Sites and mechanism for NO_x transformations in Cu-SSZ-13

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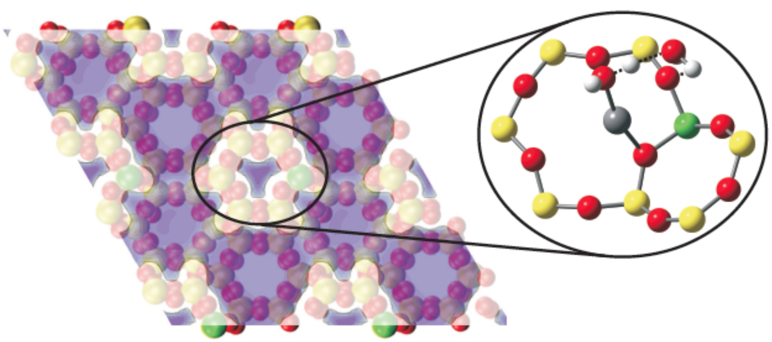

CLEERS Conference
April 29, 2015

The NSF/DoE NO_x SCR Team

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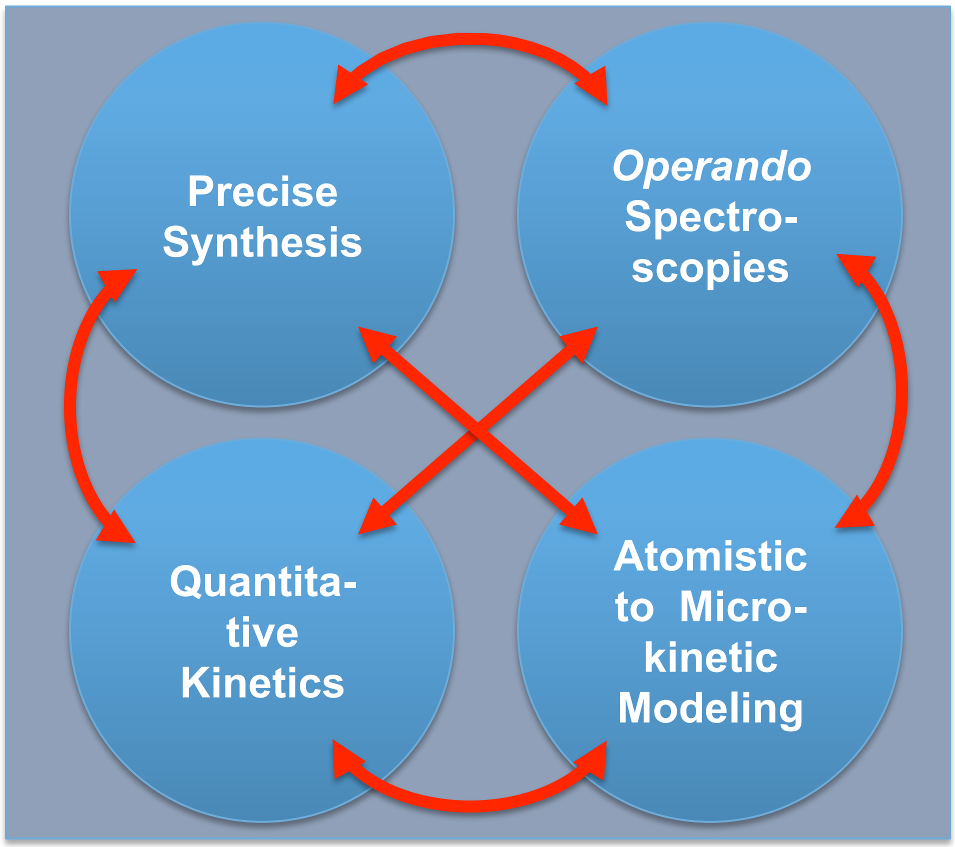
DOE-DE-EE0003977 CBET 12-58690

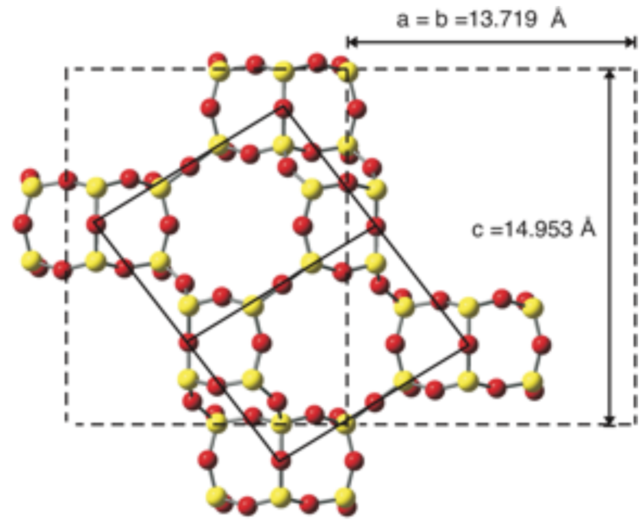
Objectives of NSF/DoE NO_x SCR Team

"This project seeks to build a **microscopically detailed** model of **catalyst performance** under all operating conditions and **throughout the life cycle** aiming to optimize engine efficiency within emission constraints and to circumvent catalyst deactivation."



Cu-SSZ-13 Zeolite

- Crystalline aluminosilicate
- AABBCCAA stacking
- 4-, 6-, and 8-membered rings
- Ion exchange sites associated with Si → Al substitutions
  - AlO_4^-/M^+, $[AlO_4^-]/M^{2+}$



- Supercell DFT simulations using Vasp
  - PAW-PW91
  - Rhombohedral cell (—): 12 Si & 24 O
  - Hexagonal cell (- -): 36 Si & 72 O

Red: O
Yellow: Si
Green: Al
White: H

Cu Exchange in Zeolite Frameworks

NH_4-SSZ-13 (Si:Al 4.5 – 25)

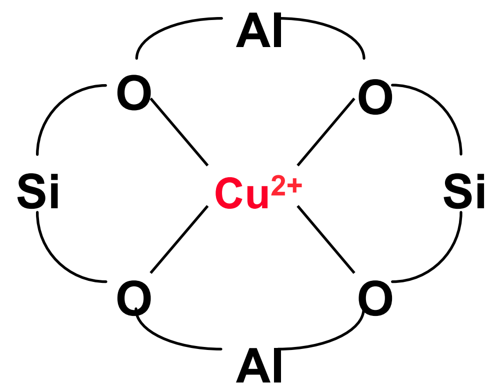
+

$Cu(NO_3)_2$ (*aq*)

(Cu^{2+})

→

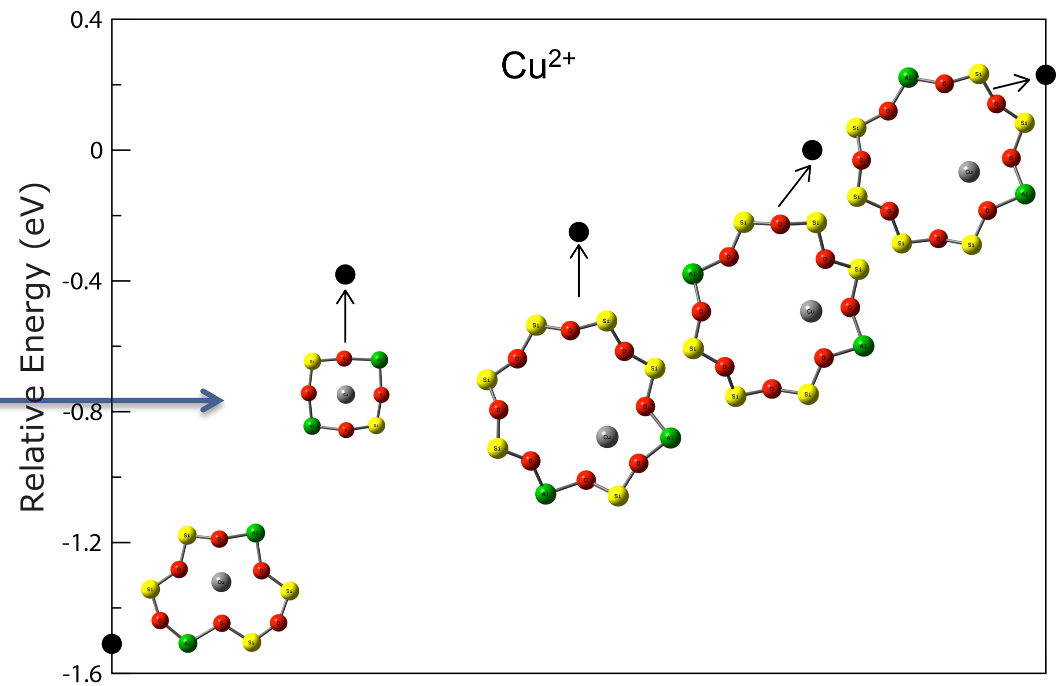
1 Cu^{2+} : 2 Al



“Z_2Cu”

