Kinetic model for NH_3 solvation, reduction and re-oxidation of active Copper sites in Cu-SSZ-13

CLEERS 2021 Workshop

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Public

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[2] Oak Ridge National Laboratory

Motivation and Background

- Evolution of emission regulations and regulatory practices requires a fundamental understanding of SCR real-world aging mechanisms and their interactions

[1] Heavy-Duty Engine and Vehicle Omnibus Regulation (ca.gov)
https://ww3.arb.ca.gov/board/books/2020/082720/20-8-2pres.pdf

HEAVY-DUTY DIESELS (>33,000 lbs GVWR)					
MY		2027-2030		2031 and subsequent	
Mileage	(miles)	@435,000	@600,000*	@435,000	@800,000*
FTP/RMC	(g/bhp-hr)	0.020	0.035	0.020	0.040
LLC	(g/bhp-hr)	0.050	0.090	0.050	0.100
Idling	(g/hr)	5	5	5	5

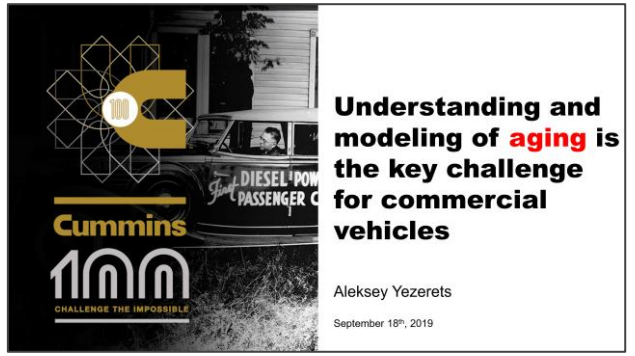
- Modeling the evolution of active sites and intrinsic SCR rates as a function of relevant real-world aging mechanisms :

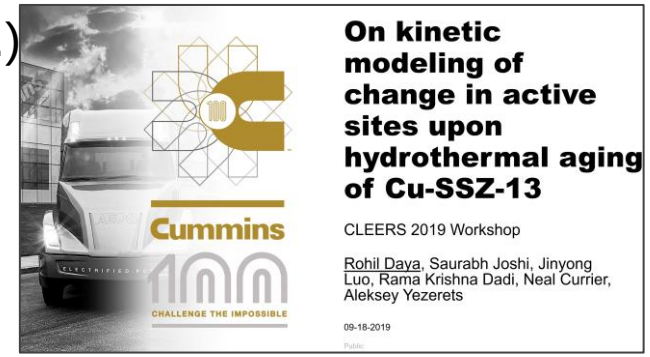
a) Allows prediction of SCR performance degradation as a function of real-world aging parameters

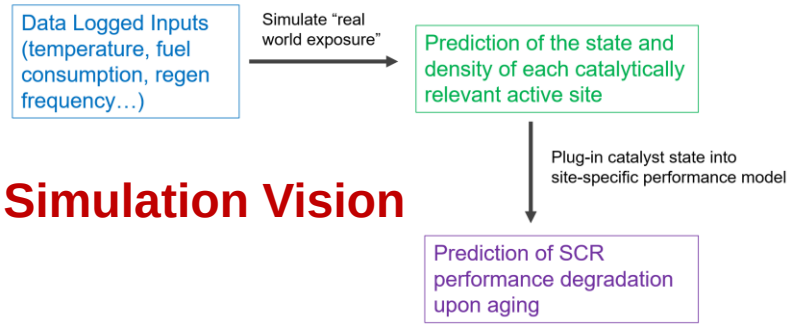
b) Mitigates proliferation of empirical catalyst kinetic models for different aging conditions and catalyst composition variables (such as Cu loading, Si/Al ratio etc.)

c) Enables rational system design, calibration and control

2019 Presentations on SCR Aging







SCR Aging Simulation Vision

Outline

- NH_3 Adsorption and Desorption Kinetics

General kinetic model framework
NH_3 TPD, NH_3 storage as a function of temperature and NH_3 pressure

- Kinetics for NO + NH_3 RHC to N_2 and OHC over NH_3-solvated ZCu sites*

Reduction of Cu^{II} sites in NO + NH_3 at all temperatures
Low-Temperature Step-2 (Standard SCR) of Cummins 4-Step Protocol[2]

- OHC Kinetics over partially-solvated and NH_3-free ZCu sites

Oxidation during Step-4 in NO + O_2

- Kinetics for NO only RHC, NH_3 only RHC, NO + NH_3 RHC to N_2O and direct OHC over ZCu sites

NO Oxidation (Step-1), NH_3 Oxidation (Step-3), N_2O Formation and High Temperature SCR (Step-2)

- NO_2 Chemistry - Fast SCR, Ammonium Nitrate and Slow SCR

- Influence of sulfur storage and sulfur aging mechanisms

Focus of today's discussion. Influence of HTA* considered

Ongoing work. Impact of HTA and sulfur

*RHC – Reduction Half Cycle
OHC – Oxidation Half Cycle
HTA – Hydrothermal Aging

[2] Kamasamudram et al. (2010). *Catalysis Today*, *151*(3-4), 212-222.

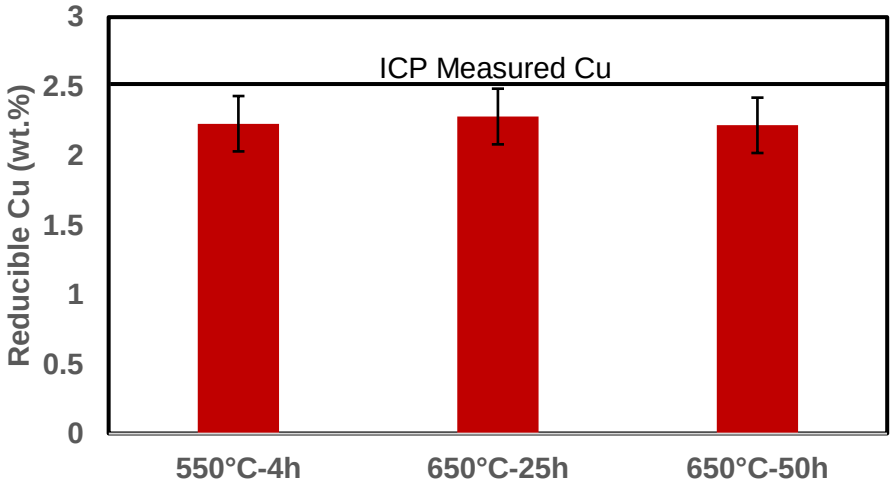
Quantification of Z_2Cu and nominally ZCuOH sites – Evolution with HTA

- Wet NO + NH_3 titration experiments utilized for quantification of total reducible Cu sites, which remain unchanged upon HTA, consistent with [3]
- Dry NO_2 adsorption and TPD experiments utilized for quantification of nominally ZCuOH sites[4], which decrease monotonically with HTA

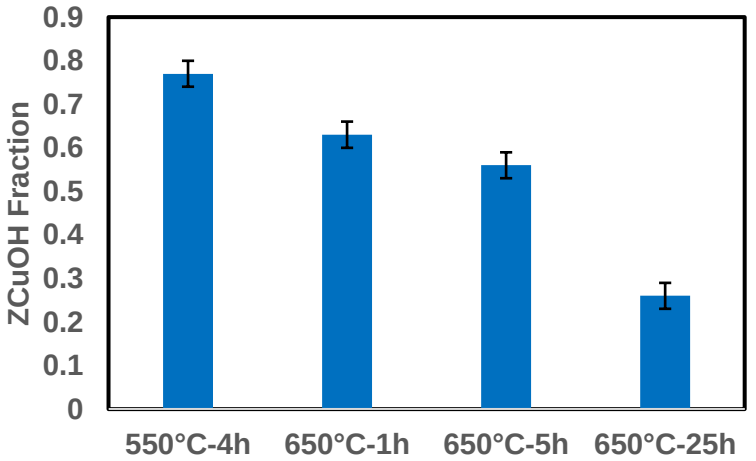
Summary of Methods to Quantify Z_2Cu (paired-Al) and ZCuOH (isolated-Al) Sites.

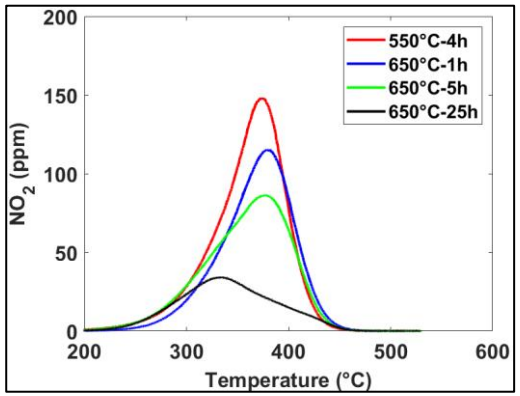
Method	Approach and Hypothesis
Cobalt titration of Al pairs	Co^{II} selectively exchanges ZH sites associated with paired framework Al ions
NH_3 titration and TPD on oxidized and reduced catalysts	Increase in Brønsted acidity quantified as a measure of Z_2Cu sites
EPR on hydrated and dehydrated catalysts	Hydrated and dehydrated EPR gives measure of total isolated Cu^{II} and Z_2Cu sites respectively
H_2-TPR on hydrated catalyst	Different reducibilities of ZCuOH and Z_2Cu lead to distinct H_2 consumption peaks as a function of temperature
DRIFTS	Change in framework T-O-T vibrations at 900 and 950 cm^{-1} upon NH_3 solvation attributed to Z_2Cu and ZCuOH respectively
NO_2 adsorption and TPD under dry conditions	NO_2 disproportionation and nitrate formation only catalyzed by ZCuOH sites
XANES	Operando XANES spectrum can be modeled as a weighted combination of pure components through multivariate curve resolution (MCR) analysis
NH_3 temperature programmed reduction (TPR)	Different reducibilities of ZCuOH and Z_2Cu lead to distinct N_2 production peaks as a function of temperature

Wet NO + NH_3 Titration



Dry NO_2 Adsorption and TPD





$$3NO_2 + 2ZCuOH \leftrightarrow NO + 2ZCuNO_3 + H_2O$$

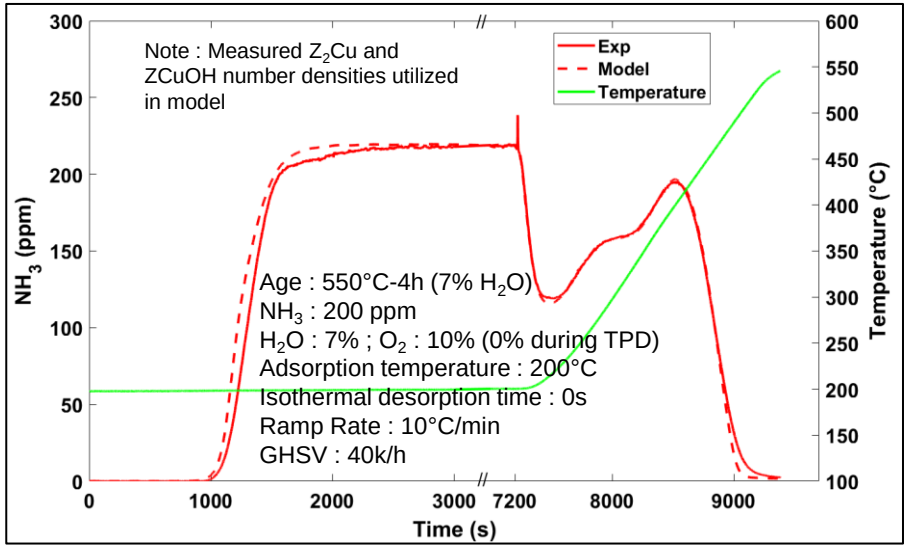
[3] Gramigni et al. (2021). *ACS Catalysis, 11,* 4821-4831

[4] Villamaina et al. (2019). *ACS Catalysis*, *9*(10), 8916-8927.

