Applications of X-Ray Absorption Techniques for Characterization of Metals, Metal Cations, and Metal Oxo Species in Catalysts

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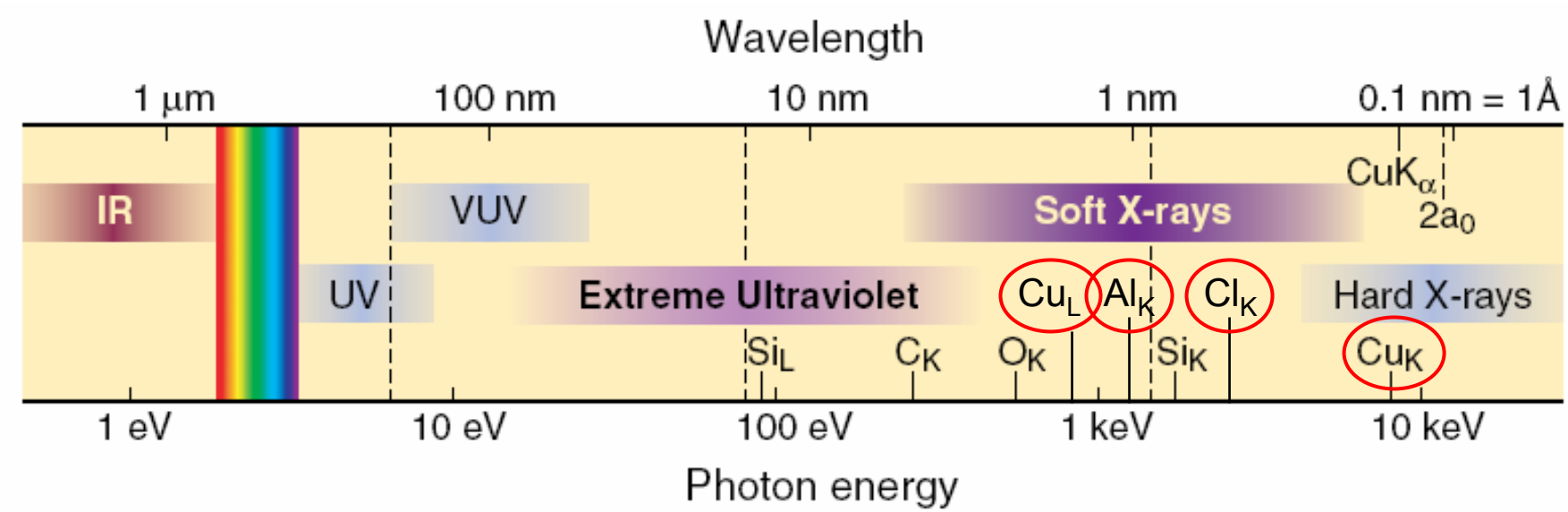
Characterization of Catalytic Active Centers

- Important characteristics
  - nuclearity of active centers
  - connectivity to nearest and next-nearest neighbors
  - geometry of active center
  - changes that occur upon adsorption or reaction
- X-Ray absorption spectroscopy
  - XANES – oxidation state and local coordination
  - EXAFS – local coordination and geometry
- X-Ray imaging
  - Spatial distribution of oxidation states

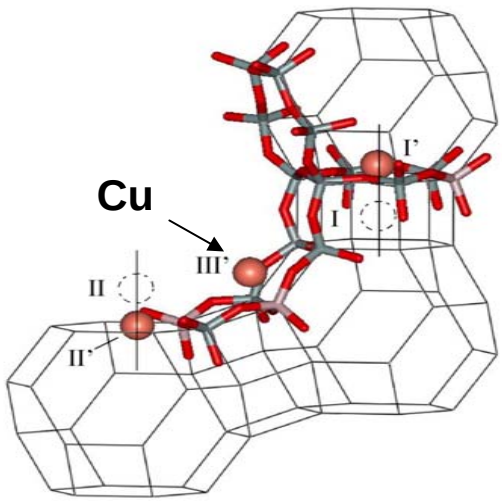
What are “Soft” and “Hard” X-rays?



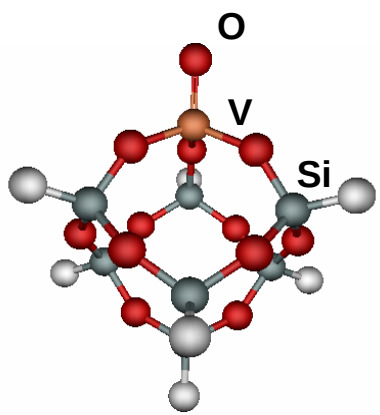
Soft X-rays
- 200 eV→ ~2000 eV
- Oxidation State
- Coordination
- In situ studies limited by short attenuation lengths

Hard X-rays
- 2000eV +
- Oxidation State
- Coordination
- In situ studies not limited by attenuation lengths

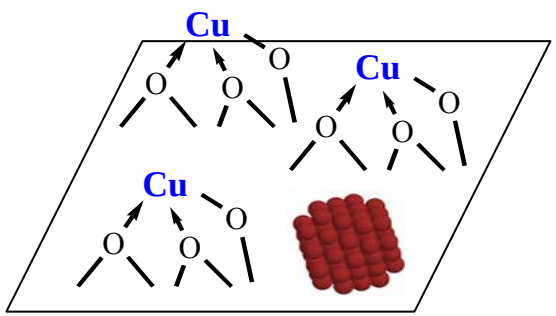
Illustrations



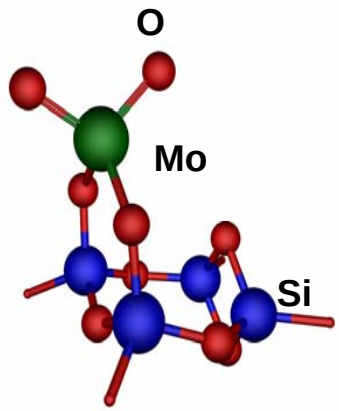
Siting of Cu^+ in Cu-Y and Cu-ZSM-5



Structure of VO_x on SiO_2



Nuclearity of Cu supported on SBA-15



Structure of MoO_x on SiO_2

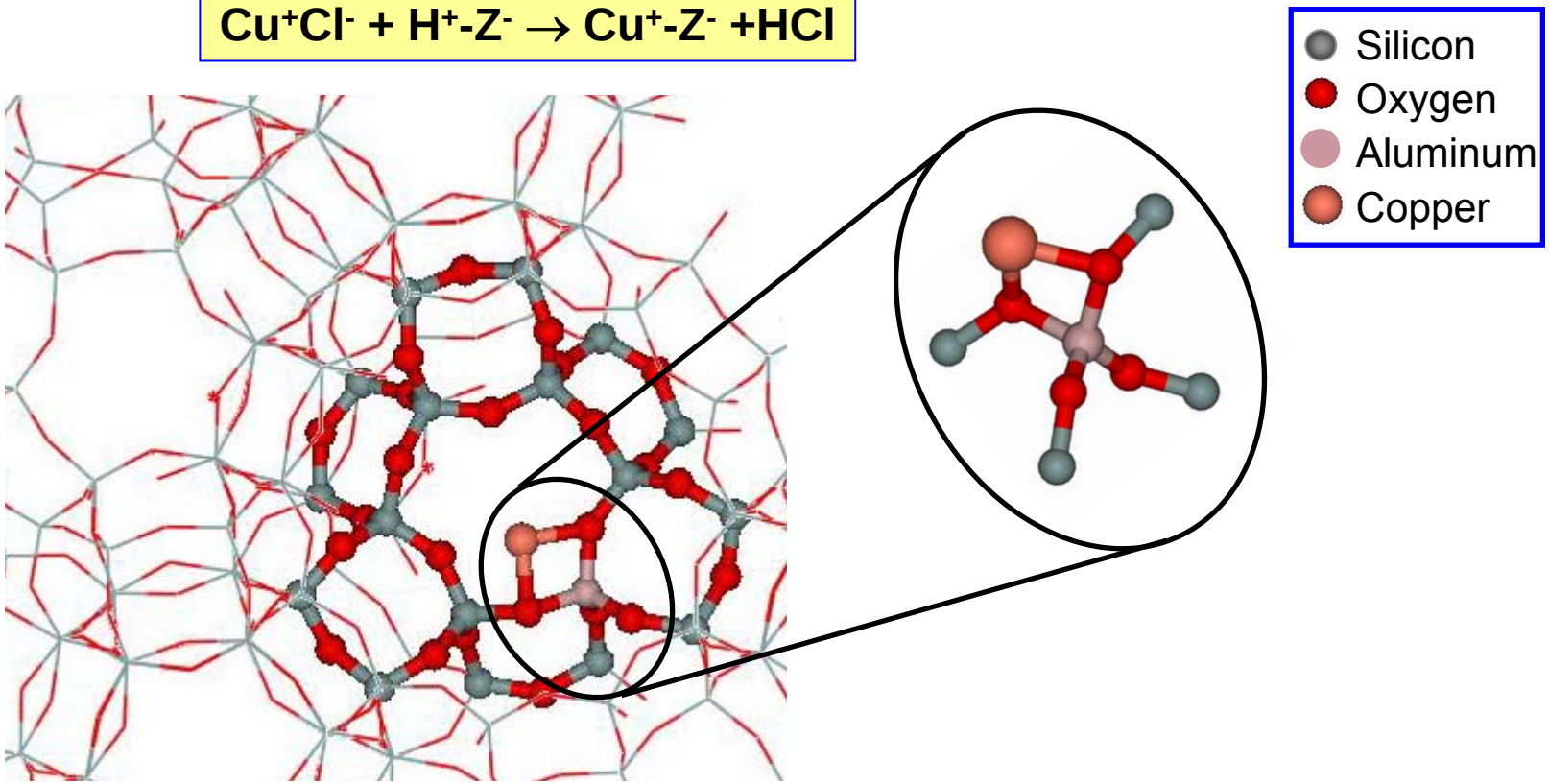
Cu-Exchanged Zeolites

- Cu-exchanged zeolites (Y and ZSM-5) are active catalysts for:
  - NO decomposition and reduction
  - Synthesis of dimethyl carbonate, dimethoxy methane, methyl formate
  - Desulfurization of diesel fuel
- The oxidation state, nuclearity, and local environment of Cu cations in zeolites is strong function of the exchange chemistry
- For structure-function studies, it is essential to obtain a complete picture of the oxidation state and local environment of Cu cations
- X-Ray absorption spectroscopy using hard and soft x-rays can provide the needed information