Cu Exchange in Zeolite Frameworks

NH_4-SSZ-13 (Si:Al 4.5 – 25**)**
+
$Cu(NO_3)_2$ (*aq*)
(Cu^{2+})



- Cu(II) exhibits a **strong preference** for binding in 6-fold rings near 2 Al
- Agreement with DFT, UV-vis, EXAFS, and XRD, acid titrations

Cu Exchange in Zeolite Frameworks

1 Cu^{2+} : 1 Al

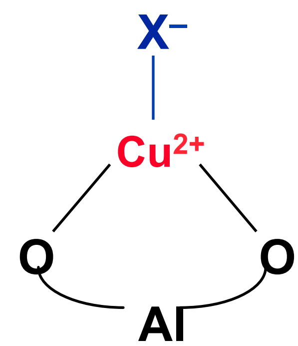
NH_4-SSZ-13 (Si:Al 4.5 – 25)

+

$Cu(NO_3)_2$ (*aq*)

(Cu^{2+})

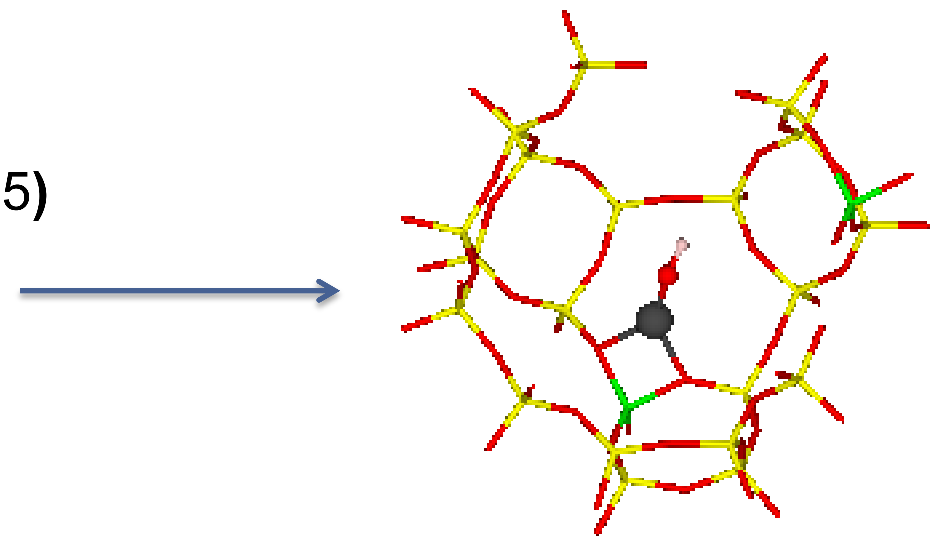
→



"ZCuX"

Cu Exchange in Zeolite Frameworks

NH_4-SSZ-13 (Si:Al 4.5 – 25**)**
+
$Cu(NO_3)_2$ (*aq*)
(Cu^{2+})

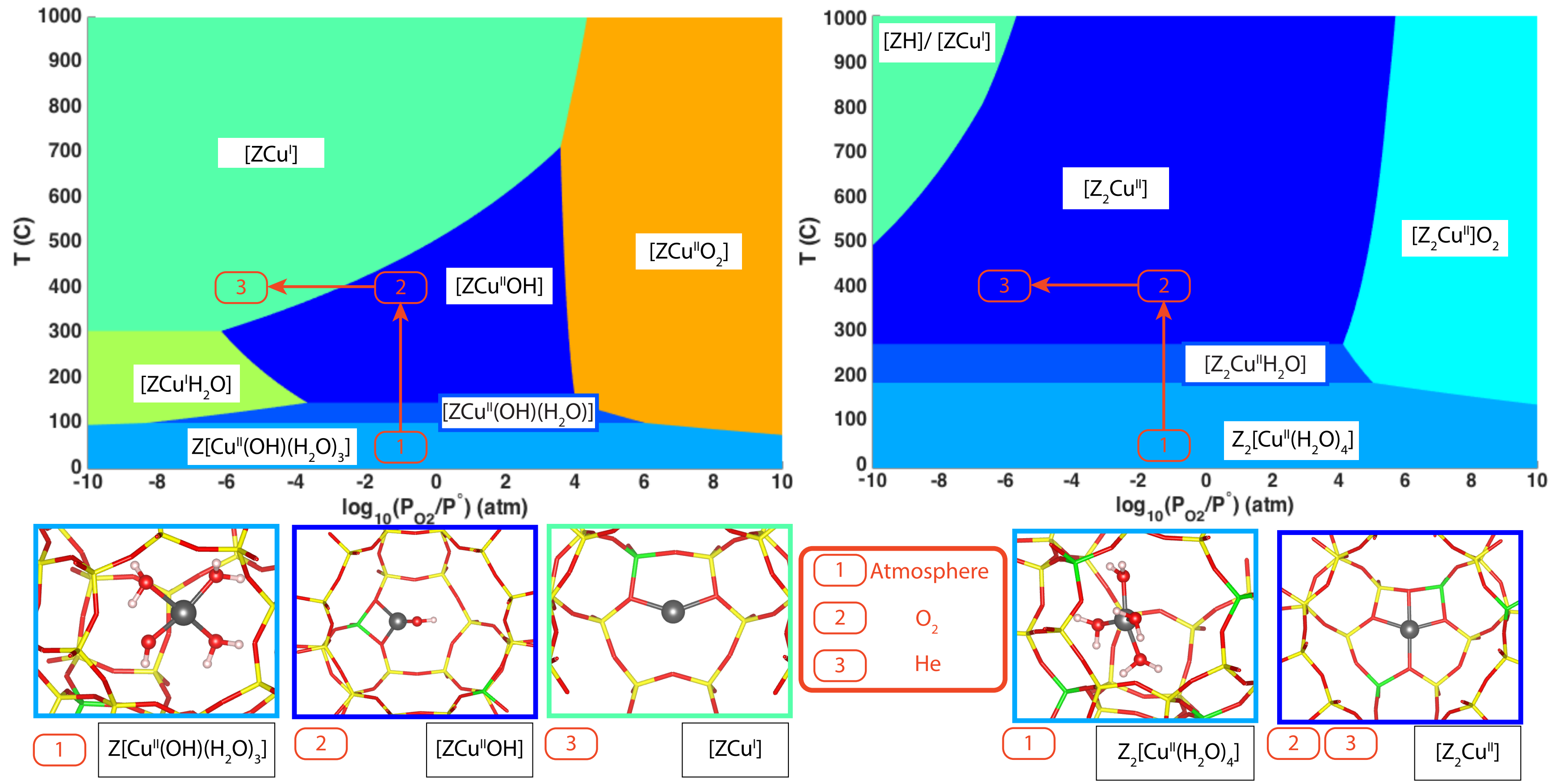


ZCuOH

- **Isolated Al** bind Cu(II) as ZCu(II)OH
- Agreement from DFT, UV-vis, EXAFS, and XRD, acid titrations

