Detailed kinetic modeling of NO_x storage and reduction with hydrogen
- Ammonia formation

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Acknowledgements

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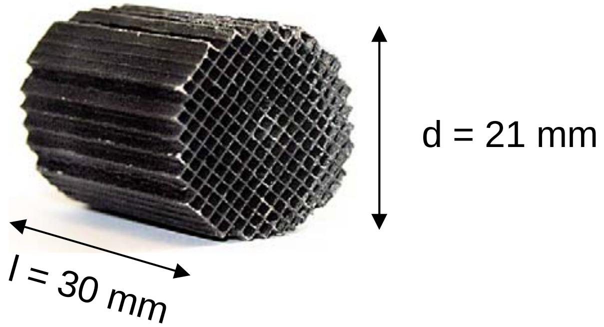
- Cummins Inc. is gratefully acknowledged for the financial support.

Outline

- Catalyst sample
- Mechanism
  - Determination of parameters
  - Submodel 1: NO oxidation
  - Submodel 2: NO_x storage
  - Submodel 3: NO_x reduction
  - Submodel 4: NO_x regeneration
- Results
  - Long cycles
  - Short cycles
- Validation
- Conclusions

Catalyst sample, Pt/Ba/Al

- Wash coat weight: 1040 mg
- 2.9 % Pt, 18% Dispersion
- 20.8 % Ba
- BET: 97 m^2/g
- Cell density: 400 cpsi
- Space velocity: 18 400 h^{-1}



Mechanism
- Determination of parameters

- Mechanisms for NO oxidation and NO_x reduction investigated separately
- Based on previous mechanism for NO_x storage
- Literature values
- Kinetic gas theory and sticking coefficient for pre-exponential factors for adsorption
- Statistical thermodynamics (partition functions) to check pre-exponential factors for adsorption/desorption
- Thermodynamic constraints
- Regression analysis

Mechanism
Sub model 1: NO oxidation

Sub model 1 developed earlier on Pt/Al_2O_3, Pt/SiO_2 and $Pt/Ba/Al_2O_3$

$$NO_{(g)} + Pt \underset{r_2}{\overset{r_1}{\leftrightarrow}} NO - Pt$$ NO adsorption and desorption.

$$O_{2(g)} + 2Pt \underset{r_4}{\overset{r_3}{\leftrightarrow}} 2O - Pt$$ O_2 adsorption and desorption.

$$NO - Pt + O - Pt \underset{r_6}{\overset{r_5}{\leftrightarrow}} NO_2 - Pt + Pt$$ NO oxidation

$$NO_2 - Pt \underset{r_8}{\overset{r_7}{\leftrightarrow}} NO_{2(g)} + Pt$$ NO_2 adsorption and desorption.

L. Olsson, H. Persson, E. Fridell, M. Skoglundh and B. Andersson, *J. Phys. Chem. B,* 105 (2001) 6895.
A. Lindholm, N. W. Currier, J. Li, A. Yezerets, and L. Olsson, *Topics in Catalysis*, 42-43 (1-4) (2007) 83.

Mechanism
Sub model 2: NO_x storage

Sub model 2 based on an earlier NO_x storage model on $Pt/Ba/Al_2O_3$

$$NO_{2(g)} + BaCO_3 \underset{r_{10}}{\overset{r_9}{\leftrightarrow}} NO_2 - BaCO_3$$
NO_2 adsorption and desorption on $BaCO_3$.

$$NO_2 - BaCO_3 \underset{r_{12}}{\overset{r_{11}}{\leftrightarrow}} BaO - NO_2 + CO_{2(g)}$$
CO_2 desorption and adsorption on $BaCO_3$.

$$NO_2 - BaO + 2NO_2 - Pt \underset{r_{14}}{\overset{r_{13}}{\leftrightarrow}} Ba(NO_3)_2 + 2Pt + NO_{(g)}$$
$Ba(NO_3)_2$ formation (disproportionation route)

$$NO_{(g)} + BaCO_3 \underset{r_{16}}{\overset{r_{15}}{\leftrightarrow}} NO - BaCO_3$$
NO adsorption and desorption on $BaCO_3$

$$NO_{(g)} + S_3 \underset{r_{18}}{\overset{r_{17}}{\leftrightarrow}} S_3 - NO$$
NO adsorption and desorption on S3

$$NO - S_3 + O - Pt \underset{r_{20}}{\overset{r_{19}}{\leftrightarrow}} NO_2 - S3 + Pt$$
Direct oxidation of NO on S3

$$NO_{2(g)} + S_3 \underset{r_{22}}{\overset{r_{21}}{\leftrightarrow}} S_3 - NO_2$$
NO_2 adsorption and desorption on S_3

- L. Olsson, H. Persson, E. Fridell, M. Skoglundh and B. Andersson, *J. Phys. Chem. B,* 105 (2001) 6895.
- A. Lindholm, N. W. Currier, J. Li, A. Yezerets, and L. Olsson, *Submitted* (2008).