NH_3 adsorption and desorption kinetics

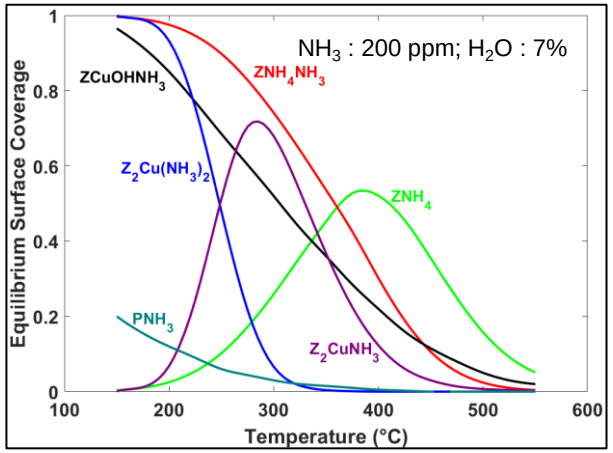
- Recent experimental studies on the SCR mechanism generally assume $Z_2Cu(NH_3)_4$ and $ZCuOH(NH_3)_3$ as the most stable Cu-amine complexes upon NH_3 solvation of an oxidized catalyst[5-7]

- Kinetic model considers up to 2 NH_3 per Z_2Cu site and up to 1 NH_3 per ZCuOH site, consistent with NH_3:Cu ratios measured from NH_3 adsorption experiments in presence of H_2O[8-10]. DFT binding energies used as initial guess[11]



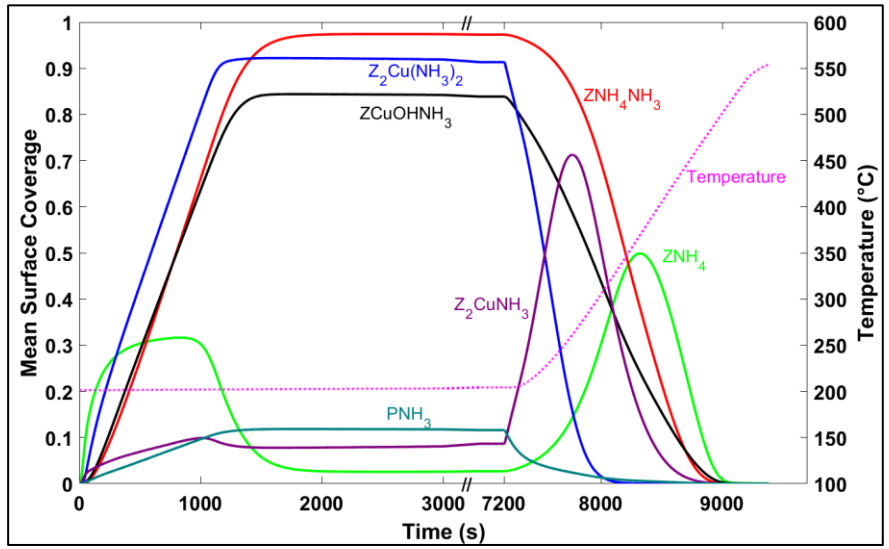
Notation used for Cu-amine complexes and attribution of Physisorbed NH_3.

Surface Species	Notation
$Z[(O_f)_y\ Cu^{II}(OH)(NH_3)(H_2O)_x]$	$ZCuOHNH_3$
$Z_2[(O_f)_{y2}Cu^{II}(NH_3)_2(H_2O)_{x2}]$	$Z_2Cu(NH_3)_2$
$Z_2[(O_f)_{y3}Cu^{II}(NH_3)(H_2O)_{x3}]$	Z_2CuNH_3
$ZNH_4(NH_3)_l$ for $l \geq 2$ $EFAl.NH_3$ $Z[(O_f)_{y4}\ Cu^{II}(OH)(NH_3)_m(H_2O)_{x4}]$ for $m \geq 2$ $Z_2[(O_f)_{y5}Cu^{II}(NH_3)_n(H_2O)_{x5}]$ for $n \geq 3$	PNH_3
$Z[Cu^{I}(NH_3)_2(H_2O)_{x6}]$	$ZCu(NH_3)_2$
$Z[(O_f)_{y7}Cu^{I}(NH_3)(H_2O)_{x7}]$	$ZCuNH_3$



NH_3 Adsorption-Desorption Thermodynamics and Kinetics.

Reaction	$K_{eq.}$ at 200 °C	$\Delta_{ads}H^0$ (kJ/mol)	$\Delta_{ads}S^0$ (J/mol-K)	A_{ads} (1/s)	A_{des} (1/s)
$NH_3 + ZH \leftrightarrow ZNH_4$	2.47e+10	−169.6 ($\alpha = 0.1$)	−158.7	5.14e+04	1e+13
$NH_3 + ZNH_4 \leftrightarrow ZNH_4NH_3$	1.97e+05	−73 ($\alpha = 0.09$)	−39.2	2.82e+01	3.14e+03
$NH_3 + P \leftrightarrow PNH_3$	6.58e+02	−48.6 ($\alpha = 0.65$)	−41	4.43e+01	6.05e+03
$NH_3 + ZCuOH \leftrightarrow ZCuOHNH_3$	2.77e+04	−117.8 ($\alpha = 0.28$)	−103.7	3.62e+01	9.51e+06
$NH_3 + Z_2Cu \leftrightarrow Z_2CuNH_3$	2.71e+07	−139.2 ($\alpha = 0.08$)	−150.2	2.76e+02	1.93e+10
$NH_3 + Z_2CuNH_3 \leftrightarrow Z_2Cu(NH_3)_2$	6.83e+04	−141.3 ($\alpha = 0.04$)	−194.4	9.63e+02	1.37e+13



Relative Free Energy of Adsorption

$$ZNH_4 > Z_2CuNH_3 > ZNH_4NH_3 > Z_2Cu(NH_3)_2 > ZCuOHNH_3 > PNH_3$$

[5] Negri et al. (2020). *Journal of the American Chemical Society*, *142*(37), 15884-15896.
[6] Clark et al. (2020). *ChemCatChem*, *12*(5), 1429-1435.
[7] Liu et al. (2020). *ChemCatChem*, *12*(11), 3050-3059.
[8] Luo et al. (2017). *Journal of Catalysis*, *348*, 291-299.
[9] Daya et al. (2020). *Applied Catalysis B: Environmental*, *263*, 118368.
[10] Daya et al. (2021). *Applied Catalysis B: Environmental*, 120444.
[11] Paolucci, et al. (2016). *Journal of the American Chemical Society*, *138*(18), 6028-6048.

Two-site framework and HTA Model

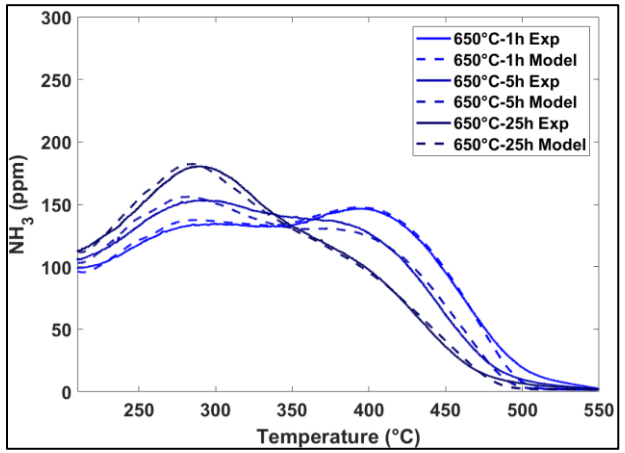
- Model structure reframed by combining Z_2Cu, ZCuOH and ZH sites into an overarching framework aluminum (Al_f) site

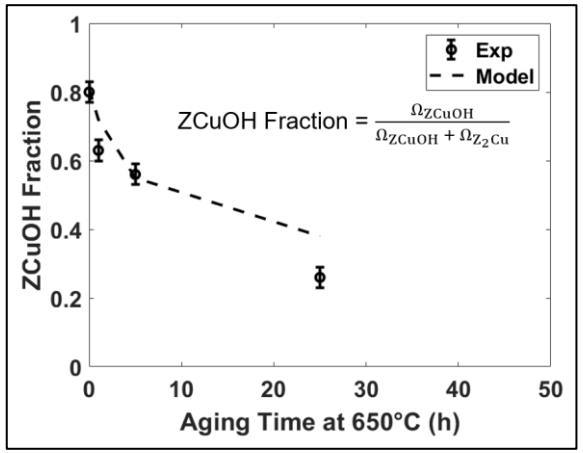
- NH_3 TPD as a function of mild HTA described within the following constraints, leading to one free parameter per HTA condition:

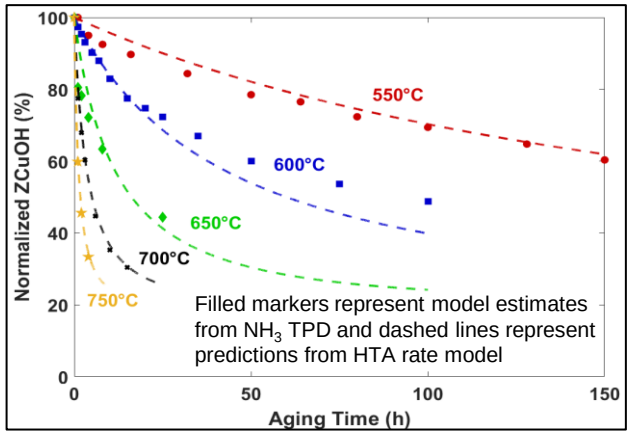
a) Kinetic parameters independent of HTA (mean-field approximation)
b) Total reducible Cu^{II} sites independent of HTA
c) Total framework Al_f insensitive to HTA (no dealumination)

List of Surfaces Species in Two-Site Kinetic Model.

Site 1 - Al_f	Site 2 - Physisorbed
ZH	$ZNH_4(NH_3)_l$ for $l \geq 2$
ZNH_4	$EFAl.NH_3$
ZNH_4NH_3	$ZCuOH(NH_3)_m$ for $m \geq 2$
ZCuOH	$Z_2Cu(NH_3)_n$ for $n \geq 3$
$ZCuOHNH_3$	
Z_2Cu	
$Z_2Cu(NH_3)$	
$Z_2Cu(NH_3)_2$	
ZCu	
$ZCuNH_3$	
$ZCu(NH_3)_2$	





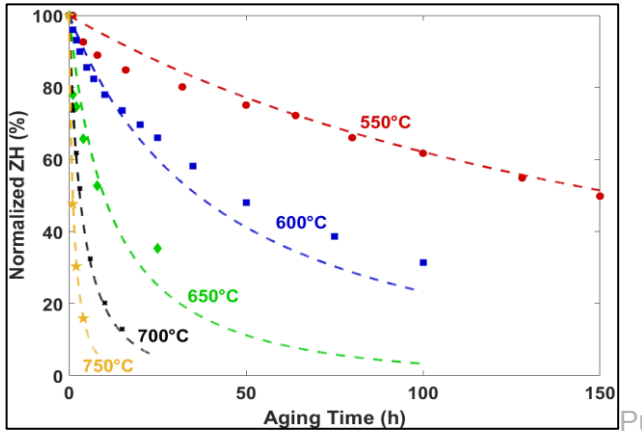


$$\Omega_{Al_f} = \Omega_{ZH} + \Omega_{ZCuOH} + 2\Omega_{Z_2Cu}$$

$$\Theta_{ZH} = \frac{\Omega_{ZH}}{\Omega_{Al_f}}$$

$$\theta_{ZCuOH} = \frac{\Omega_{ZCuOH}}{\Omega_{Al_f}}$$

$$\theta_{Z_2Cu} = \frac{2\Omega_{Z_2Cu}}{\Omega_{Al_f}}$$



NH_3 : 200 ppm
H_2O : 7% ; O_2 : 10% (0% during TPD)
Adsorption temperature : 200°C
Isothermal desorption time : 0s
Ramp Rate : 10°C/min
GHSV : 40k/h

- Offset between the loss of ZCuOH sites and the loss of ZH sites is accounted for by introducing a correction factor μ

$$ZCuOH + (1-\mu)ZH \rightarrow Z_2Cu + H_2O - \mu ZH$$

$$\frac{-d\Omega_{ZCuOH}}{dt} = r_{HTA} = 5.09{*}10^5 e^{\frac{-175425}{RT}} \theta_{ZCuOH}\theta_{ZH}\Omega_{Al_f}$$

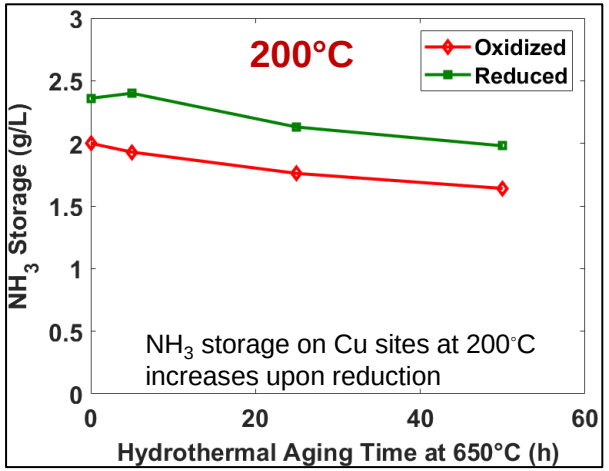
$$\mu = 0.14$$

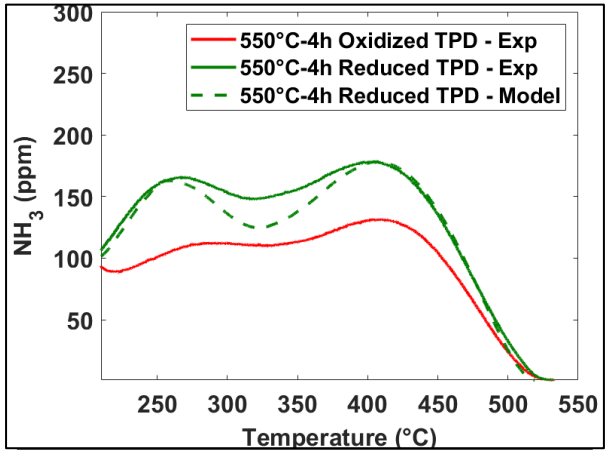
Note:
All HTA in 7% H_2O

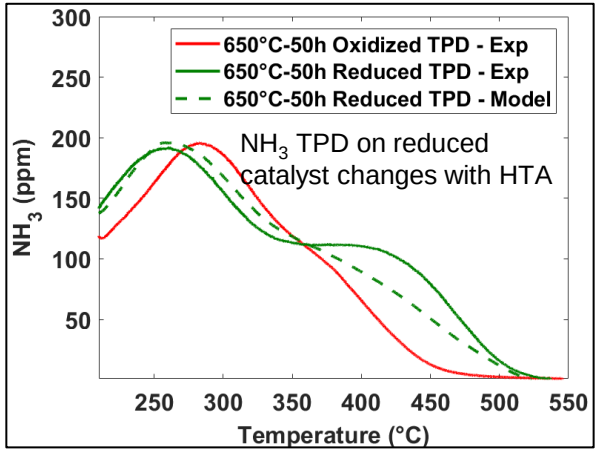
[10] Daya et al. (2021). *Applied Catalysis B: Environmental*, 120444.

