# An Efficient Methodology for Global SCR Kinetic Model Tuning

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Analysis and Testing Technology

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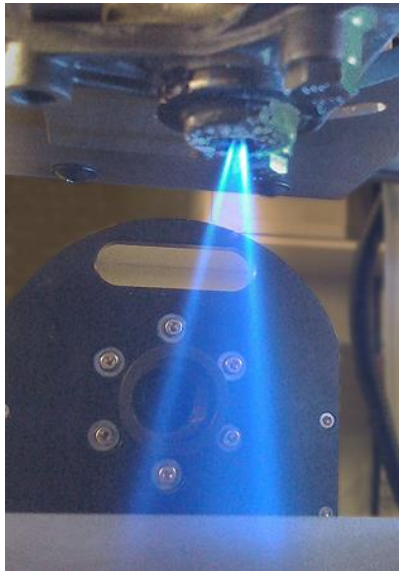

# Background/Challenges

- Lack understanding of **reaction mechanism** and kinetics over wide range of reaction conditions
- Complex reaction network
- Non-linear phenomena of chemical reactions
- Reactions couple with mass transfer and heat transfer

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# Lab Reactor vs Reactor Model

- Lab Reactor (steady state condition)

**Bulk Gas**: $N_2$, $CO_2$, $H_2O$, $O_2$
**Emission Gas**: $NH_3$, NO, $NO_2$, $N_2O$
**Flow Rate, Pressure, T**

→

**Formulations**
**Geometric parameters**

→

**FTIR:**
$NH_3$, NO, $NO_2$, $N_2O$

**Input (variables: *x*)** | Catalyst (f) | **Output (responses: y)**

- Reactor Model

$$y = f(x : \alpha, \beta)$$

$$x : \begin{cases} \text{T, P, Total gas flow rate} \\ \text{Concentration of } O_2, H_2O, CO_2 \\ \text{Concentration of cat. in } NH_3, NO, NO_2, N_2O \end{cases}$$

$\alpha$ : Catalyst geometry parameters : Length, Diameter, CPSI, Wall thickness, Washcoat thickness

$\beta$ : Kinetic parameters (depend on formulations)

$y$ : cat. out $NH_3$, NO, $NO_2$, $N_2O$

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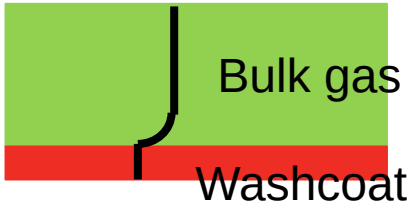
**What is the function "*f*"?**

# "$f$" is the Reactor Model

- **Control Equations for Reactor Model (SS)**
  - Gas Phase: $$\frac{d\bar{c}_j}{d\bar{V}} = -a_1 k_{g,j}\left(\bar{c}_j - \bar{c}_{j,s}\right)$$
  - Surface: $$a_1 k_{g,j}\left(\bar{c}_j - \bar{c}_{j,s}\right) - a_3 \sum \nu_{ij}\, r_i''\left(C_{-ref}\bar{c}_s\right) = 0$$
  - Adsorption Site: $$a_3 \sum \nu_{i\theta}\, r_i''\left(C_{-ref}\bar{c}_s\right) = 0$$




  - **Assumptions**:
    - Stable catalyst
    - Isothermal conditions
    - Single adsorption site for only NH3
    - Interal diffusion lumped into global kintics

- **Kinetic Model ($r_i''$ )**
  - To decide # of reactions to model with appropriate rate expressions ($r_i''$ ) and calibrated kinetic parameters

# List of Chemical Reactions Modeled for VSCR

| | **Reactions** | |
|---|---|---|
| 1 | $NH_3 + S_1 <-> NH_3\text{-}S_1$ | **$NH_3$ adsorption and desorption**(reversible) |
| 2 | $2NH_3\text{-}S_1 + 1.5O_2 -> N_2 + 3H_2O + 2S_1$ | **$NH_3$ oxidation** |
| 3 | $NO + 0.5\ O_2 <-> NO_2$ | NO oxidation(reversible) |
| 4 | $4\ NH_3\text{-}S_1 + 4\ NO + O_2 -> 4\ N_2 + 6\ H_2O + 4\ S_1$ | **Standard SCR** |
| 5 | $2\ NH_3\text{-}S_1 + NO + NO_2 -> 2\ N_2 + 3\ H_2O + 2\ S_1$ | **Fast SCR** |
| 6 | $2\ NH_3\text{-}S_1 + 2.5\ O_2 -> 2NO + 3\ H_2O + 2\ S_1$ | $NH_3$ oxidation to NO |
| 7 | $2NH_3\text{-}S_1 + 2NO + 1.5O_2 -> 2N_2O + 3H_2O + 2S_1$ | $N_2O$ formation |

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# Simplification - kinetics

- Using global kinetics instead of micro-kinetics
  - Example to use

$$r = \frac{(kinetic\ \ factor)(driving\ \ force)}{adsorption\ \ \text{group}} \qquad r = \frac{(A \cdot e^{-E/R \cdot T})(C_A^{\alpha} C_B^{\beta})}{1 + K_A \cdot C_A} \cdots$$

Instead of

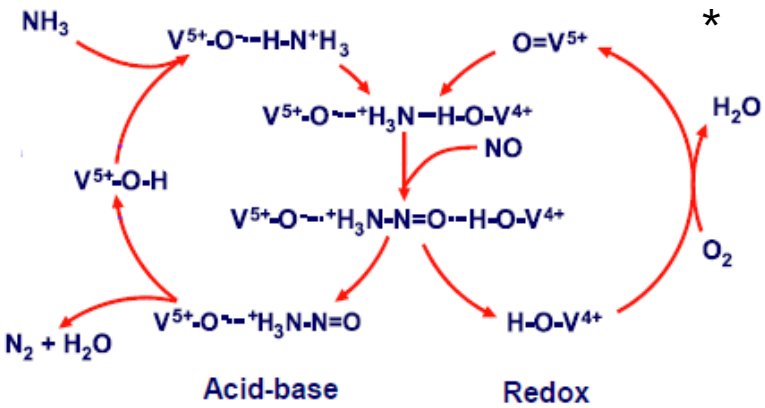
$$\text{Rate} = \frac{\alpha^2}{\beta}[\gamma - (\gamma^2 + \beta S/\alpha)^{1/2}]^2$$

$$\alpha = \frac{k_2 k_3 P_{NO} K_1 P_{NH_3}}{(k_{-2} + k_3 P_{NO})(1 + K_6 P_{H_2O} + K_1 P_{NH_3}) + k_2 K_1 P_{NH_3}}$$

$$\beta = 16 k_4 k_5 P_{O_2}$$

$$\gamma = (2 k_5 P_{O_2})^{1/2} + (k_4)^{1/2}$$

$S$ = ratio of V=O to $V^{5+}$–OH sites on the clean, fully oxidized catalyst (assumed to be equal to 0.1 in the present study),