Cu-Exchanged Zeolite

- **Cu-Y, Cu-ZSM-5, and Cu-Mord were prepared by solid-state exchange (SSIE)**

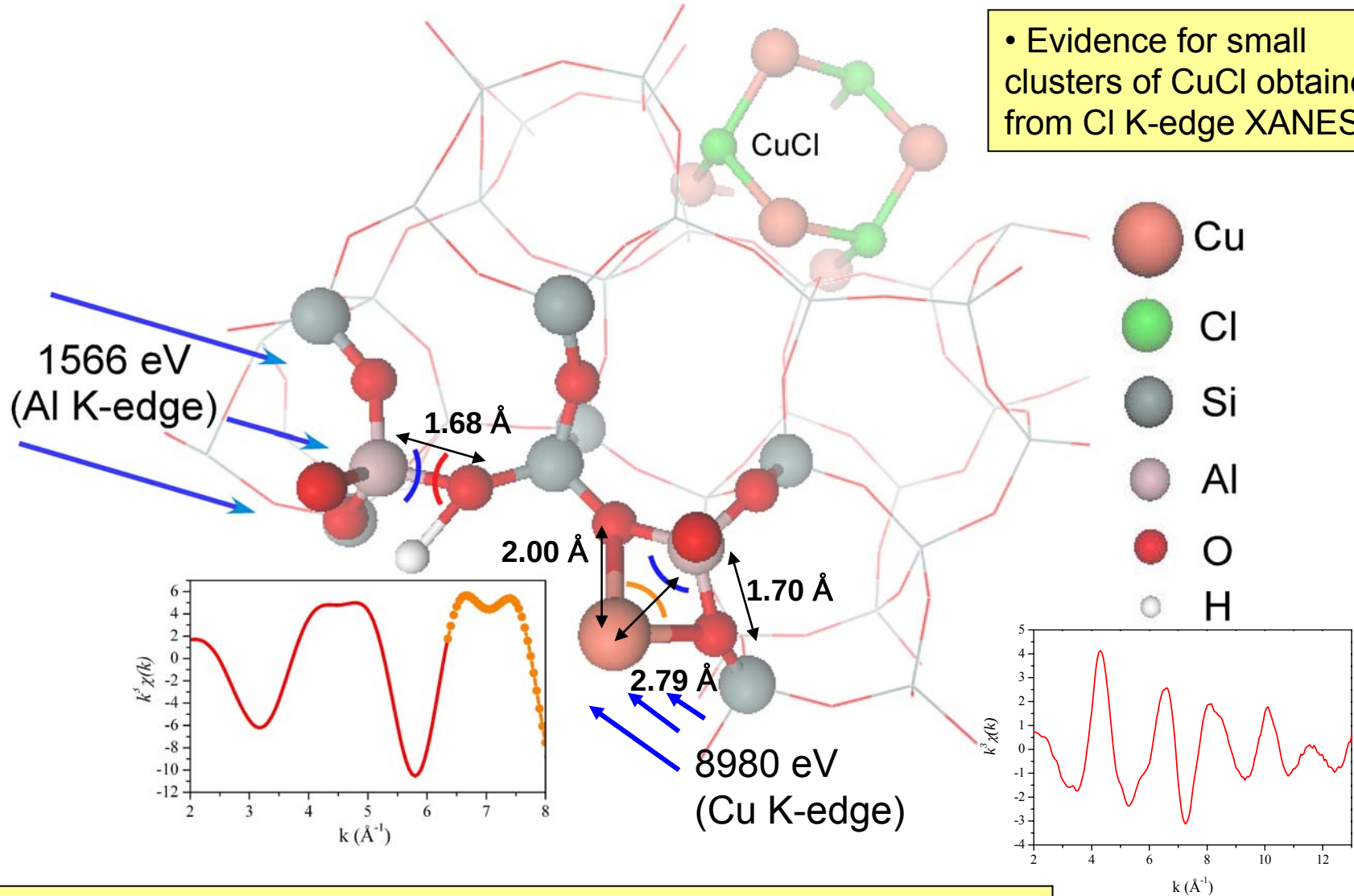
$$Cu^{+}Cl^{-} + H^{+}\text{-}Z^{-} \rightarrow Cu^{+}\text{-}Z^{-} + HCl$$



- What is the local structure and oxidation state of Cu?
- Is CuCl occluded in the pores?
- Does the coordination of Cu^{+} change upon adsorption of CO?

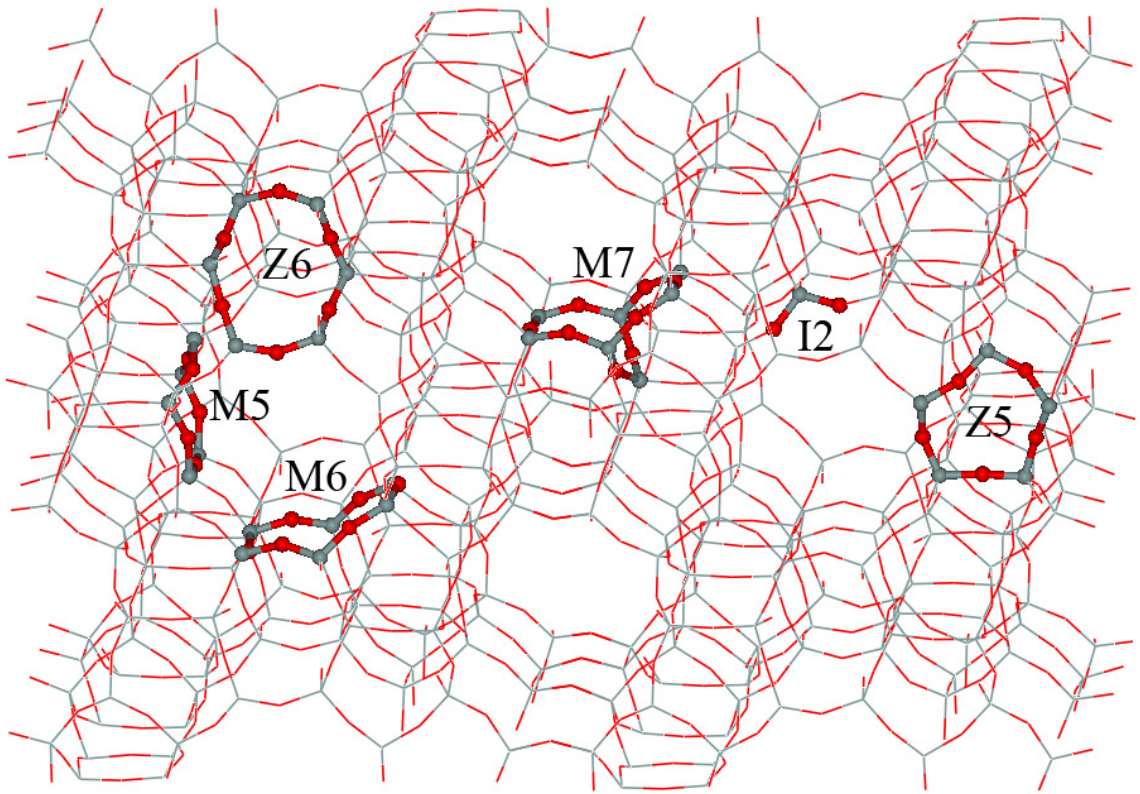
Cu and Al Site Geometries from Cu and Al EXAFS