Chemically Distinct Cu(II) Sites

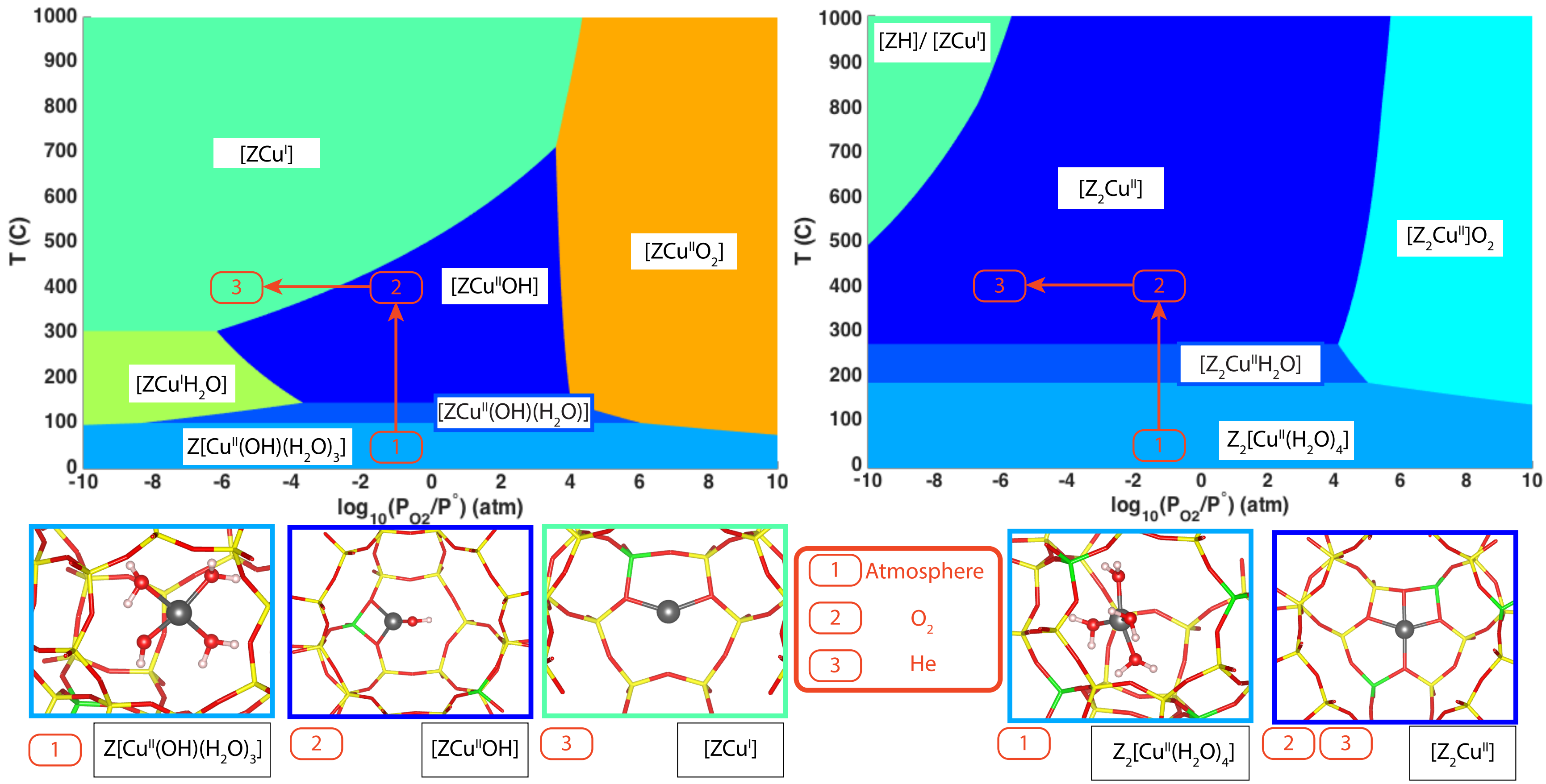
ZCuOH | **Z_2Cu**



1:1 Cu:H exchange | *1:2 Cu:H exchange*

Chemically Distinct Cu(II) Sites

ZCuOH Z_2Cu



Hydrated at ambient   ***Hydrated at ambient***

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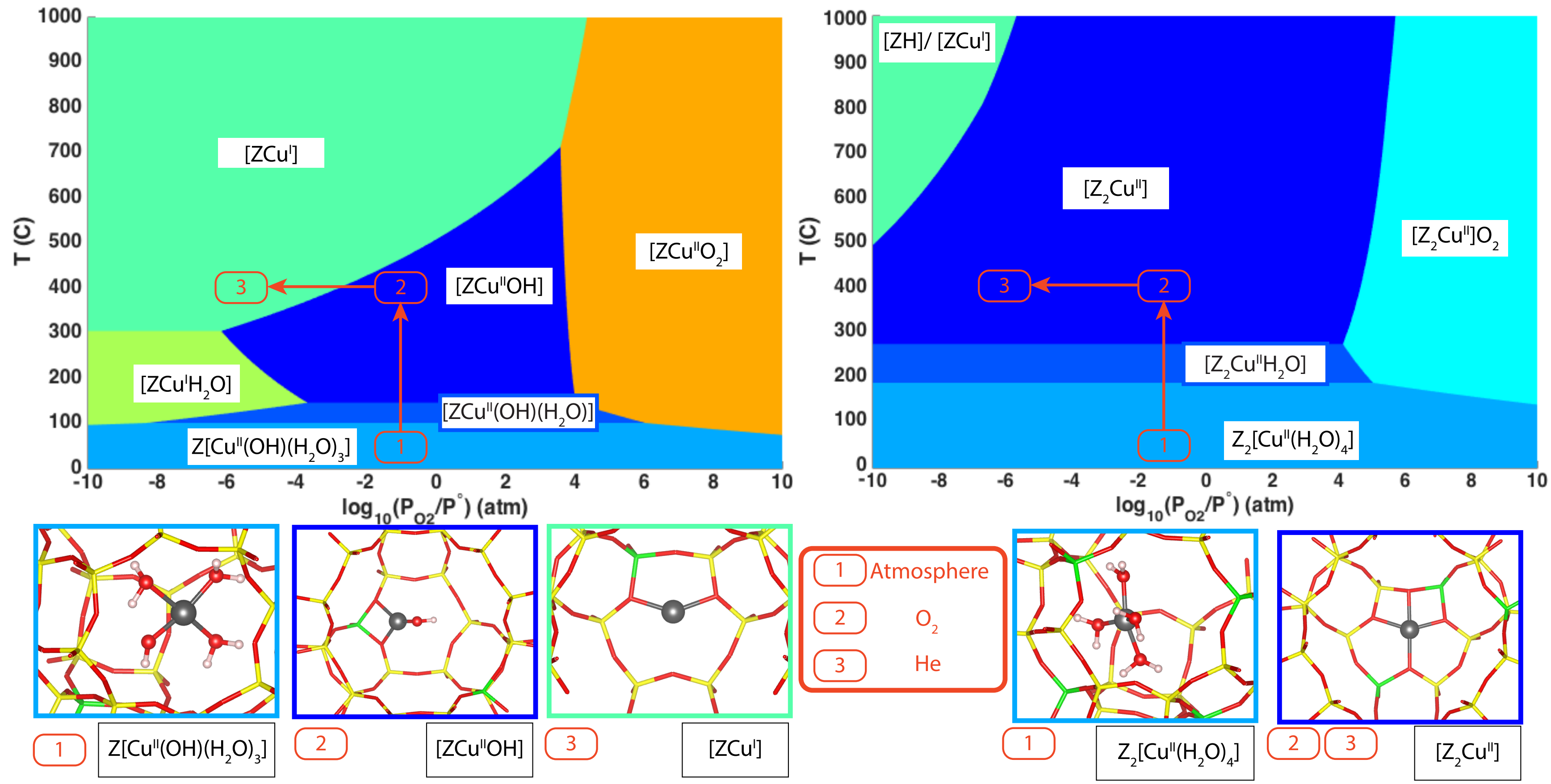
Chemically Distinct Cu(II) Sites