- Lump internal mass transfer effect into kinetics

*http://www.topsoe.com

Dumesic et al, J. Catal, 1996

# Data Fitting

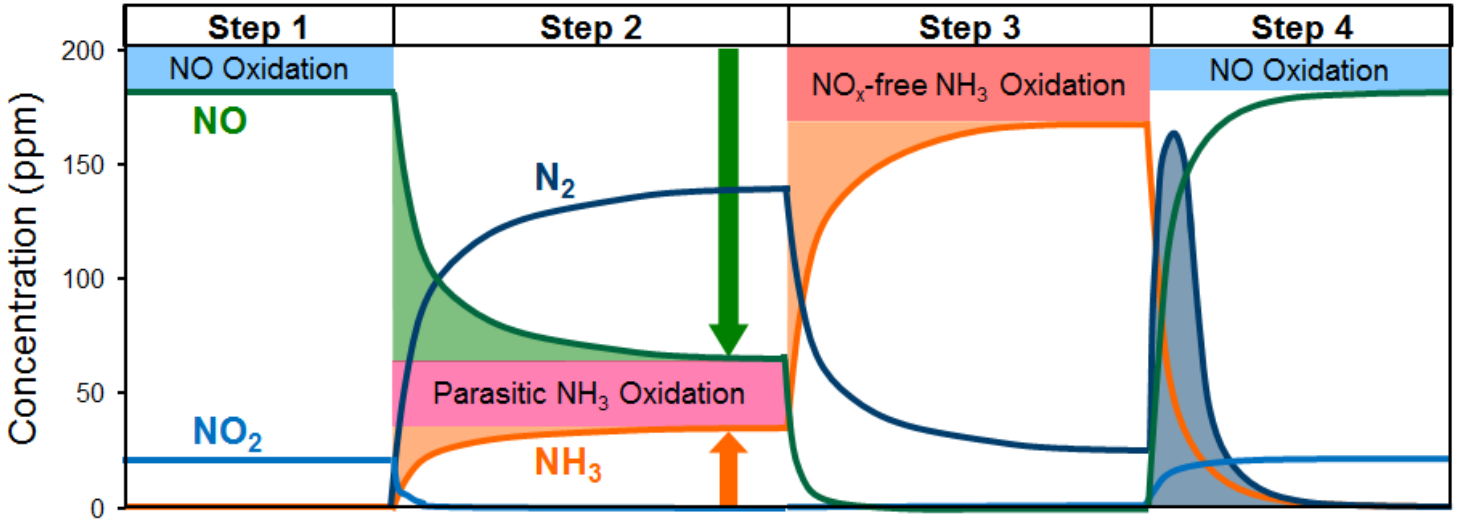
- Numerically solving differential equations
- Minimizing differences between **measured** values and **calculated** values by varying kinetic parameters

$$\min_{\beta}\left(\sum[(y^{\exp} - y^{cal}(x:\alpha,\beta))]^2\right)$$

# Experimental

- **Reaction conditions:**
  - **$NH_3$ TPD**
  - **Standard SCR; fast SCR; NO oxidation; $NH_3$ oxidation**
  - **$NO_x$, 100~1000 ppm**
  - **$NO_2/NO_x$ =0, 0.25, 0.5**
  - **ANR sweep: ANR=0.6~1.4**
  - **$O_2$ effect: 4~13%**
  - **T: 170~500 °C**

**Cummins 4-step Protocol***




*Kamasamudram et al., Catalysis Today 151 (2010) 212-222

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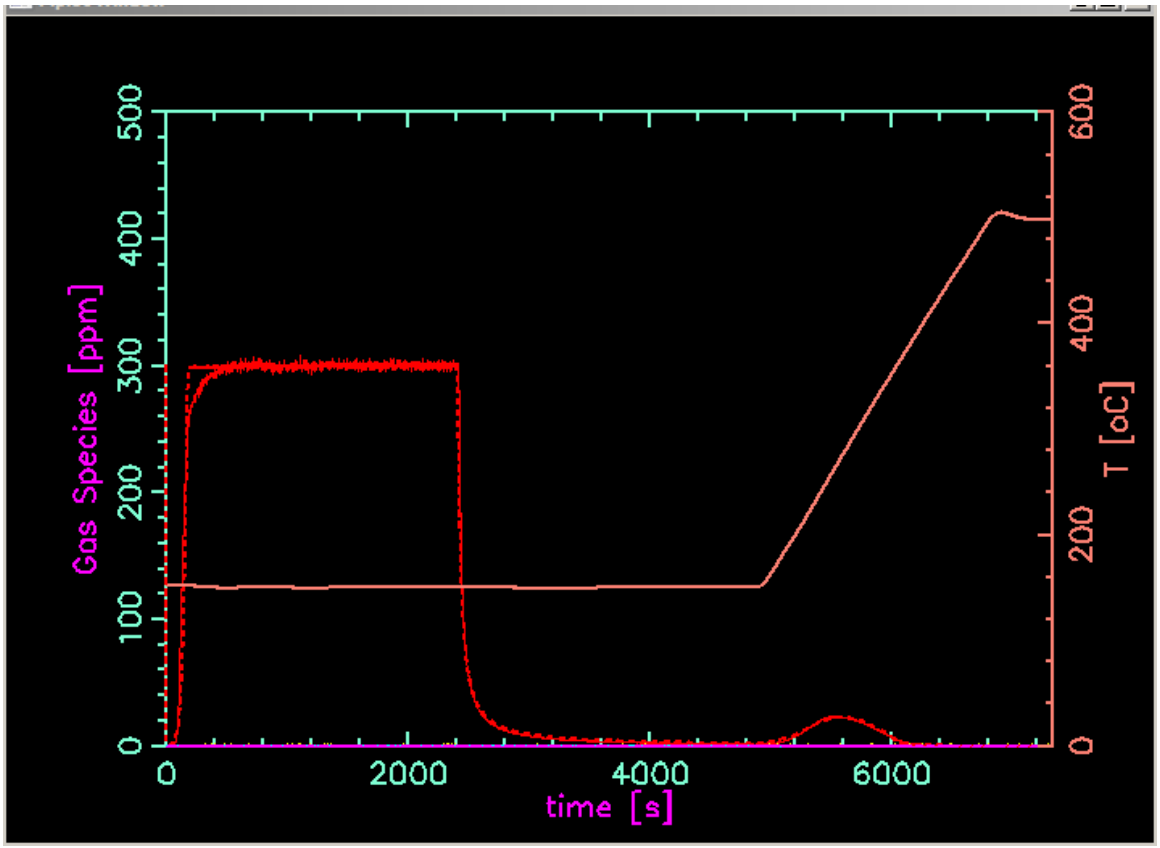
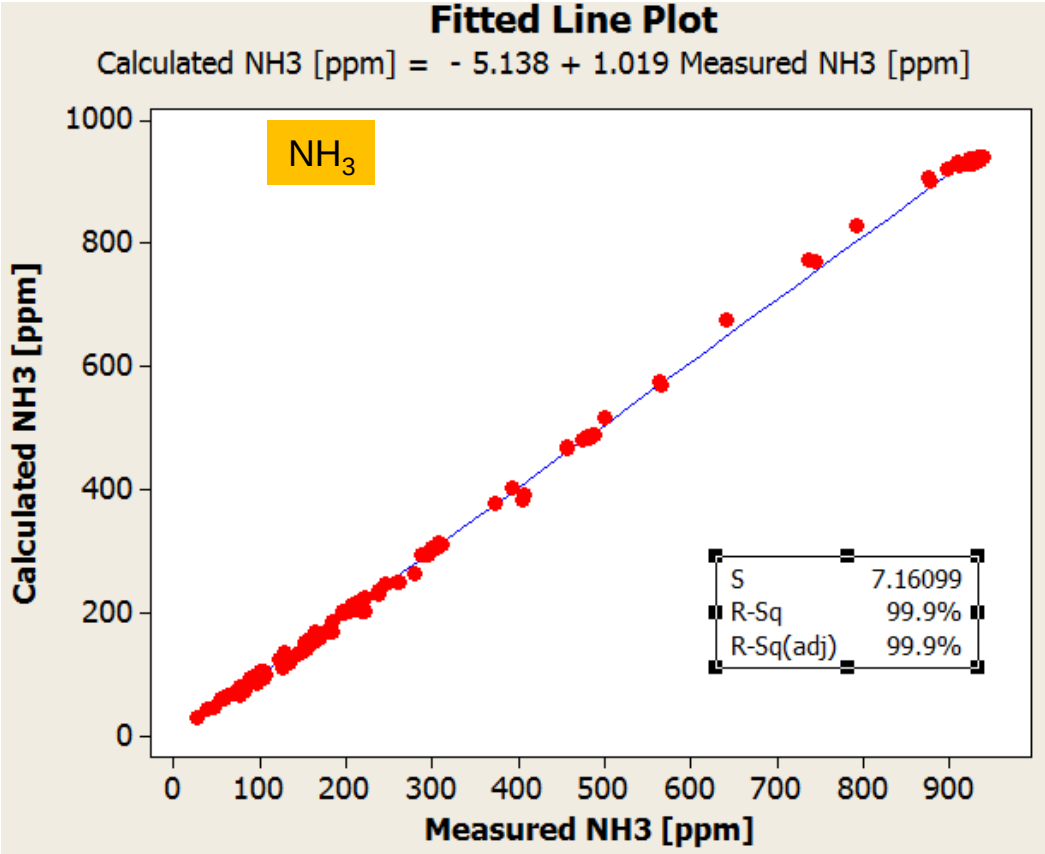
# $NH_3$ TPD: $NH_3 + S_1$ <---> $NH_3$-$S_1$

