Model Development and its Application for a Cu-CHA Catalyst

M. Bendrich, A. Scheuer, R. E. Hayes, M. Votsmeier

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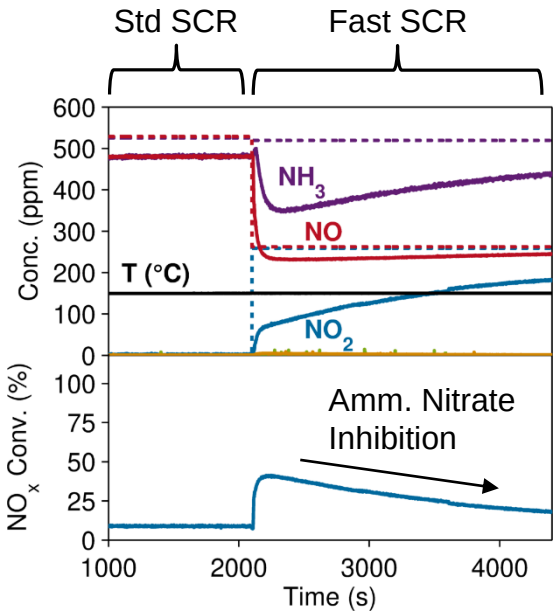
18.09.2019

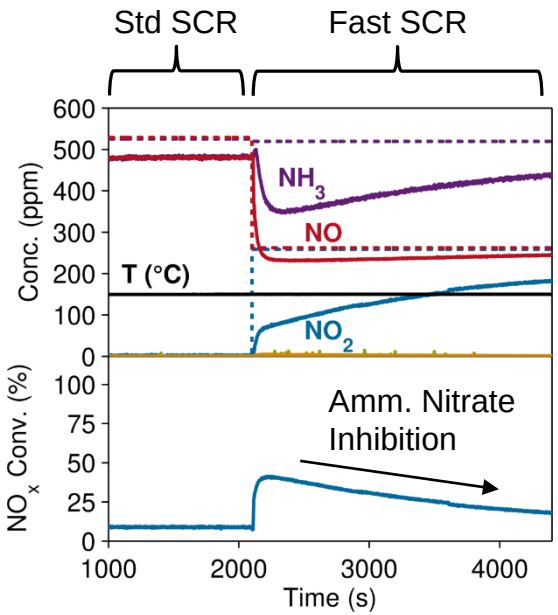
Cu-CHA Challenge: Ammonium Nitrate



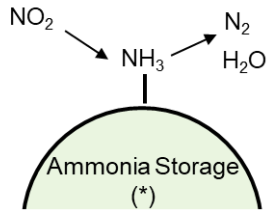
„One challenge of SCR catalysts at temperatures below 200°C is that ammonium nitrate accumulates on Cu-zeolite catalysts“

– US DOE 2017 Annual Merit Review

Cu-CHA Challenge: Ammonium Nitrate



Goal: Extend SCR mechanism to include ammonium nitrate

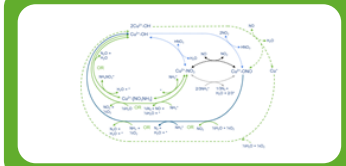


$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$

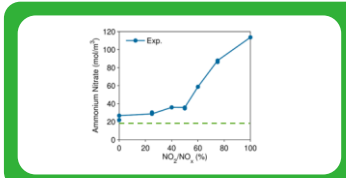
„One challenge of SCR catalysts at temperatures below 200°C is that ammonium nitrate accumulates on Cu-zeolite catalysts“

– US DOE 2017 Annual Merit Review

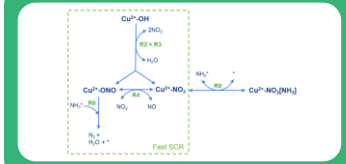
Overview of Presentation



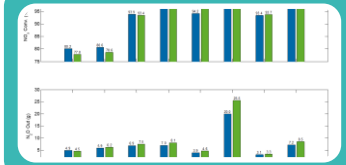
SCR mechanism with nitrates



Validate predicted amount of amm. nitrate



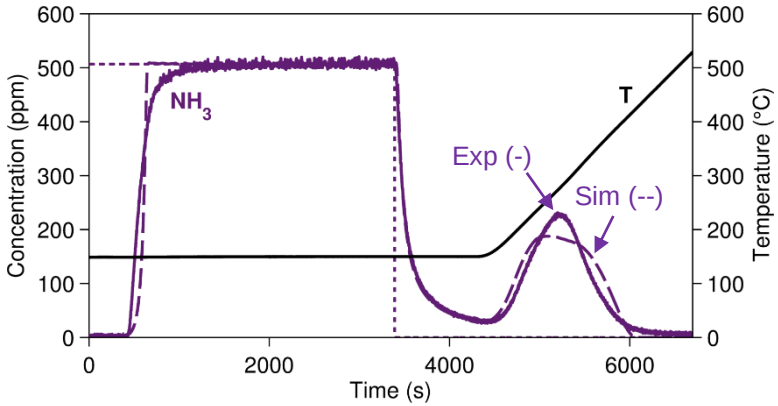
Demonstrate increased SCR performance due to nitrate buffer



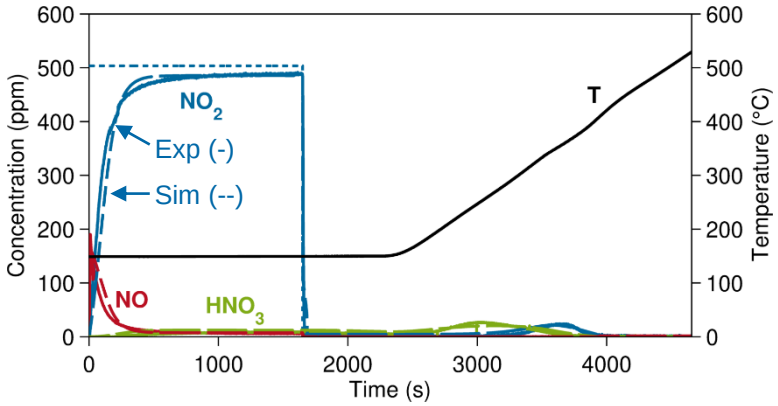
Model predictability for a wide range of driving cycles (no additional calibration)