Increased NH_3 coordination on Cu sites upon reduction

- Reduction of isolated Cu^{II} sites leads to the formation of NH_3 solvated ZCu sites. NH_3 stored on ZCu sites and ZH sites can be quantified by performing a TPD experiment. This is labeled a *Reduced TPD*, to differentiate it from the typical NH_3-TPD experiment on an oxidized catalyst (labeled *Oxidized TPD* for comparison)

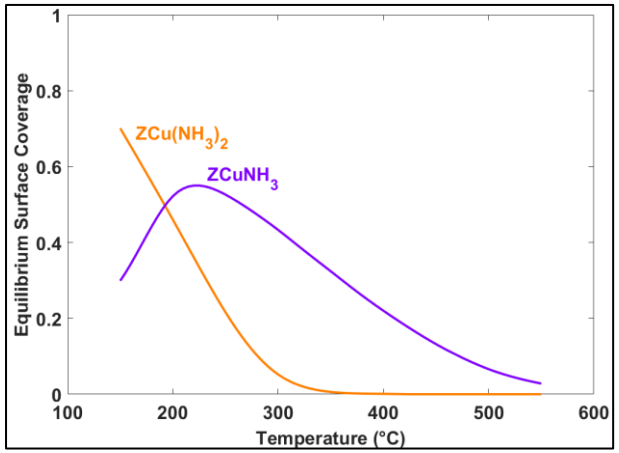






NH_3 : 200 ppm ; H_2O : 7%
Adsorption temperature : 200°C
Isothermal desorption time : 0s
Ramp Rate : 10°C/min
GHSV : 40k/h

- Experimental results contradict DFT literature reporting higher NH_3 coordination on Cu^{II} sites relative to Cu^{I} sites[11-13]. Kinetic model considering up to 2 NH_3 per ZCu site with DFT binding energies[11] captures reduced TPD, and predicts change in NH_3 coordination on ZH sites with HTA



NH_3 Adsorption-Desorption Thermodynamics and Kinetics on ZCu Sites.

Reaction	K_{eq}. at 200 °C	$\Delta_{ads}H^0$ (kJ/mol)	$\Delta_{ads}S^0$ (J/mol-K)	A_{ads} (1/s)	A_{des} (1/s)
$NH_3 + ZCu \leftrightarrow ZCuNH_3$	1.42e+05	−139.2 (α = 0.45)	−125.8	1.90e+03	7.07e+09
$NH_3 + ZCuNH_3 \leftrightarrow ZCu(NH_3)_2$	4.41e+03	−130.2 (α = 0.27)	−170.7	2.94e+03	2.42e+12

Relative Mobility

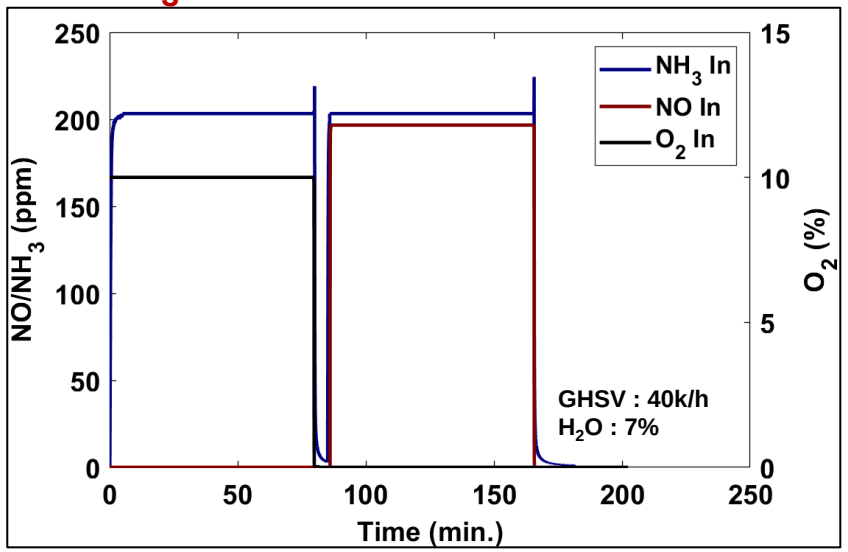
$$ZCu(NH_3)_2 > ZCuOHNH_3 > ZCuNH_3 > Z_2Cu(NH_3)_2 > Z_2CuNH_3$$

[10] Daya et al. (2021). *Applied Catalysis B: Environmental*, 120444.
[11] Paolucci, et al. (2016). *Journal of the American Chemical Society*, *138*(18), 6028-6048.
[12] Chen et al. (2018). *Journal of catalysis*, *358*, 179-186.
[13] Chen et al. (2019). *Topics in Catalysis*, *62*(1), 93-99.

$NO + NH_3$ RHC

Reduction of NH_3-solvated Cu^{II} sites follows second order kinetics with HTA independent rates[3,14]

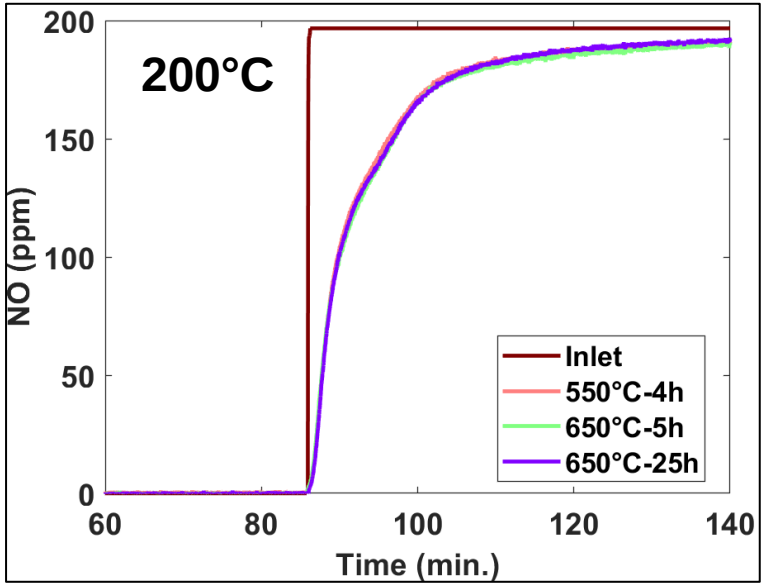
NH_3 First Titration Protocol

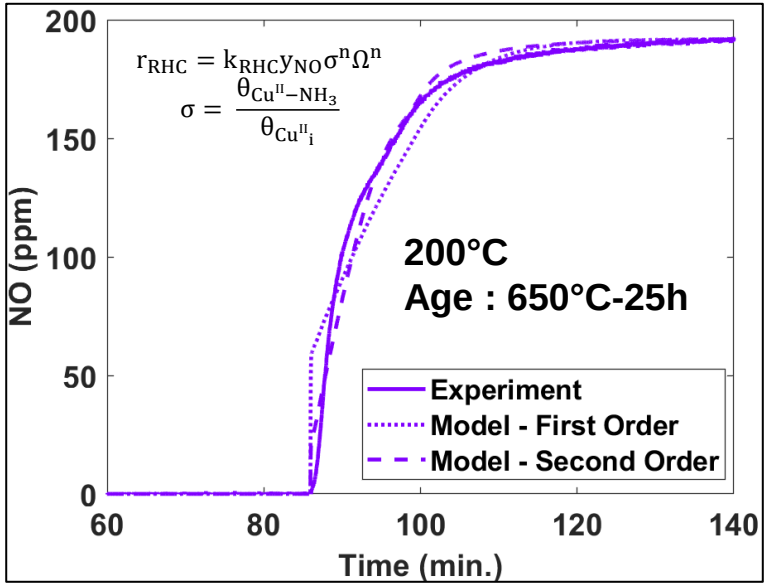


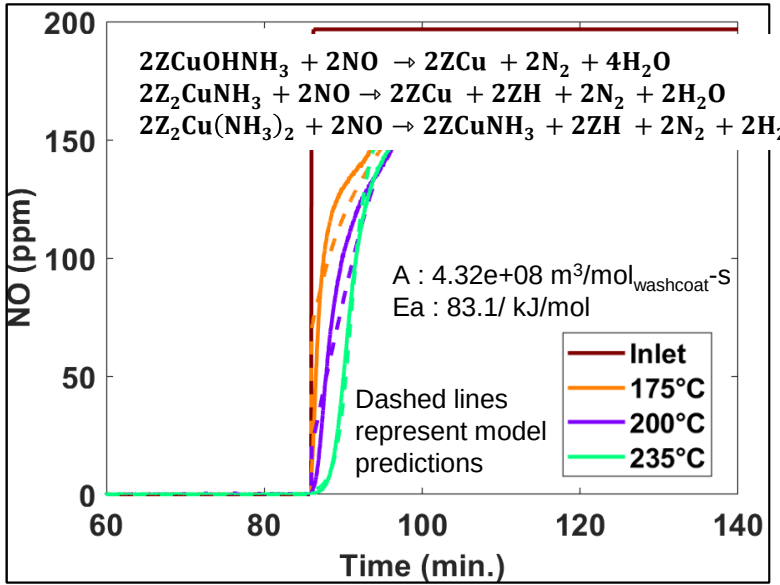
- Identical reduction rates on Z_2Cu and ZCuOH. No involvement of NH_3 on ZH sites
- Second order rate in Cu^{II} describes NO consumption better than first order rate. Further confirmation by linear dependence of first order rate constant on Cu loading
- Hydrolysis reaction proposed in [15]:

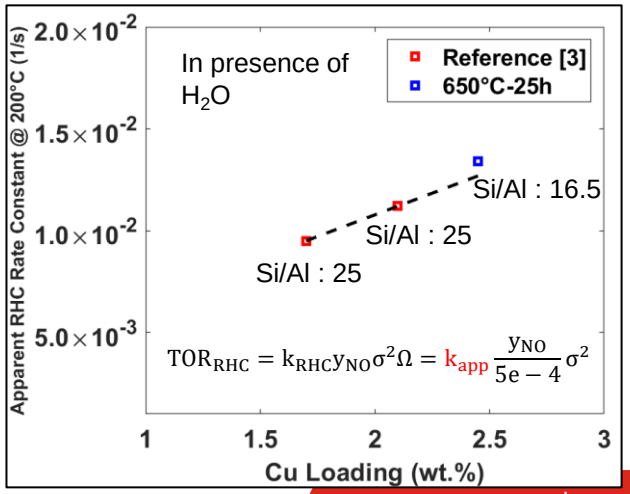
$$Cu^{2+}(NH_3)_4 + H_2O \leftrightarrow Cu^{2+}(OH)^-(NH_3)_3 + NH_4^+$$

NO consumption independent of HTA[3,14] Reduction rate order w.r.t Cu^{II}[3,14]





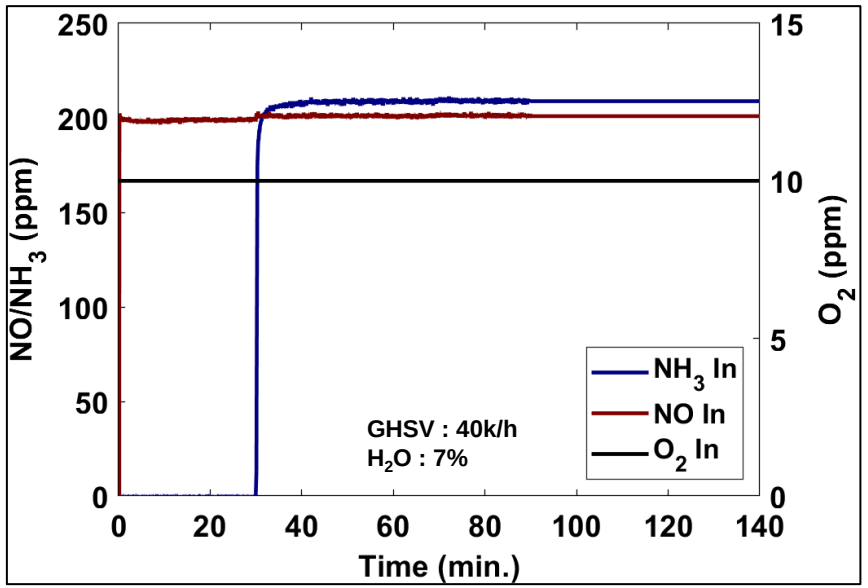




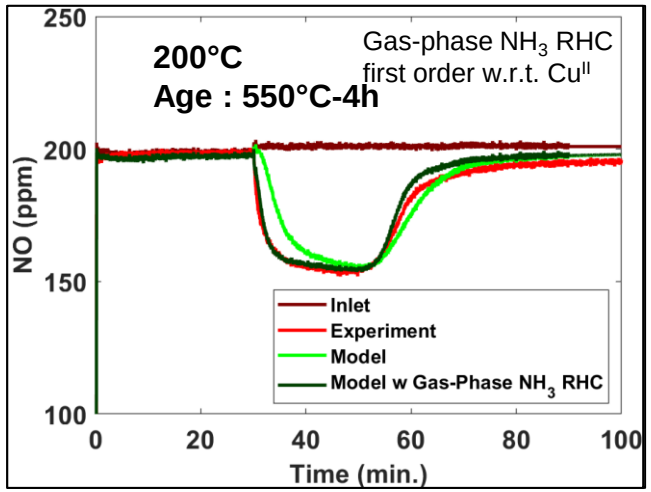
[3] Gramigni et al. (2021). *ACS Catalysis*, *11*, 4821-4831.
[14] Joshi et al. 2020 CLEERS Presentation
[15] Hu et al. (2021). *ACS Catalysis*, *11*, 11616-11625.