Mechanism
Sub model 3: NO_x reduction

Sub model 3 developed earlier on Pt/SiO_2

$$H_{2(g)} + 2Pt \underset{r_{24}}{\overset{r_{23}}{\leftrightarrow}} 2H - Pt$$ H_2 adsorption and desorption on Pt

$$O - Pt + 2H - Pt \overset{r_{25}}{\rightarrow} H_2O - Pt + 2Pt$$ H_2O formation on Pt

$$H_2O_{(g)} + Pt \underset{r_{27}}{\overset{r_{26}}{\leftrightarrow}} H_2O - Pt$$ H_2O desorption and adsorption on Pt

$$NO - Pt + Pt \underset{r_{29}}{\overset{r_{28}}{\leftrightarrow}} N - Pt + O - Pt$$ NO dissociation on Pt

$$2N - Pt \overset{r_{30}}{\rightarrow} N_{2(g)} + 2Pt$$ N_2 formation on Pt

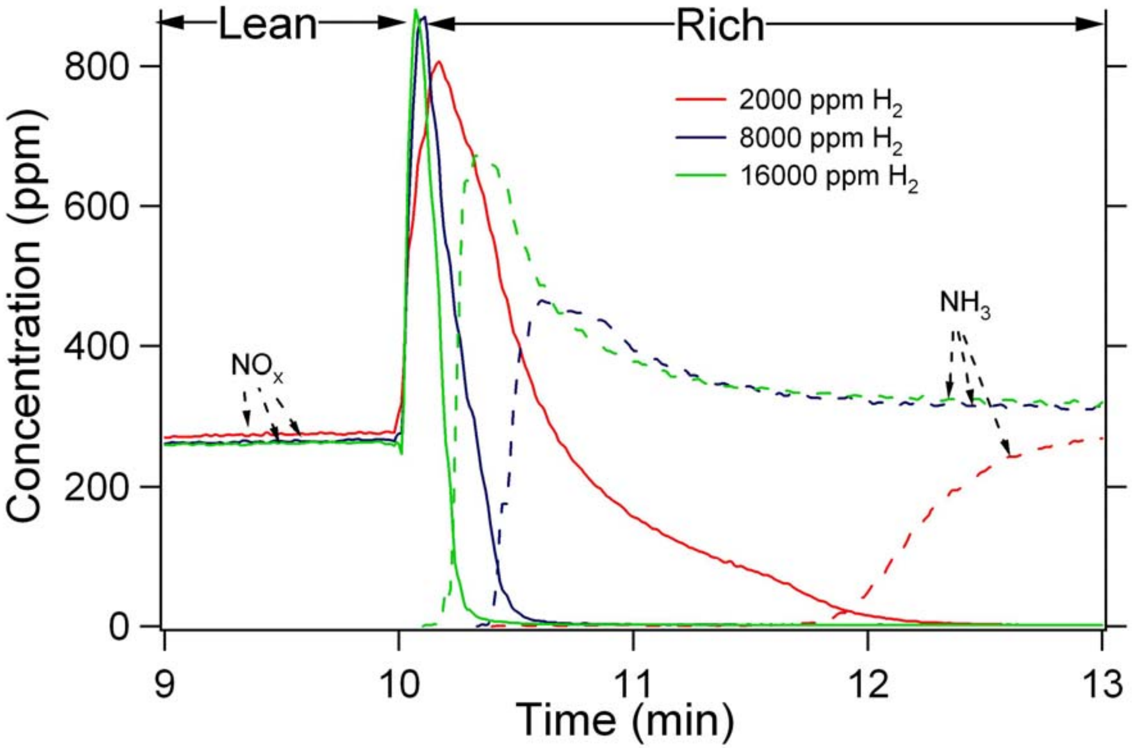
$$N - Pt + 3H - Pt \overset{r_{31}}{\rightarrow} NH_3 - Pt + 3Pt$$ Ammonia formation on Pt

$$NH_{3(g)} + Pt \underset{r_{33}}{\overset{r_{32}}{\leftrightarrow}} NH_3 - Pt$$ Ammonia adsorption and desorption on Pt

A. Lindholm, N. W. Currier, J. Li, A. Yezerets, and L. Olsson, *Topics in Catalysis*, 42-43 (1-4) (2007) 83.

Effect of hydrogen concentration

Pt/Ba/Al - 400 °C



- **Ammonia observed when NO_x close to 0**
- **Decreasing the hydrogen concentration ⇒ longer time before NH_3 is detected**

A. Lindholm, N. W. Currier, E. Fridell, A. Yezerets, and L. Olsson, Applied Catalysis B . Environmental, 75 (1-2) (2007) 78.