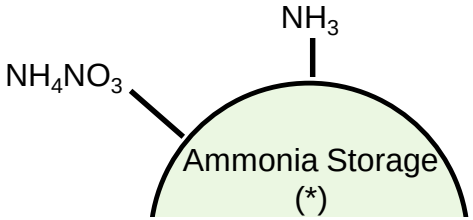
Goal: Extend Model to Include Nitrates

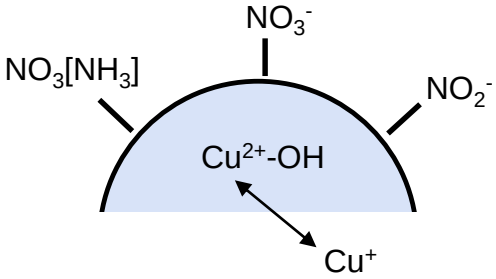
Current Model: Adsorption of Ammonia



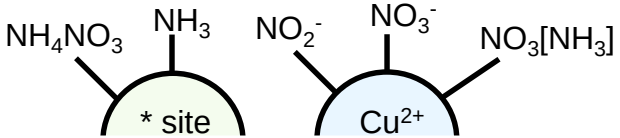
Extension: Adsorption of Nitrates

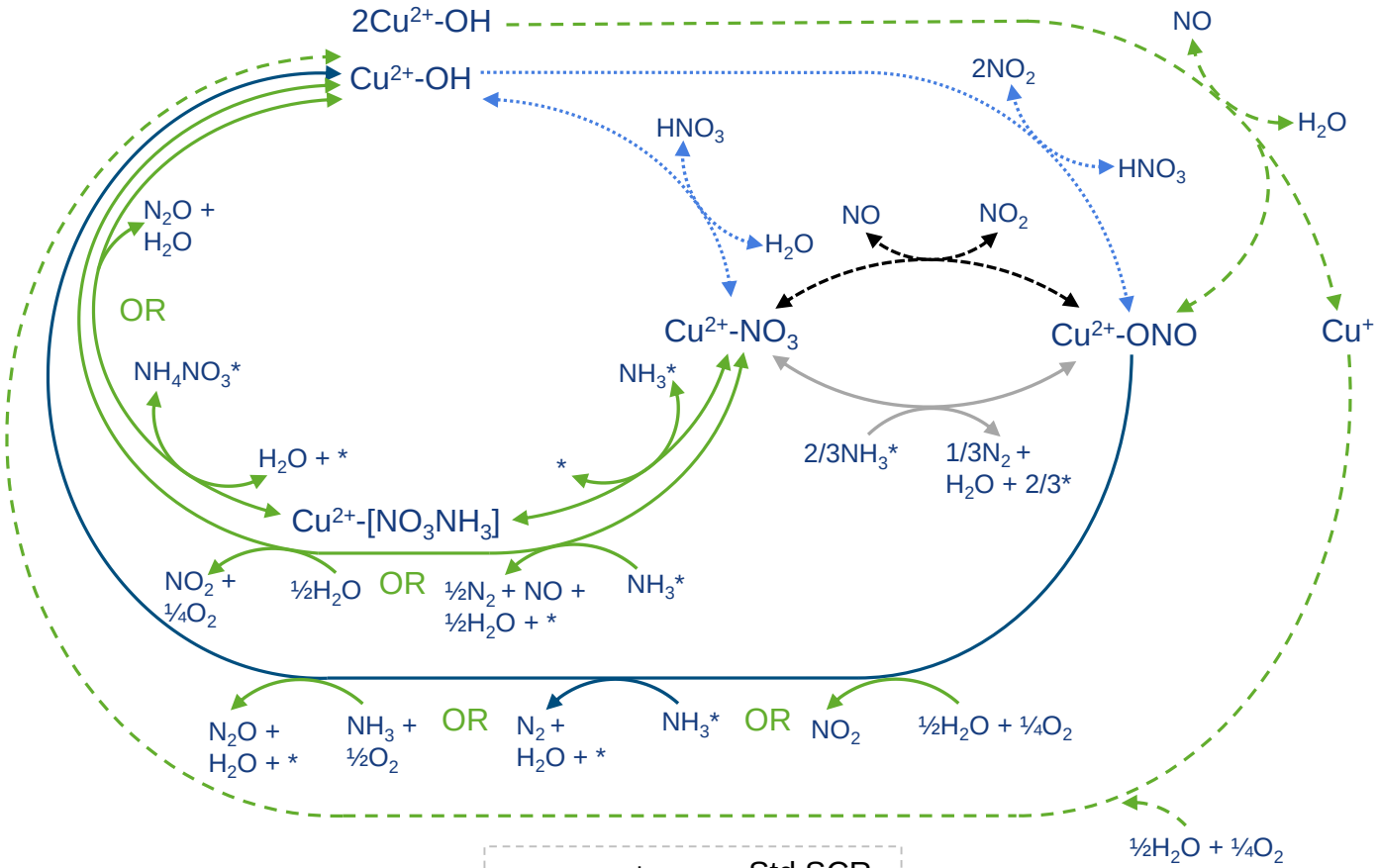






Mechanism

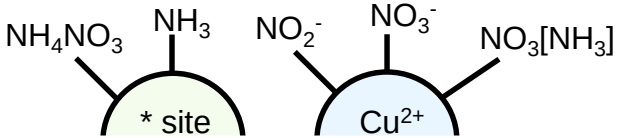




+ = Std SCR
+ + = Fast SCR
+ + = NO_2 SCR

Mechanism published as:
M. Bendrich, A. Scheuer, R. E. Hayes, M. Votsmeier, Unified mechanism model for Standard SCR, Fast SCR, NO_2 SCR over a copper chabazite catalyst, Applied Catalysis B: Environmental 222 (2018) 76-87.

Fast SCR



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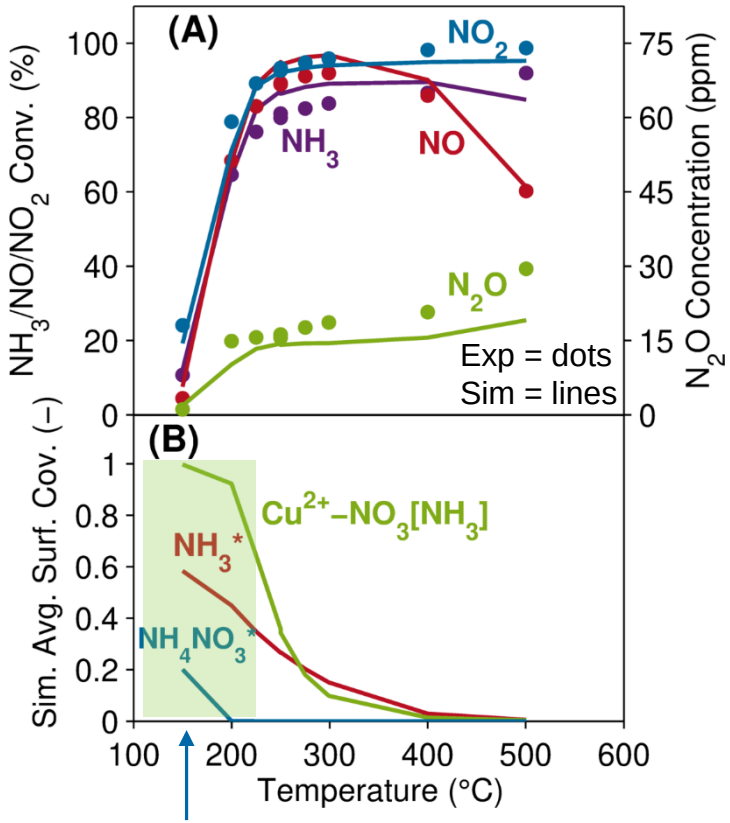
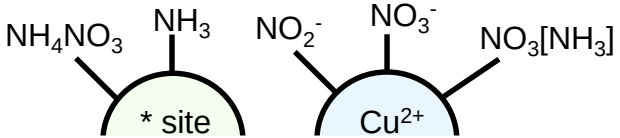
Model captures steady state data



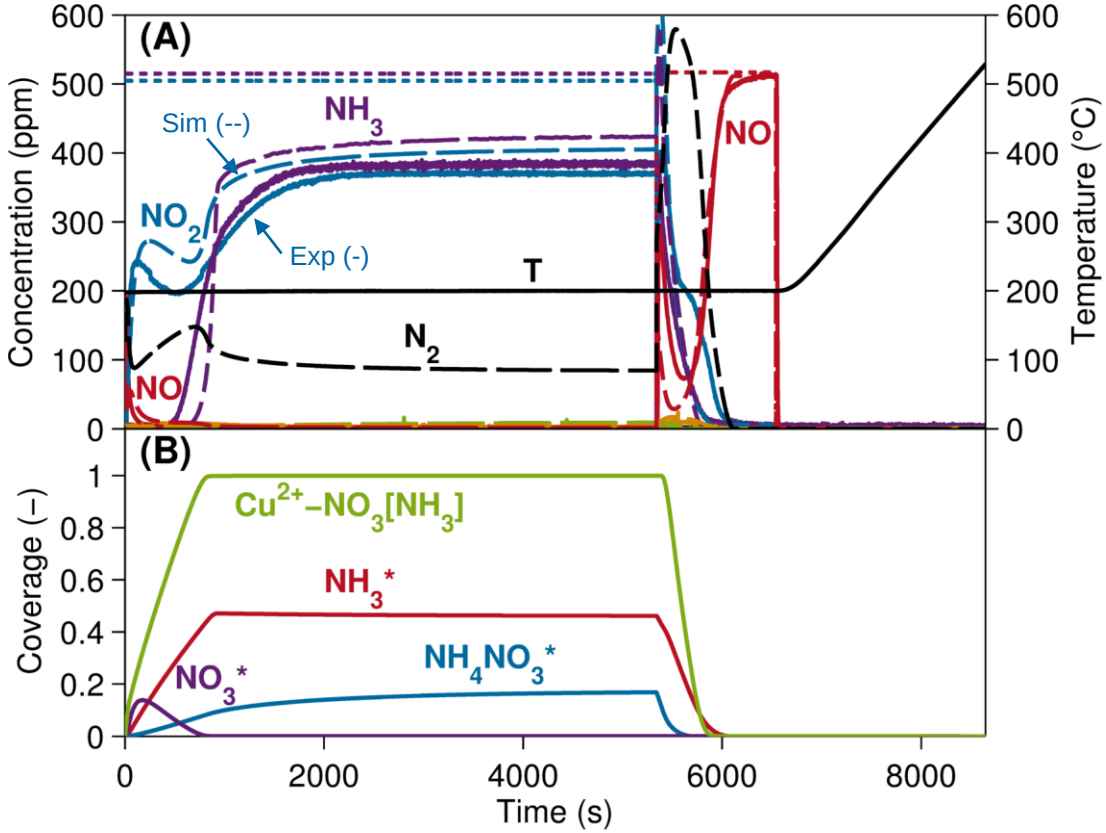
Ammonium nitrate inhibits activity at steady state

2*R1	$2NH_3 + 2^* \leftrightarrow 2NH_3^*$
R2+R3	$2NO_2 + 2Cu^{2+} – OH \leftrightarrow Cu^{2+} – ONO + Cu^{2+} – NO_3 + H_2O$
R4r	$Cu^{2+} – NO_3 + NO \leftrightarrow NO_2 + Cu^{2+} – ONO$
2*R6	$2Cu^{2+} – ONO + 2NH_3^* \rightarrow 2N_2 + 2H_2O + 2Cu^{2+} – OH + 2^*$
Sum:	$\mathbf{2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O}$

