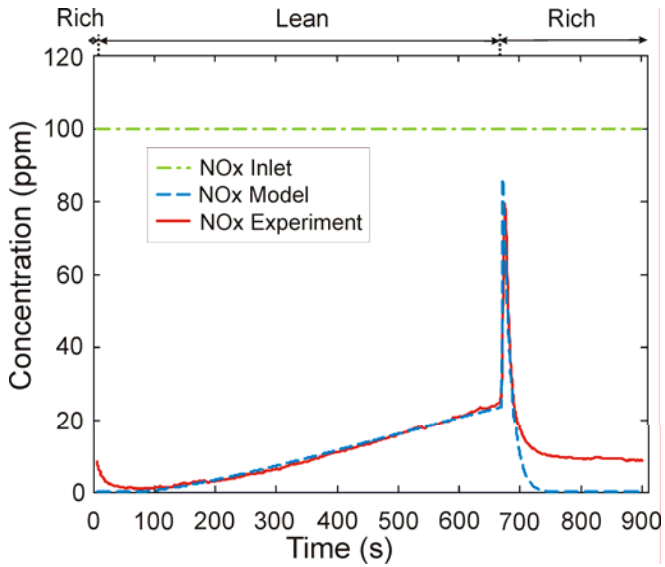




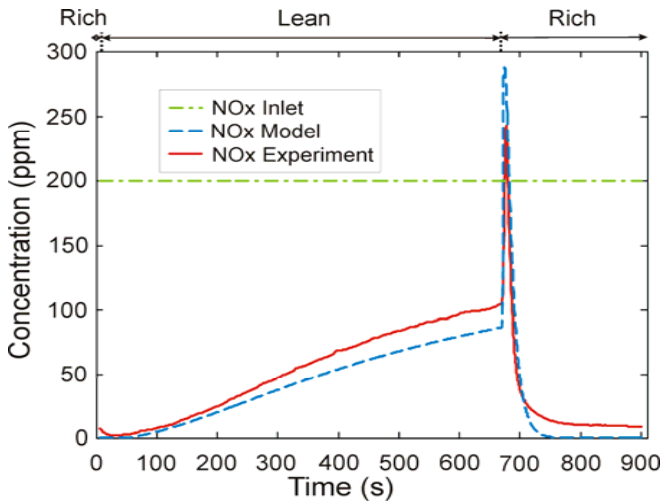

Catalyst-out concentrations for 200 C, measurements and simulations

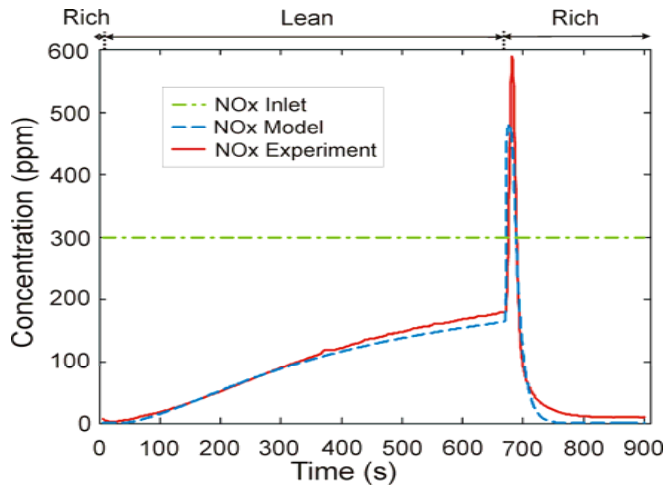


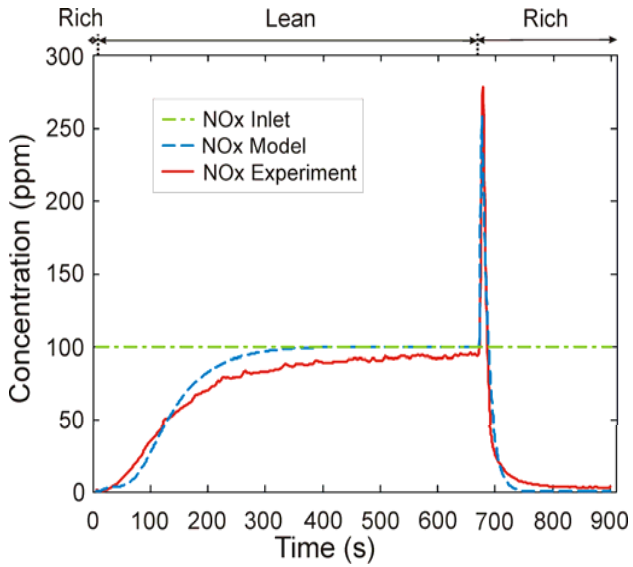





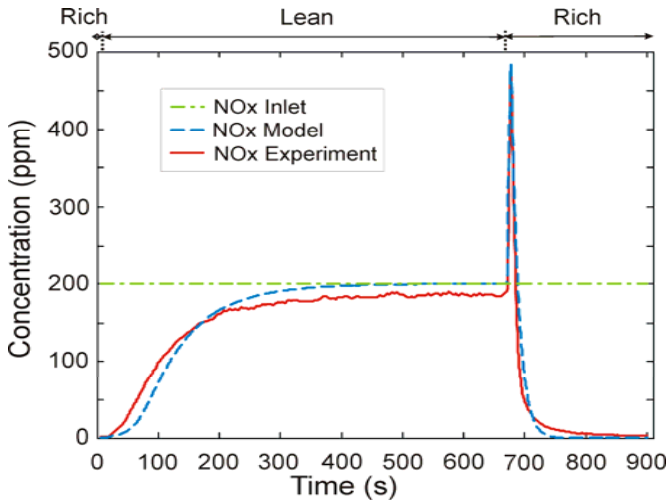

Catalyst-out concentrations for 400 C, measurements and simulations

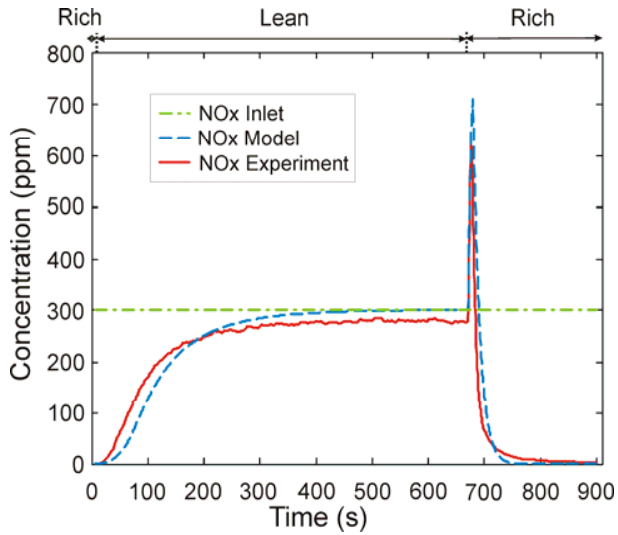