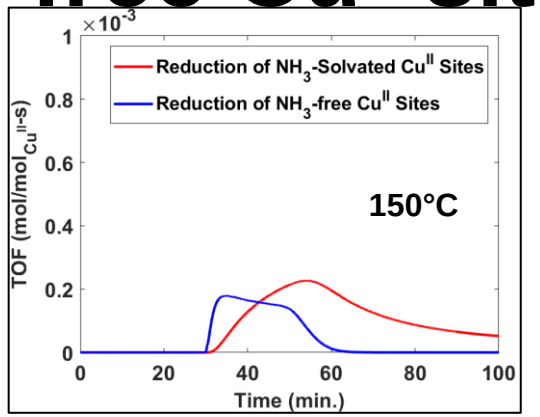
Additional pathway for reduction of NH_3-free Cu^{II} sites with gas-phase NH_3

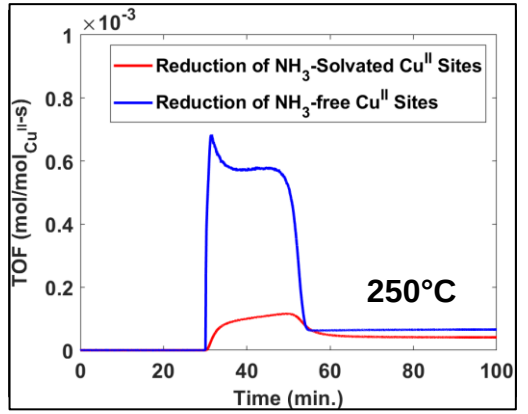
NO First Titration Protocol

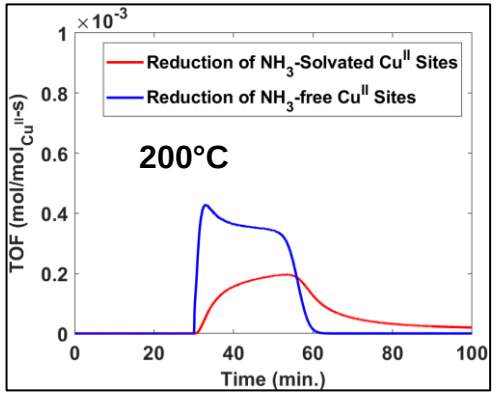


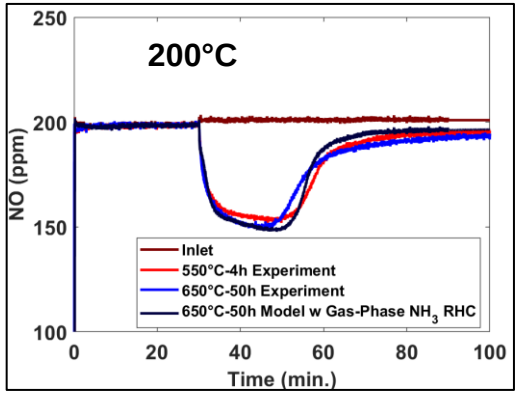
NO consumption during Cu^{II} reduction











- NO consumption at onset of NH_3 introduction can be explained by a gas-phase NH_3 RHC route, likely associated with HONO intermediate[16,17]
- Rate of reduction of NH_3-free Cu^{II} sites insensitive to HTA, and increases in significance with temperature

$$ZCuOH + NO \leftrightarrow ZCu + HONO$$

$$HONO + NH_3 \rightarrow NH_4NO_2$$

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

$$ZCu + 0.25O_2 + 0.5H_2O \rightarrow ZCuOH$$

Final global reaction:

$$NO + NH_3 + 0.25O_2 \rightarrow N_2 + 1.5H_2O$$

$$ZCuOH + NH_3 + NO \rightarrow ZCu + N_2 + 2H_2O$$
$$Z_2Cu + NH_3 + NO \rightarrow ZCu + ZH + N_2 + H_2O$$

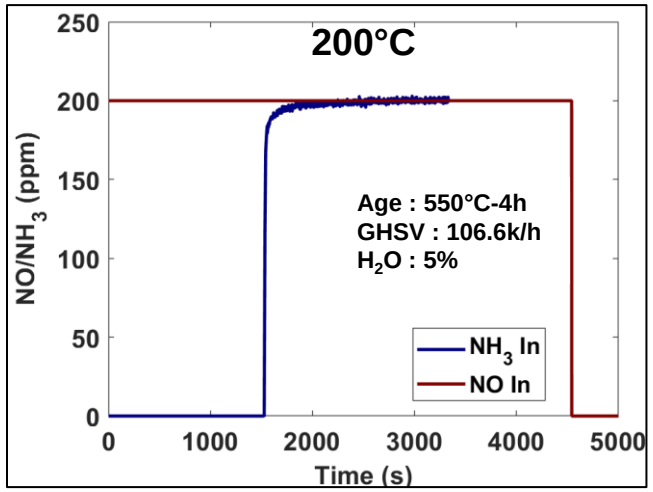
A : 6.11e+12 1/s
Ea : 65.2/ kJ/mol

[16] Chen et al. (2020). *ACS Catalysis*, *10*(10), 5646-5656.
[17] Daya et al. (2021). *Reaction Chemistry & Engineering*, *6*(6), 1042-1052.

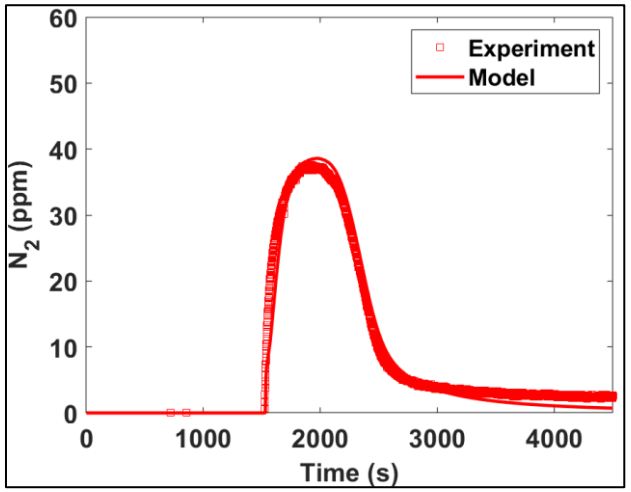
NO + NH_3 RHC Kinetics validated with measured N_2 at all temperatures

Experiments performed at ORNL

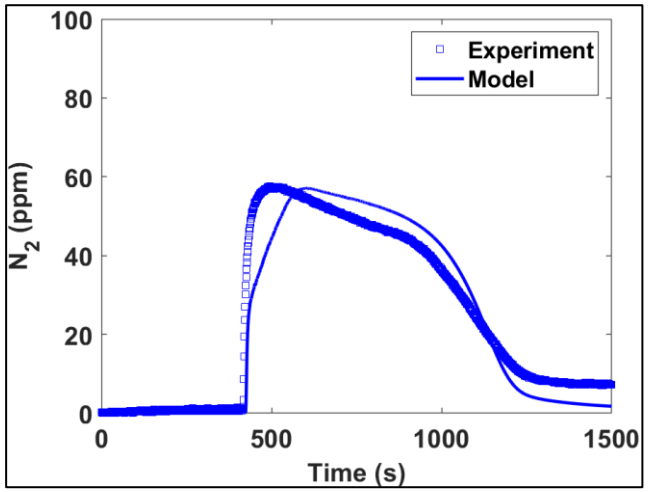
NO First Titration Protocol



200°C



250°C



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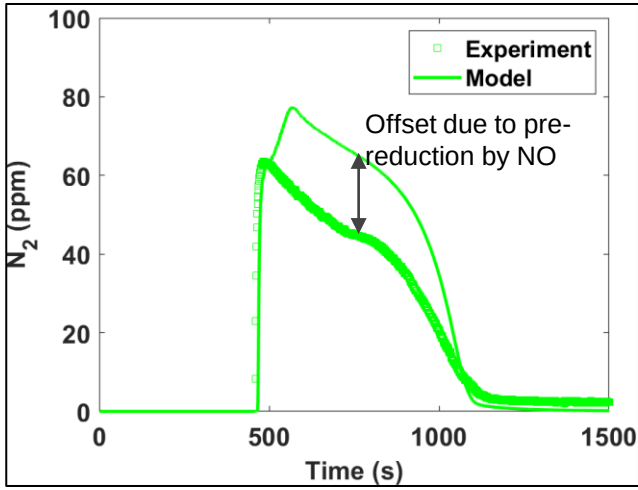
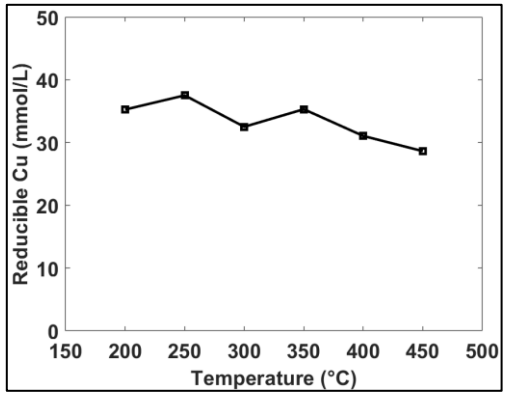
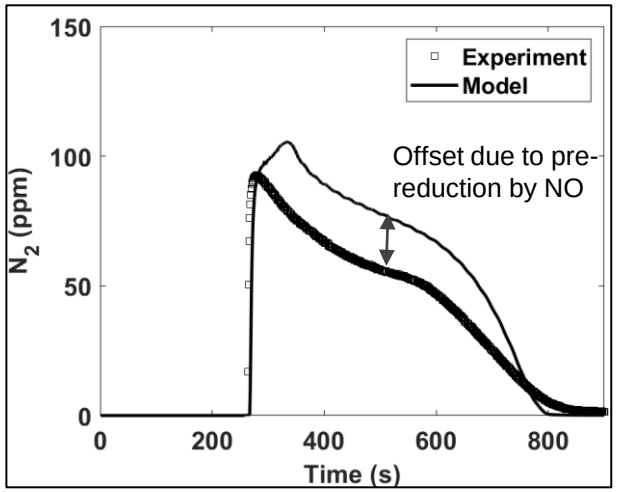


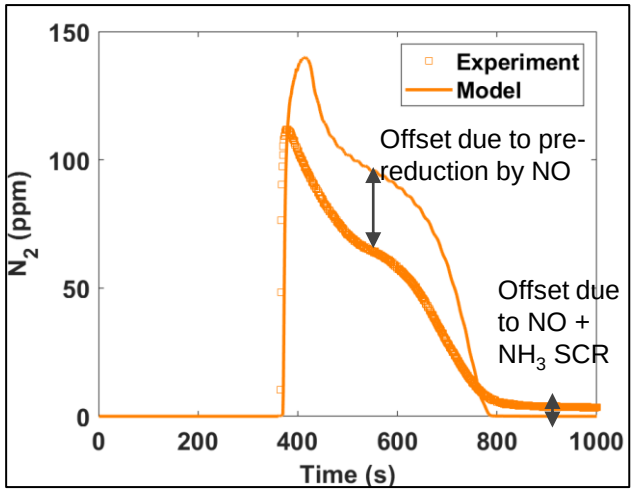
Measured reducible Cu from integrated N_2