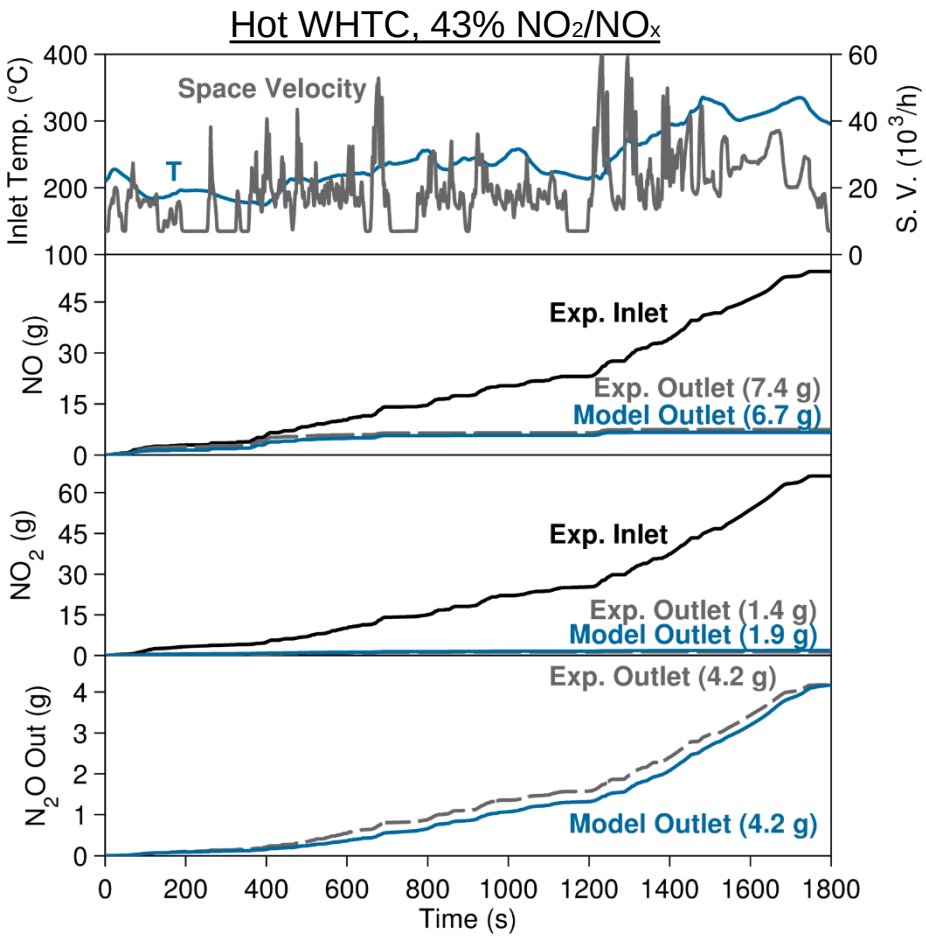
Transient NO_2 SCR



Model captures transients due to ammonia and nitrate storage

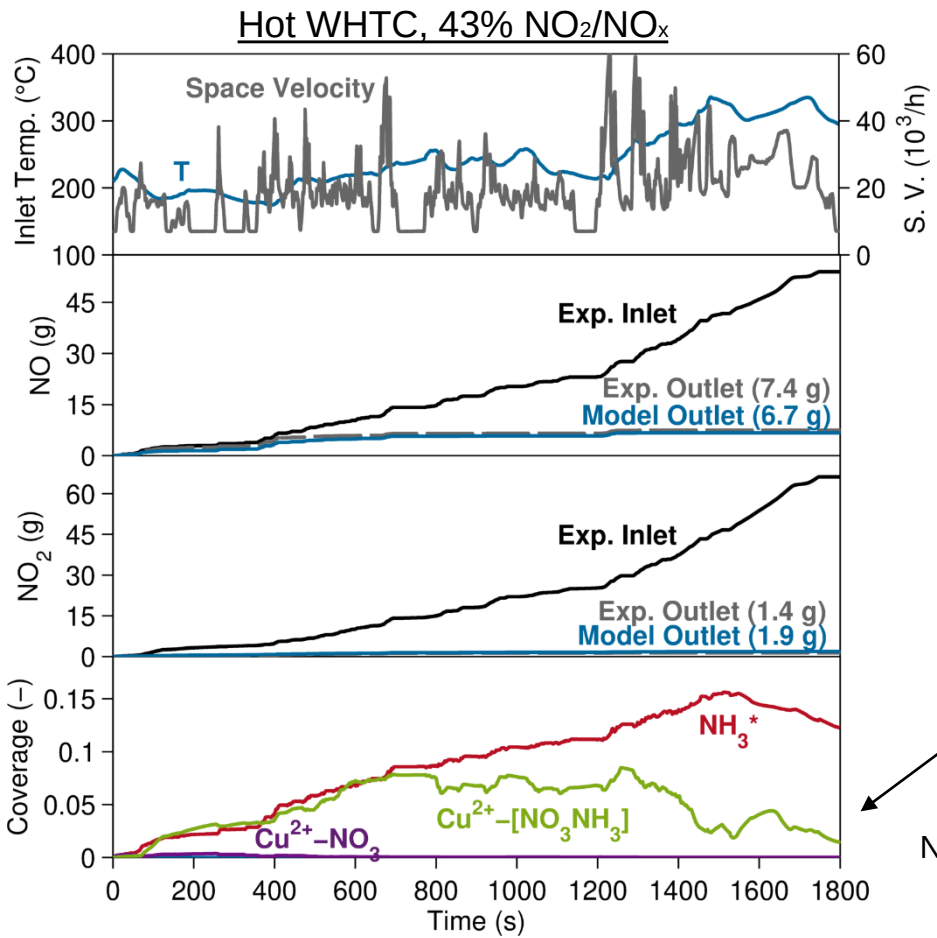


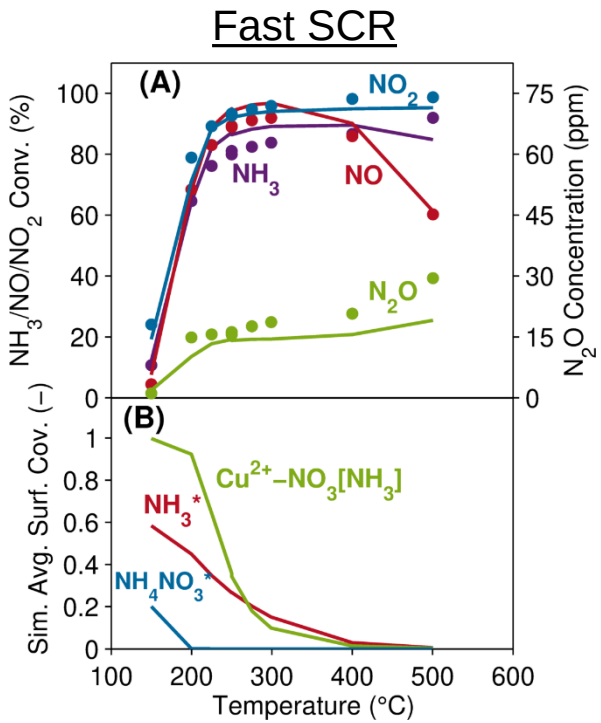
Predictive Simulation of WHTC



- Mechanism applied to driving cycle without any reparameterization
- Model predicts cumulated emissions

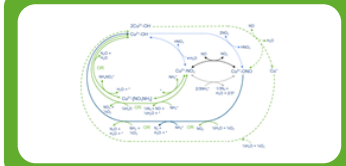
Predictive Simulation of WHTC





Why does so little Amm. Nitrate form during WHTC?

Overview of Presentation



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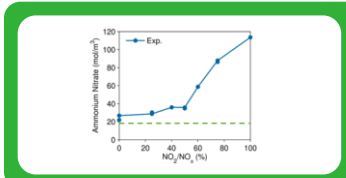

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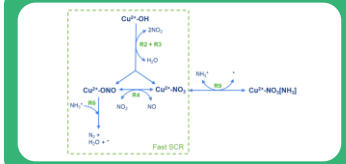

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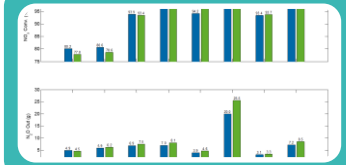
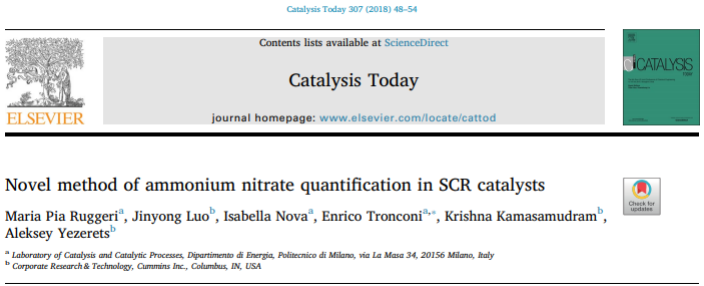


Model predictability for a wide range of driving cycles (no additional calibration)

How much AN forms during steady state?


Catalysis Today 307 (2018) 48–54

Contents lists available at ScienceDirect

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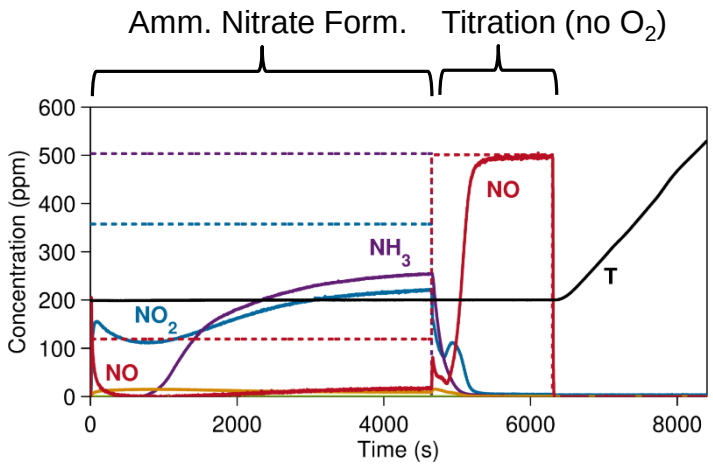
Novel method of ammonium nitrate quantification in SCR catalysts

Maria Pia Ruggeri[a], Jinyong Luo[b], Isabella Nova[a], Enrico Tronconi[a,*], Krishna Kamasamudram[b], Aleksey Yezerets[b]

[a] Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, via La Masa 34, 20156 Milano, Italy
[b] Corporate Research & Technology, Cummins Inc., Columbus, IN, USA



Method from Ruggeri et al. (2018)