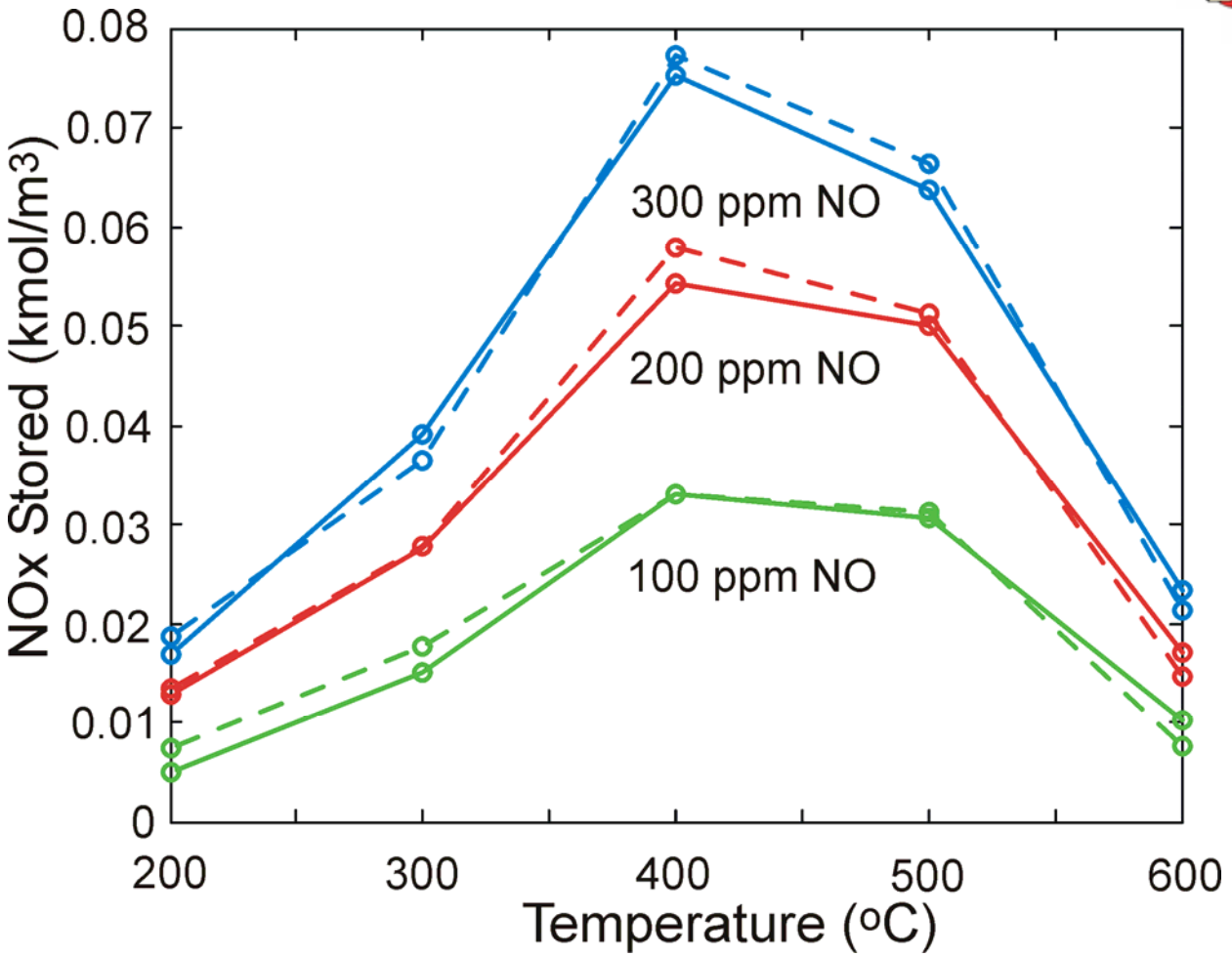



Catalyst-out concentrations for 600 C, measurements and simulations



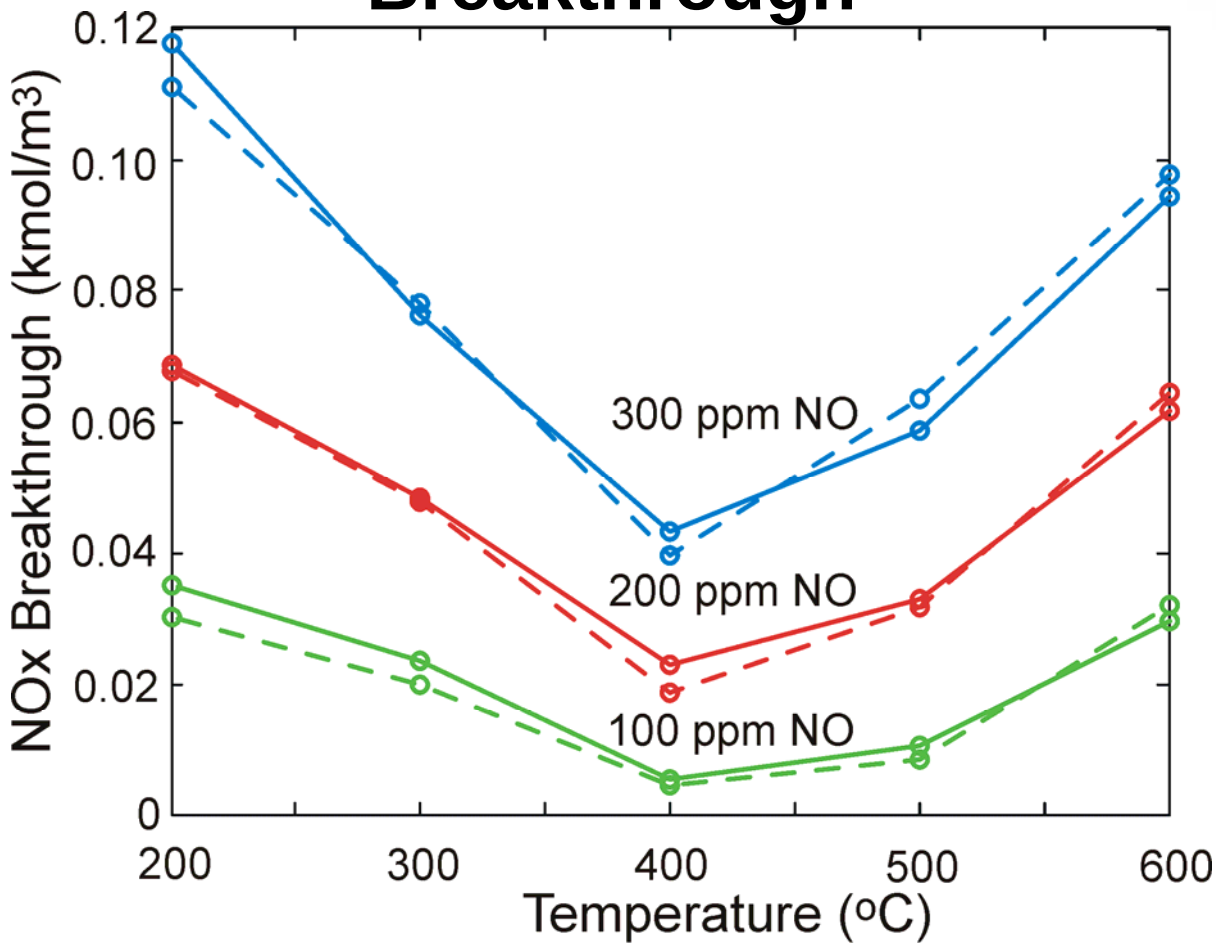



# NOx Storage




- Storage drops off at higher temperatures

# Integrated NOx Breakthrough

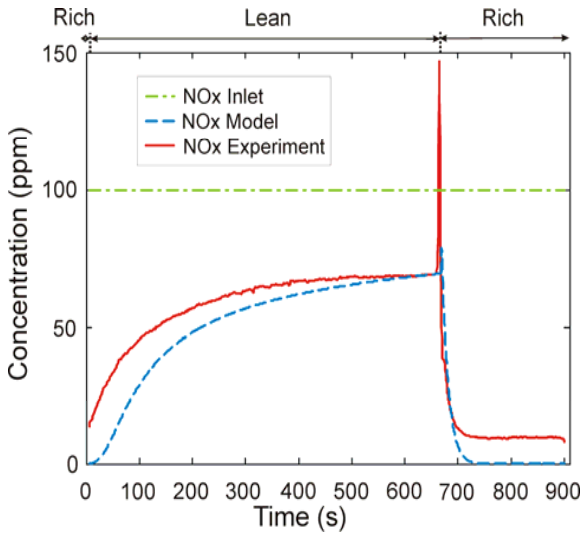



- Maximum storage occurs at 400 C

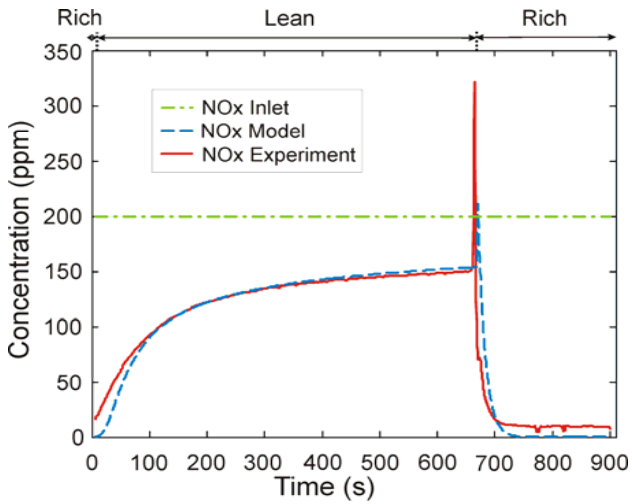
# Summary

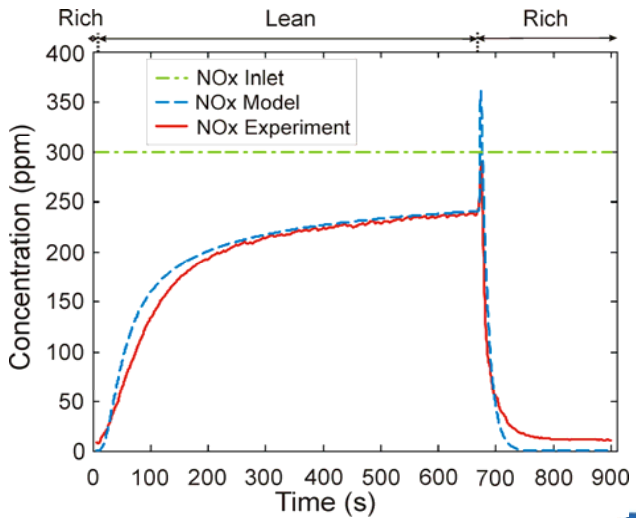