- Evidence for small clusters of CuCl obtained from Cl K-edge XANES

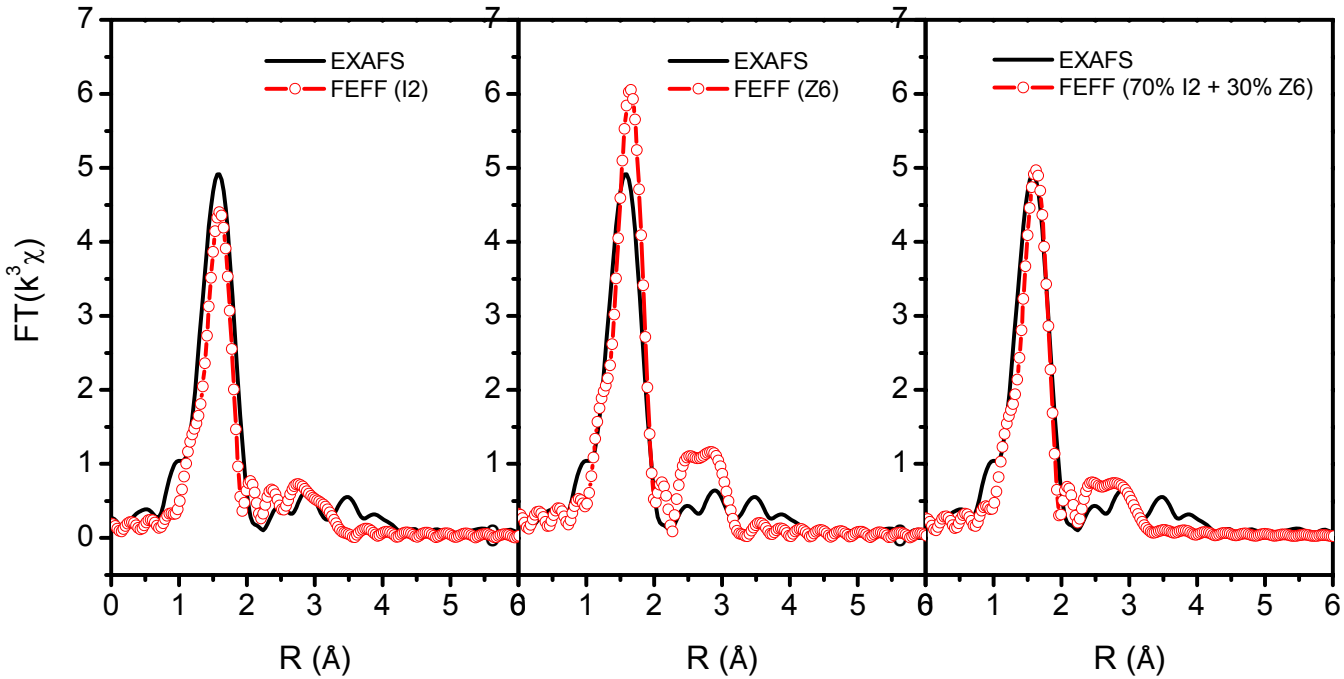


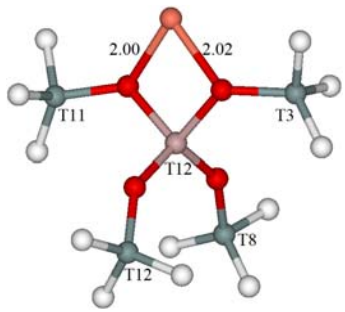
- Cu and Al EXAFS provide an average view of site geometery

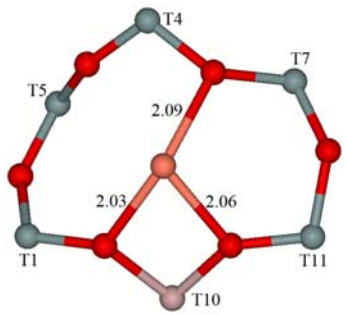
Possible Cations-Exchange Sites in ZSM-5



Distribution of Cu^+ Sites in ZSM-5

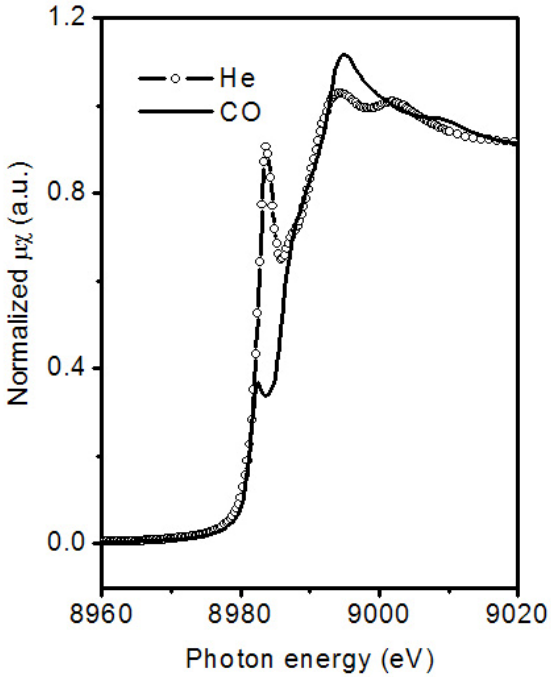


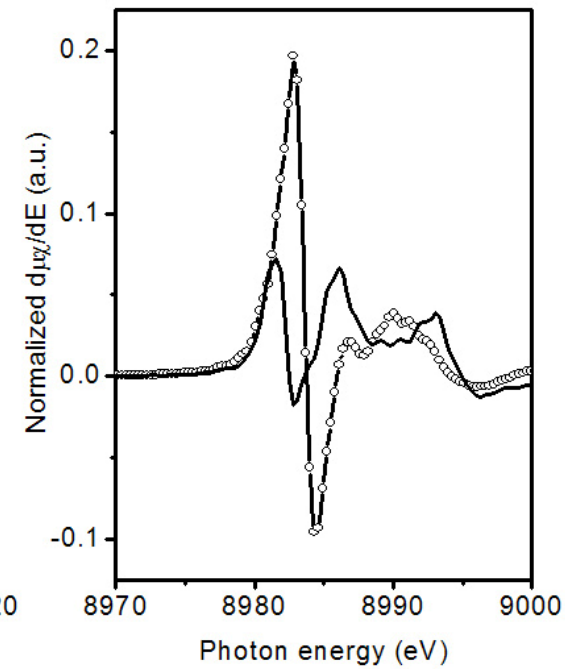


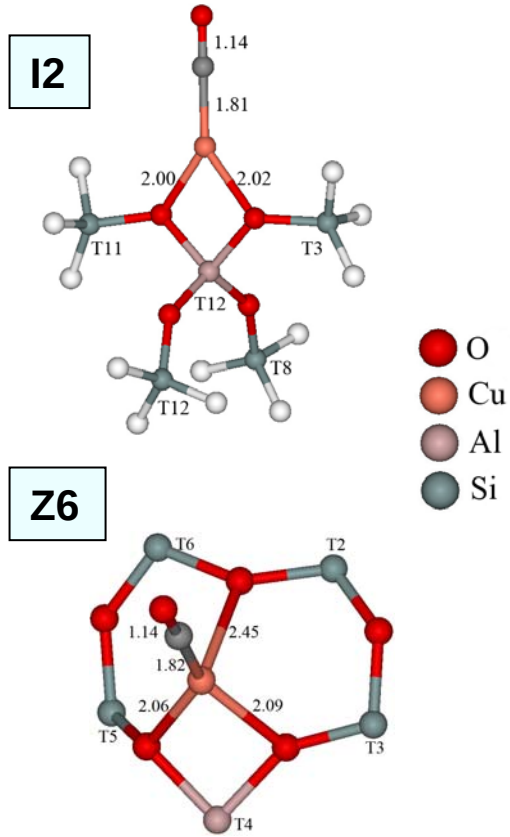


- Simulation of the EXAFS pattern suggest that 70% of Cu^+ is in I2 sites and 30% in Z6 sites