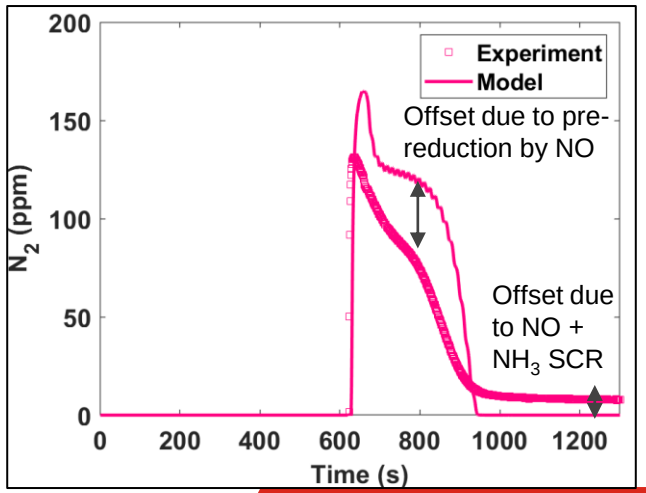
350°C



400°C



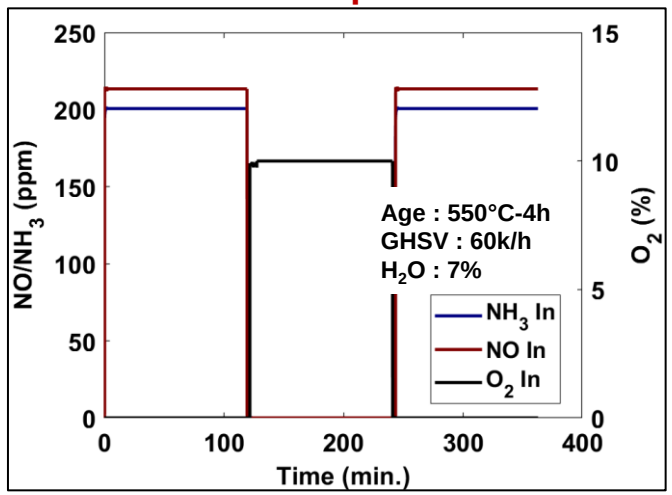
450°C



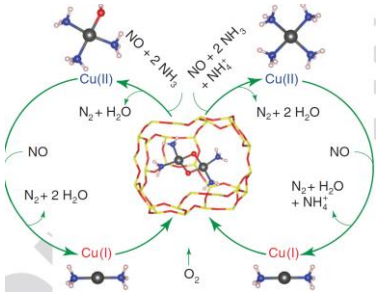
OHC over NH_3-solvated ZCu sites

Cu^{II}-dimer formation in OHC proceeds with significant NH_3 desorption

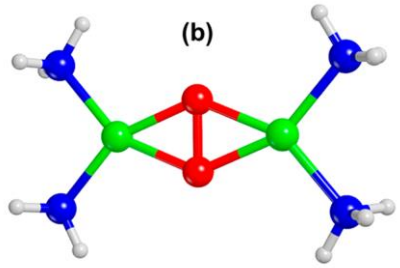
RHC1 → O_2 Only OHC → RHC2 Sequence



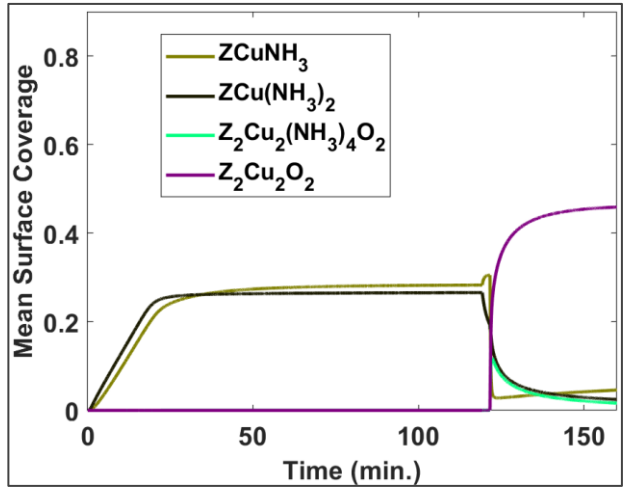
Cu^{II}-dimer requirement for OHC[18]

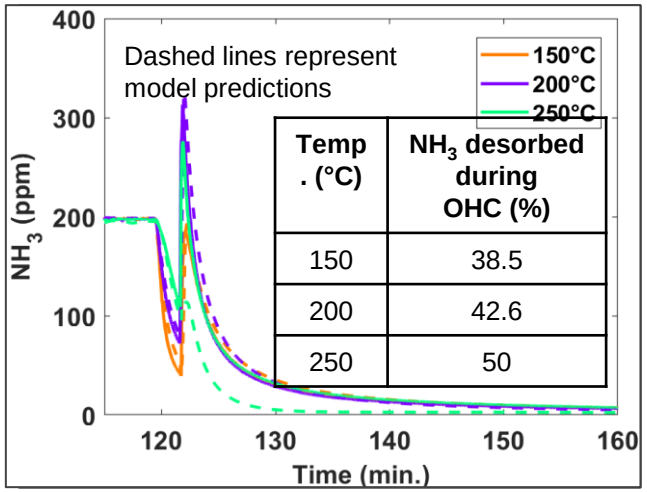


Structure of Cu^{II}-dimer[19]



side-on μ-η_2,η_2-peroxo diamino dicopper(II)





Temp. (°C)	NH_3 desorbed during OHC (%)
150	38.5
200	42.6
250	50

Reaction	Rate Expression	Ea (kJ/mol)	$\Delta_{ads}H^0$ (kJ/mol)	$\Delta_{ads}S^0$ (J/mol-k)
$2ZCu(NH_3)_2 + O_2 \leftrightarrow Z_2Cu_2(NH_3)_4O_2$	$r_{f_{dimer}} = k_{f_{dimer}} y_{O_2} (\frac{\theta_{ZCu(NH_3)_2}}{\theta_{Cu^{II}_i}})^2 \Omega_{ZCu}^2$ $r_{b_{dimer}} = k_{b_{dimer}} \frac{\theta_{Z_2Cu_2(NH_3)_4O_2}}{\theta_{Cu^{II}_i}} \Omega_{ZCu}$	E_{fdimer} = 30.5[18] E_{bdimer} = 110 (α = 0.23)	-79[20]	-126[20]
$Z_2Cu_2(NH_3)_4O_2 \leftrightarrow Z_2Cu_2O_2 + 4NH_3$	$r_{2f_{dimer}} = k_{2f_{dimer}} \frac{\theta_{Z_2Cu_2(NH_3)_4O_2}}{\theta_{Cu^{II}_i}} \Omega_{ZCu}$ $r_{2b_{dimer}} = k_{2b_{dimer}} y_{NH_3} \frac{\theta_{Z_2Cu_2O_2}}{\theta_{Cu^{II}_i}} \Omega_{ZCu}$	$E_{2fdimer}$ = 117.2 (α = 0.26) $E_{2bdimer}$ = 0	-117.2	-168

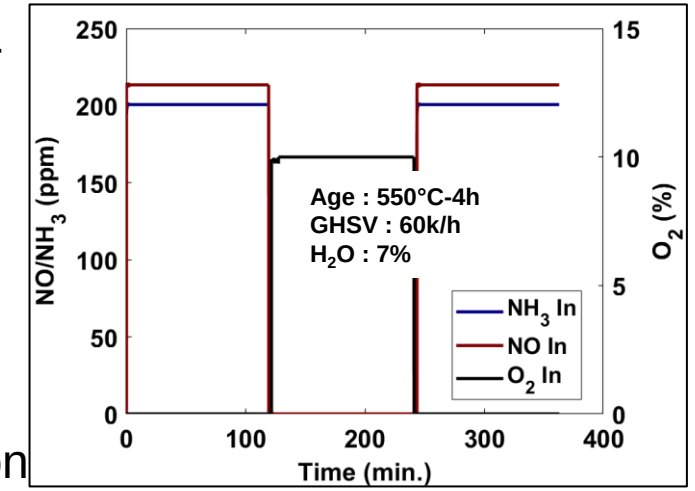
[18] Paolucci et al. (2017). *Science*, *357*(6354), 898-903.
[19] Negri et al. (2020). *Journal of the American Chemical Society*, *142*(37), 15884-15896.
[20] Wang et al. (2021) *ChemCatChem*. (https://doi.org/10.1002/cctc.202100253)

Reduction of Cu^{II} dimer requires 1 NO per Cu^{II}

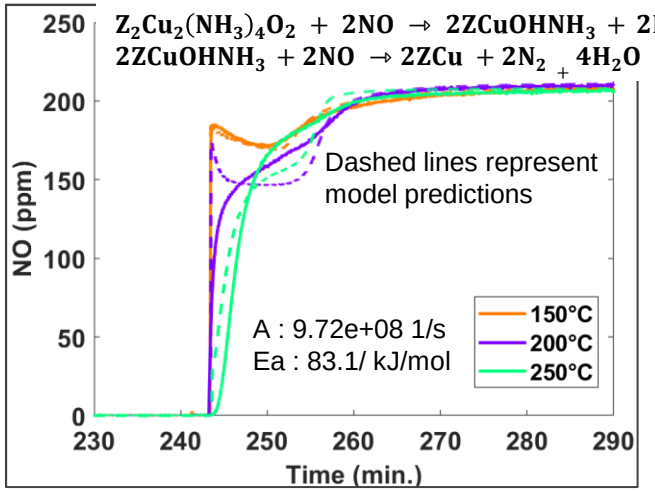
- Reduction of Cu^{II}-dimer consumes identical NO as reduction of nominally Z_2Cu and ZCuOH
- O_2 desorption from Cu^{II}-dimer competes with Cu^{II}-dimer reduction by NO

- Dimer reduction by NO appears to be slower under SCR conditions, requiring modified kinetic parameters

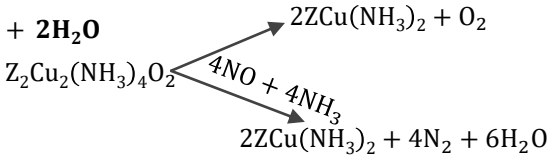
RHC1 → O_2 Only OHC → RHC2 Sequence



NO + NH_3 Titration of Cu^{II}-dimer



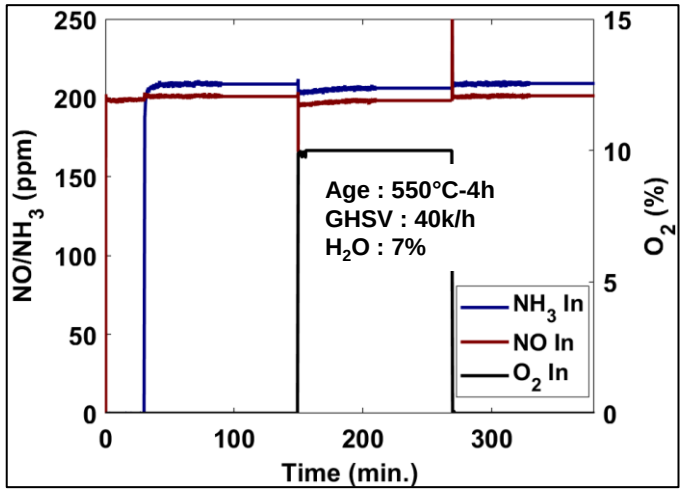
Parallel Cu^{II} dimer reduction routes



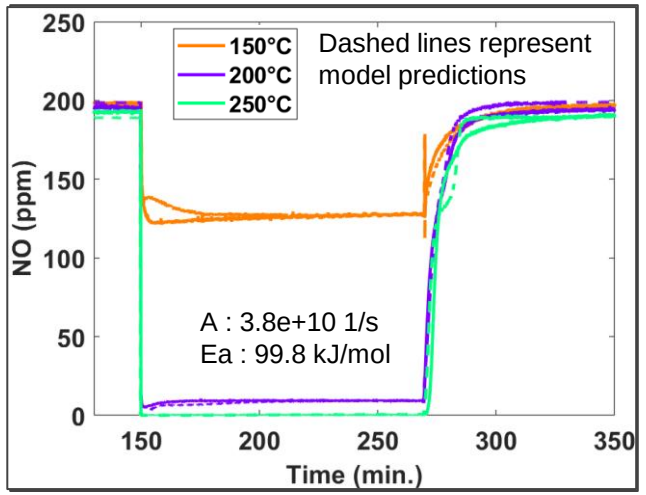
Temp. (°C)	NO/Cu^{II} from RHC1	NO/Cu^{II} from RHC2
150	0.74	0.77
200	0.82	0.86
250	1.04	1.04

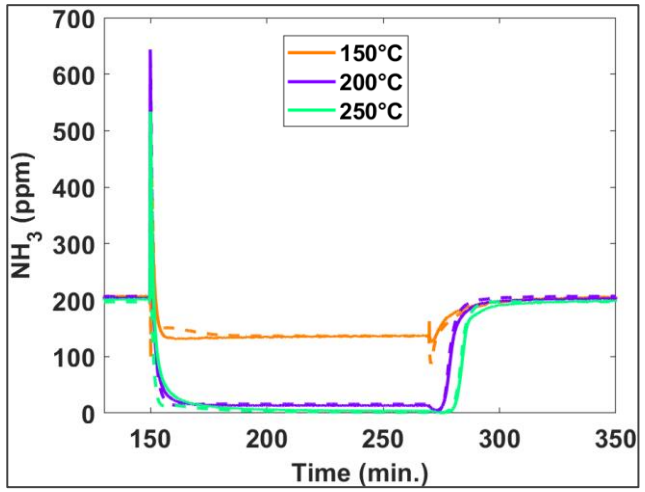
Note:
NO/Cu^{II} ratios < 1 at low temperatures associated with re-oxidation by trace O_2 and/or excess H_2O