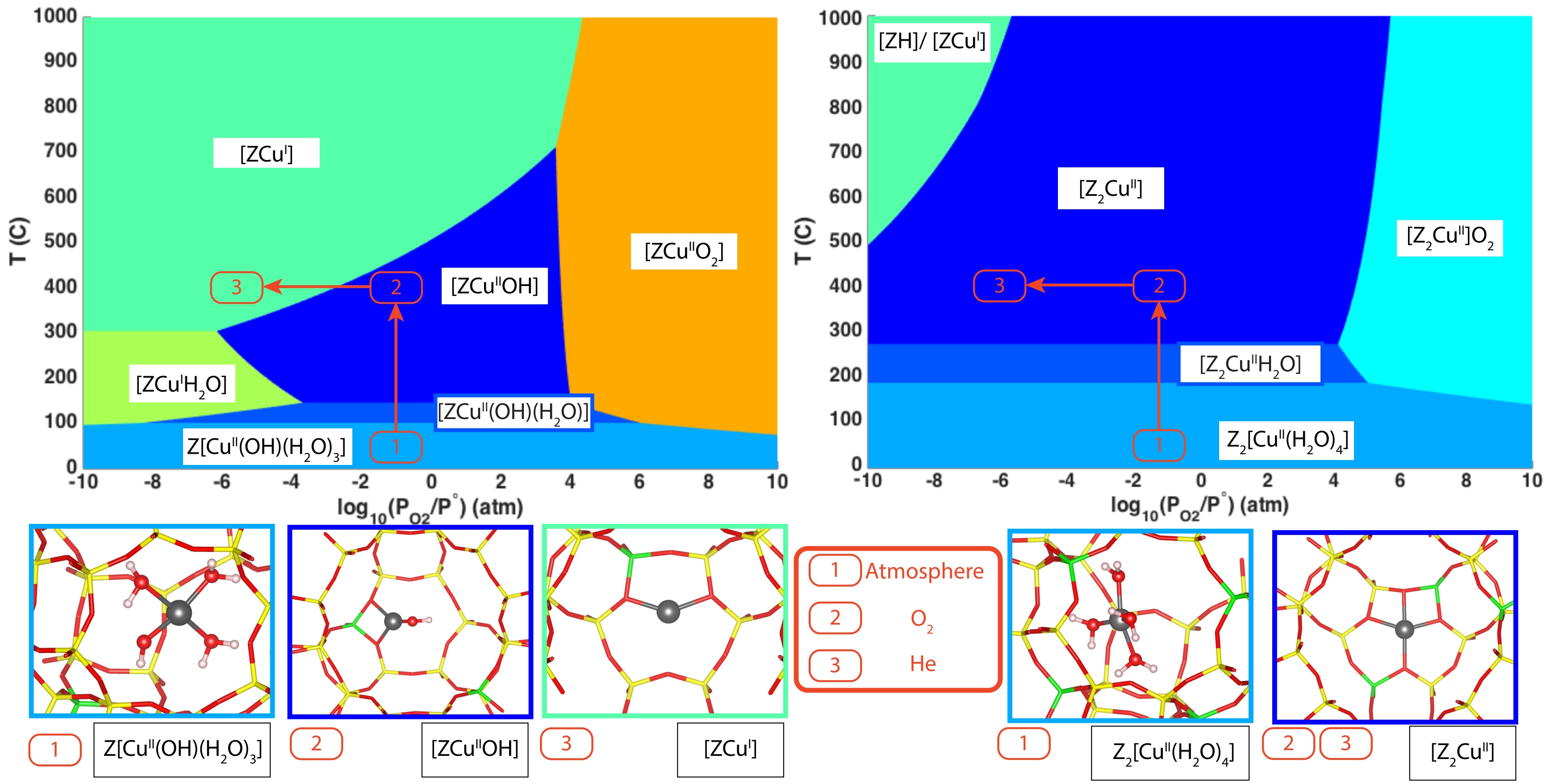
ZCuOH | **Z_2Cu**



Dehydrate at elevated T | *Dehydrate at elevated T*

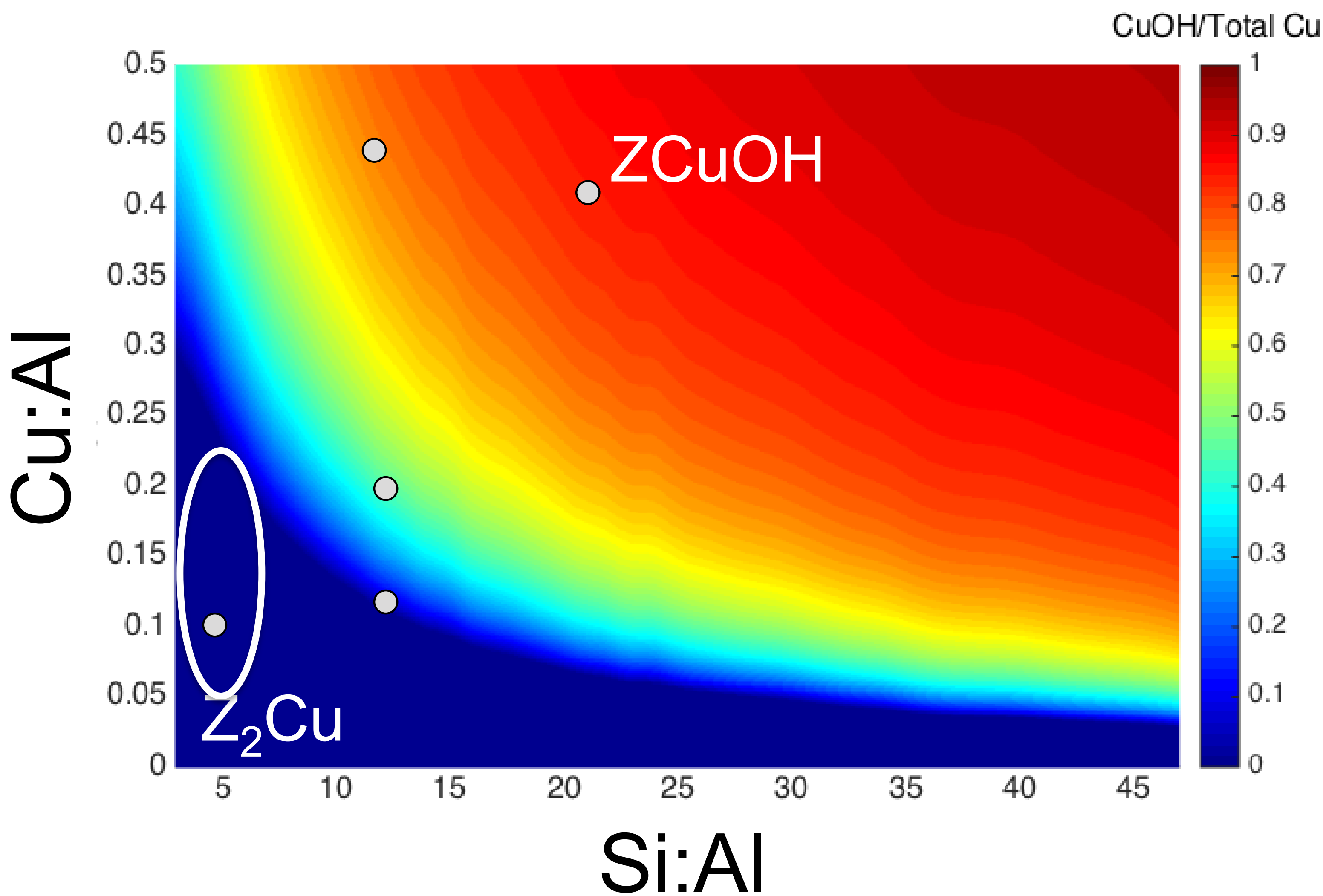
Chemically Distinct Cu(II) Sites

ZCuOH **Z_2Cu**

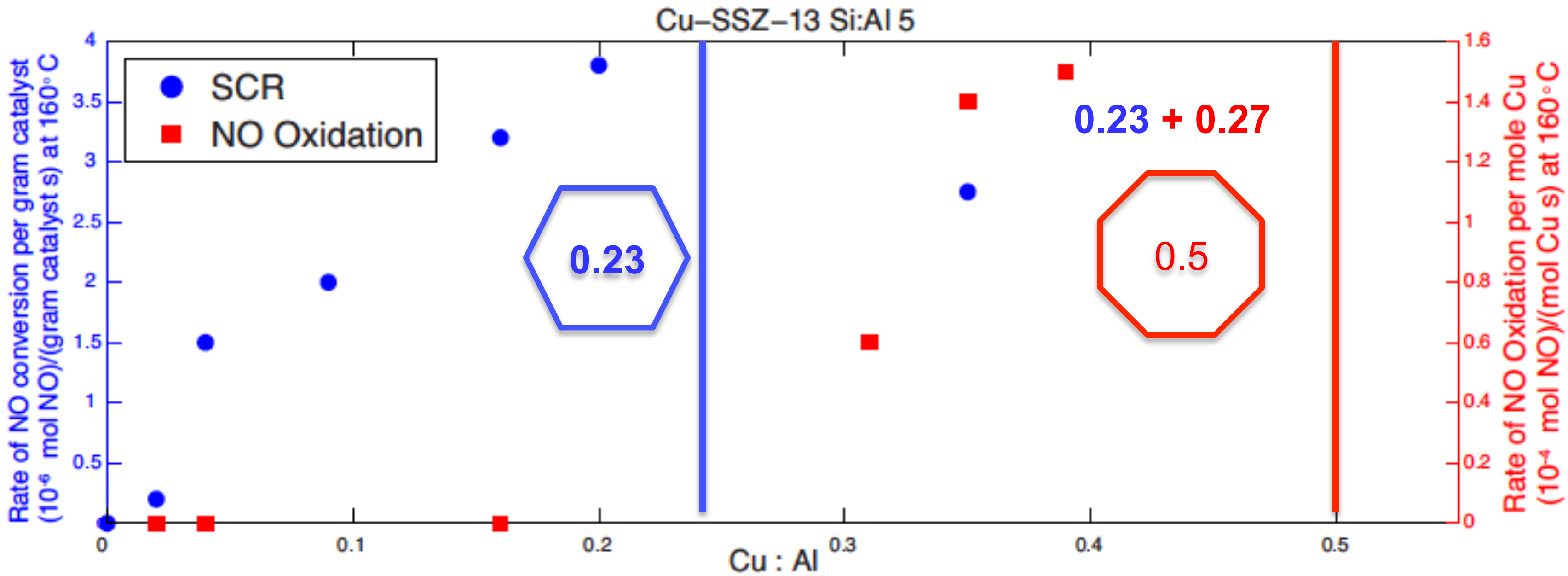


Auto-reducible *Not reducible*

Single/paired Al sites vs. Si:Al ratio



Rates vs. Cu Loading @ Si:Al 5:1



- Standard SCR activity scales with number of isolated Cu^{2+} in 6-MR
- Dry NO oxidation activity scales with Cu oxo species at higher Cu loadings

Bates *et al.* J. Catal. **2014**, 312, 87–97.