Change in Cu^+ Coordination upon CO Adsorption in Cu-ZSM-5

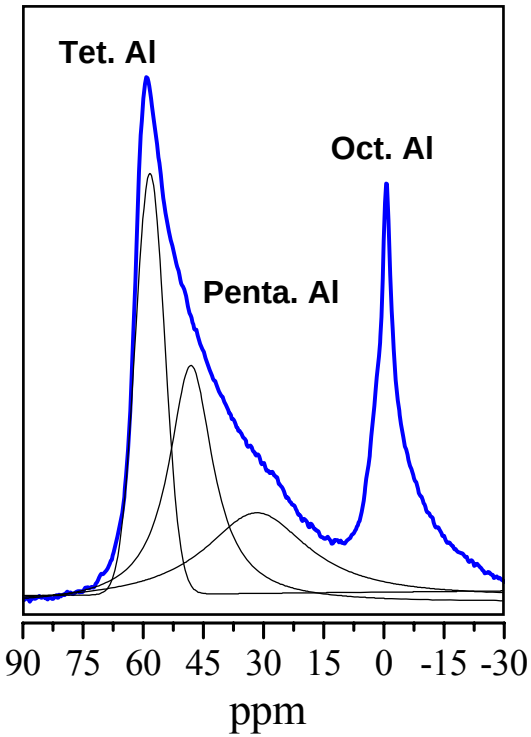


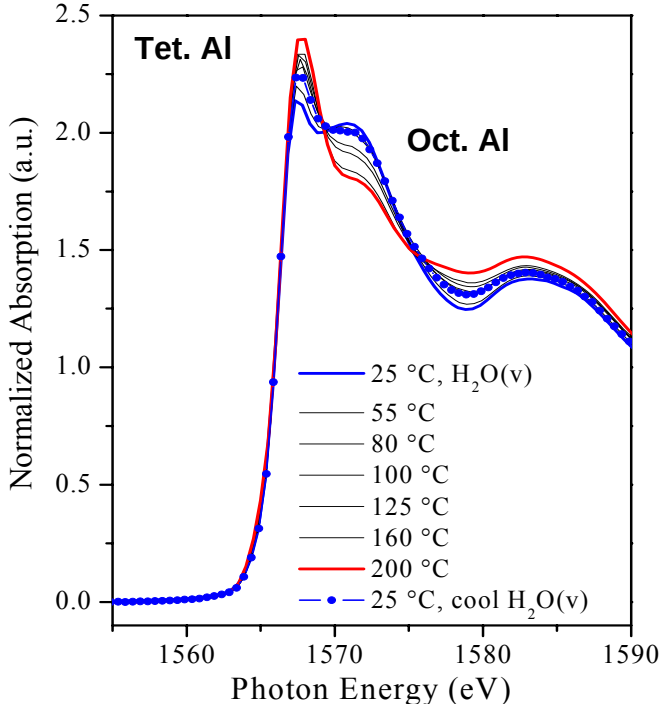


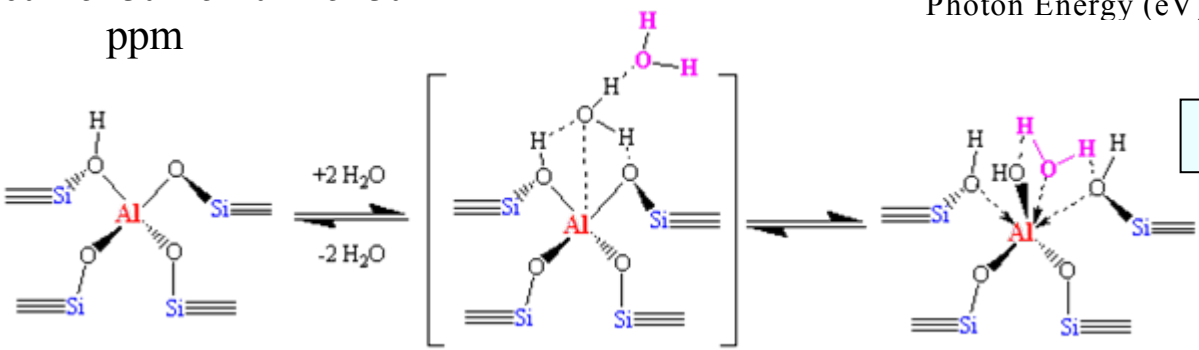


- Position of preedge feature is characteristic of Cu^+
- CO adsorption increases the total coordination of Cu^+ from 2 to 3, causing a decrease in the intensity of the preedge XANES feature