NO → RHC1 → NO + NH_3 + O_2 → RHC2 Sequence



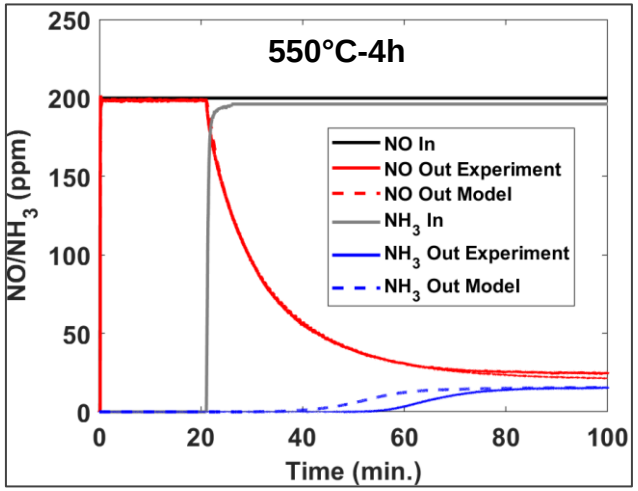
Standard SCR over reduced catalyst

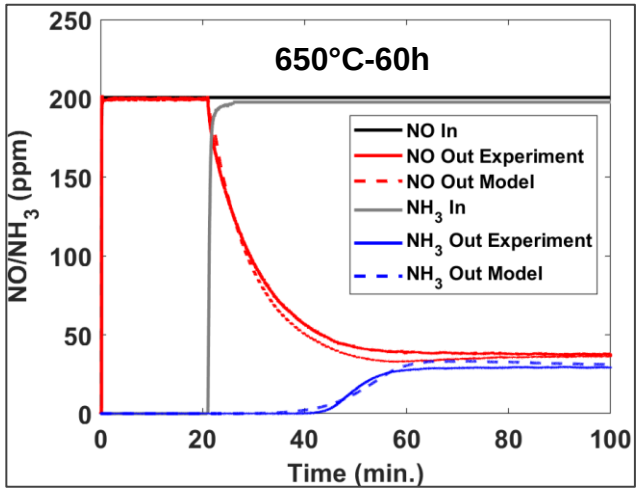




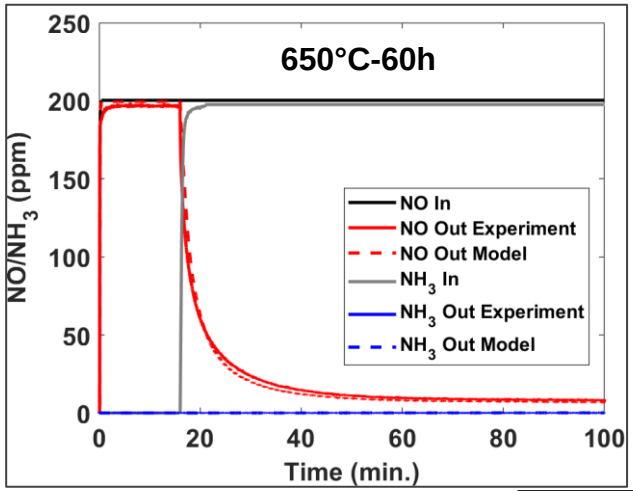
Model validation of transient NO_x conversion during standard SCR over an oxidized catalyst

190°C



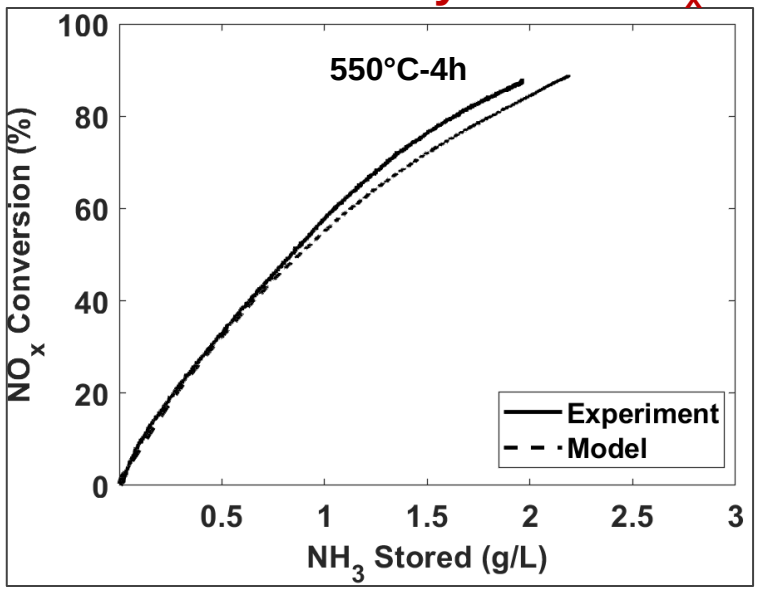


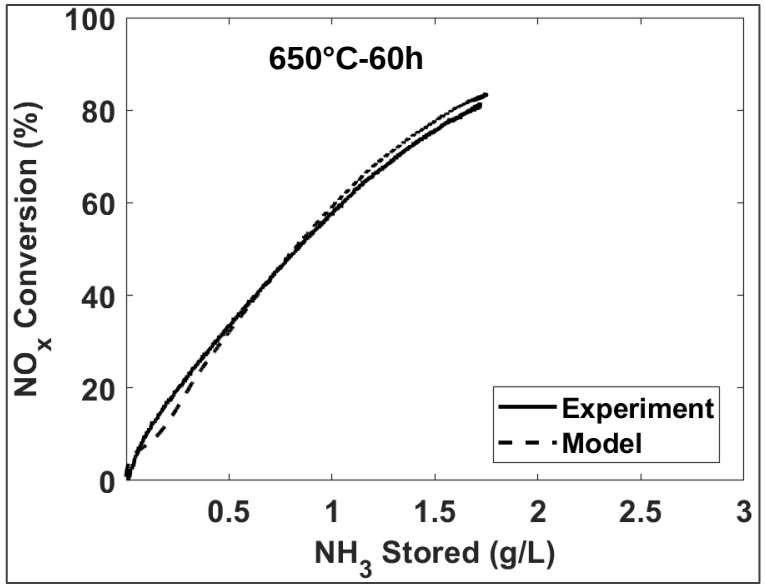
235°C



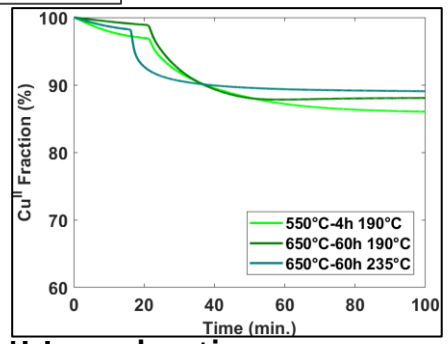
NH_3 : 200 ppm
NO : 200 ppm
O2 : 10%
H_2O : 7%
GHSV : 60k/h

Dynamic NO_x Conversion at 190°C





Cu^{II} Fraction

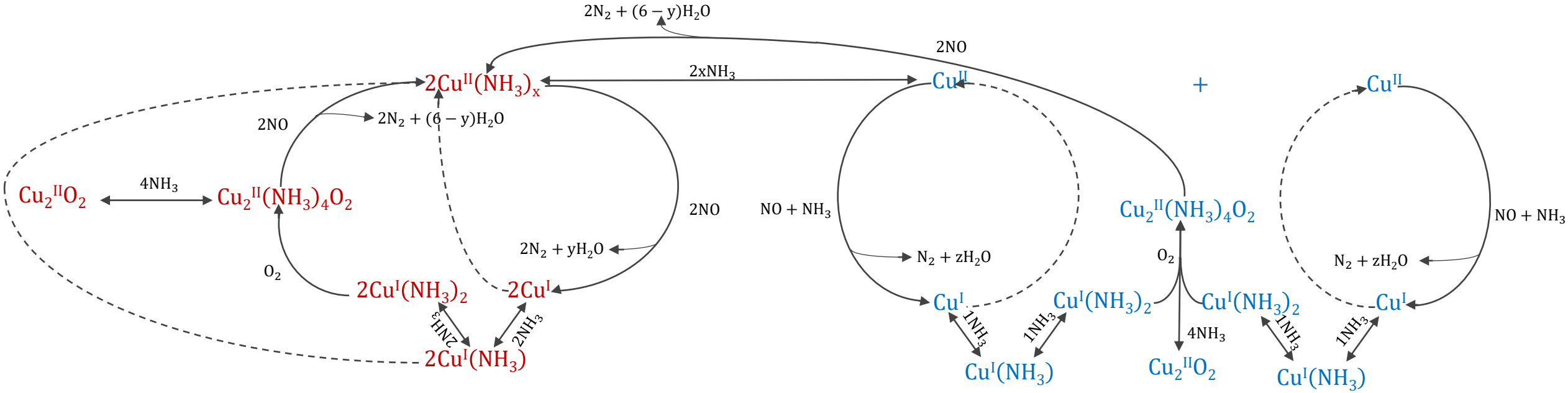


- Kinetic model of NH_3 solvation, reduction and re-oxidation of active Copper sites accurately predicts low-temperature transient SCR NO_x conversion as a function of HTA

Standard SCR redox cycle from NO + NH_3 RHC and OHC over NH_3-solvated ZCu sites

NH_3-solvated Cu^{II} sites

NH_3-free Cu^{II} sites



Dashed lines represent OHC over partially solvated and NH_3-free ZCu sites, likely involving Brønsted NH_3

Note:

x represents temperature and Cu^{II} speciation dependent NH_3 solvation of Cu^{II} sites. x range : [1-2]

y represents Cu^{II} speciation dependent H_2O produced upon reduction of two NH_3-solvated Cu^{II} sites. y range : [2-4]

z represents Cu^{II} speciation dependent H_2O produced upon reduction of one NH_3-free Cu^{II} site. z range : [1-2]

This picture of standard SCR is simplified, and does not include :

1. Intermediates (HONO, NH_2NO etc.)
2. All dimeric and multimeric surface species (Z_2Cu_2O, $Z_2Cu_2O(NH_3)_2$, $Z_2Cu_2O_2(NH_3)_2$ etc.)

Cummins

Backup Slides

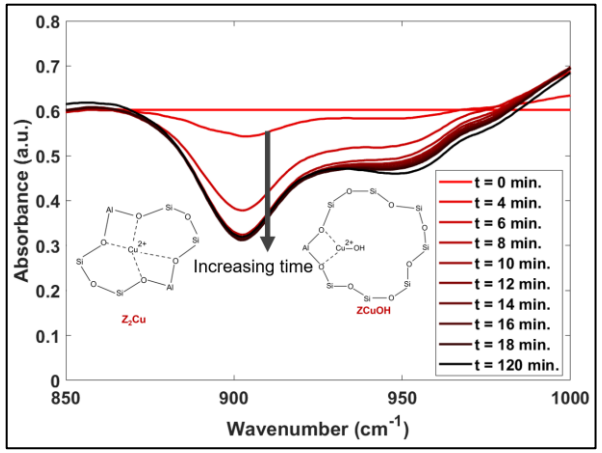
Summary of SCR redox activation barriers from DFT