Mechanism
Sub model 4: NO_x regeneration

$$6H-Pt+Ba(NO_3)_2+CO_{2(g)}\xrightarrow{r_{34}}2NO-Pt+BaCO_3+3H_2O-Pt+Pt$$

$$4H-Pt+BaO-NO_2+CO_{2(g)}\xrightarrow{r_{35}}0.5N_{2(g)}+BaCO_3+2H_2O-Pt+2Pt$$

$$4H-Pt+2BaCO_3-NO\xrightarrow{r_{36}}N_{2(g)}+2BaCO_3+2H_2O-Pt+2Pt$$

$$2H-Pt+NO_2-S_3\xrightarrow{r_{37}}NO-Pt+S_3+H_2O-Pt$$

$$4H-Pt+2NO-S_3\xrightarrow{r_{38}}N_{2(g)}+2S_3+2H_2O-Pt+2Pt$$

Reduction of stored NO_x species to form NO or N_2

$$2NH_3-Pt+3O-Pt\xrightarrow{r_{39}}N_{2(g)}+3H_2O_{(g)}+5Pt$$

Ammonia oxidation on Pt

$$2NH_3-Pt+Ba(NO_3)_2+Pt\xrightarrow{r_{40}}1.5N_{2(g)}+BaO-NO_2+3H_2O-Pt$$

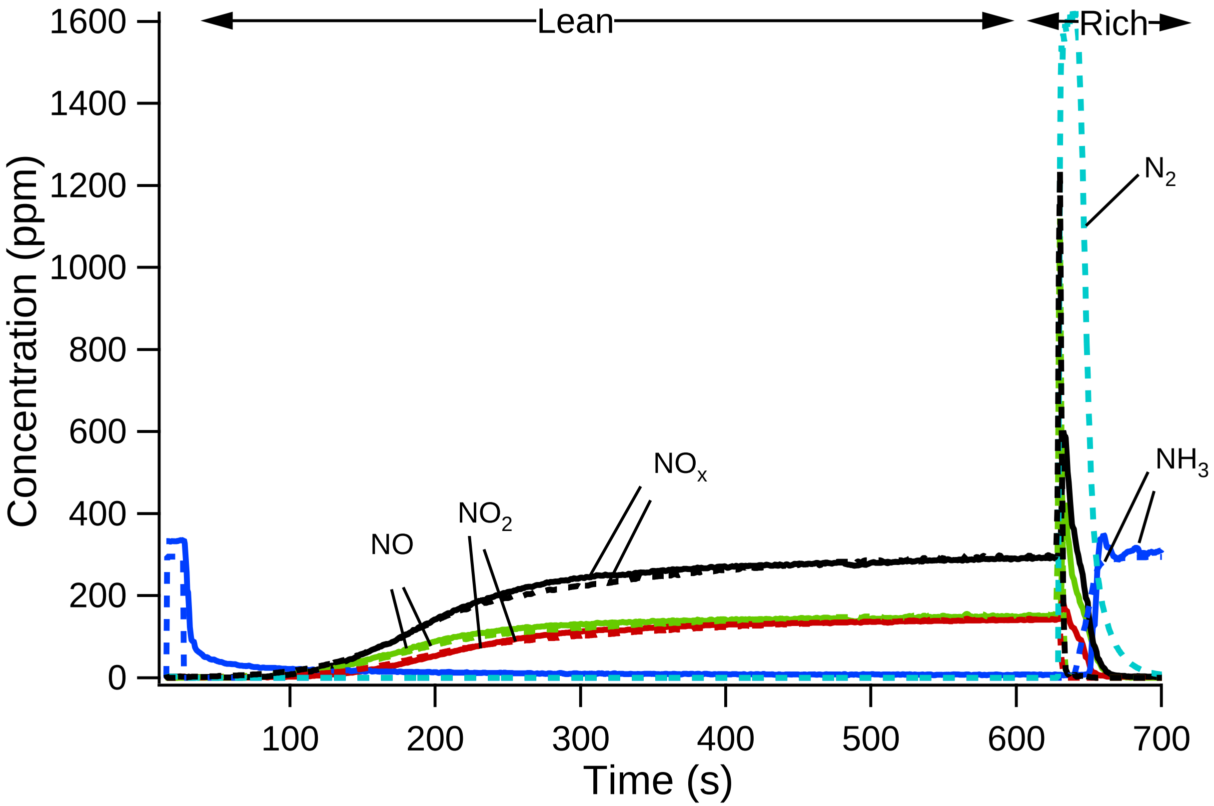
$$4NH_3-Pt+3NO_2-BaO+2Pt+3CO_{2(g)}\xrightarrow{r_{41}}3.5N_{2(g)}+3BaCO_3+6H_2O-Pt$$