Al Coordination change in H-USY







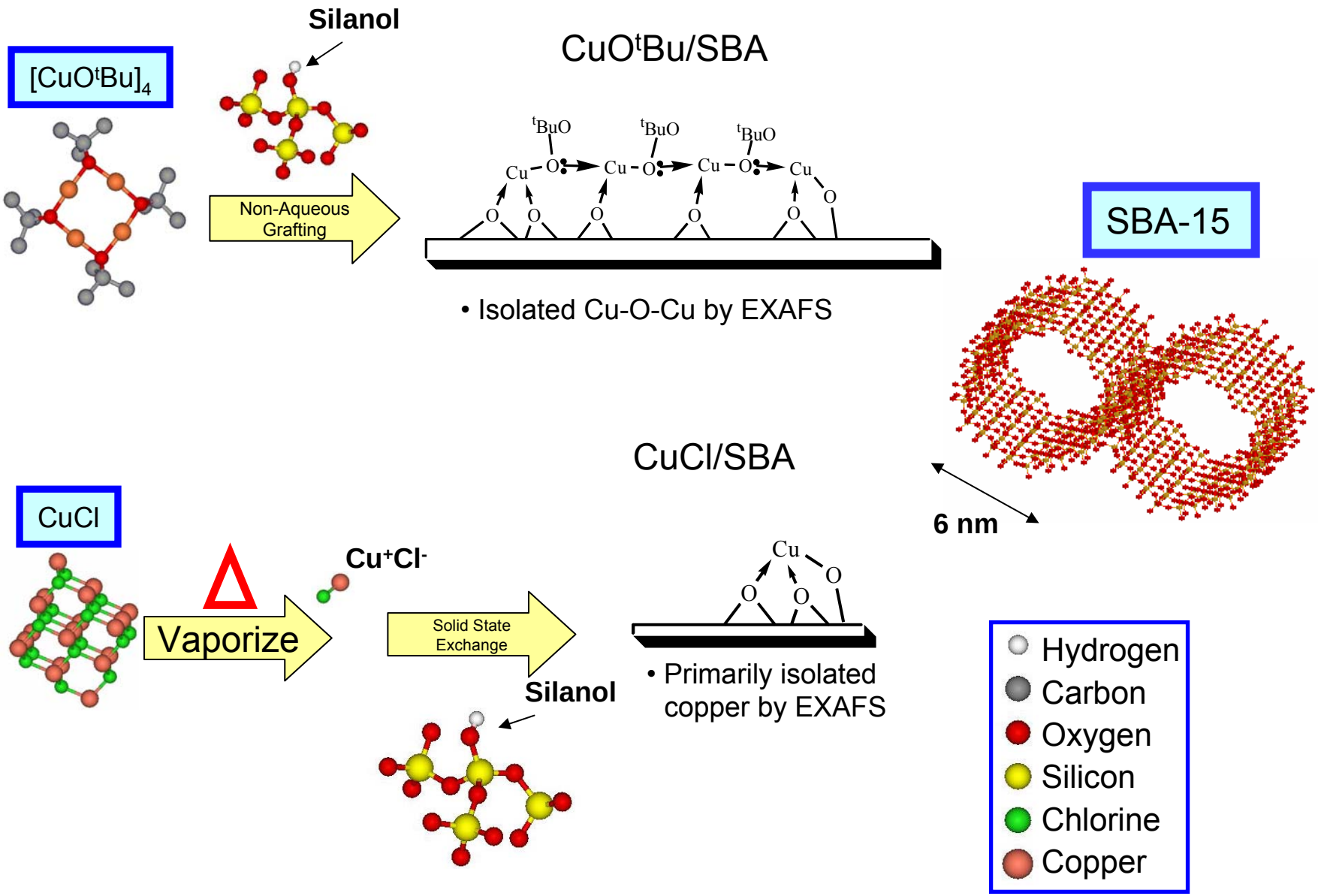
[H_2O]/[Al] = 2

Tetrahedral Al

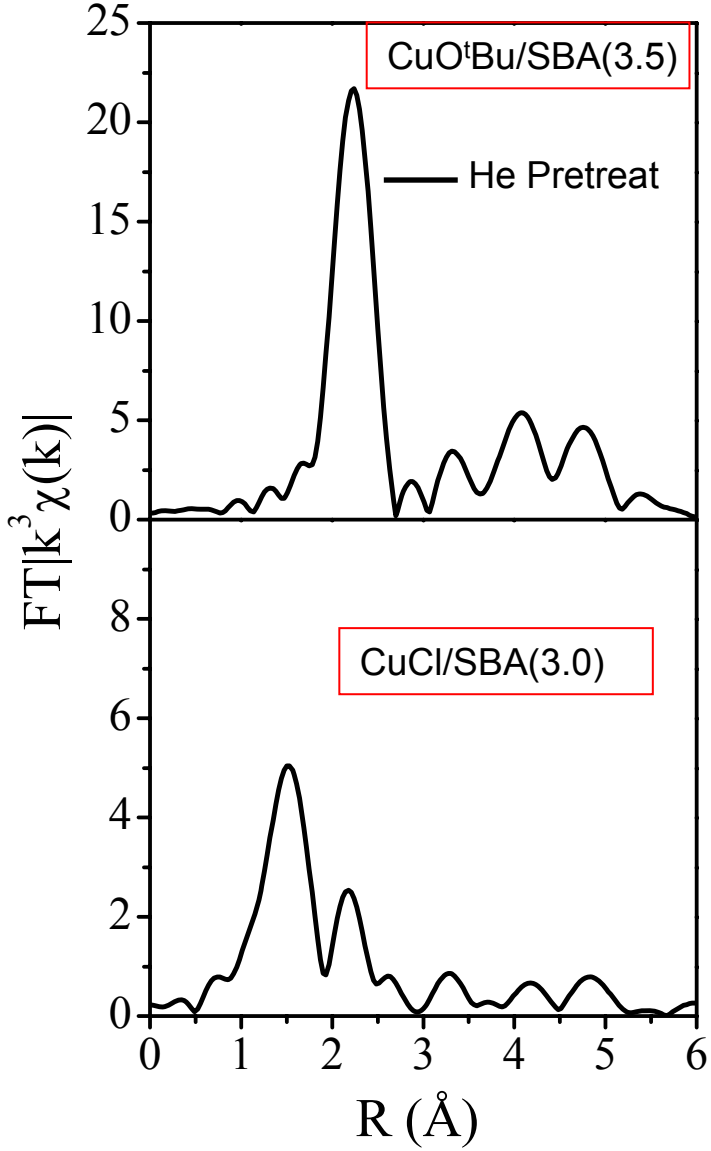
Octahedral Al

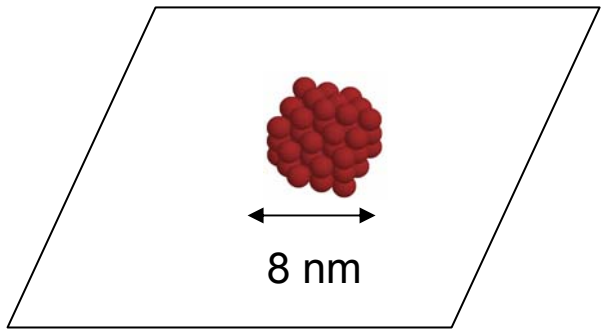
Dehydration

Preparation of Cu/SBA-15

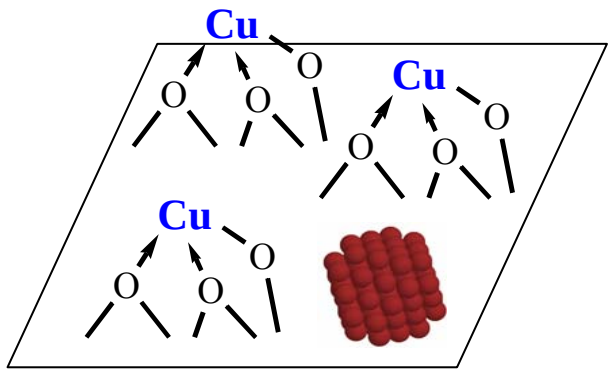


Local Cu after He pretreatment at 673 K





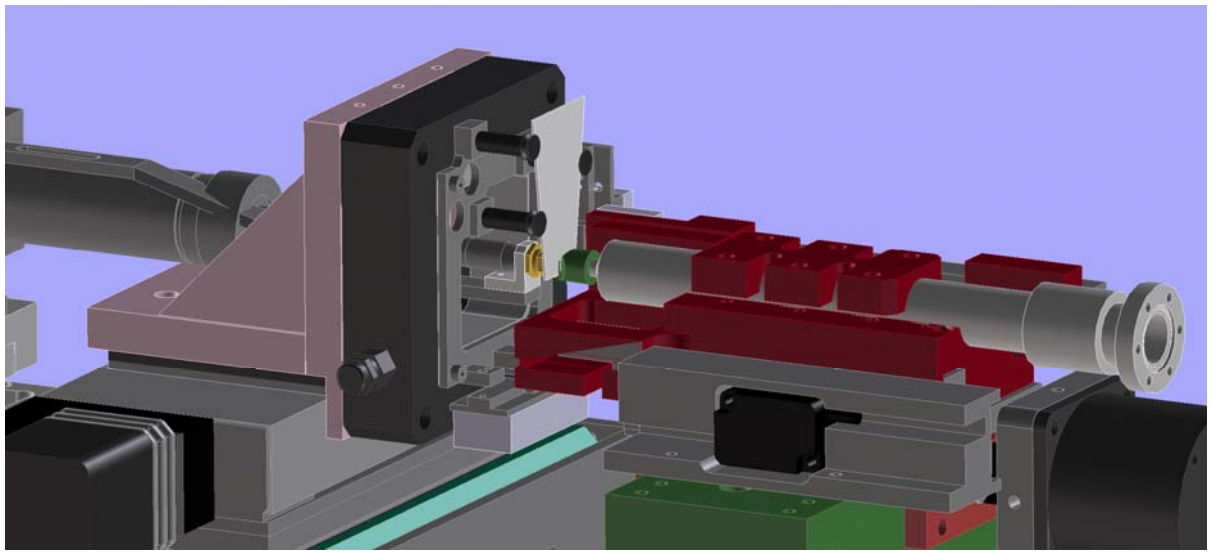
100% of Cu is in the particle form



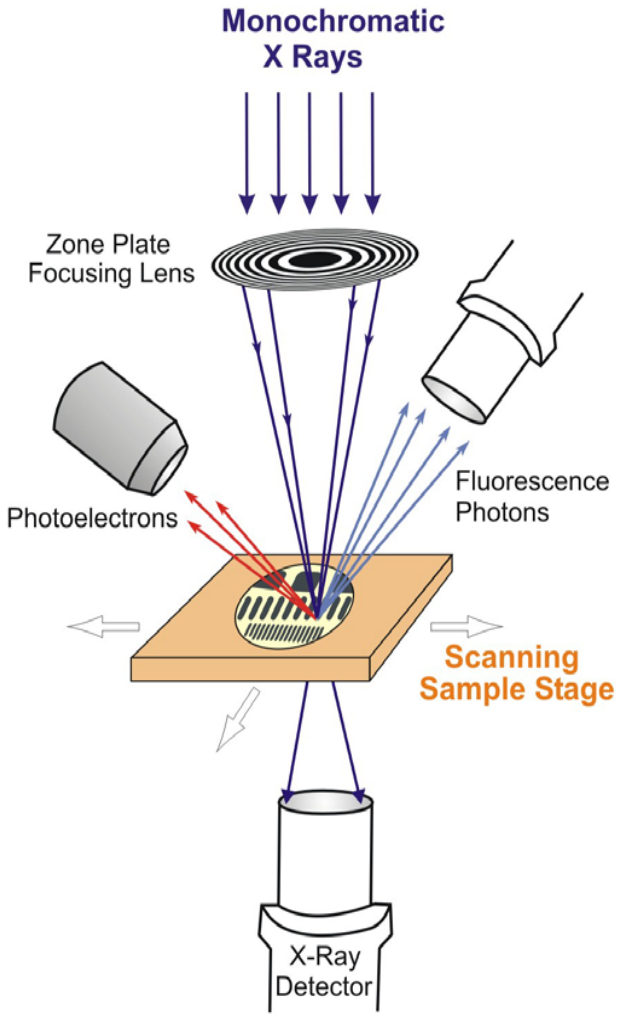
90% of Cu is in the atomic form

Scanning Transmission X-ray Microscope (STXM)

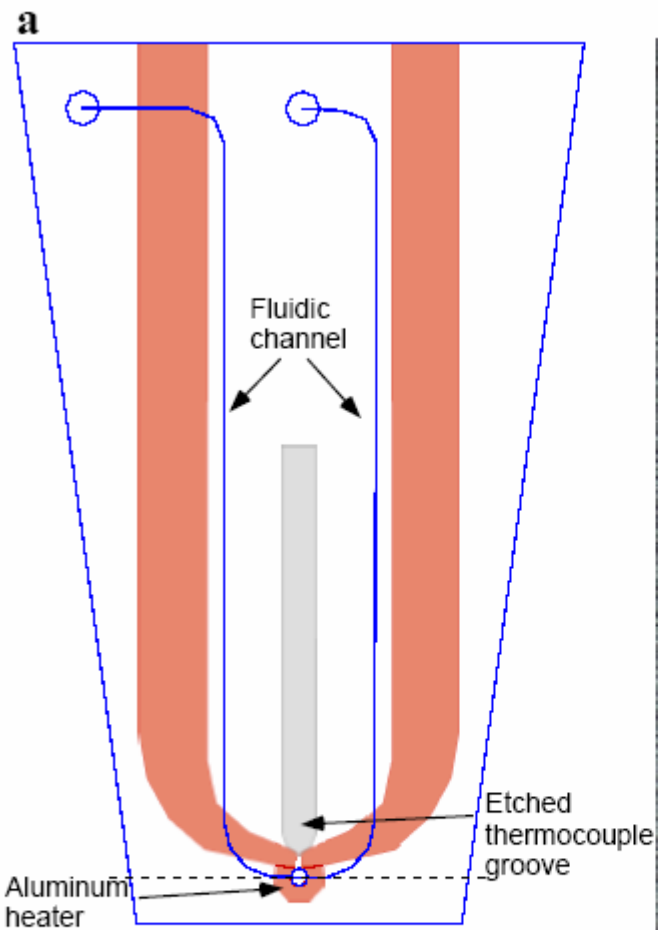
- Ability to image individual catalyst particles and collect local spectrum
- X-ray absorption spectra of individual particles can be compared to the bulk absorption of catalysts by removal of the Zone plate