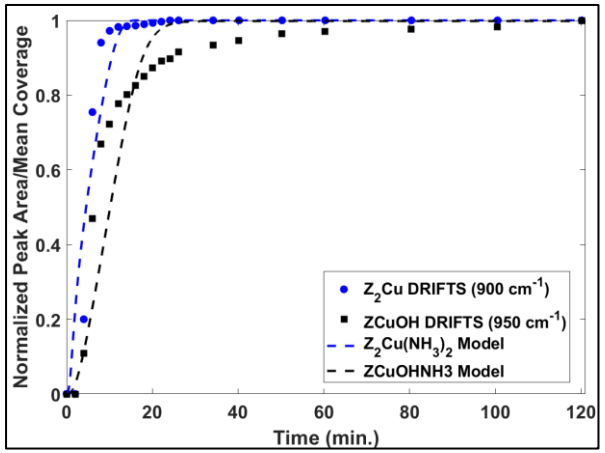
Category	Reactants	Products	DFT Activation Barriers [kJ/mol]
RHC on Z_2Cu	$NO + Z_2Cu(NH_3)_4$	$ZH + ZCu(NH_3)_3(H_2NNO)$	74[11]
	$NO + Z_2Cu(NH_3)_4$	$ZNH_4 + ZCu(NH_3)_2(H_2NNO)$	40[25]
	$NO + Z_2Cu(NH_3)_2$	$ZH + ZCu(NH_3)(H_2NNO)$	70[25]
	$NO + NH_3 + Z_2Cu$	$ZH + ZCu + NH_2NO$ (via ZNO)	52.7[24] (free energy)
RHC on ZCuOH	$NO + ZCuOH(NH_3)_3$	$H_2O + ZCu(NH_3)_2(H_2NNO)$	71[11]
	$NO + 2ZCuOH(NH_3)_3$	$HONO + ZCu(NH_3)_3 + ZCuOH(NH_3)_3$	60[20]
	$NO + ZCuOH(NH_3)_3$	$HONO + ZCu(NH_3)_3$	32[20]
	$NO + ZCuOH(NH_3)_2$	$ZCu(NH_3)_2HONO$	30[22] (free energy)
	$NO + ZCuOH(NH_3)_2$	$ZCu(NH_3)(H_2NNO) + H_2O$	105.9[22] (free energy)
	$NO + ZCuOH(NH_3)$	$ZCu(NH_3)(HONO)$	38[25]
	$ZCu(NH_3)(HONO)$	$ZCu(H_2NNO)$	131[25]
OHC	$O_2 + ZCu(NH_3)_2$	$Z_2Cu_2(NH_3)_4O_2$	35[18], 47[25], 61.75[12], 20[21], 33[23] (free energy), 32[16]
	$O_2 + ZCu(NH_3)_2 + NO$	$Z_2Cu_2(NH_3)_4O(ONO)$	20.26[12]
	$Z_2Cu_2(NH_3)_4O_2 + NO$	$Z_2Cu_2(NH_3)_4O(ONO)$	42.45[12], 46[21]
	$Z_2Cu_2(NH_3)_4O_2 + 2NO$	$2ZCu(NH_3)_2(ONO)$	36[16]
	$Z_2Cu_2(NH_3)_4O(ONO)$	$ZCu(NH_3)_2(NO_3) + ZCu(NH_3)_2$	60.8[12], 51[21]
	$ZCu(NH_3)_2(NO_3) + NO$	$ZCu(NH_3)_2(ONO) + NO_2$	47[21]
	$ZCu(NH_3)_2(ONO) + NO + NH_3$	$HONO + ZCu(NH_3)_2 + N_2 + H_2O$	60[16]
HONO and NH_2NO decomposition	$HONO + NH_3$ in gas-phase	$N_2 + 2H_2O$	140[16]
	$HONO + NH_3$ over ZH	$N_2 + 2H_2O$	5[16]
	$HONO + NH_3$ over NH_4	$N_2 + 2H_2O$	37[16]
	$HONO + ZCu(NH_3)_3$	$ZCu(NH_3)_2 + N_2 + 2H_2O$	17-25[20], 119[16]
	$ZCu(NH_3)_2HONO$	$ZCu(NH_3) + N_2 + 2H_2O$	37[22]
	NH_2NO decomposition over ZH	$N_2 + H_2O$	37[16]
	NH_2NO decomposition over ZNH_4	$N_2 + H_2O$	5[16]
Reactions on NH_3 Free Cu	$ZCu + NO + O_2$	$ZCuNO_3$	55[25], 104[26] (free energy)
	$ZCuNO_3 + NO$	$ZCuONO + NO_2$	71[25], 65[26]

[11] Paolucci et al. (2016). *Journal of the American Chemical Society*, *138*(18), 6028-6048.
[12] Chen et al. (2018). *Journal of catalysis*, *358*, 179-186.
[20] Hu et al. (2021) *Angewandte Chemie,133*(13), 7273-7280.
[21] Liu et al. (2020). *Catalysis Science & Technology, 10*(11), 3586-3593..
[18] Paolucci et al. (2017). *Science*, *357*(6354), 898-903.
[22] Gao et al. (2017). *Journal of the American Chemical Society*, *139*(13), 4935-4942.
[23] Chen et al. (2018). *Catalysis Science & Technology*, *8*(8), 2131-2136.
[16] Chen et al. (2020). *ACS Catalysis*, *10*(10), 5646-5656.
[24] Crandell et al. (2017). *Dalton Transactions*, *46*(2), 369-377.
[25] Zhao et al. (2021). *Catalysis Science & Technology.*
[26] Janssens et al. (2015). *ACS catalysis*, *5*(5), 2832-2845.

NH_3 adsorption is faster and saturates earlier on Z_2Cu sites relative to ZCuOH sites

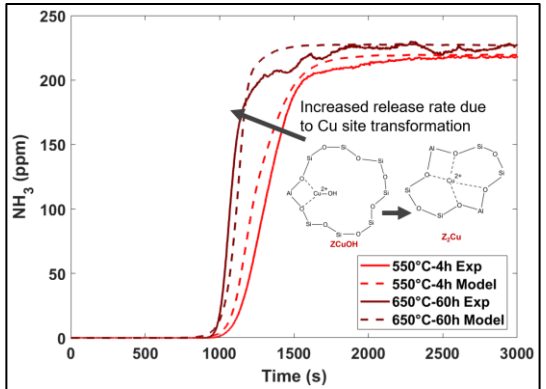
- NH_3 solvation leads to changes in the relative absorbance at wavenumbers of 900 cm^{-1} and 950 cm^{-1}, associated with Z_2Cu and ZCuOH sites respectively. Plotting the relative changes in peak areas, normalized to the steady-state spectrum at 120 min, shows an earlier approach to saturation for Z_2Cu sites relative to ZCuOH sites, consistent with model predictions

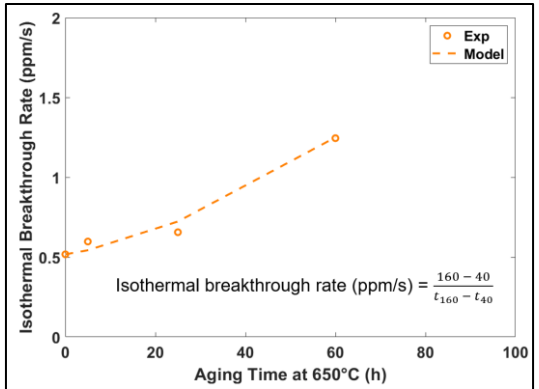




In-Situ DRIFTS Conditions
Age : 650°C-50h in 7% H_2O
Flow : 100 cc/min
Mass of powder : 35 mg
NH_3 feed : 200 ppm
Temperature : 100°C
H_2O : 0%

- Increased net NH_3 adsorption rates on Z_2Cu sites are also observed during isothermal adsorption events, quantified by NH_3 breakthrough rates. Upon HTA, the NH_3 breakthrough rate increases due to predominance of Z_2Cu sites

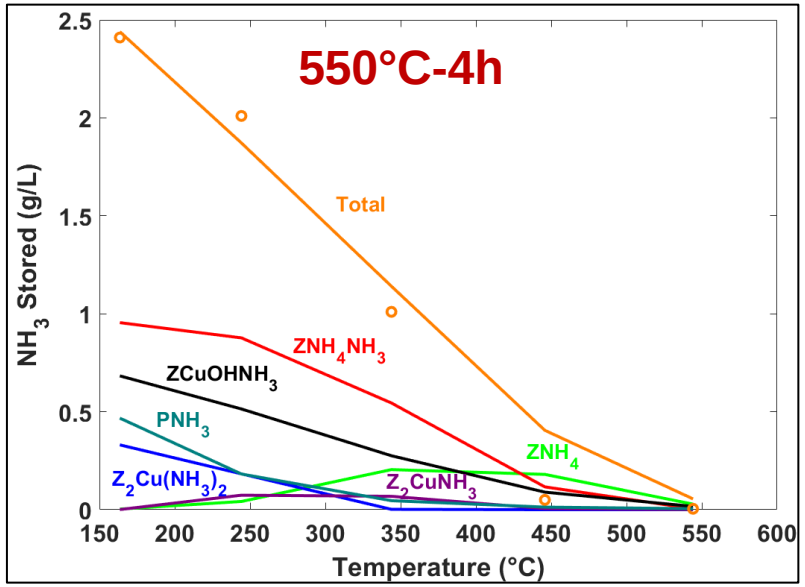


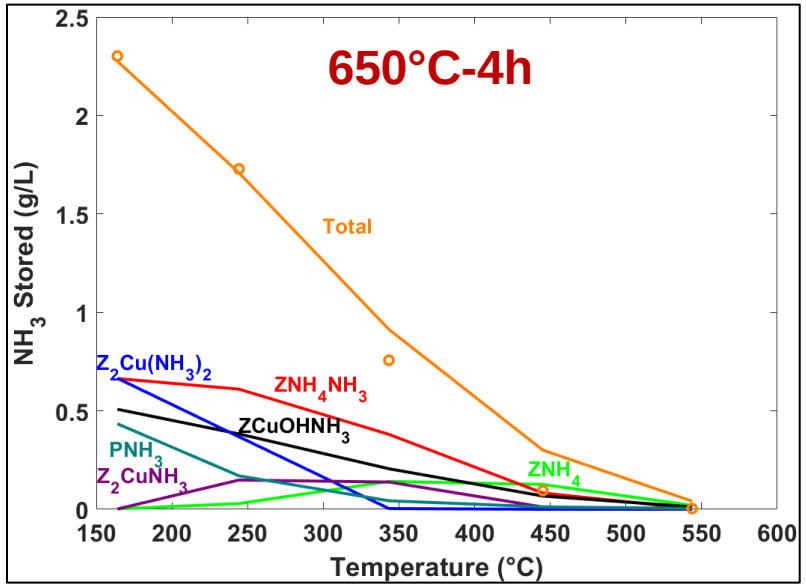


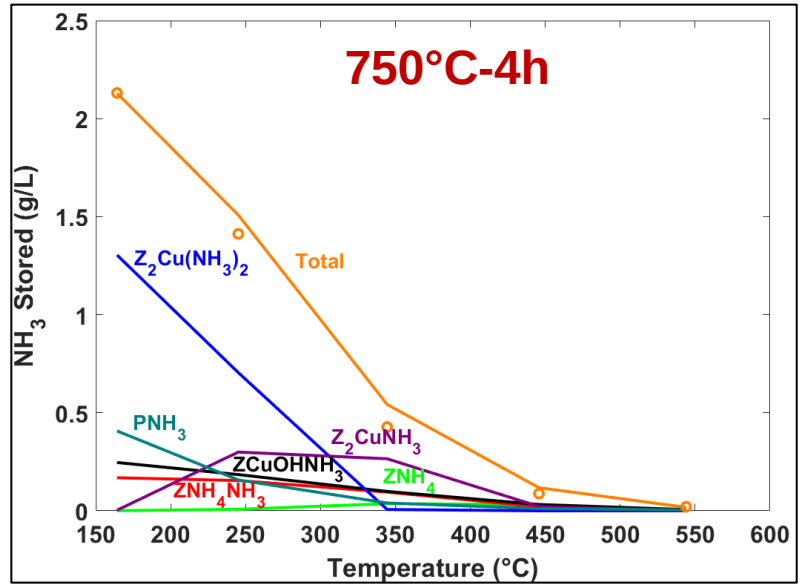
NH_3 : 200 ppm
H_2O : 7% ; O_2 : 10% (0% during TPD)
Adsorption temperature : 200°C
SV : 40k/h

Evolution of total and site-specific storage with HTA

- For the resulting number densities of Z_2Cu, ZCuOH, ZH and Physisorbed sites, the storage model was validated with temperature dependent NH_3 storage data at different HTA temperatures





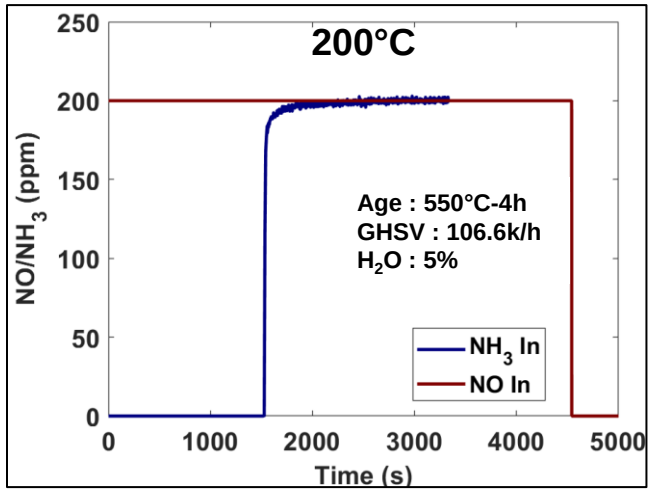


- While ZNH_4NH_3 and $ZCuOHNH_3$ are the primary NH_3 containing species at low temperatures on the 550°C-4h aged catalyst, hydrothermal aging at 750°C for 4 h leads to a predominant contribution of $Z_2Cu(NH_3)_2$ to NH_3 storage below 250°C