$NH_4NO_3 + NO \rightarrow NO_2 + 2H_2O + N_2$ λ1

$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$ λ2

$NO_{in} - NO_{out} = \lambda 1 + \lambda 2$

$NO_{2,out} = \lambda 1 - \lambda 2$

AN react = λ1

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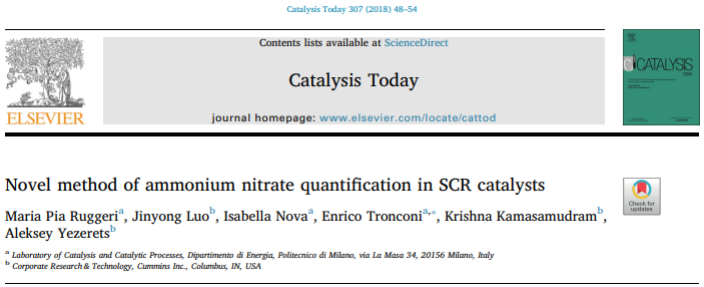
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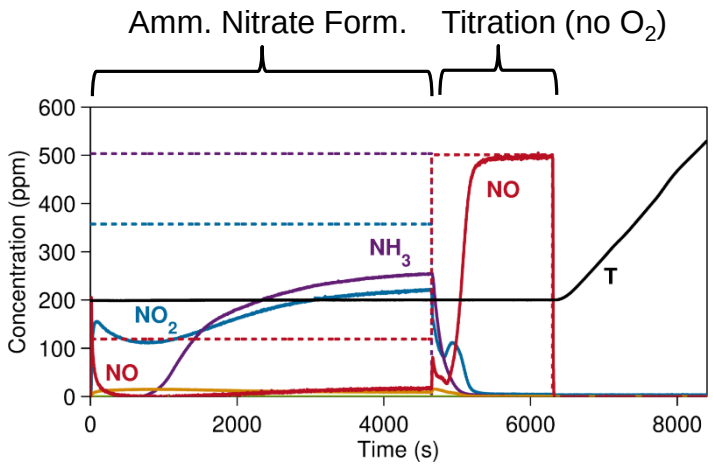
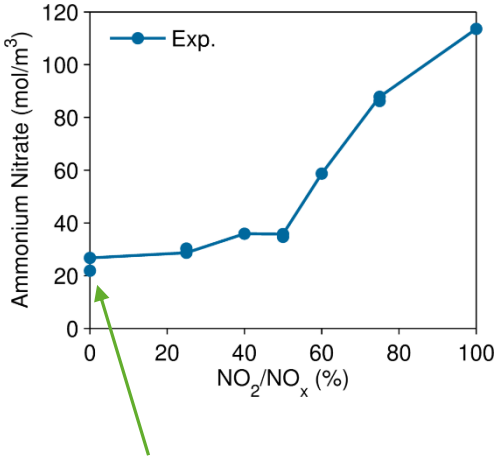
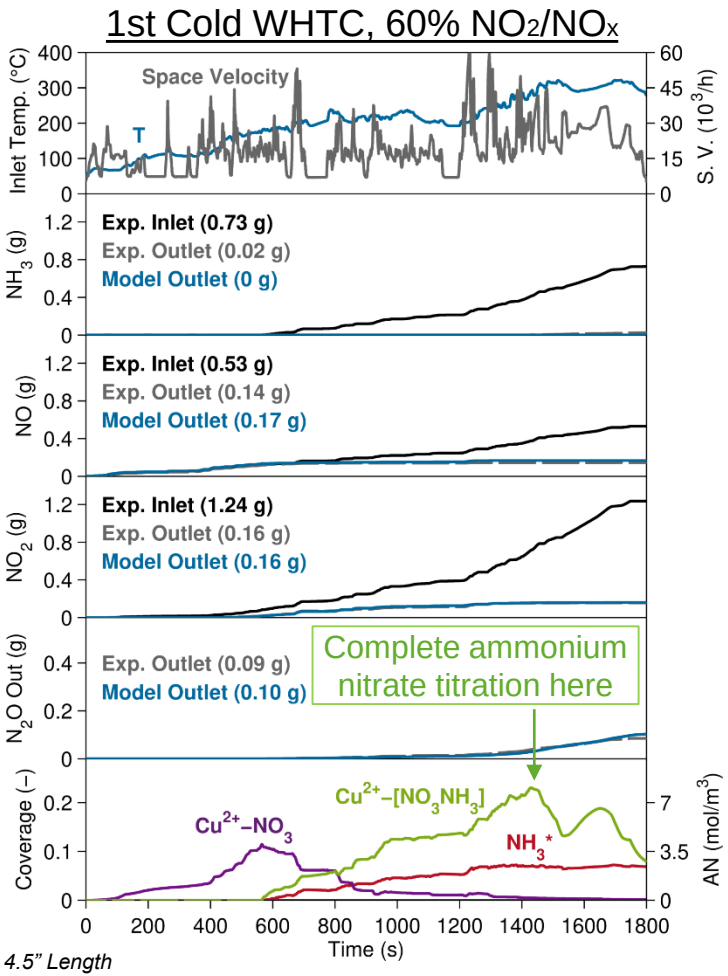


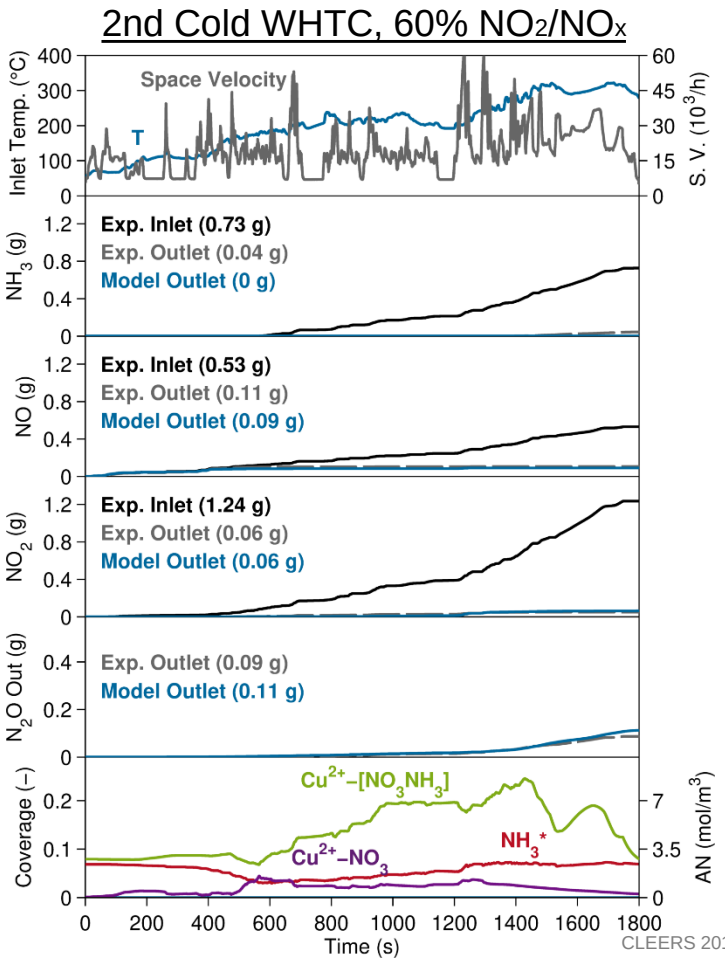
Steady State AN Formation
at 200°C, α = 1



Cu^{2+}-OH + NO + NH_3* → N_2 + $2H_2O$ + Cu^+

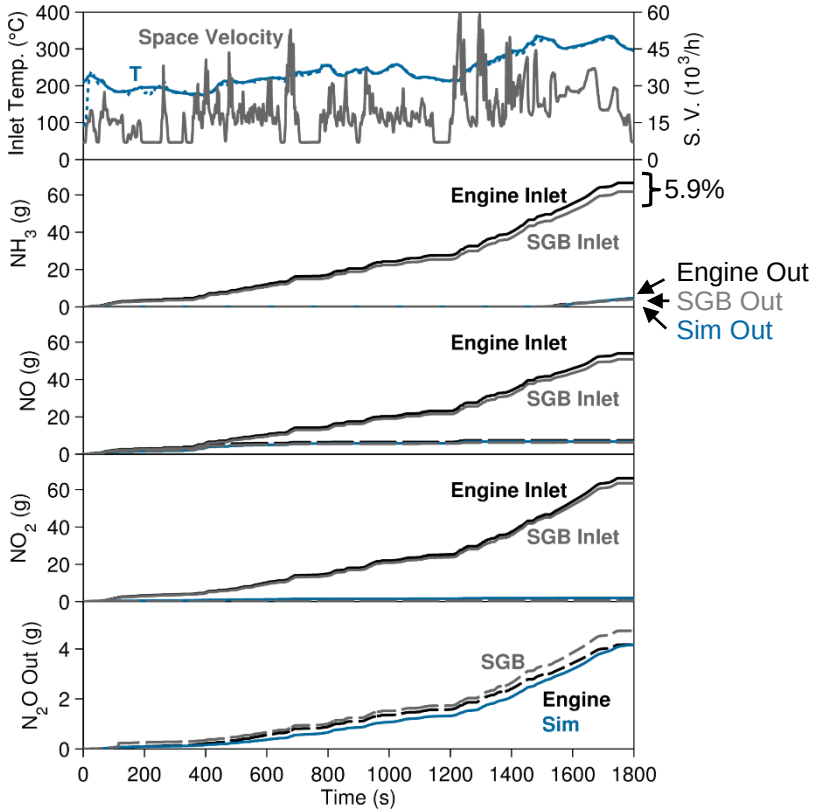
How much AN forms during cold WHTC?