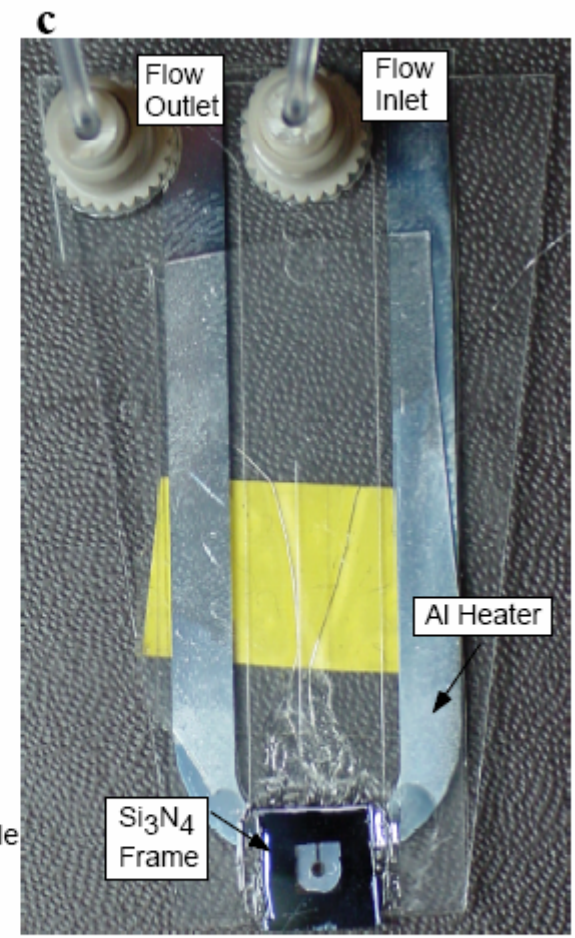


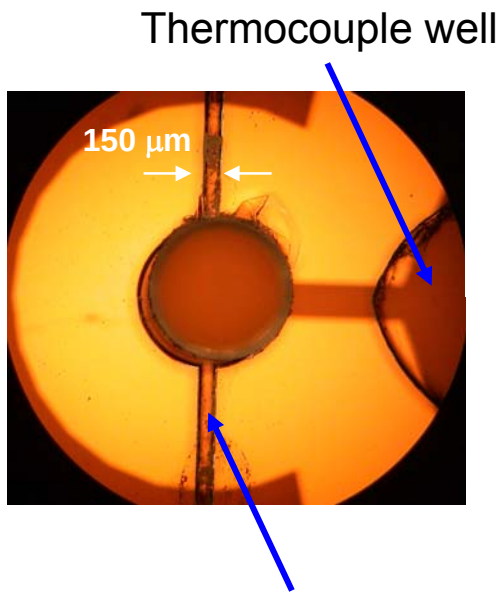
- 40 nm beam size
- 200 – 2000 eV

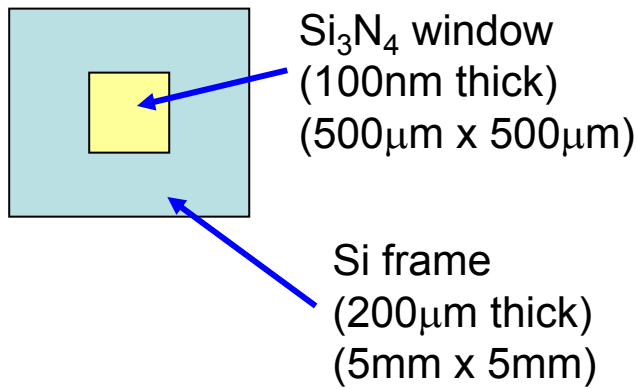


In-Situ Cell for Soft X-Ray Studies

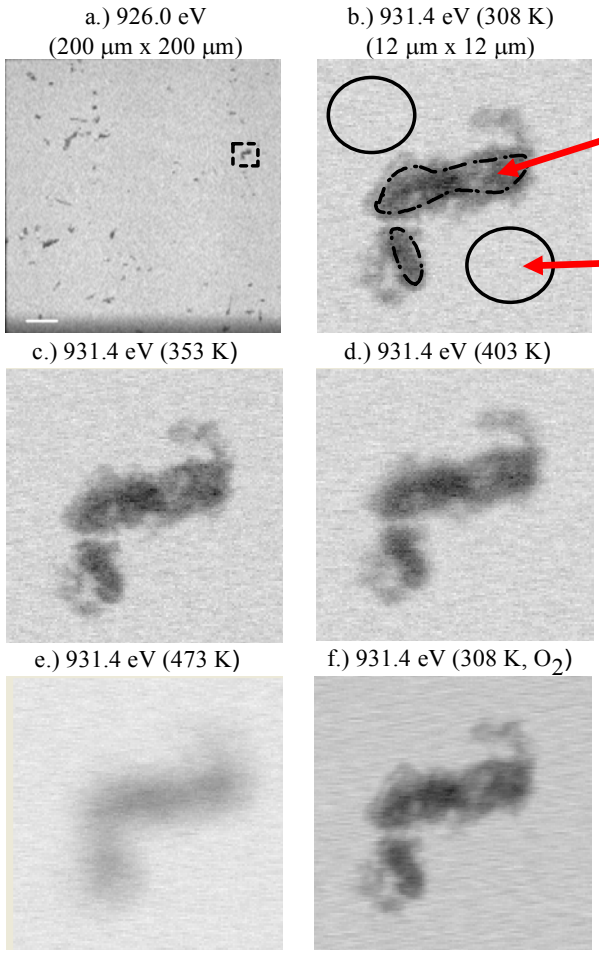








In-Situ STXM applied to the Reduction of Cu cations on silica from Cu(II) to Cu(I)



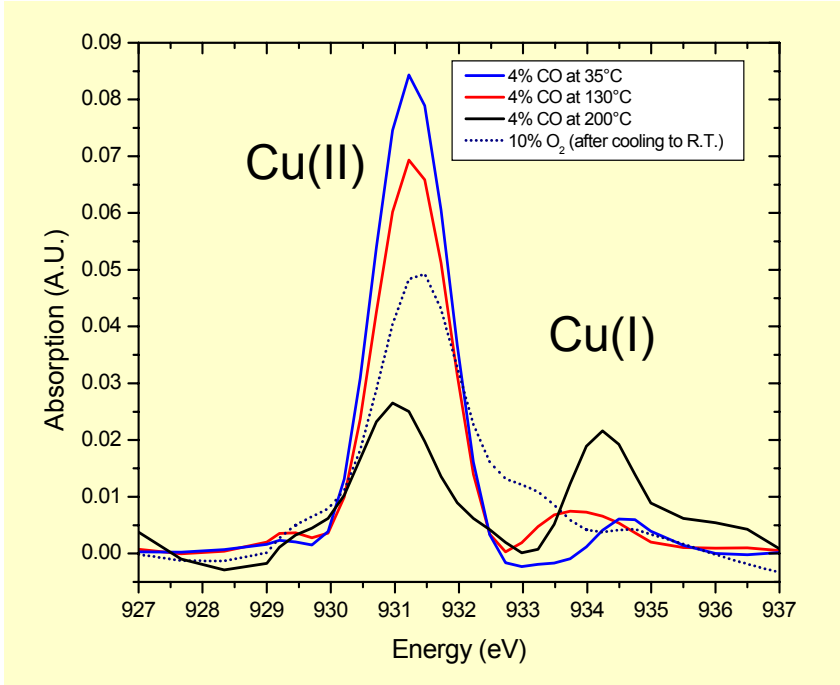
$\bar{I}$

$\bar{I}_0$

$$A = \ln(\bar{I}_0/\bar{I})$$

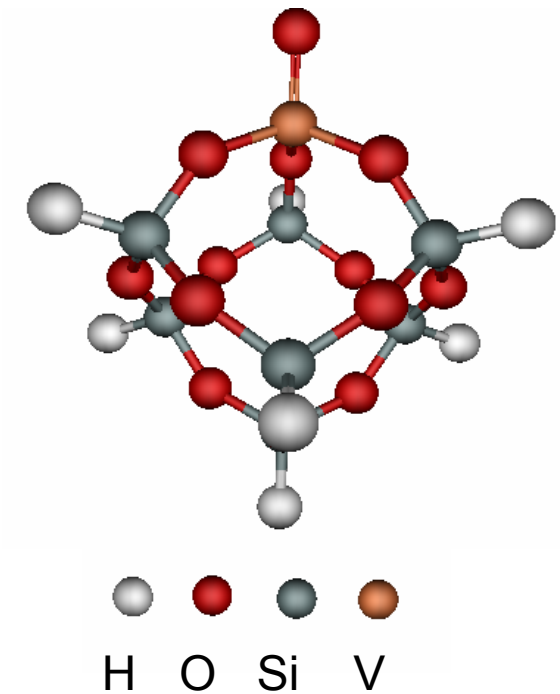
STXM images of Cu/SBA-15 taken at the Cu^{2+} peak

$$CO + 2CuO \rightarrow Cu_2O + CO_2$$



In situ L_3 edge XANES of Cu/SiO_2 taken during CO reduction and O_2 oxidation: P = 1 atm; T = 35-200°C

A Model for Isolated Vanadate Species



	Theory	Experiment
r(V=O)	1.58 Å	1.58±0.03 Å [a]
r(V-O)	1.76 Å	1.79±0.02 Å [a]
ν(V=O)	1035 cm^{-1}	1030-1040 cm^{-1} [a]
ν(V-O-Si)	991 cm^{-1}	980 cm^{-1} [a]
D_1 band	506 cm^{-1}	495 cm^{-1} [b]
D_2 band	611 cm^{-1}	606 cm^{-1} [b]

[a] <1 V/nm^2 on VO_x/SiO_2: Bronkema, J.; Bell, A. T. *J. Phys. Chem. C* **2007**, *111*, 420

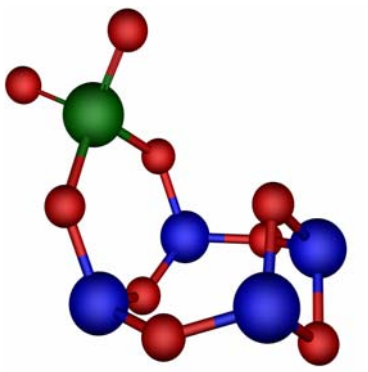
[b] Amorphous SiO_2: Phillips, J. C. *Phys. Rev. B* **1986**, *33*, 4443 & **1987**, *35*, 6409

- VO_4 attached to silsesquioxane is a good model for VO_x/SiO_2

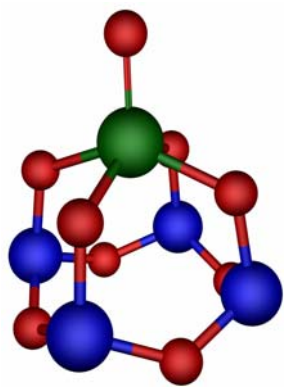
A. Goodrow and A. T. Bell, J. Phys. Chem. C, 2007