Ammonia SCR

A. Lindholm, N. W. Currier, J. Li, A. Yezerets, and L. Olsson, *Submitted* (2008).

Results

Long NO_x storage cycles, 400°C



Lean: 300ppm NO, 8% O_2, 3% CO_2, 3% H_2O, 600s

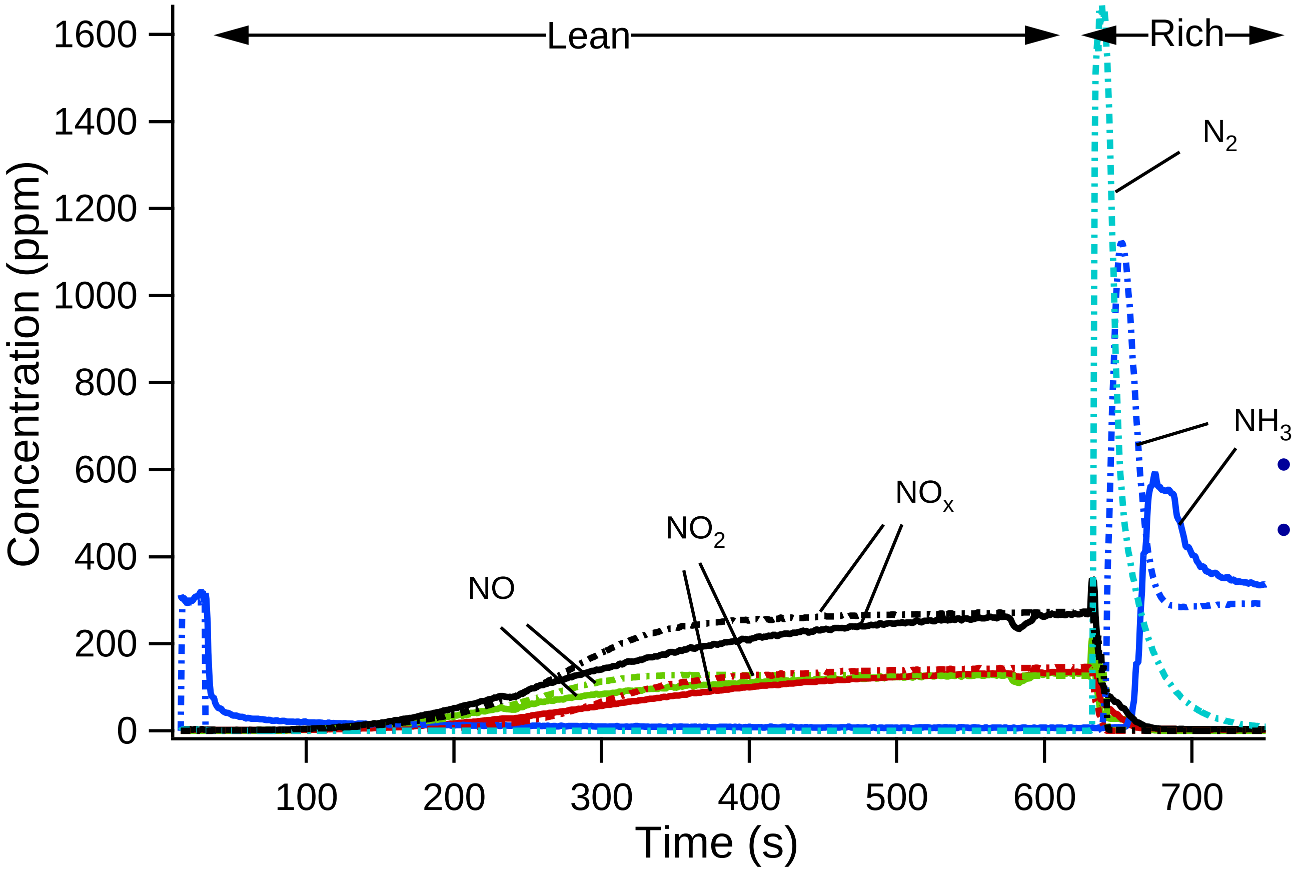
Rich: 300ppm NO, 8000 ppm H_2, 3% CO_2, 3% H_2O, 300s

- Solid lines: Experiment
- Dashed lines: Simulation

A. Lindholm, N. W. Currier, J. Li, A. Yezerets, and L. Olsson, *Submitted* (2008).

Results

Long NO_x storage cycles, 300°C



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Rich: 300ppm NO, 8000 ppm H_2, 3% CO_2, 3% H_2O, 300s