$$r_1 = A_{1,2} e^{\left(-E_{1,6}/RT\right)} C_{NH_3}(1-\theta) - A_{1,3} e^{\left(-E_{1,4}(1-\alpha\theta)/RT\right)} \theta$$



# $NH_3$ oxidation




| Species | R-Sq [%] | Mean differece [ppm] | 95% CI for mean difference [ppm] |
|---|---|---|---|
| NH3 | 99.9 | 0.370 | (-0.788, 1.527) |

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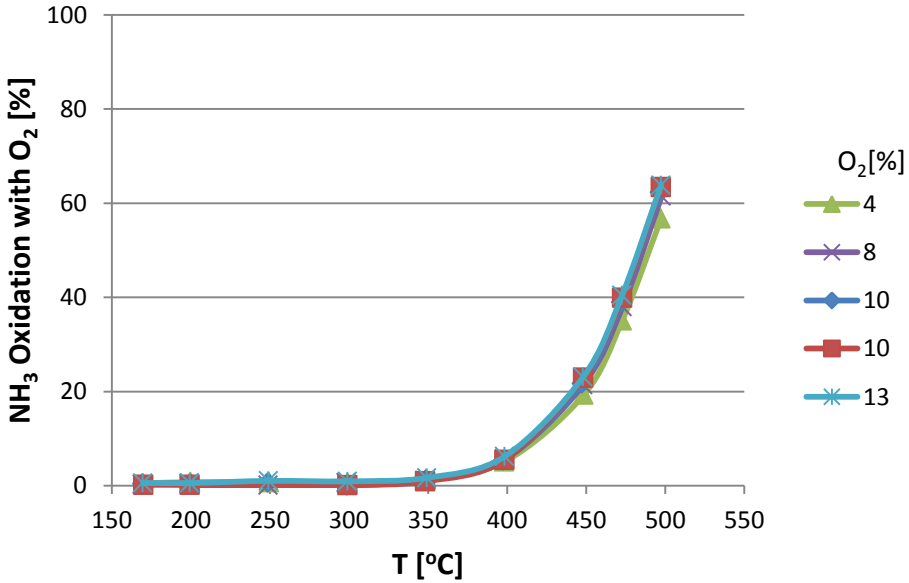
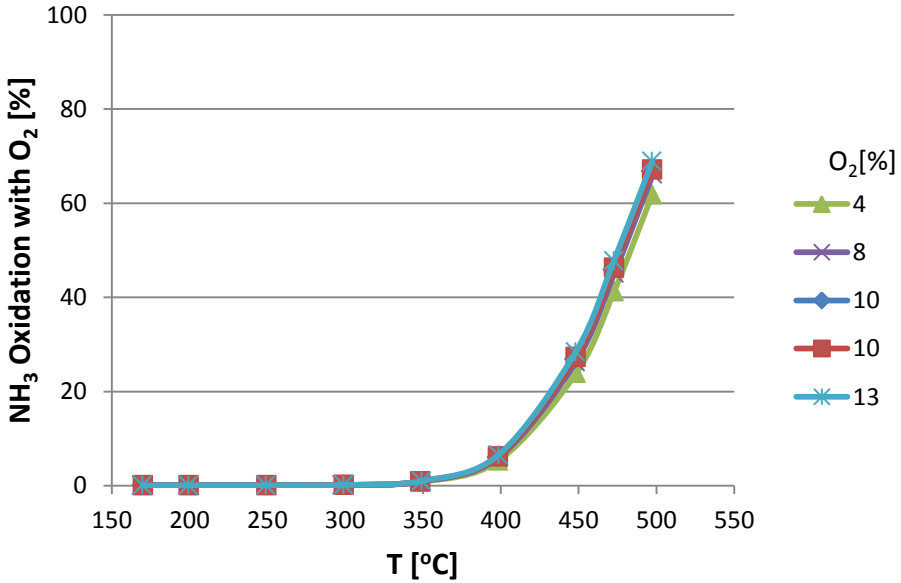
# $NH_3$ oxidation