Operando XANES and EXAFS

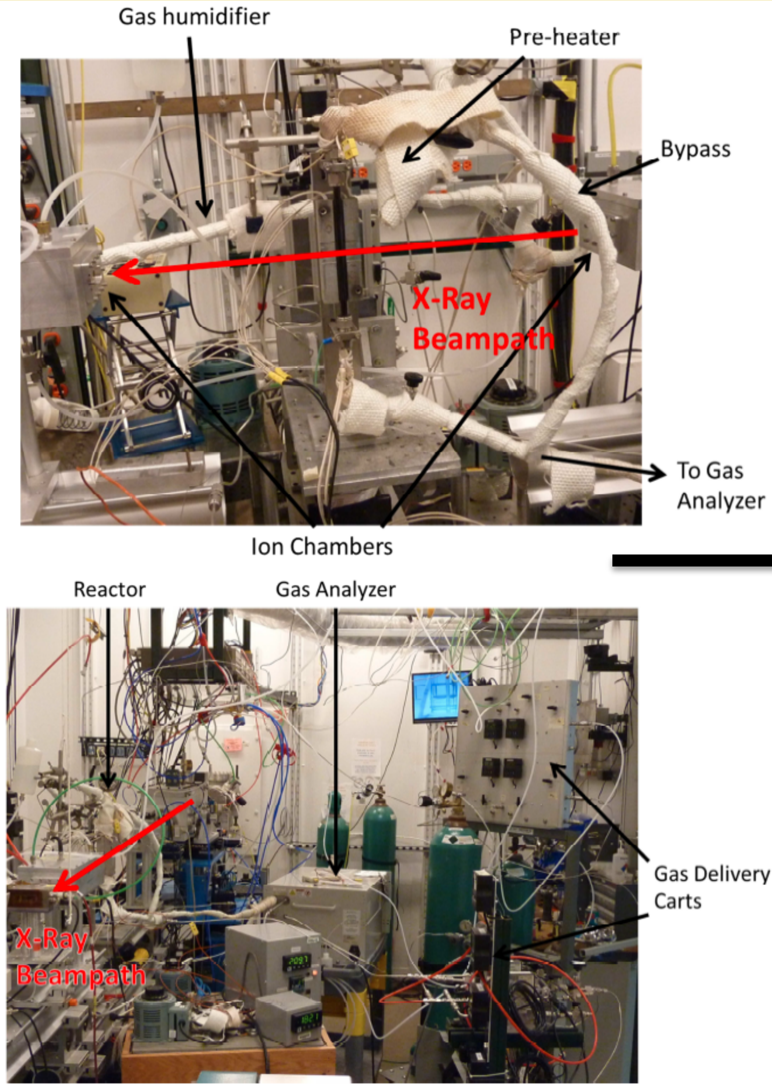
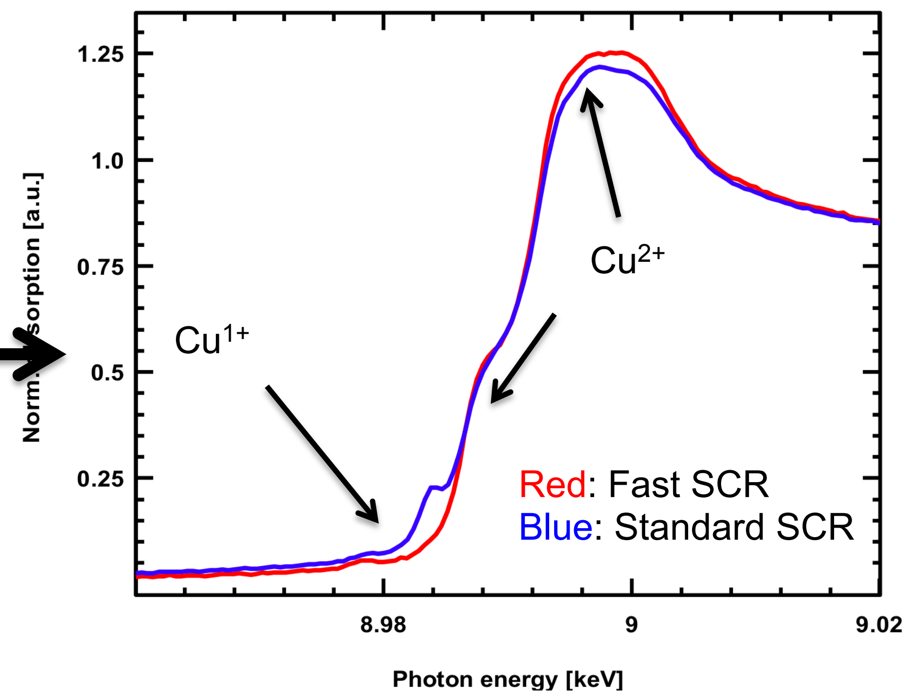


Figure S5:

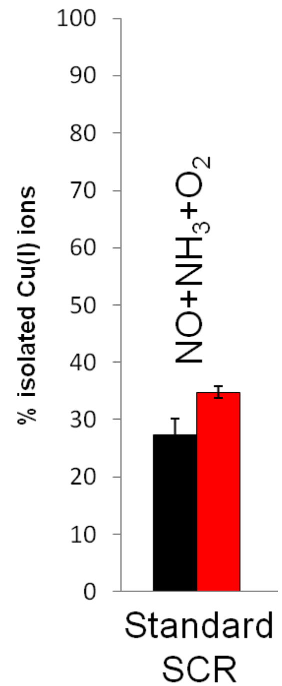
XANES vs. SCR Conditions



McEwen *et al.* Catal. Today, **2012** 184

Cutoff Experiments

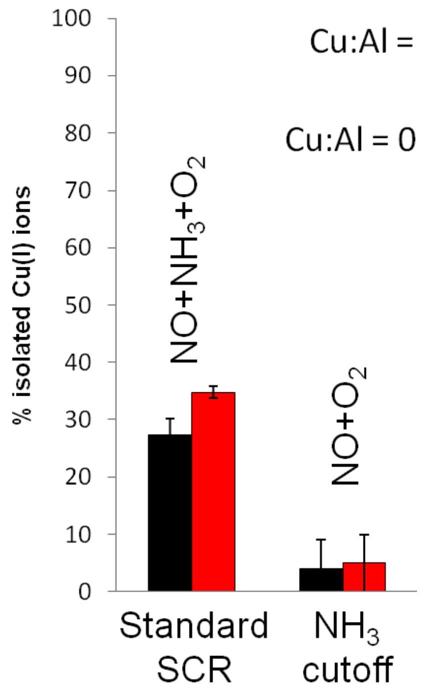
Operando XANES
Ribeiro group, Purdue



- Both Cu^{+} and Cu^{2+} present at standard SCR conditions

Cutoff Experiments

Operando XANES
Ribeiro group, Purdue



- Both Cu^{+} and Cu^{2+} present at standard SCR conditions
- Activity vanishes and $Cu^{+} \rightarrow 0$ with NH_3 cut off