Structural Models for Isolated MoOx Species

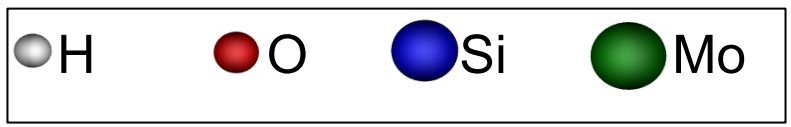
- Isolated molybdate species have been described to be either di-oxo or mono-oxo species based on experimental observation
- Theoretical calculations show that both species are possible



Di-oxo species

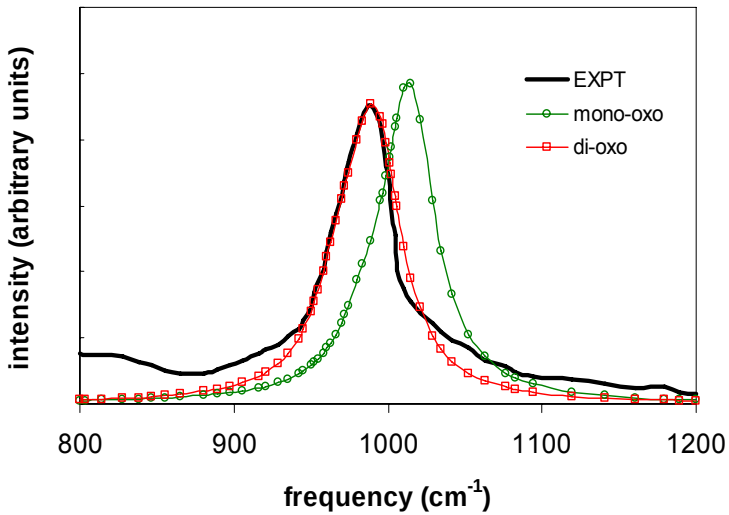


Mono-oxo species

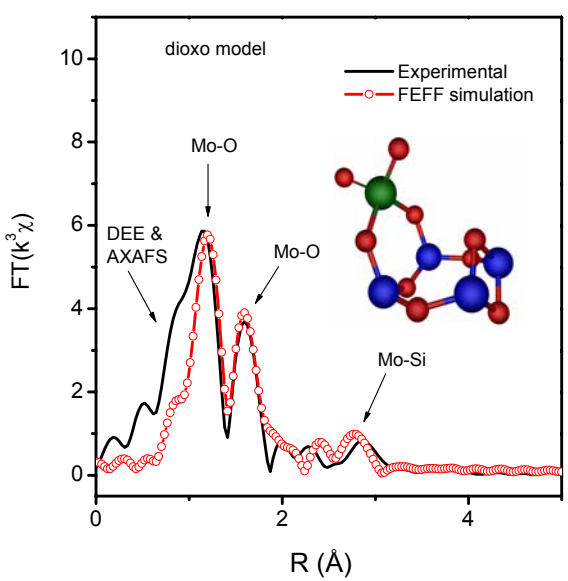


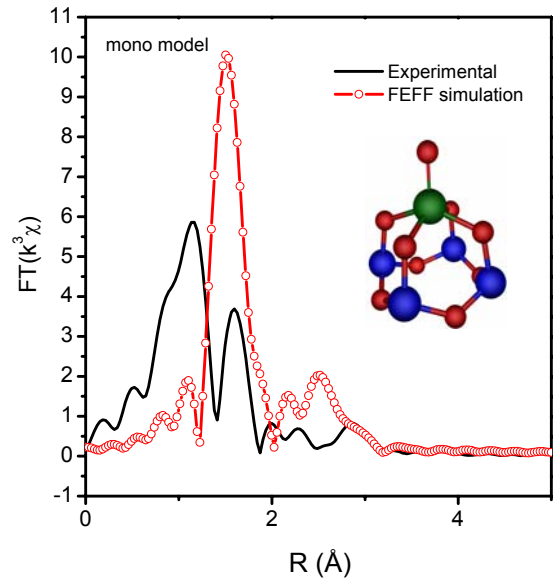
- The structural form of isolated molybdates can be determined by simulating both structures and comparing calculated properties with those observed experimentally

Structure of Isolated MoO_x Species on SiO_2



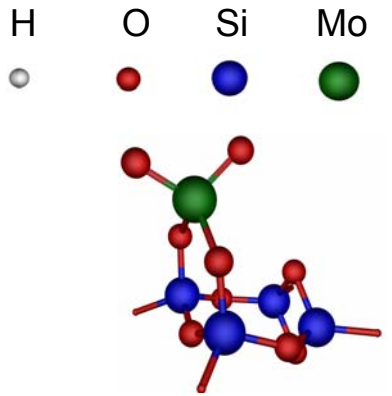
- Simulations of EXAFS and Raman data are based on quantum chemical predictions of site geometry and vibrational frequencies





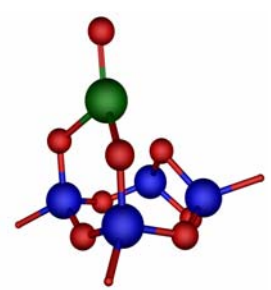
- Comparisons of simulations with experimental data (Raman, XANES, and EXAFS) indicated that isolated MoOx species on SiO_2 are di-oxo structures

Evidence for Dioxo MoO_x Species

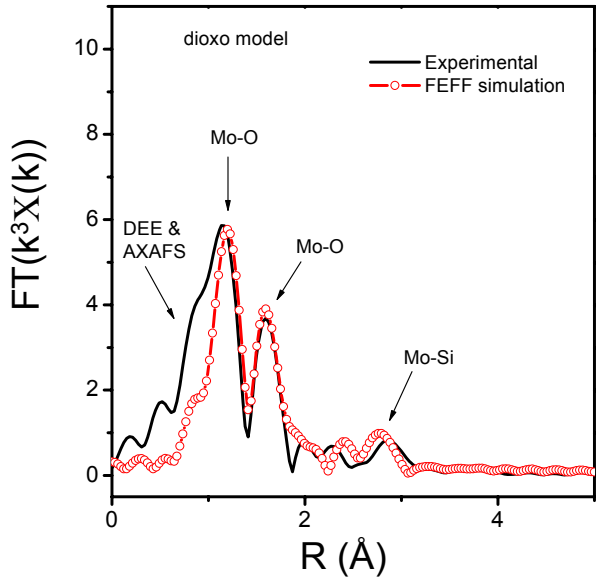


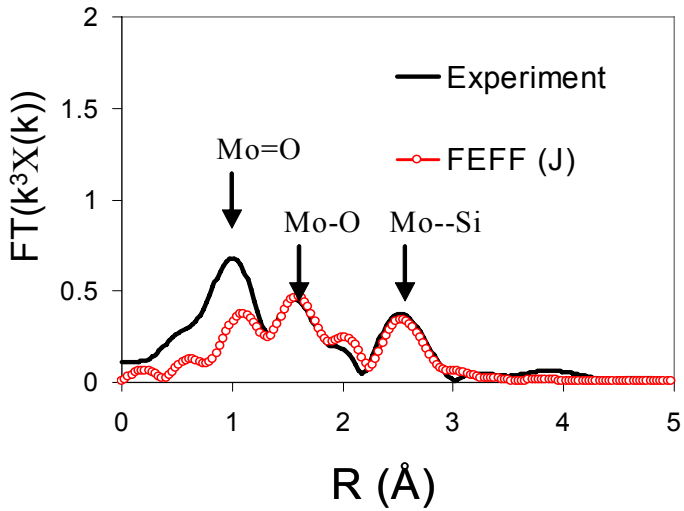
di-oxo [$=Mo(=O)_2$]

$+H_2$
$-H_2O$



Reduced [=Mo=O]





S. Chempath and A. T. Bell, J. Phys. Chem., **2006**

- Simulation of EXAFS patterns confirm the presence of dio-oxo molybdate species

Conclusions

- XANES provides information on site oxidation state and symmetry before and after interactions with adsorbates
- STXM can be used to image particles at a given oxidation state of an element
- EXAFS provides information on site coordination, geometry and identity of nearest neighbors
- Interpretation of EXAFS data are strongly aided by simulation of x-ray scattering data using models of the absorption site geometry based on quantum chemical calculations