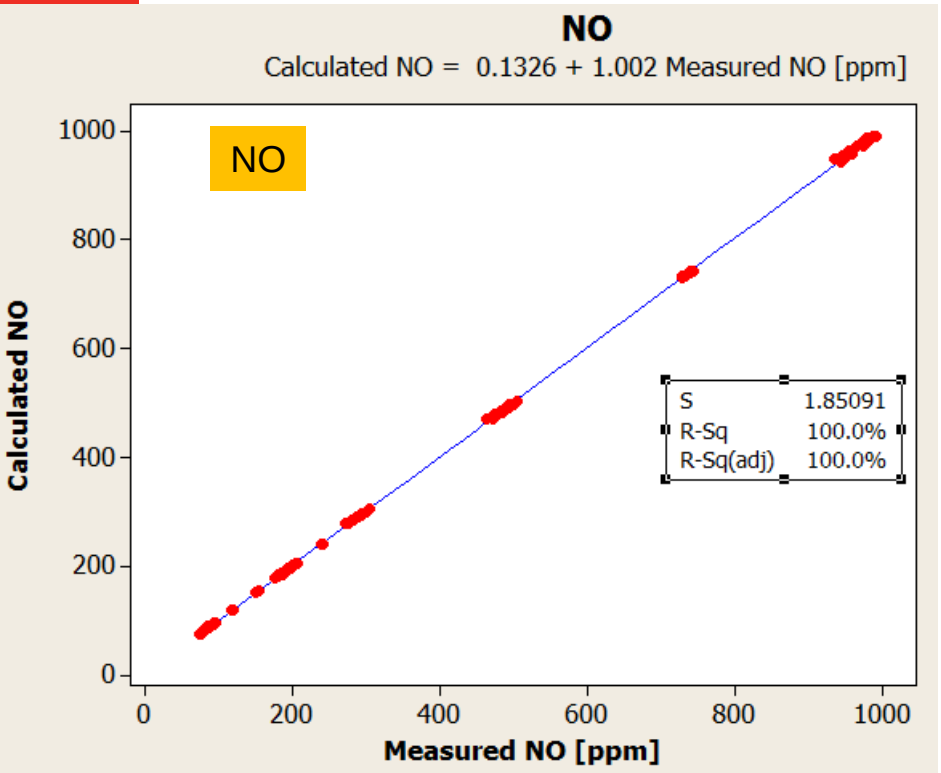
## Experimental

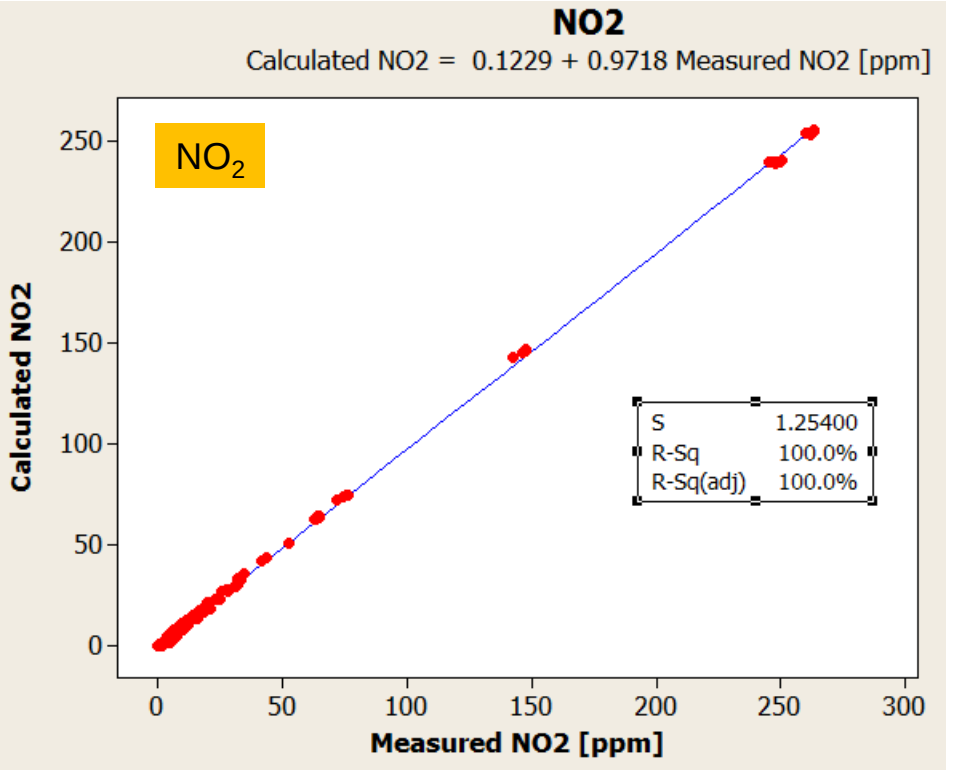



## Model Fit



# NO oxidation



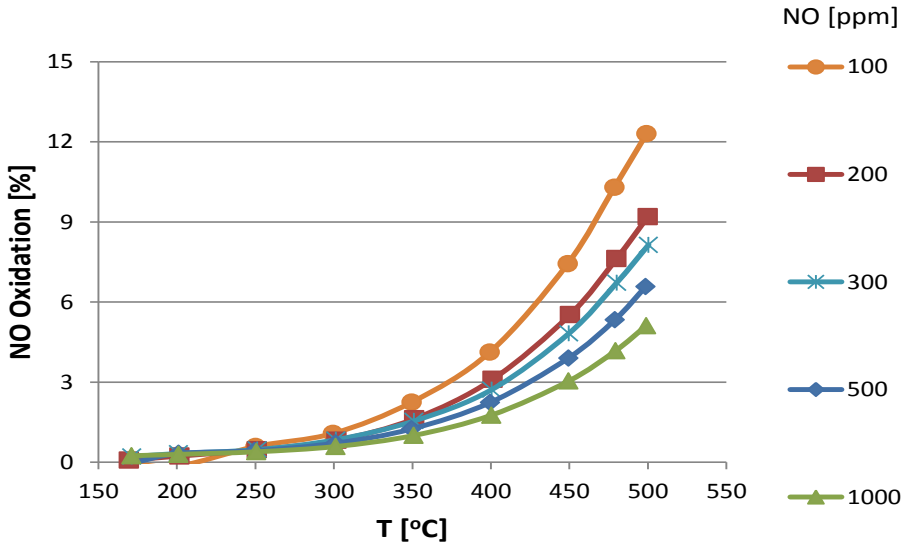



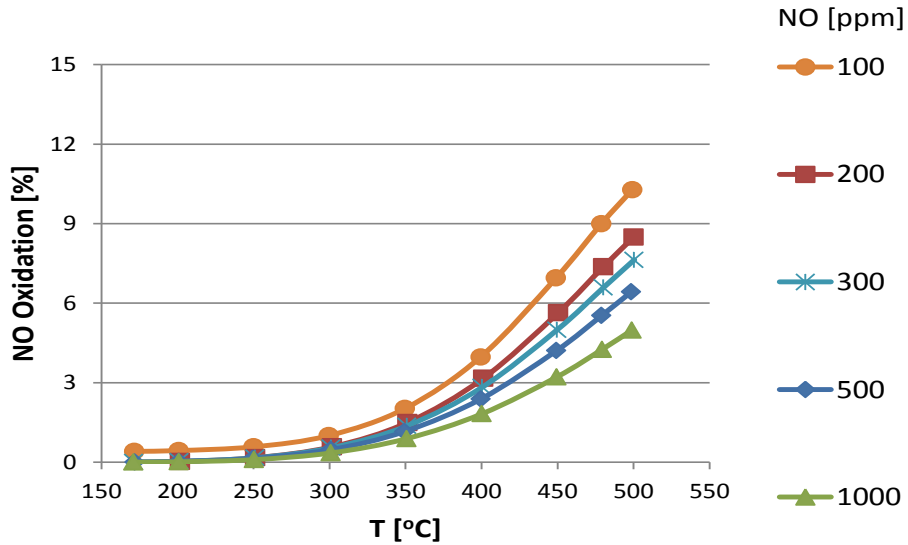

| Species | R-Sq [%] | Mean differece [ppm] | 95% CI for mean difference [ppm] |
|---|---|---|---|
| NO | 100.0 | 0.703 | (0.452, 0.954) |
| $NO_2$ | 100.0 | -0.966 | (-1.279, -0.654) |