2" Diameter, 4.5" Length

WHTC Performance at Engine, SGB, Sim.



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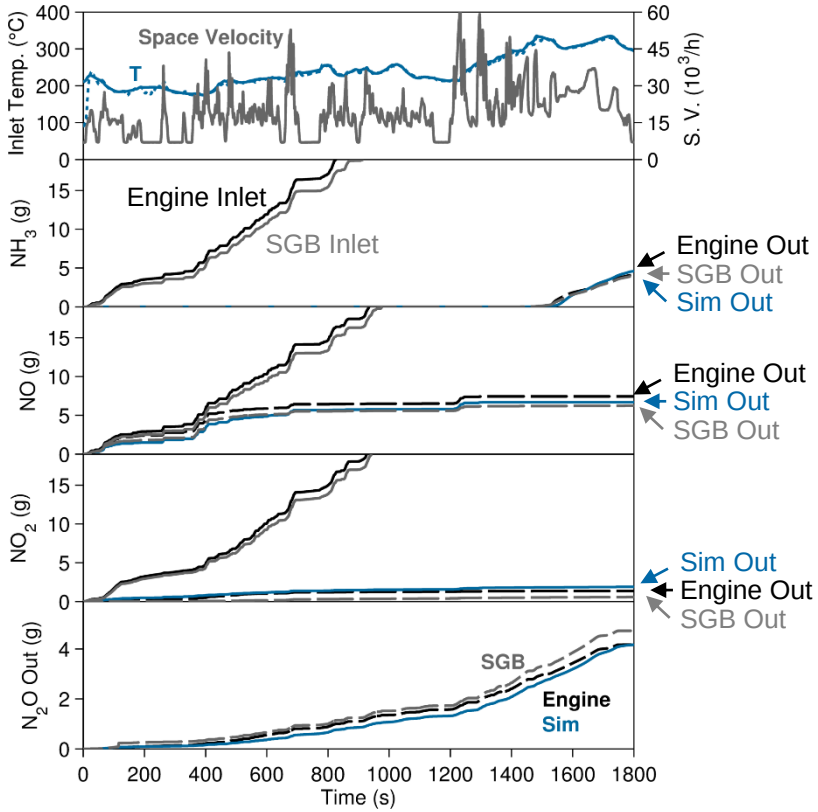

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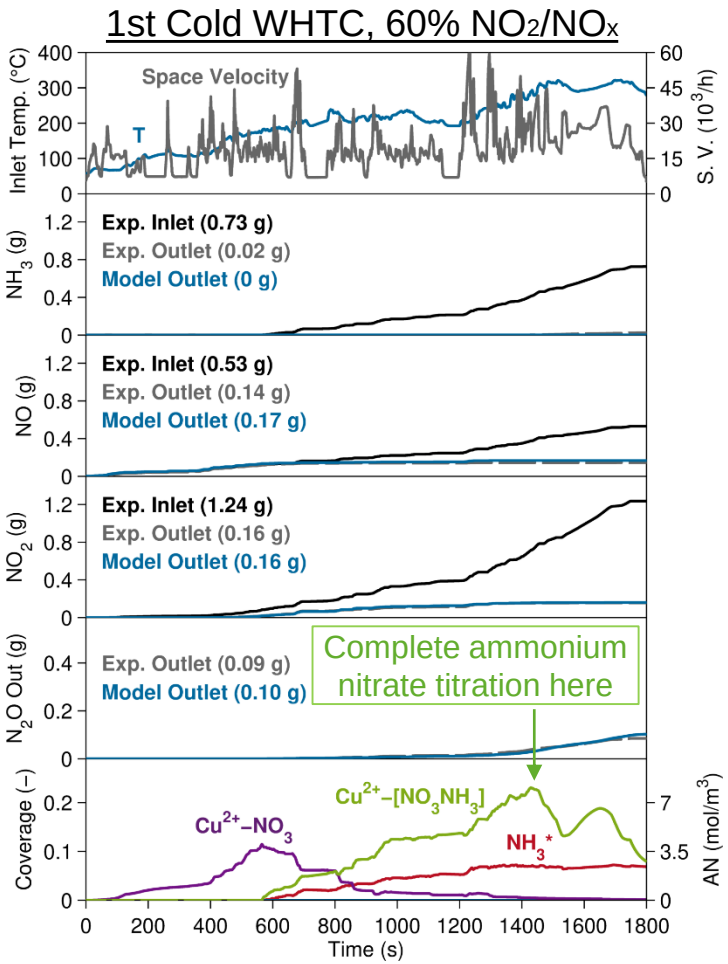
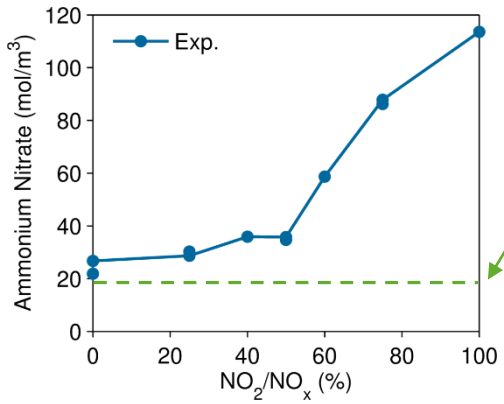
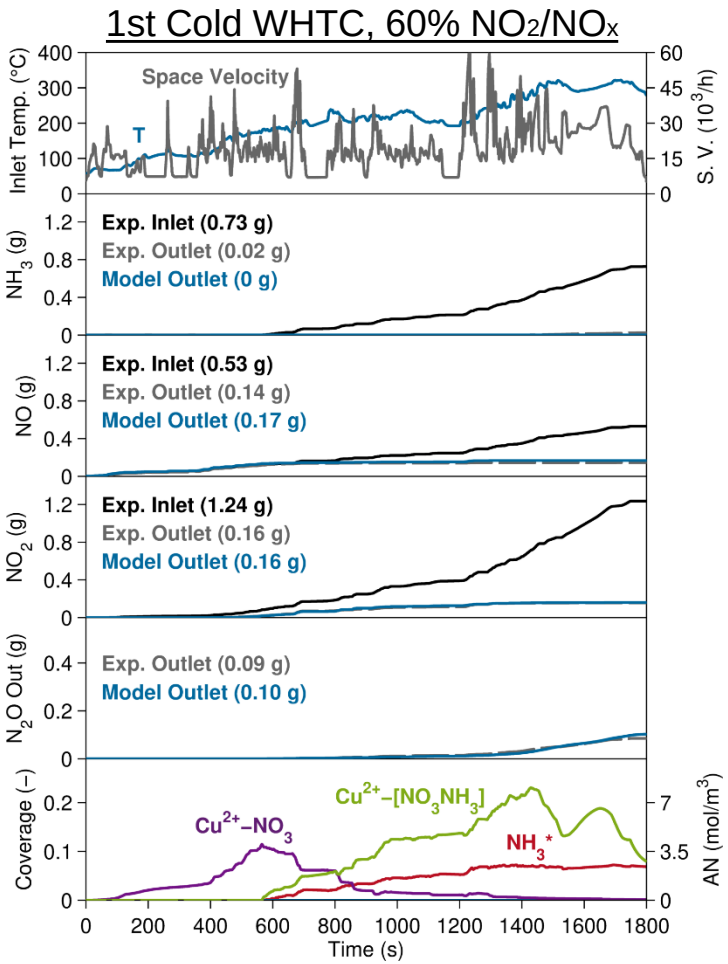




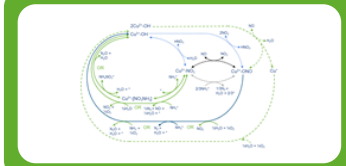
19 mol/m³ amm. nitrate measured

How much AN forms during cold WHTC?

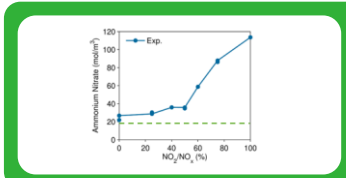


- Used driving cycle test bench to validate that little ammonium nitrate forms during cold WHTCs with high NO_2/NO_x

Overview of Presentation



SCR mechanism with nitrates



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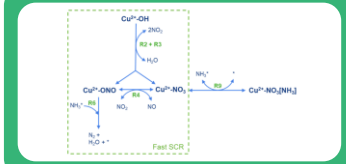