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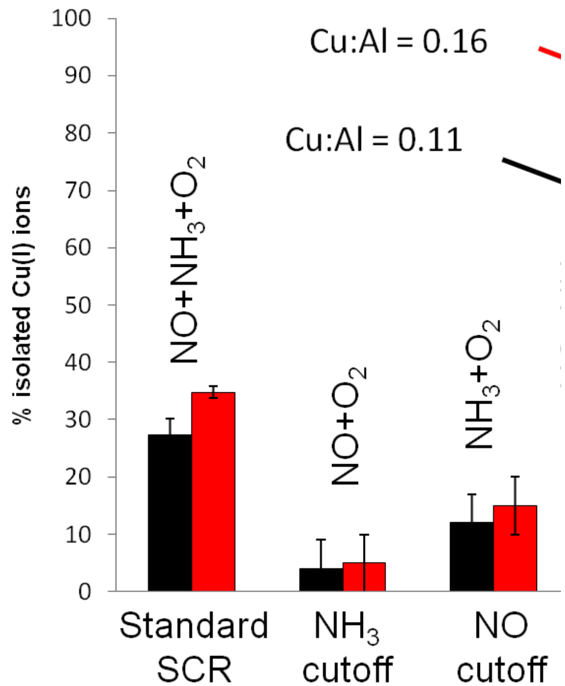
Cutoff Experiments

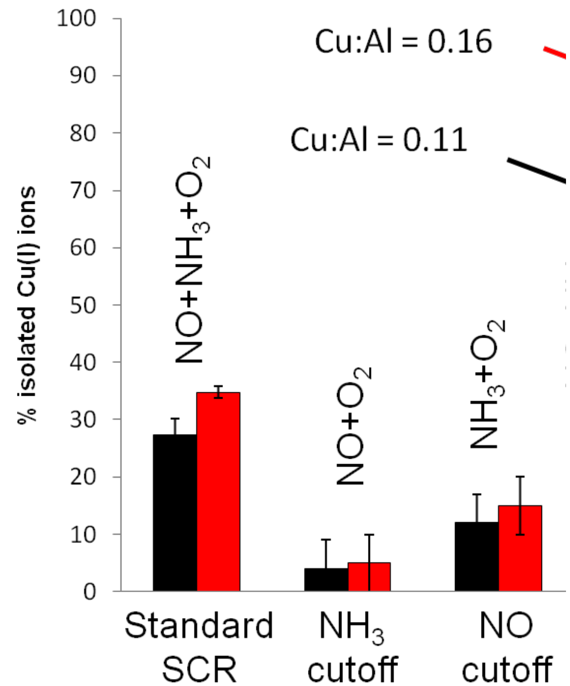
Operando XANES
Ribeiro group, Purdue



- Both Cu^{+} and Cu^{2+} present at standard SCR conditions
- Activity vanishes and $Cu^{+} \rightarrow 0$ with NH_3 cut off
- Activity vanishes and $Cu^{+} \downarrow$ with NO cut off

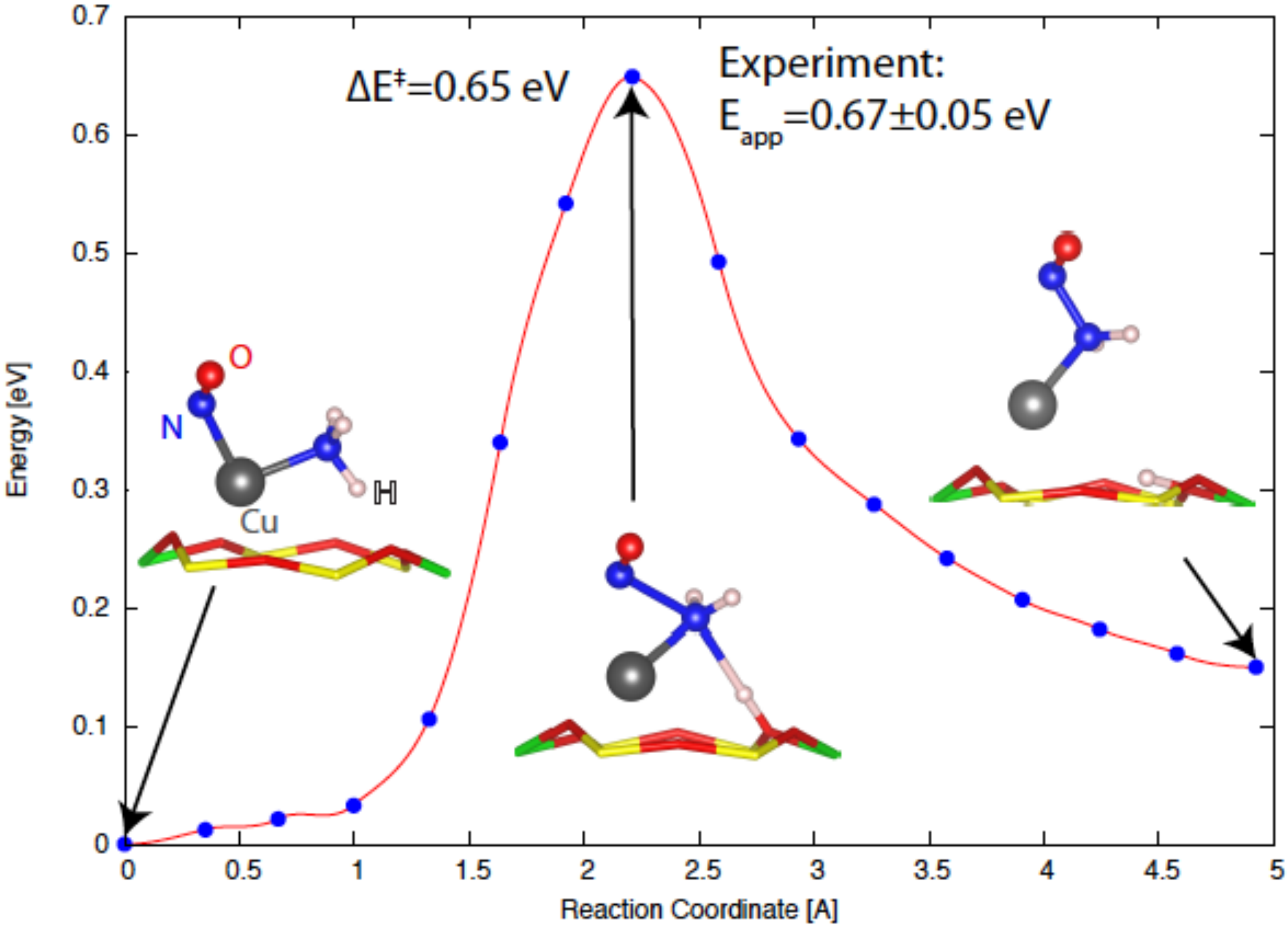
Cutoff Experiments

Operando XANES
Ribeiro group, Purdue

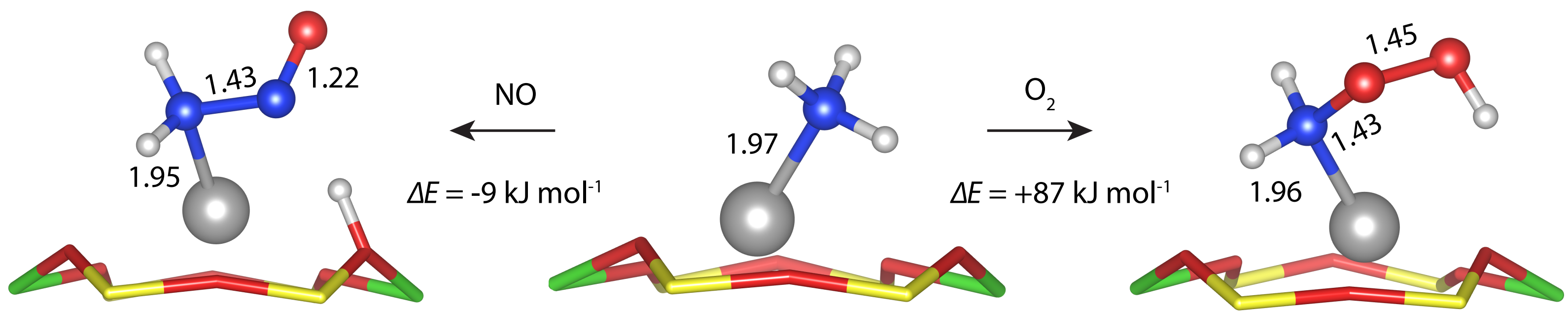


- Both Cu^{+} and Cu^{2+} present at standard SCR conditions
- Activity vanishes and $Cu^{+} \rightarrow 0$ with NH_3 cut off
- Activity vanishes and $Cu^{+} \downarrow$ with NO cut off
- NO <u>and</u> NH_3 involved in reduction half reaction