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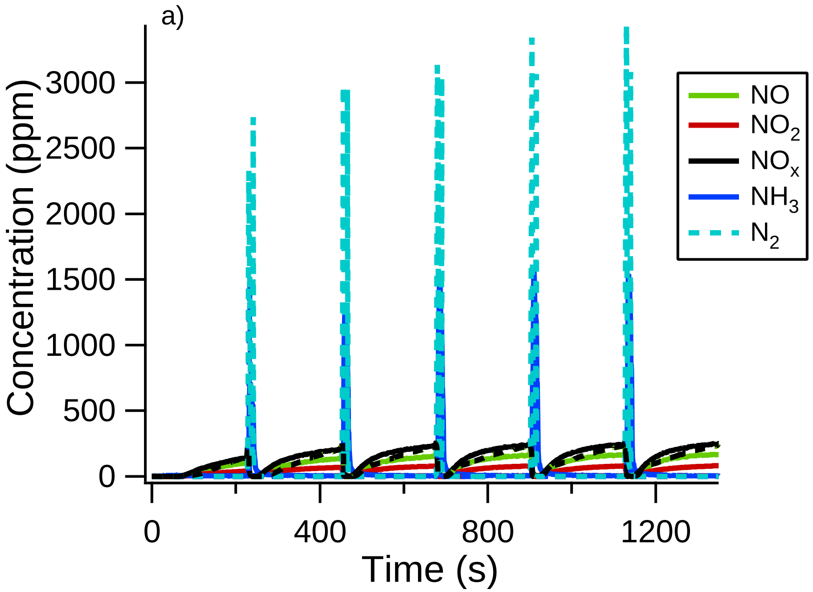
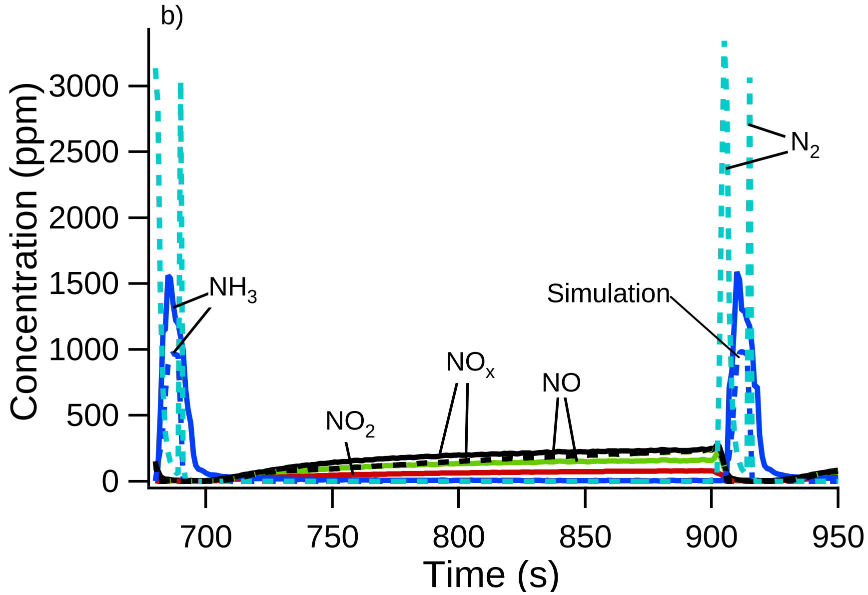
Results