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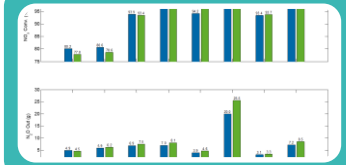
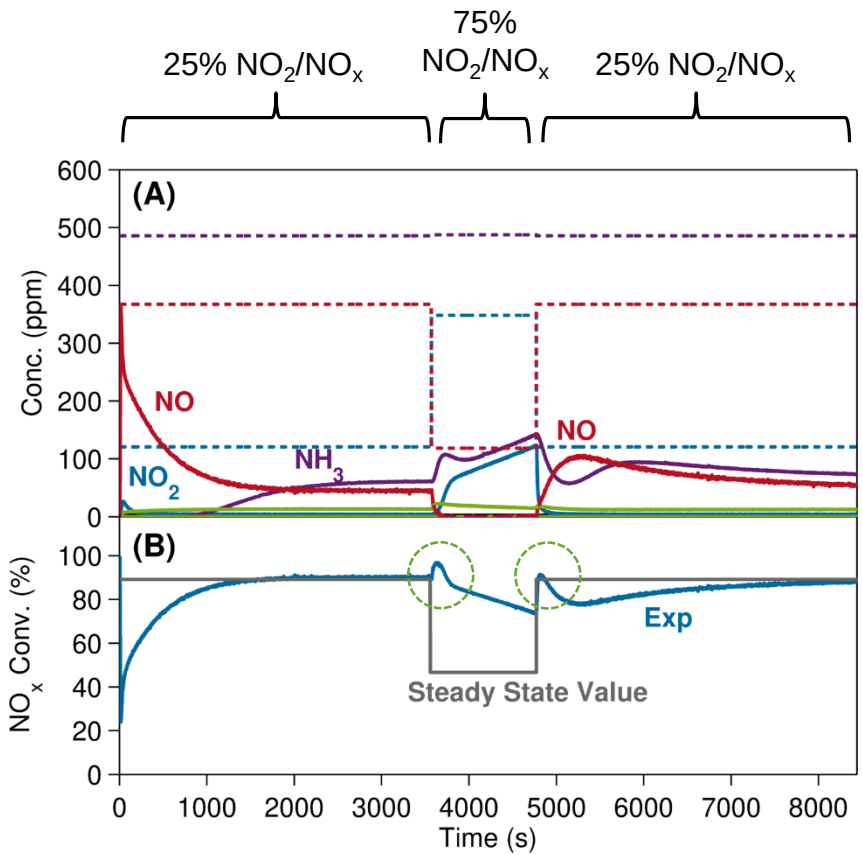


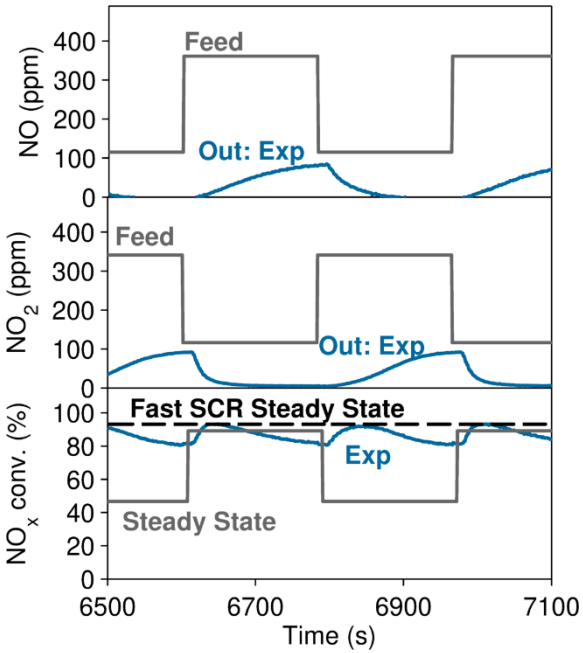
Model predictability for a wide range of driving cycles (no additional calibration)

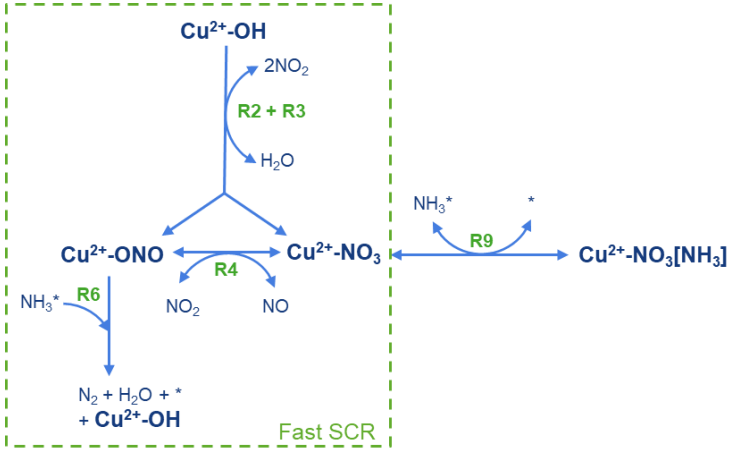
Changing NO_2/NO_x Conditions

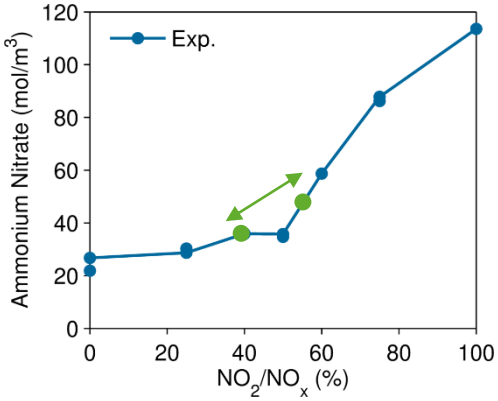


Changing NO_2/NO_x Conditions

3 minute step change, 200°C

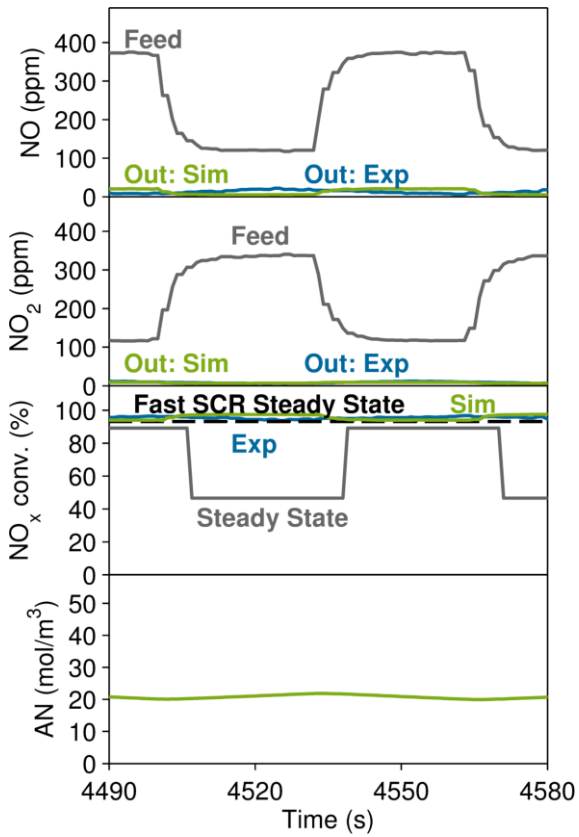


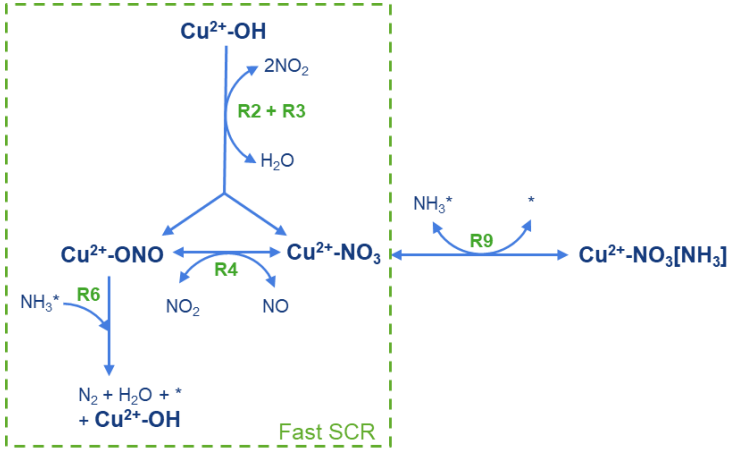


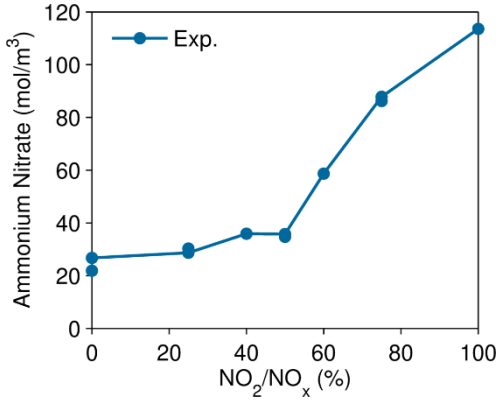


Changing NO_2/NO_x Conditions

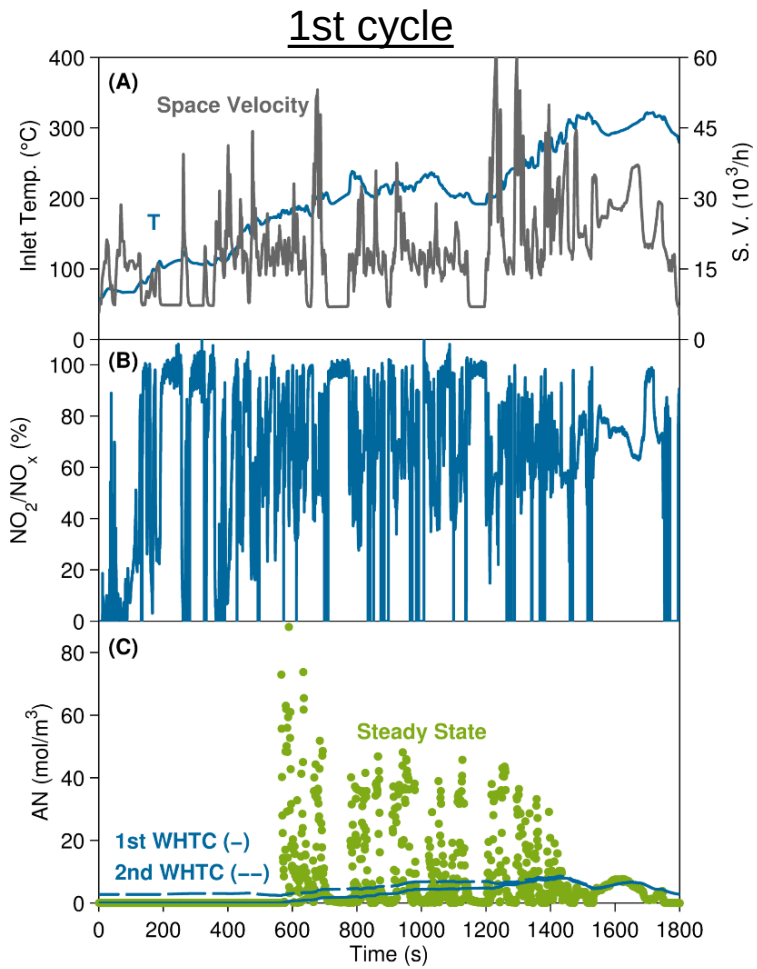
30 second step change, 200°C





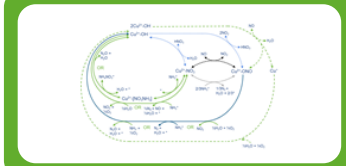


Why does little AN form during WHTC?