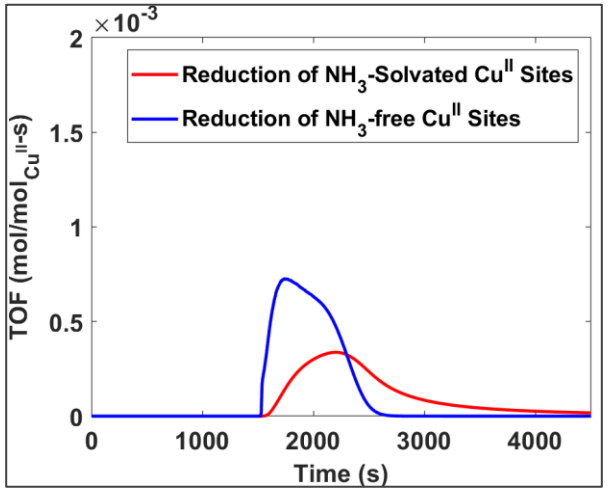
Note:
All HTA in 7% H_2O

$NO + NH_3$ RHC Kinetics predict the increased contribution of gas-phase NH_3 route with temperature

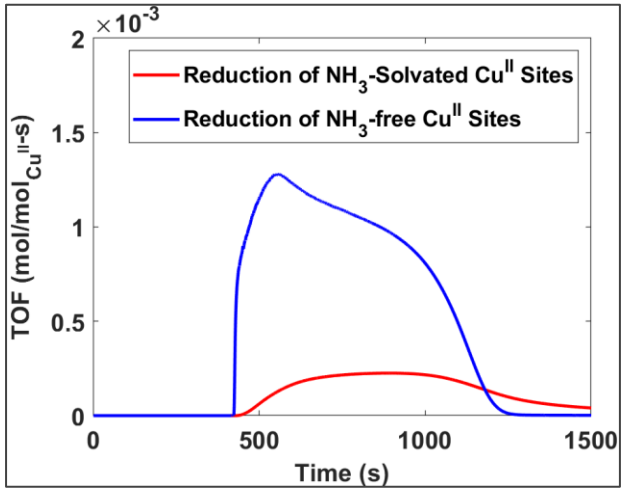
NO First Titration Protocol



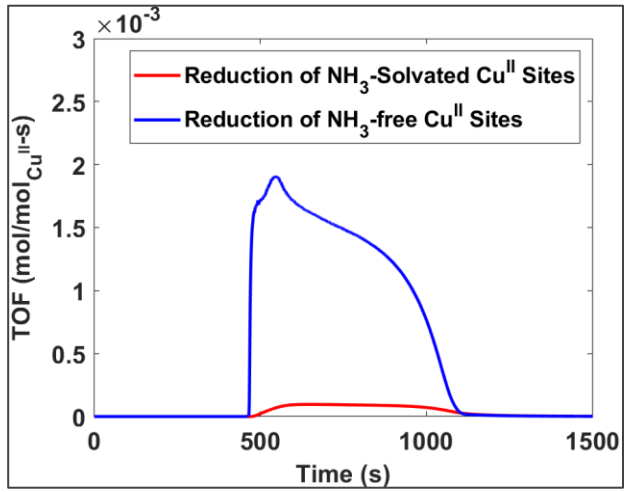
200°C



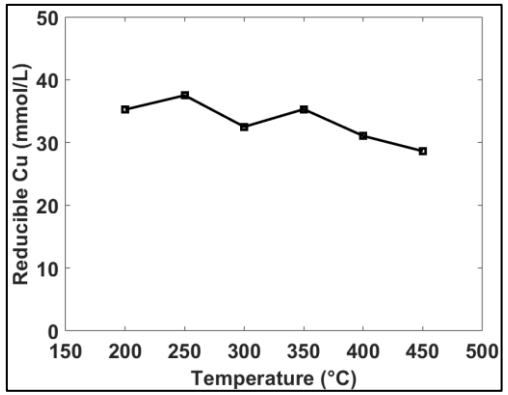
250°C



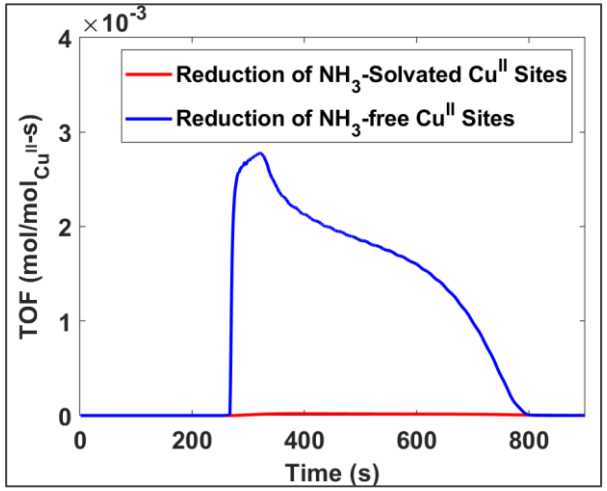
300°C



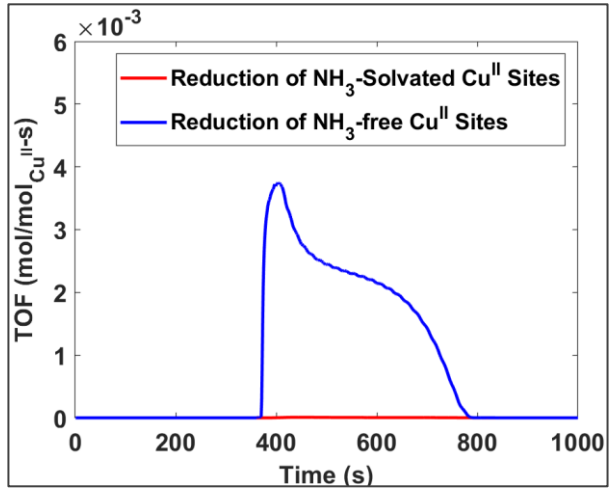
Measured reducible Cu from integrated N_2



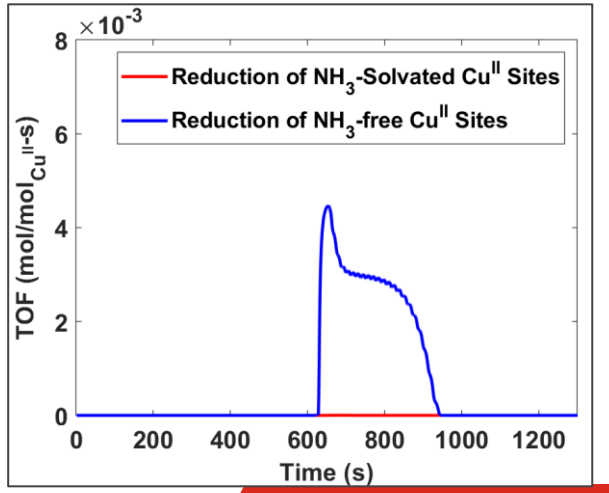
350°C



400°C

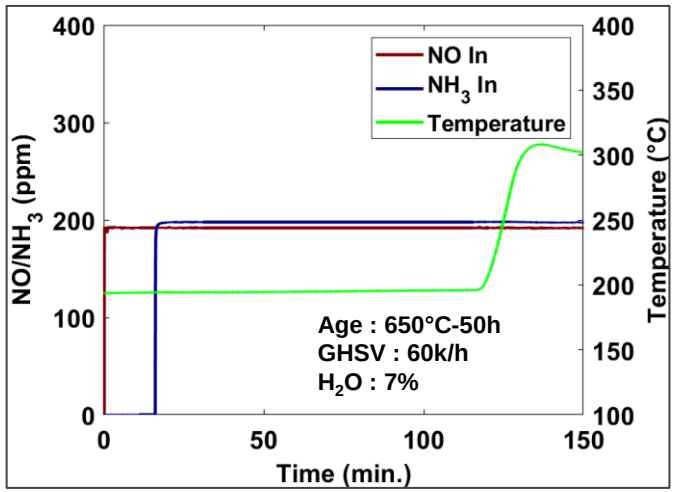


450°C

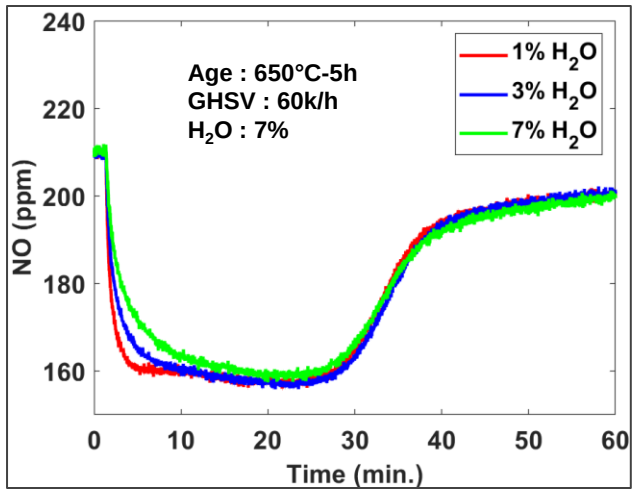


$NO + NH_3$ RHC rate first order in NO and inhibited by H_2O

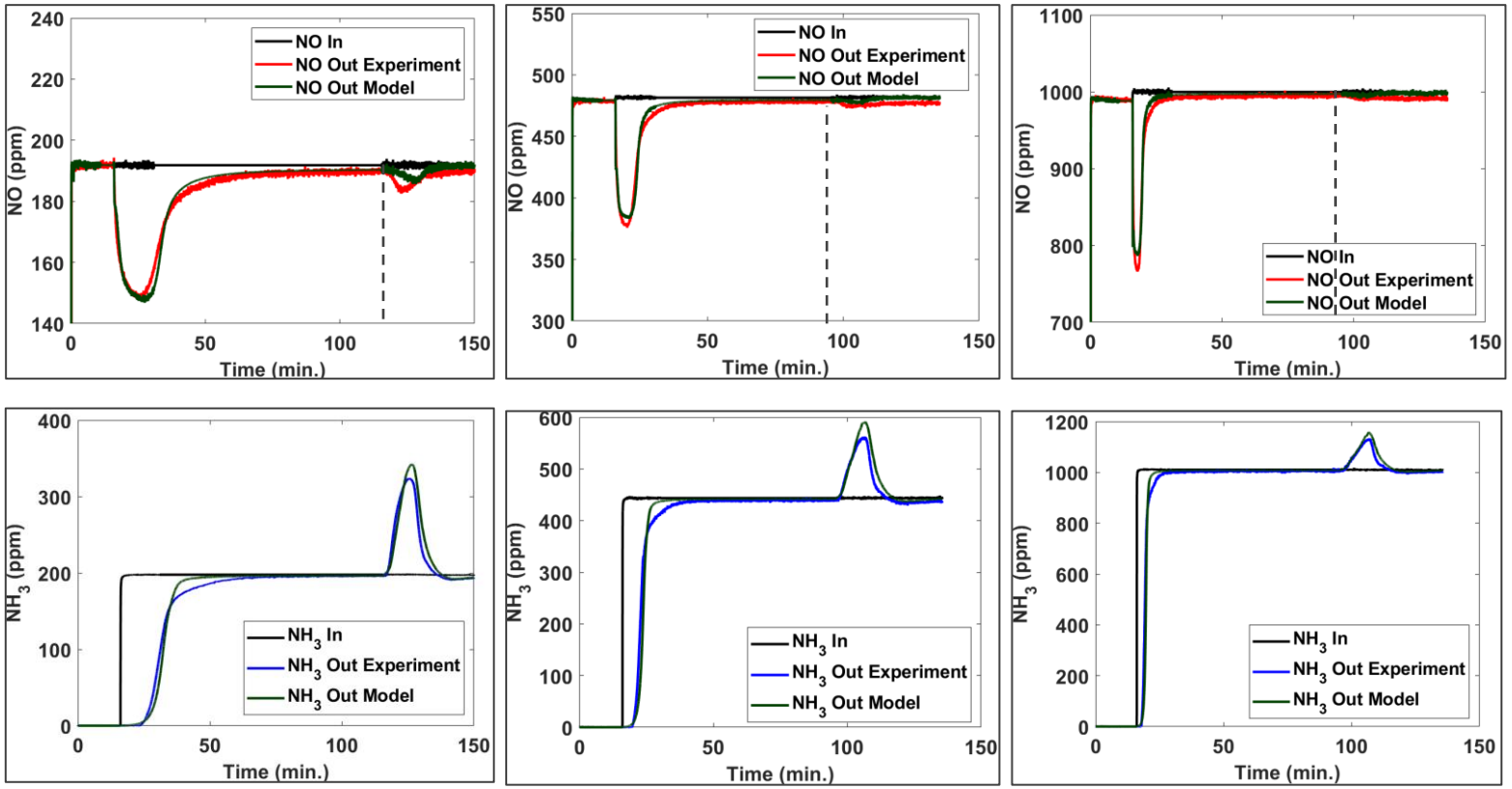
$NO + NH_3$ TPR Protocol (200 ppm)



Influence of H_2O Pressure on NO Consumption during RHC



200 ppm | 500 ppm | 1000 ppm



- Reduction of Cu^{II} sites by $NO + NH_3$ follows first order kinetics, as confirmed by model predictions on the influence of NO pressure
- Additional NO consumption during TPR observed for 200 ppm feed, confirming incomplete reduction of Cu^{II} sites during isothermal titration as a result of minor re-oxidation
- Faster initial NO consumption observed at lower H_2O pressures, confirming the inhibiting role of H_2O in reduction of Cu^{II} sites