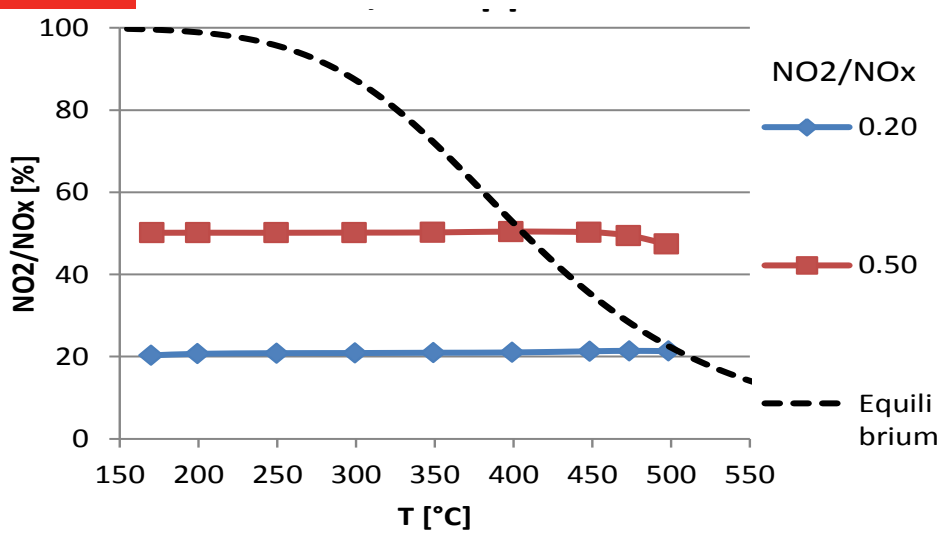
# NO oxidation

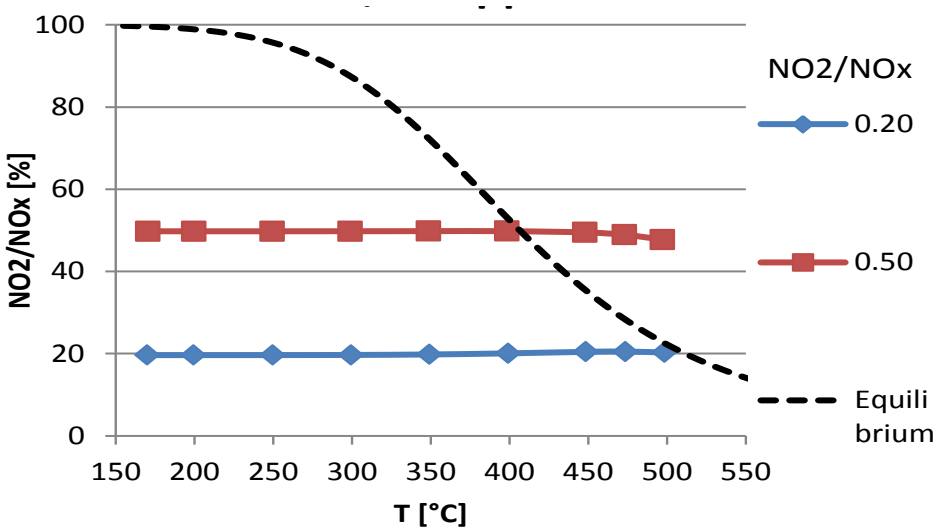
## Experimental

## Model Fit

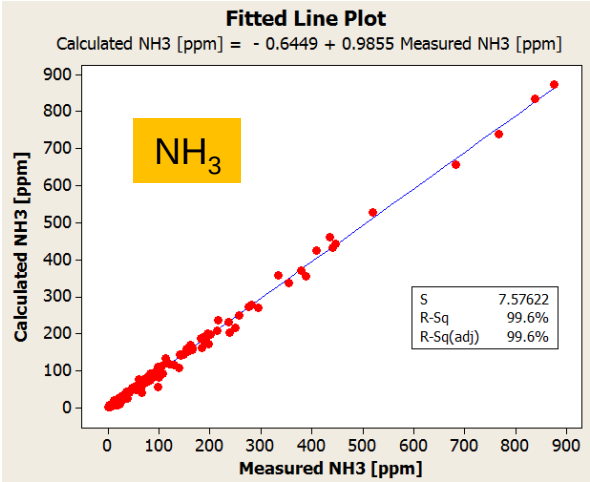


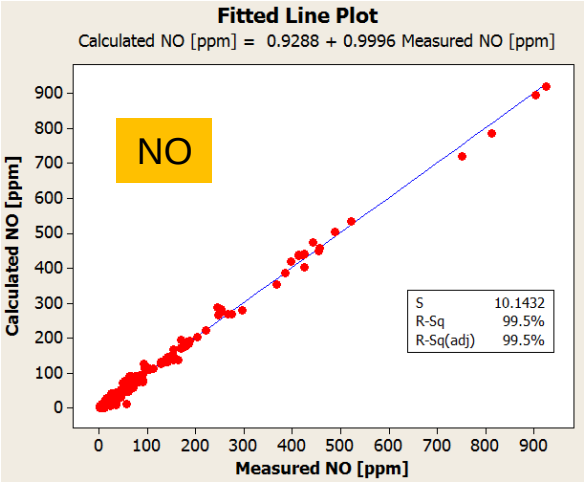



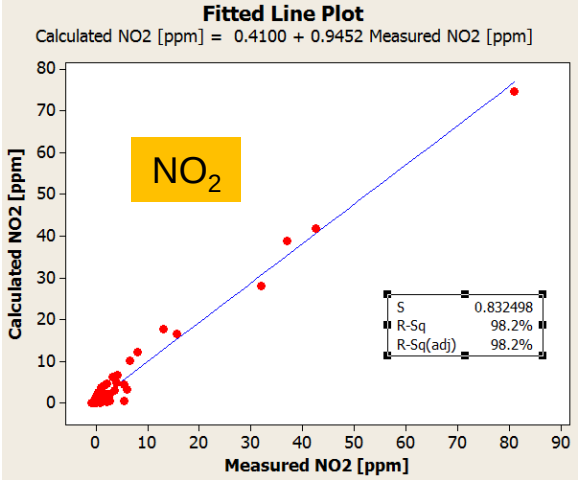



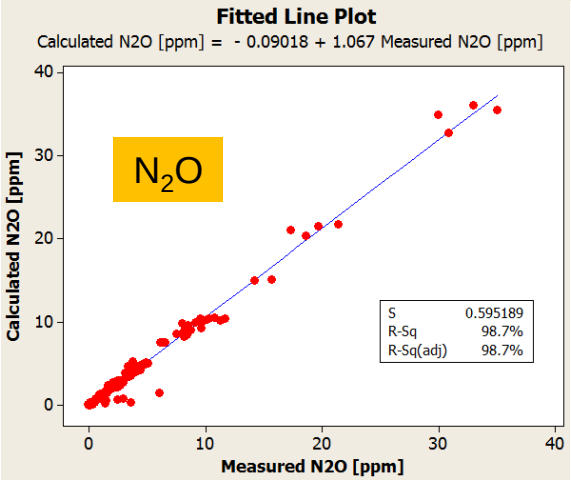



# SCR



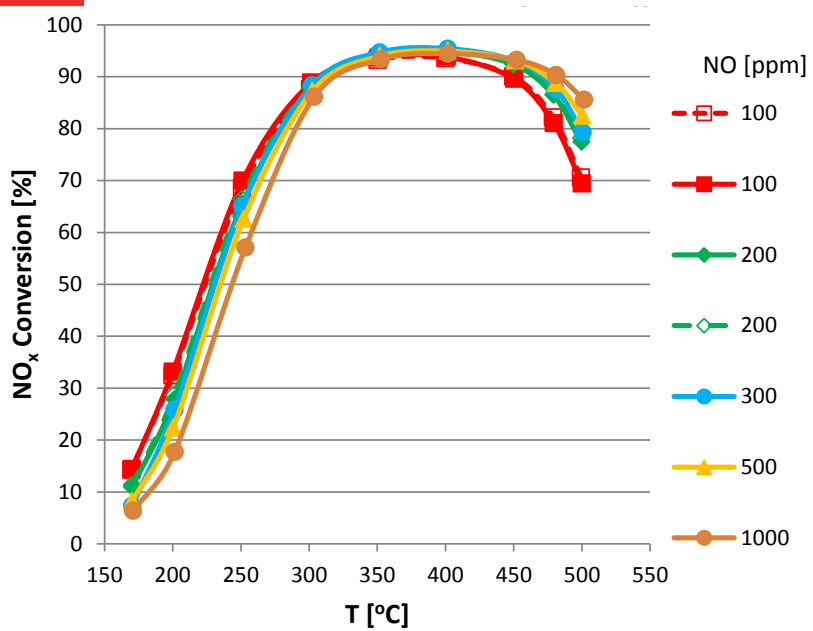