- Global kinetic model was developed for two component lean NOx traps using flow reactor experiments.
- Reactor experiments used
  - with five different temperatures between 200-600°C and
  - three different NO concentrations
  - were used CO2 and water were present.
  - Regeneration was performed with CO as a reductant.
- Model used:
  - One reaction step for the storage process for each storage material
  - A shrinking core model was used for describing the variation in mass-transfer for each of the storage components.
- Observed:
  - The maximum storage occurred at 400°C,
  - and at lower temperatures the storage/regeneration was kinetically limited.
  - The storage decreased at higher temperatures (600°C), because at these high temperatures the nitrates start to become unstable and carbonate formation is favored.
- The model was able to describe the experimental features of all 15 experiments very well and the results show that the model can describe multi-adsorber lean NOx traps in a broad temperature range.

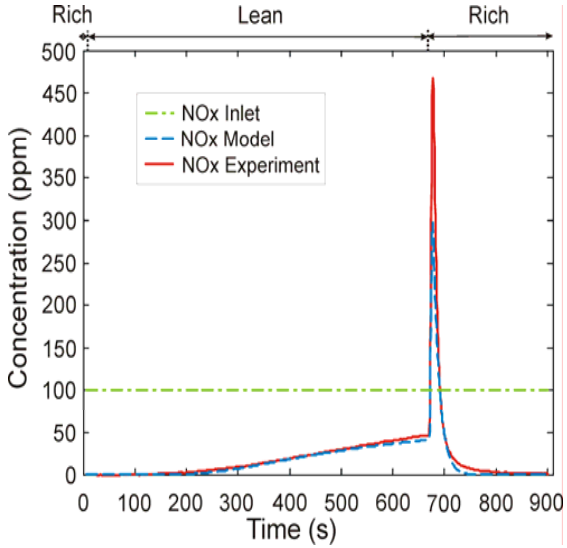
# Backup Slides




Catalyst-out concentrations for 300 C, measurements and simulations






Catalyst-out concentrations for 500 C, measurements and simulations