Co-adsorbate induced Cu^{2+} reduction

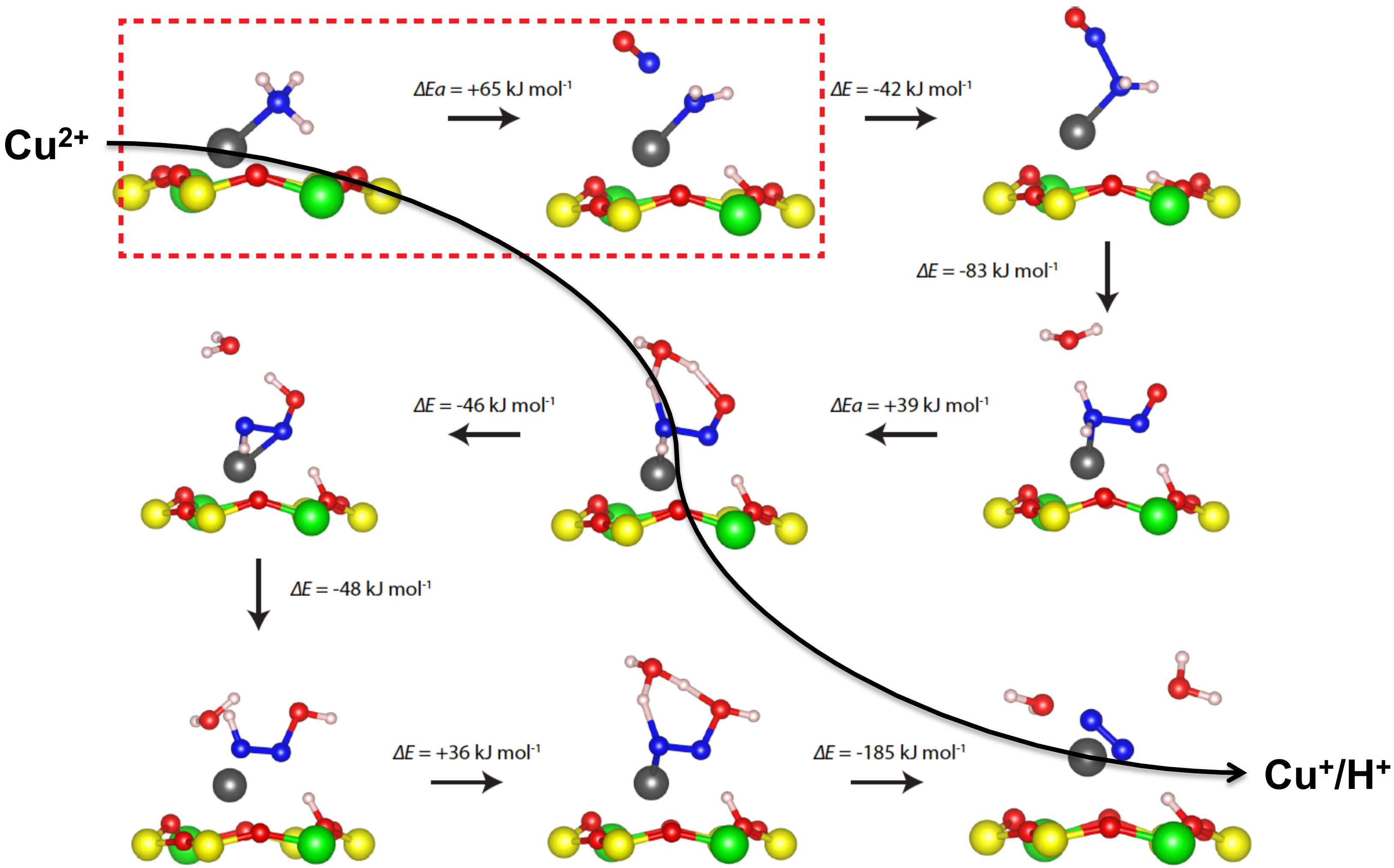


Co-adsorbate induced Cu^{2+} reduction

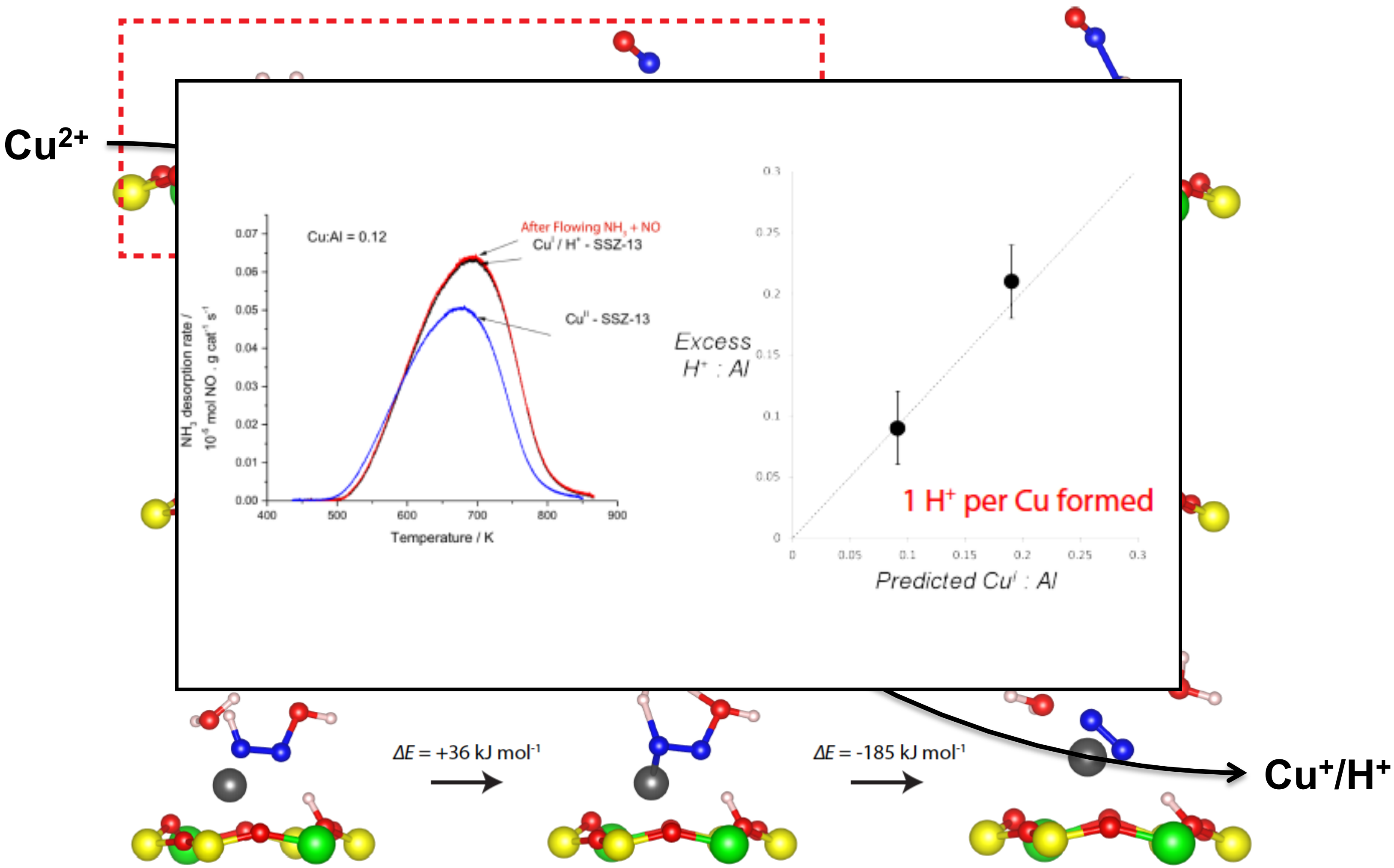


- NO/NH_3 co-adsorption not favored, not reducing
- NO promotes NH_3 dissociative adsorption
  - Reduces $Cu^{2+} \rightarrow Cu^{+}$
  - H_2NNO intermediate familiar from thermal SCR
  - Creates transient Brønsted acid sites
- O_2 does not promote same dissociation
  - Origin of selective NH_3 oxidation