Short NO_x storage cycles, 200°C





Lean: 300ppm NO, 8% O_2, 3% CO_2, 3% H_2O, 210s,

Rich: 300ppm NO, 16000 ppm H_2, 3% CO_2, 3% H_2O, 15s

- Solid lines: Experiment
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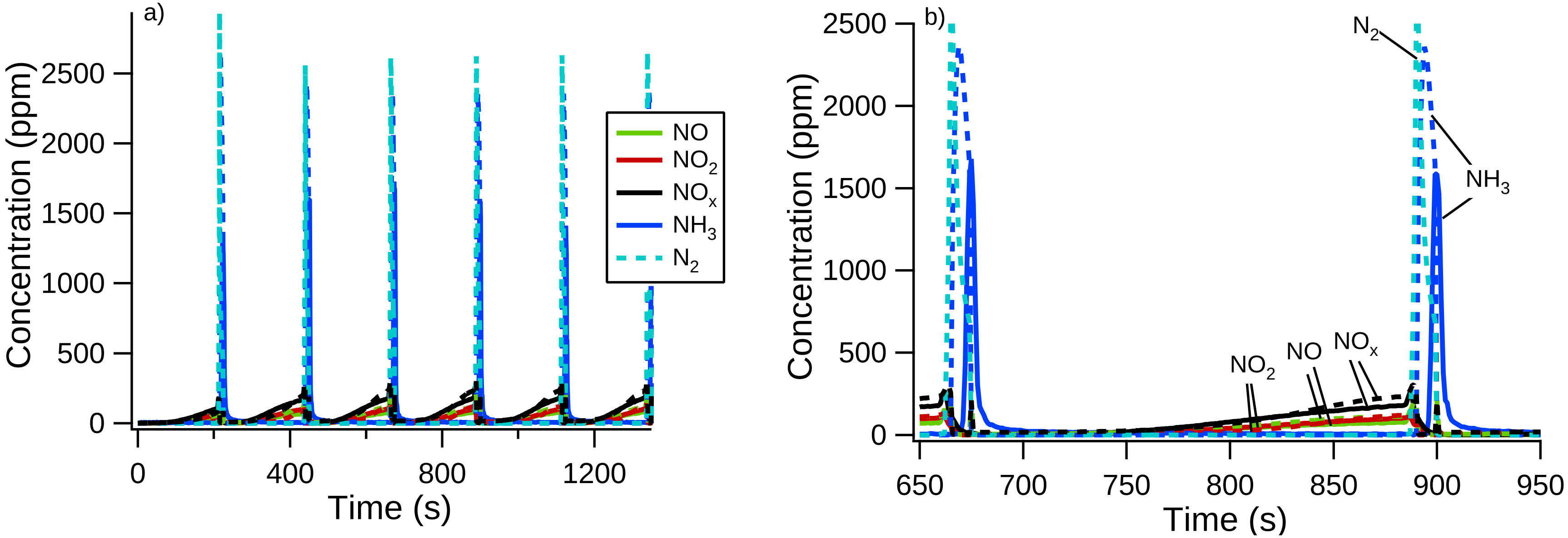
Results
Short NO_x storage cycles, 300°C



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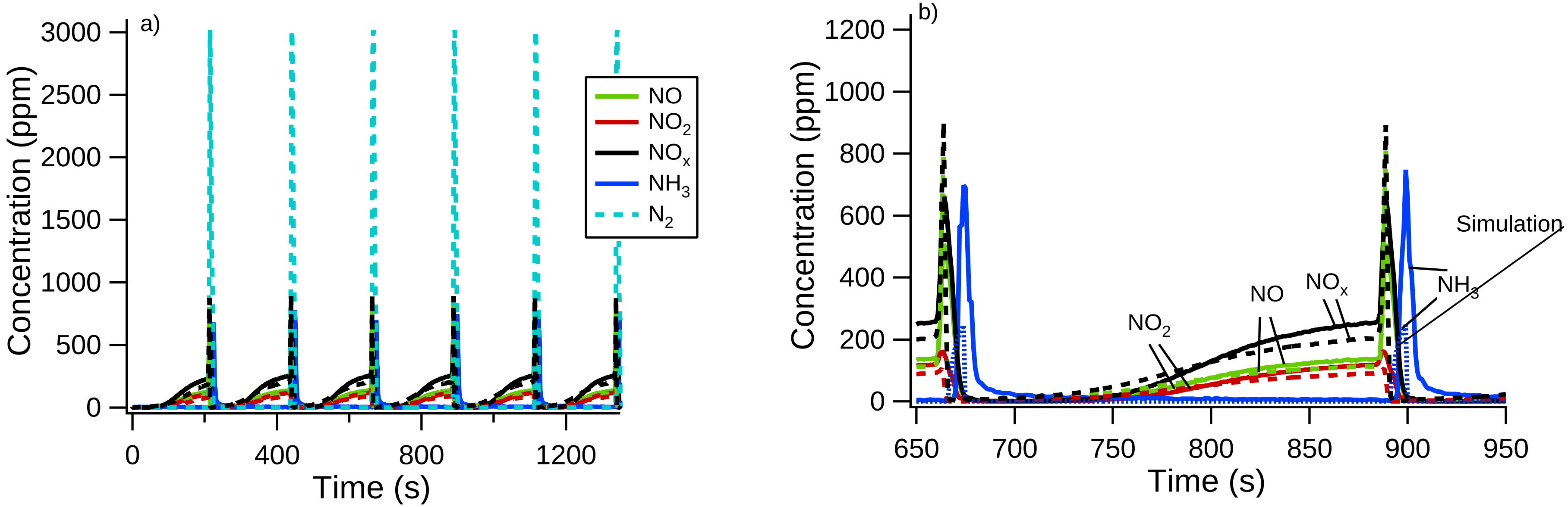
Results