- Cu-CHA can act as a buffer during fluctuating NO_2/NO_x ratios
- Little ammonium nitrate forms owing to fluctuating NO_2/NO_x conditions

Overview of Presentation



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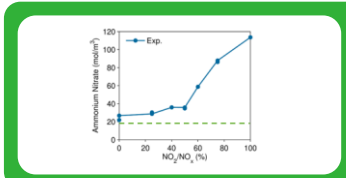

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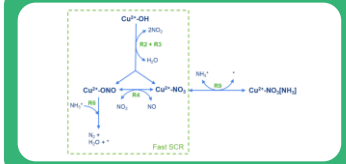
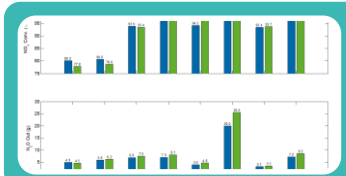
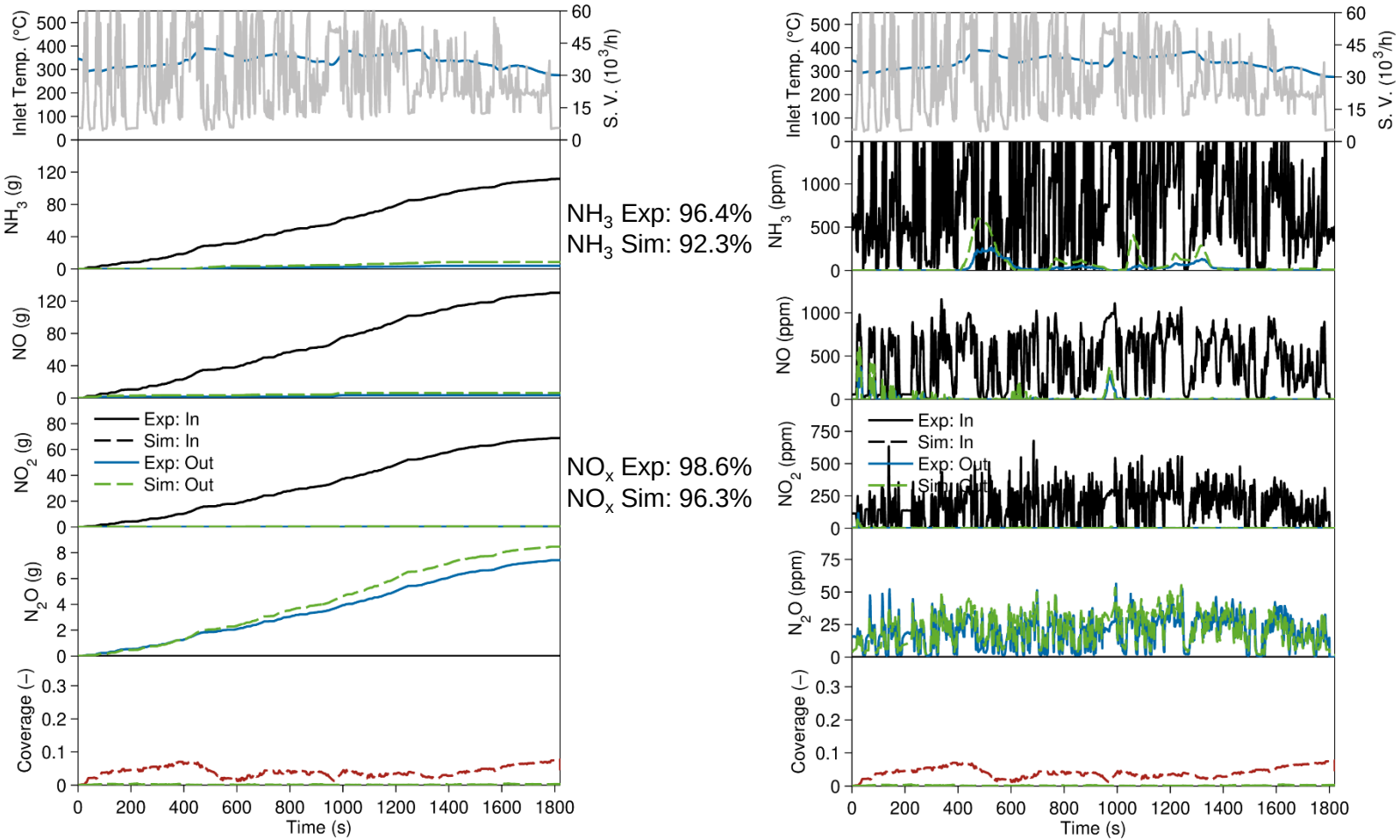


Demonstrate increased SCR performance due to nitrate buffer

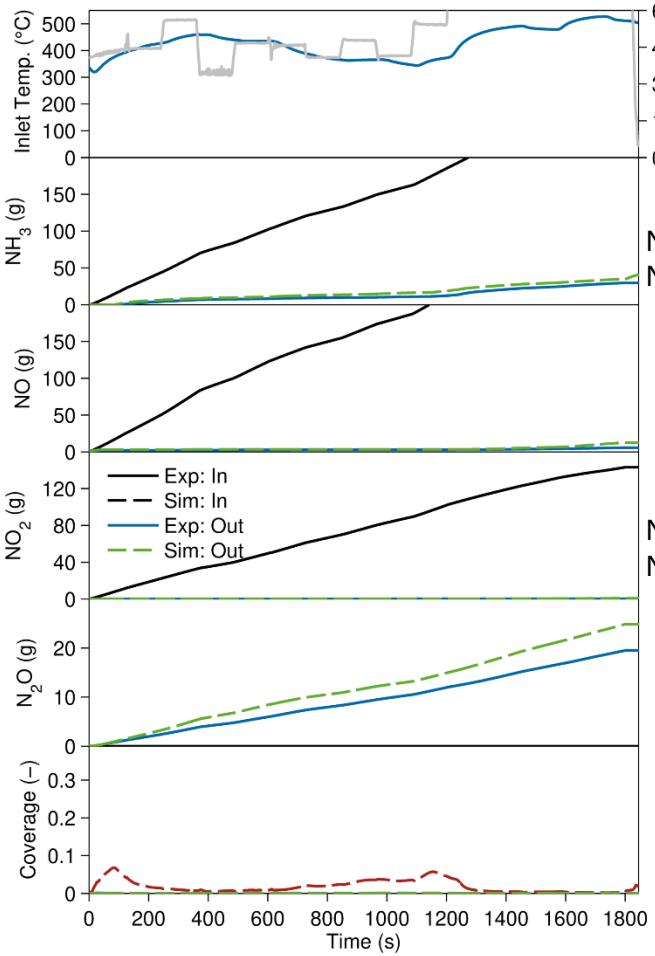


Model predictability for a wide range of driving cycles (no additional calibration)