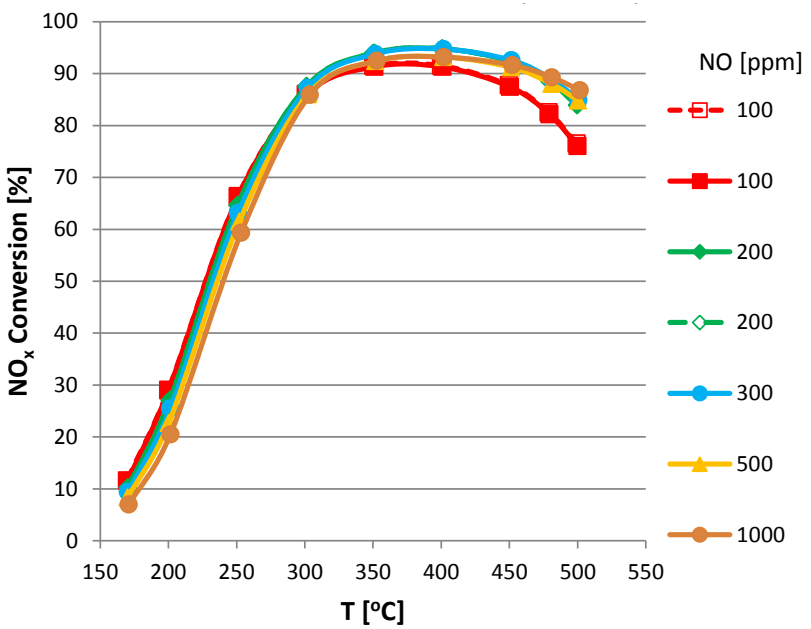

| Species | R-Sq [%] | Mean differece [ppm] | 95% CI for mean difference [ppm] |
|---|---|---|---|
| $NH_3$ | 99.6 | -1.687 | (-2.611, -0.763) |
| NO | 99.5 | 0.897 | (-0.305, 2.099) |
| $NO_2$ | 98.2 | 0.3665 | (0.2593, 0.4737) |
| $N_2O$ | 98.7 | 0.0772 | (-0.0036, 0.1580) |