Short NO_x storage cycles, 400°C



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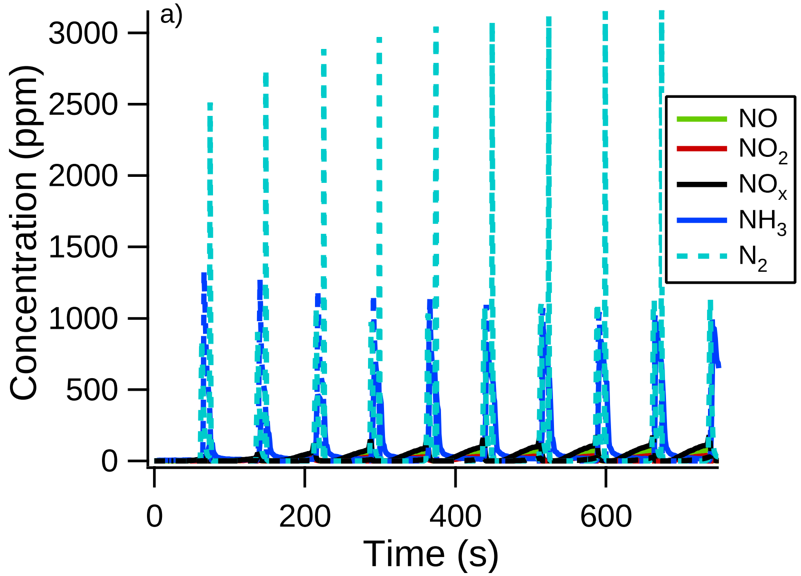
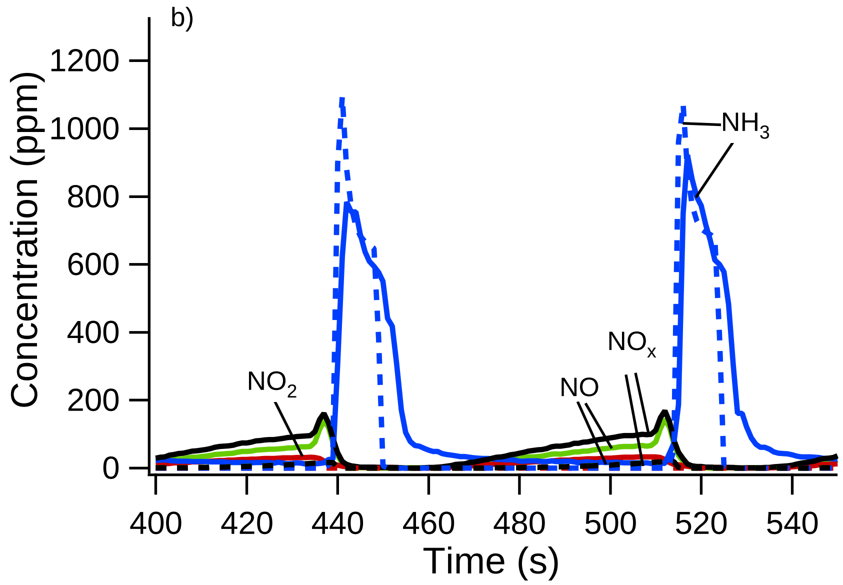
Validation
Short NO_x storage cycles, 200°C