Driving Cycle Prediction at Engine: ETC

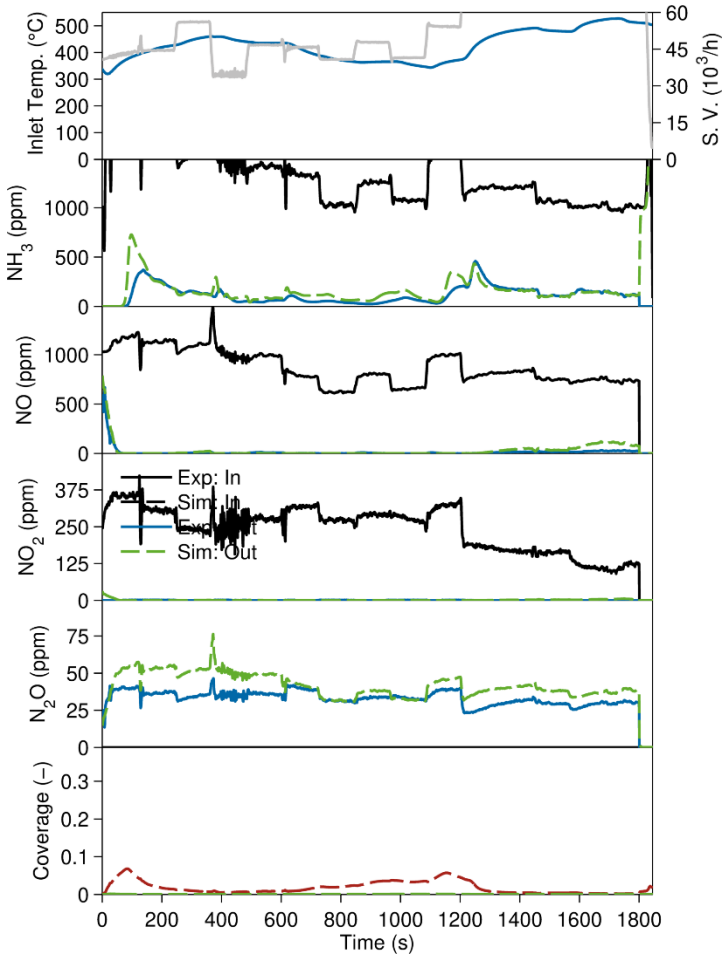


Driving Cycle Prediction at Engine: WNTE

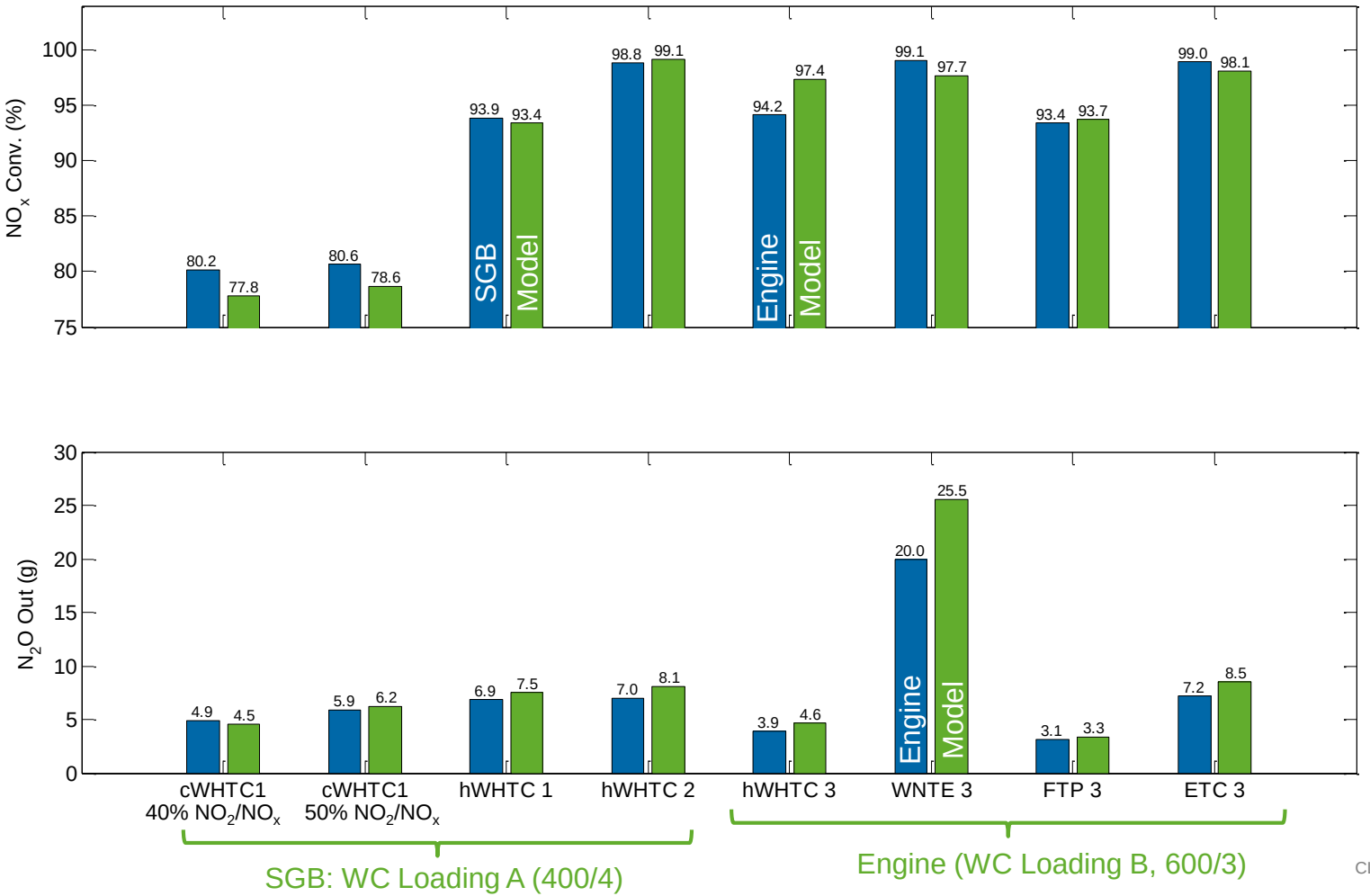


NH_3 Exp: 90.2%
NH_3 Sim: 86.7%

NO_x Exp: 99.1%
NO_x Sim: 97.1%

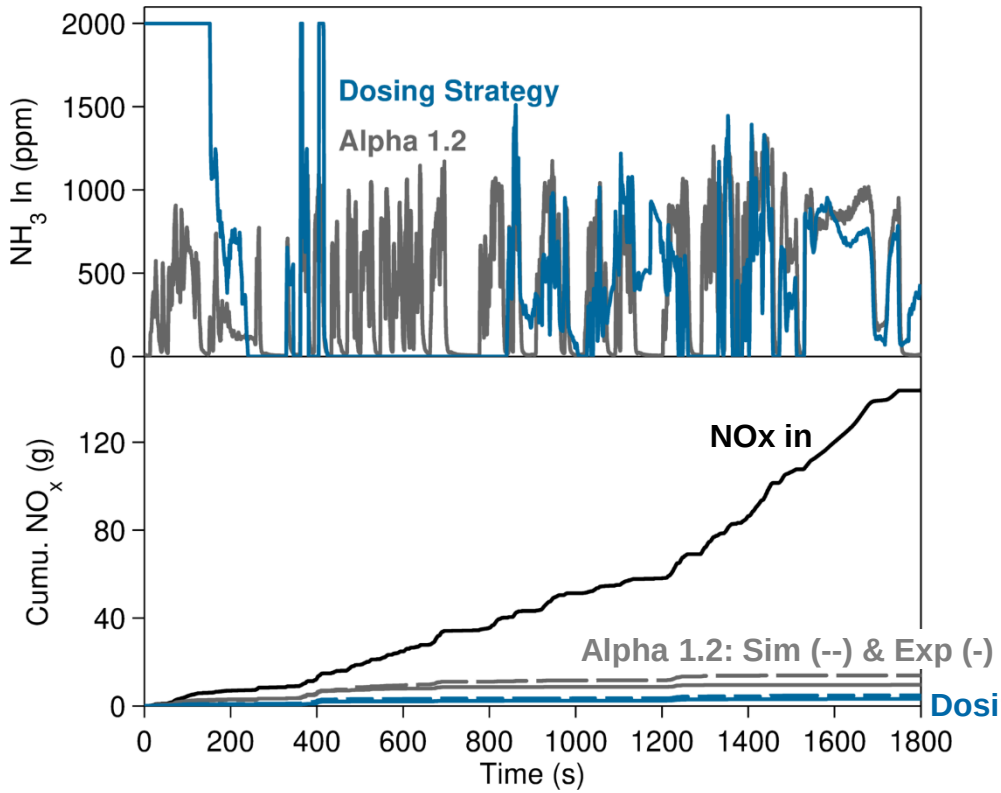


Driving Cycle Prediction



Driving Cycle Prediction

Ammonia Dosing Strategy



NO_x Conversion

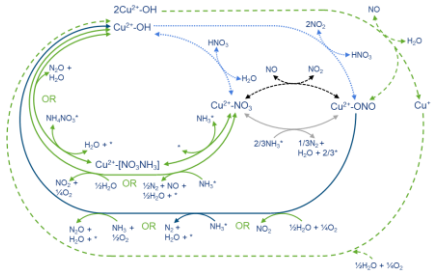
	Exp.	Sim.
α = 1.2	93.3%	90.3%
NH_3 Dosing	97.7%	96.7%

- Model applied to optimize entities of look-up table for simple feedback controller
- Model predicts increase in NO_x conversion for new dosing strategy

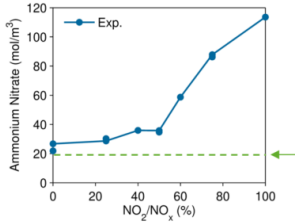
Ammonia dosing strategy published as:
B. Opitz, M. Bendrich, A. Drochner, H. Vogel, R. E. Hayes, J. F. Forbes, M. Votsmeier, Simulation study of SCR catalysts with individually adjusted ammonia dosing strategies, Chemical Engineering Journal 264 (2015) 936-944.

Summary & Conclusions

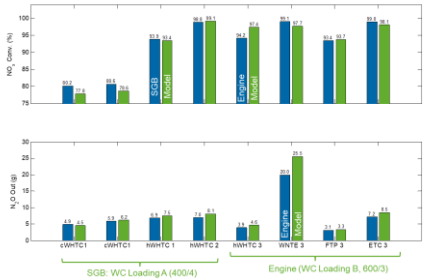
- Developed dual-site mechanism that captures SCR dynamics



- Demonstrated & validated that a minimal amount of ammonium nitrate forms during WHTC compared to steady state
  - Ammonium nitrate is not inhibitive during driving cycles
  - Nitrates act as buffer during fluctuating NO_2/NO_x conditions



- Model predicts wide range of driving cycles for Cu-CHA catalysts (different washcoat loadings & cpsi) without any additional recalibration



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