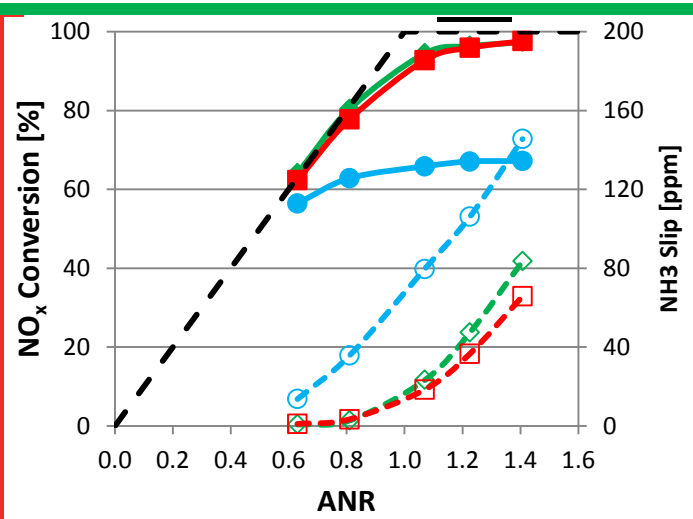
# SCR

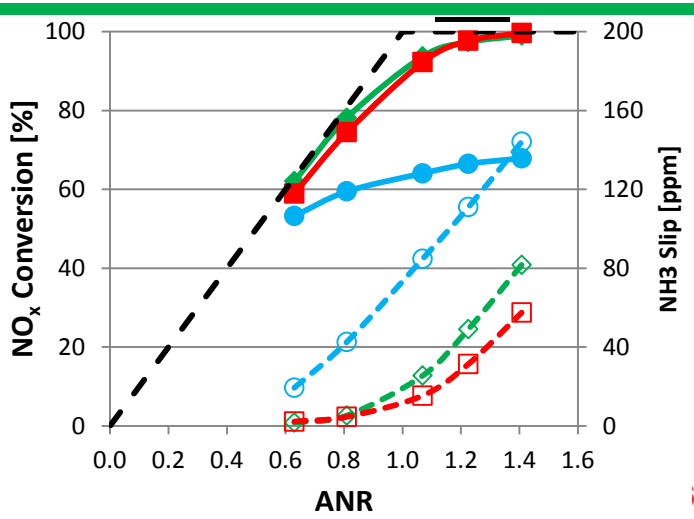
## Experimental




## Model Fit

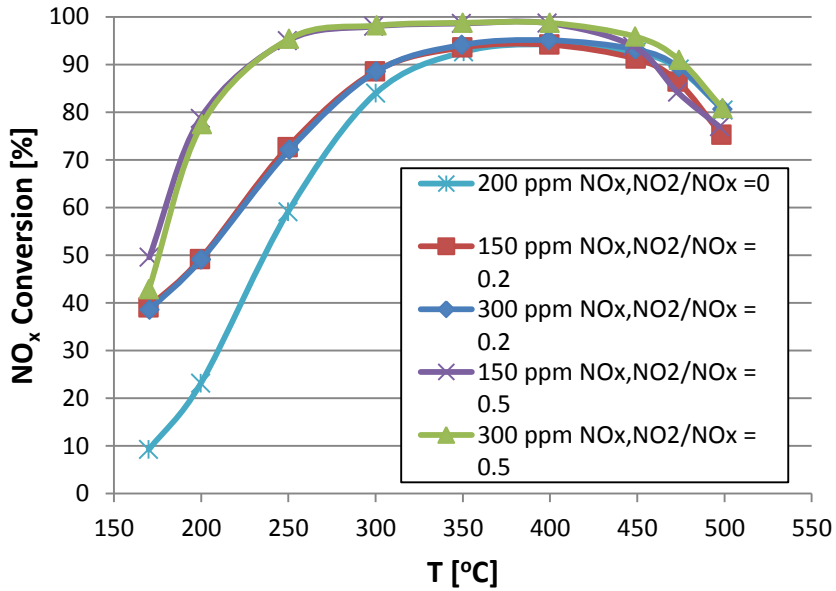


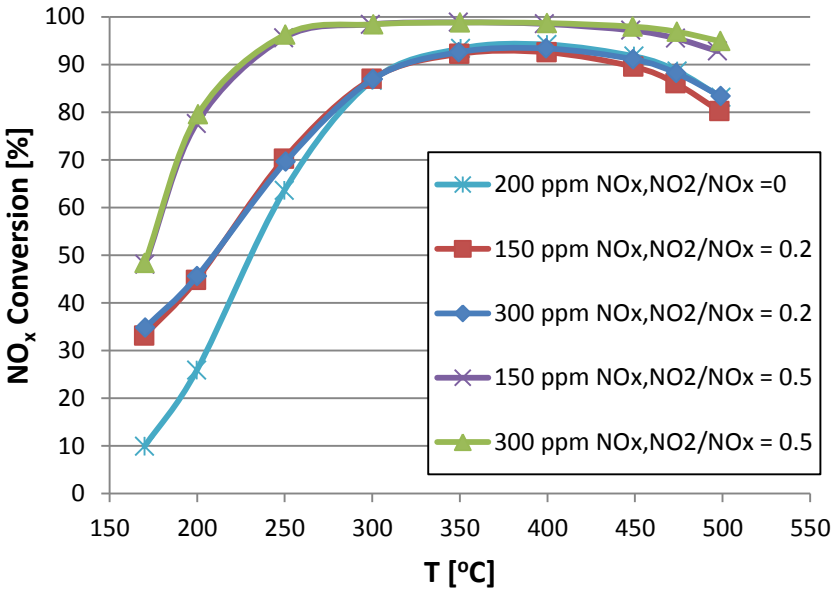



# Effect of $NO_2/NO_x$ ratio for SCR

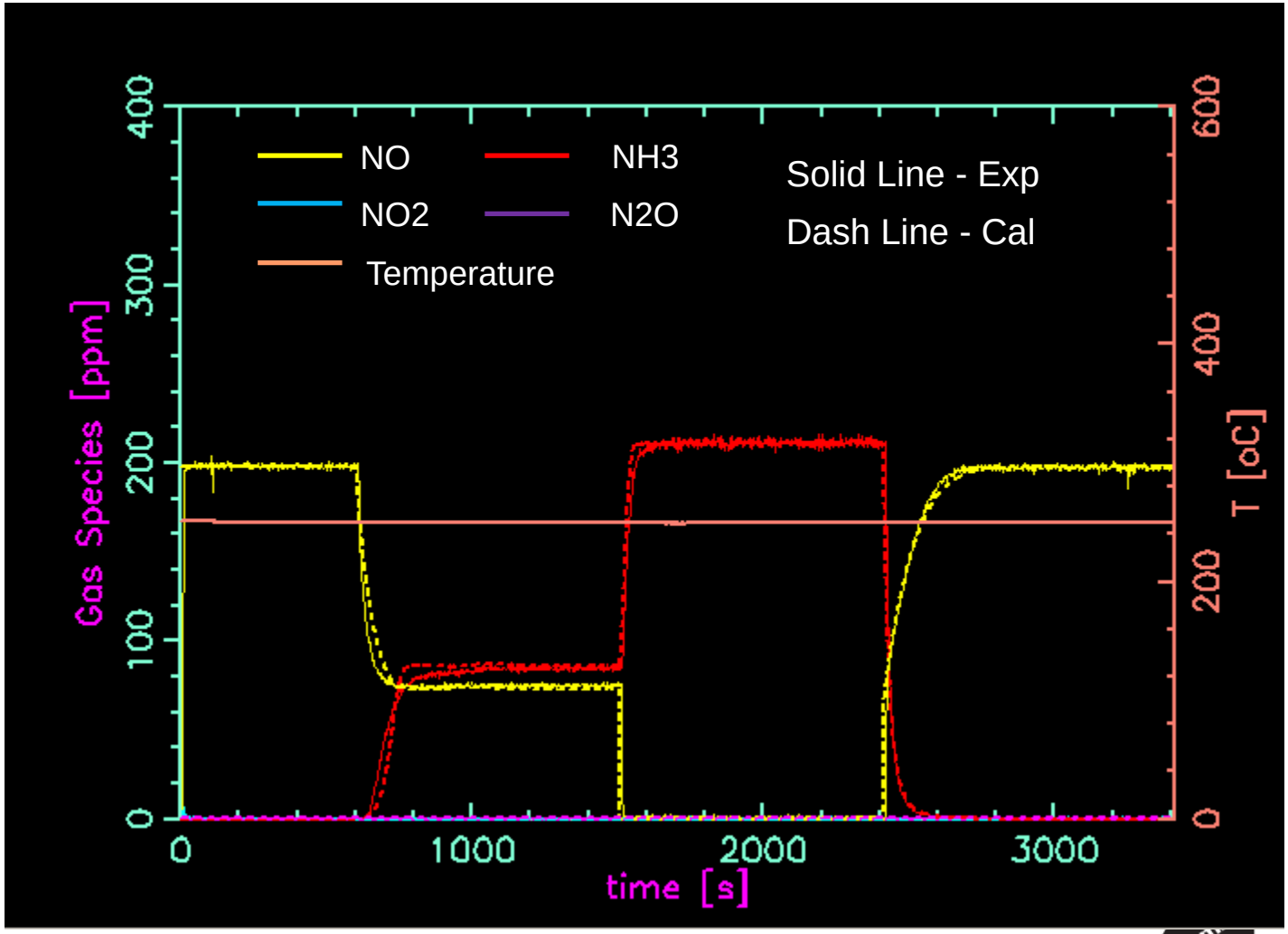
## Experimental




## Model Fit



# 4-step protocol simulation@250 C

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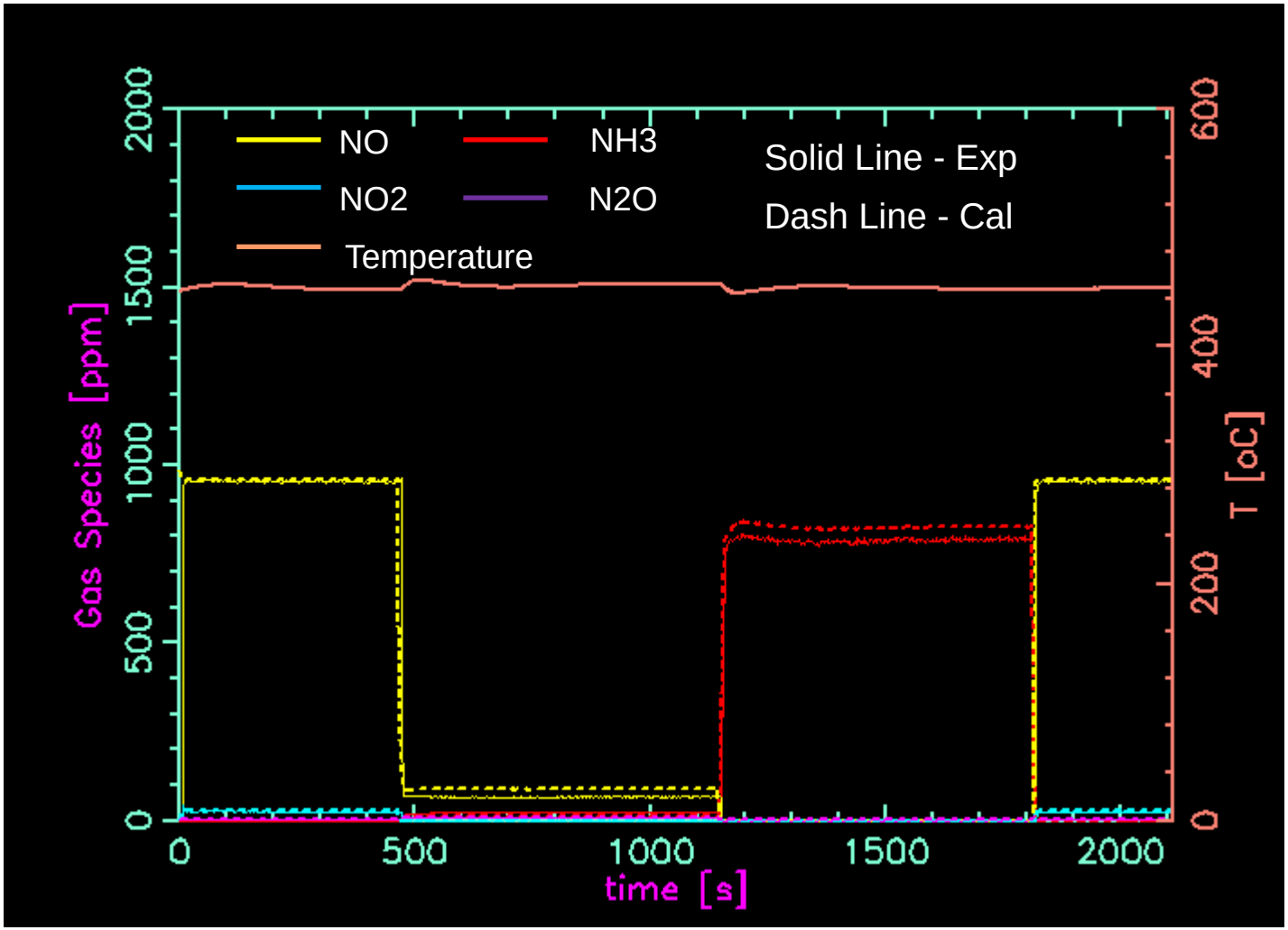
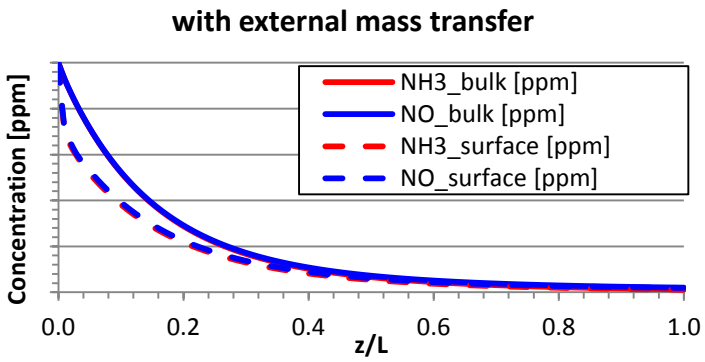
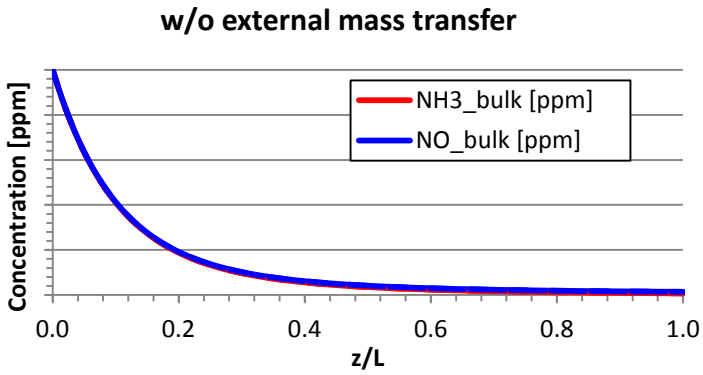
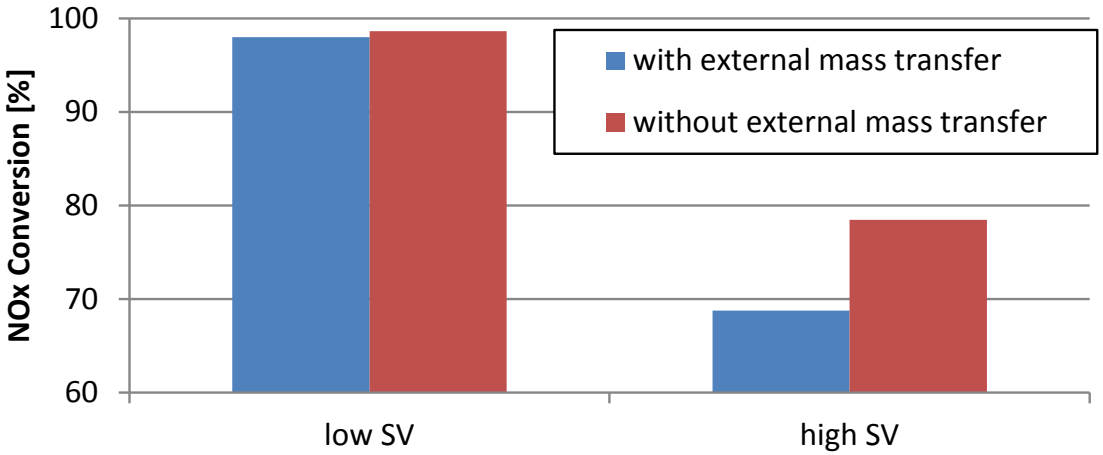
# 4-step protocol simulation@450C



# Effect of external mass transfer



# Summary

- A methodology was developed for efficiently tuning global SCR kinetics and demonstrated for a washcoated VSCR catalyst over wide range of conditions

- External mass transfer are more apparent at catalyst entrance than catalyst exit

- The NOx conversion will be more affected by external mass transfer at high T and high SV based on simulation

# Acknowledgements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  - Dr. Ramya Vedaiyan
  - Mr. Apoorv Kalyankar


- **Literature**

  - Olsson et al. Applied Catalysis B: Environmental 81 (2008) 203–217
  - Guthenke, Tronconi et al. Advances in Chemical Engineering, Volume 33, 2007, Pages 103-211,280-283
  - Sampara, PhD Thesis: Global Reaction Kinetics for Oxidation and Storage in Diesel Oxidation Catalysts2008
  - Kamasamudram et al., Catalysis Today 151 (2010) 212-222
  - Dumesic et al. J. Catal. 1996
  - Many others…


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# Thank you!

# Questions?

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