$H_2NNO^* \rightarrow N_2 + H_2O$



$H_2NNO^* \rightarrow N_2 + H_2O$



Cutoff Experiments

Operando XANES
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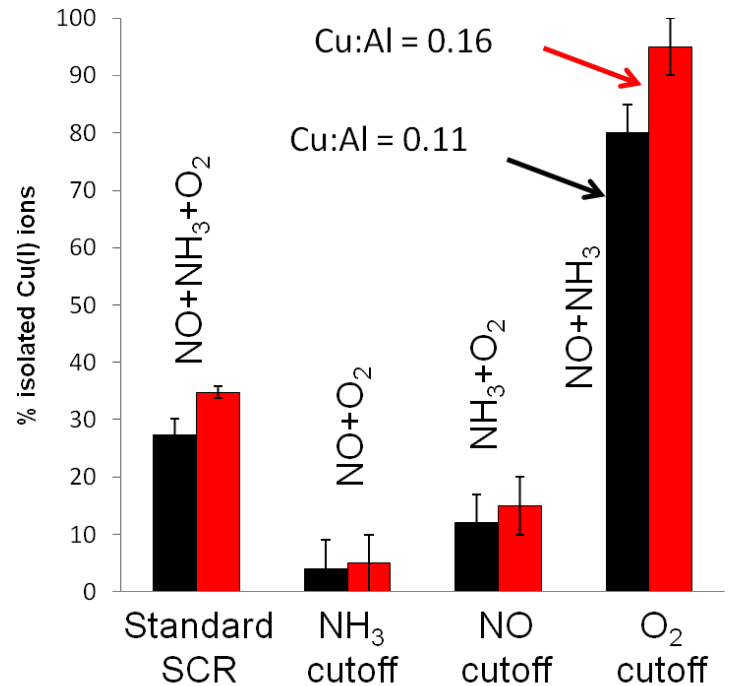
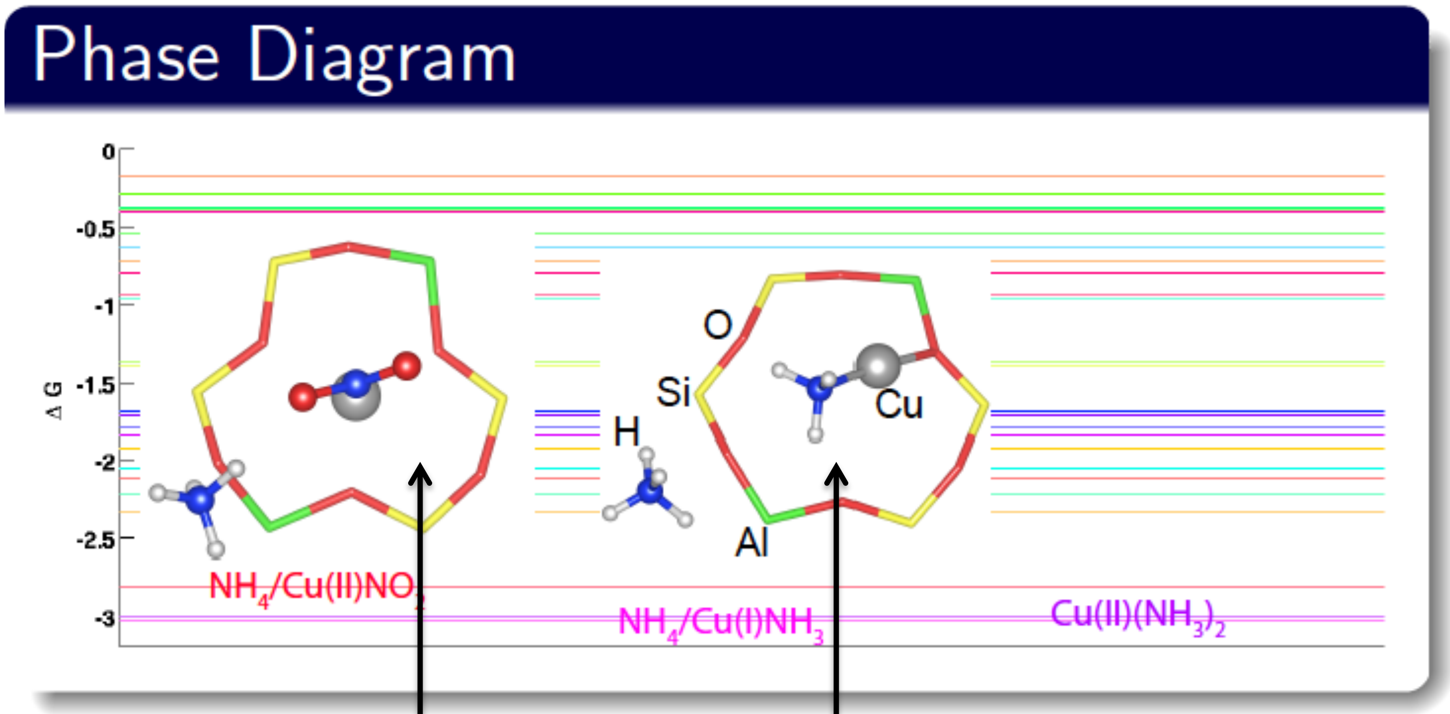


- Activity vanishes and $Cu^+ \rightarrow 1$ with O_2 cut off
- O_2 participates in oxidation half reaction

Thermodynamic screening for intermediates



Co-adsorbed Cu(II)-NO_2 and NH_4^+

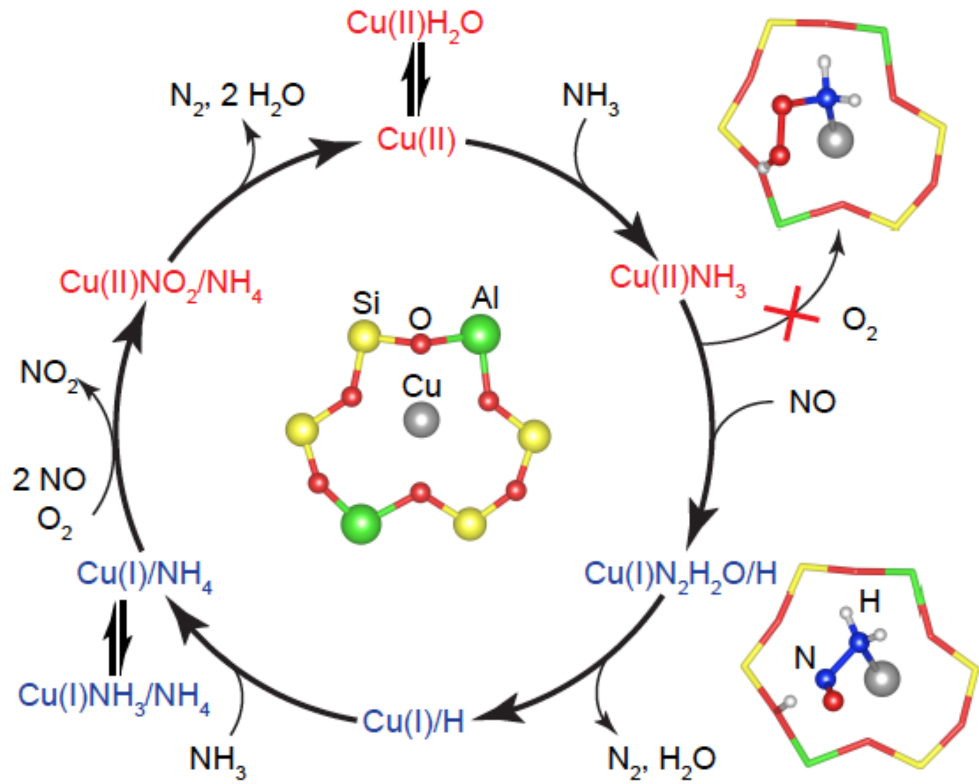
Proper stoichiometry to decompose to N_2 + H_2O

Adsorbed Cu(I)-NH_3

Consistent with observed NH_3 inhibition

Z_2Cu SCR Redox Mechanism

- NO_x SCR involves Cu oxidation and reduction half reactions
- Half-reaction rates comparable at 200˚C and standard SCR conditions
- Only proximal Brønsted acid sites are catalytically important
- N_2 generated in each half reaction
- Elementary steps remain to be detailed



Paolucci *et al. Angew. Chemie* **2014**, *53*, 11828

Postscript

- Some (computational and experimental) evidence for
  - a separate NO oxidation site, possibly a Cu_xO_y cluster
- Opportunities
  - Full kinetic model (in process)
  - Sulfur chemistry (in process)
  - Improve low *T* activity by site number/type optimization
  - Improve high *T* activity by tuning site against NH_3 oxidation
  - Other small pore zeolites/SAPOs
  - Other exchanged metals
- Calls into question some of our basic notions of static, single “active sites” in catalysis