Lean: 300ppm NO, 8% O_2, 3% CO_2, 3% H_2O, 60s,

Rich: 300ppm NO, 16000 ppm H_2, 3% CO_2, 3% H_2O, 15s

- Solid lines: Experiment
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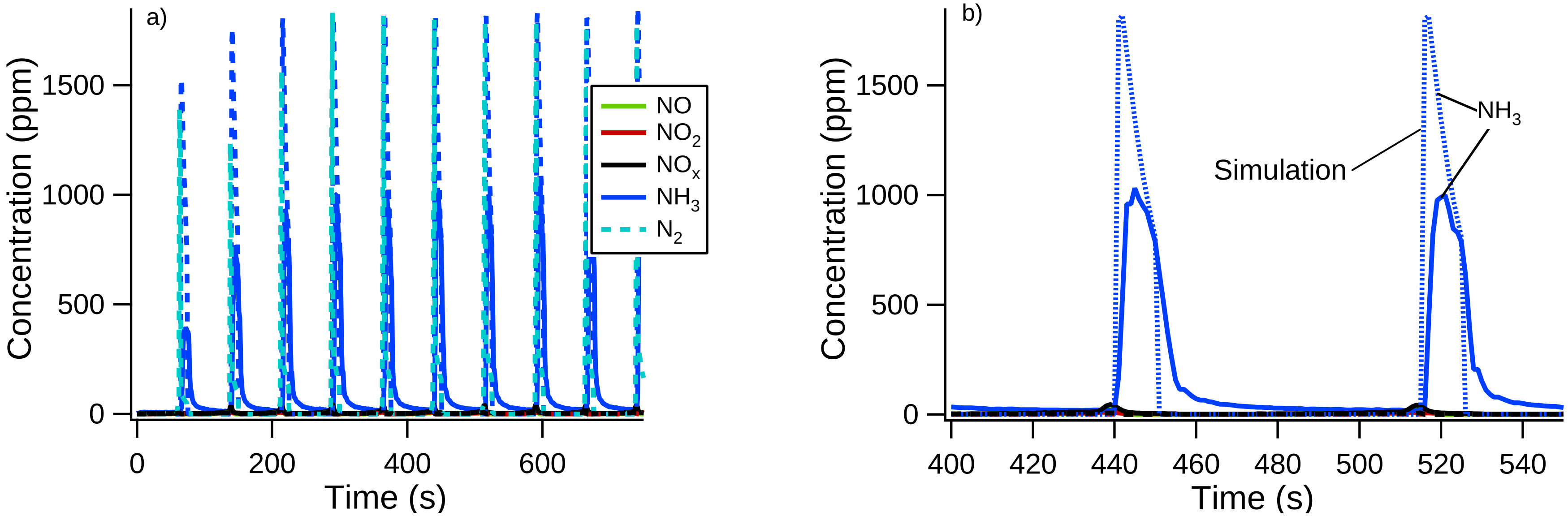

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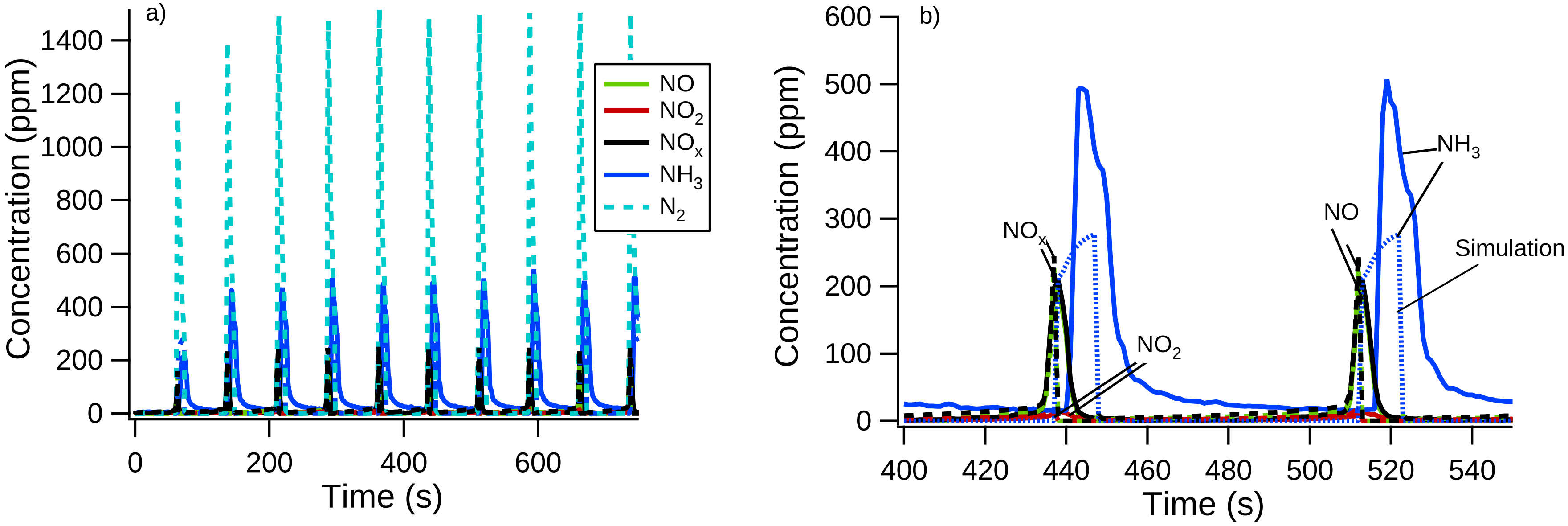
Validation
Short NO_x storage cycles, 400°C



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Conclusions

- A detailed kinetic model for NO_x storage and reduction with hydrogen in the presence of H_2O and CO_2 was developed
- The model is based on four sub-models: (i) NO oxidation, (ii) NO_x storage, (iii) NO_x reduction and (iv) NO_x regeneration
- Model includes NH_3 production on Pt sites
- The delay in time for the ammonia production is explained by SCR reactions between NH_3 and stored NO_x
- Model developed using both long cycles (Lean 600s, Rich 300s) and short cycles (Lean 210s, Rich 15s)
- Validation with short cycles (Lean 60s, Rich 15s)