Acknowledgements

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Ian Drake

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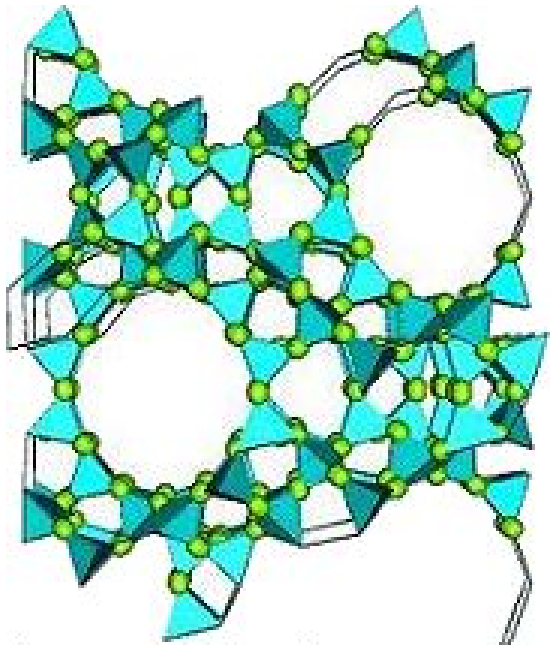
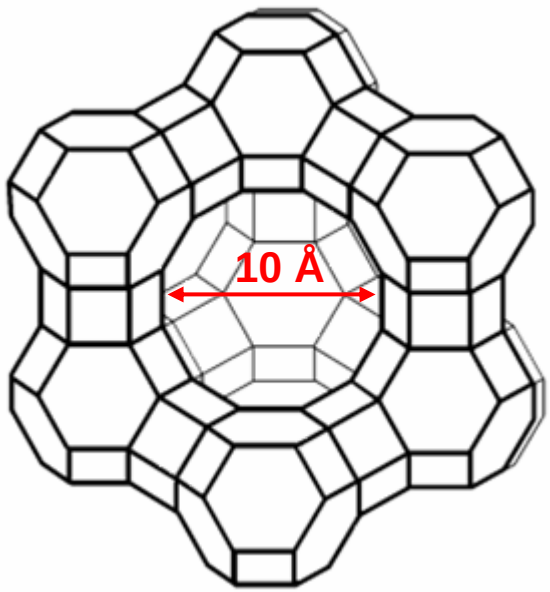
BP Methane Conversion Cooperative

The Framework Structure of Y Zeolite



Corner-sharing tetrahedra – SiO_4^- and AlO_4^{2-}



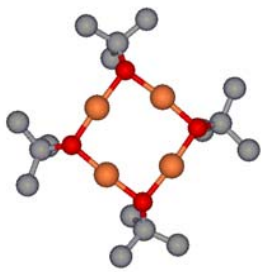
Pore structure

Unit Cell Formula: $H_{52}Al_{52}Si_{140}O_{394}$

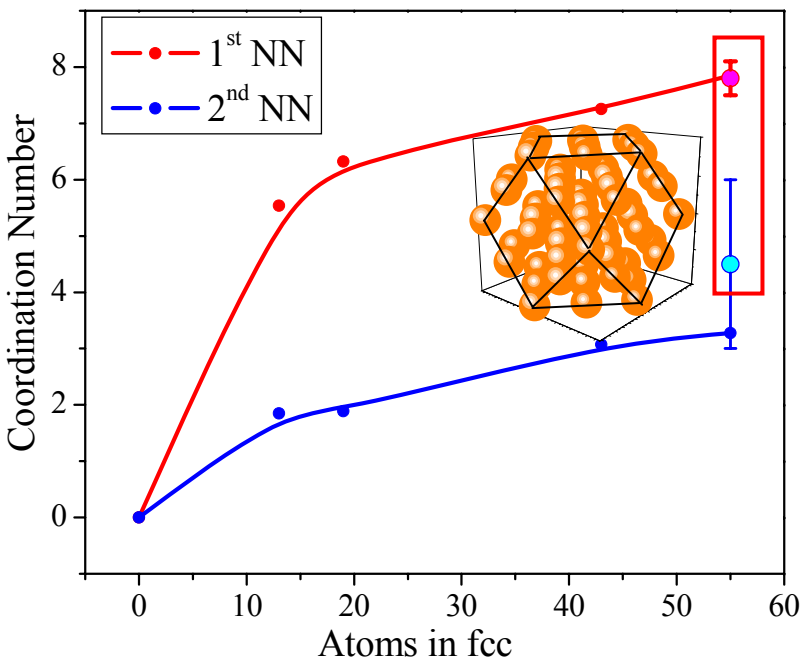
Bronsted acid site: ≡Si-O(**H**)-Al≡

Thermolysis of $[CuO^tBu]_4$ grafted material gives Cu nanoparticles

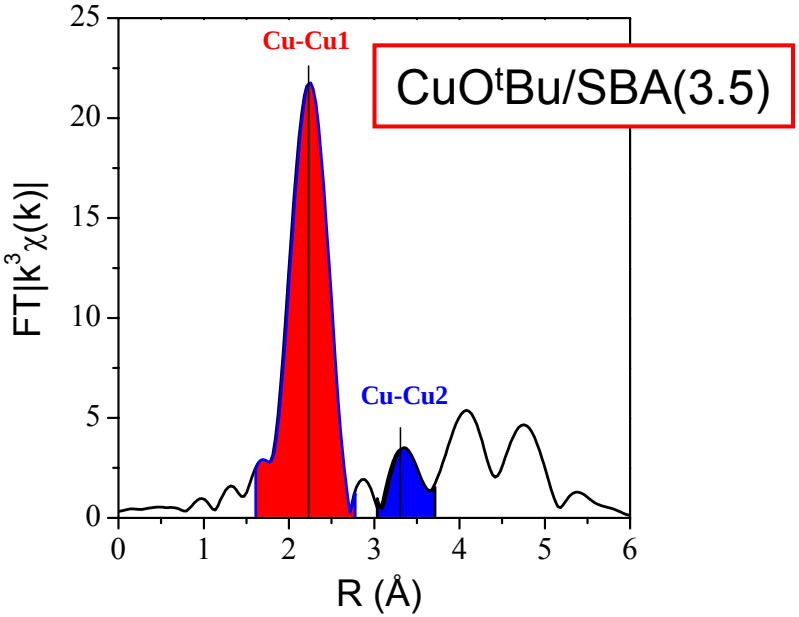
$[CuO^tBu]_4$



Grafted on SBA-15 and heated in He (573 K, 1hr)

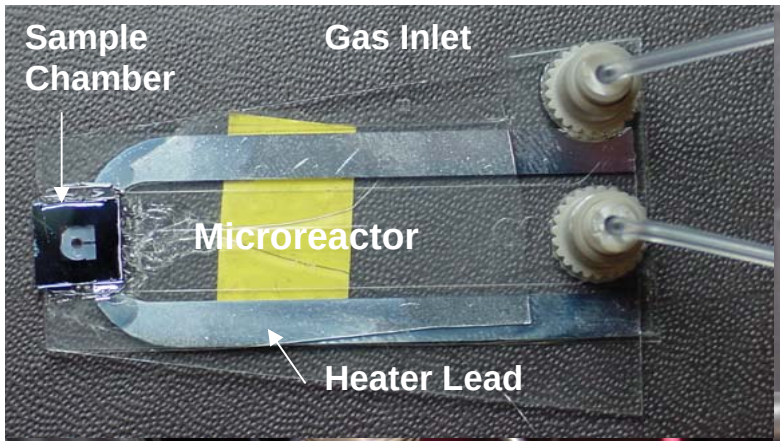


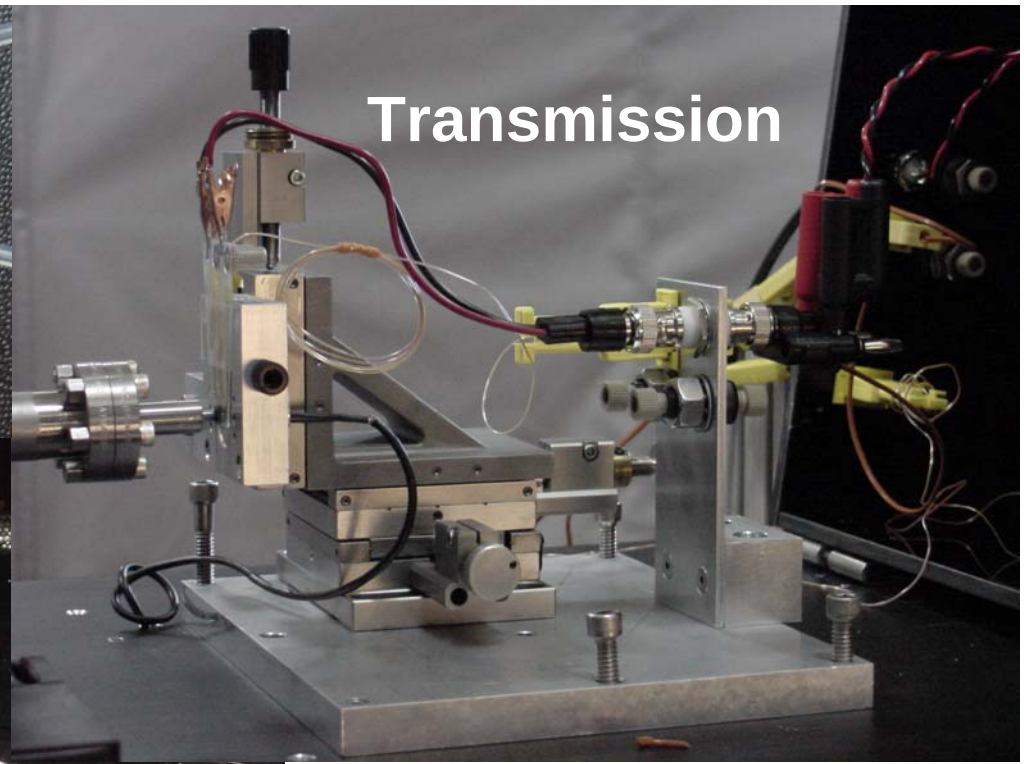
Montano, P. A.; Shenoy, G. K.; Alp, E. E.; Schulze, W.; Urban, J. *Phys Rev. Let.* **1986**, *56*, 2076.

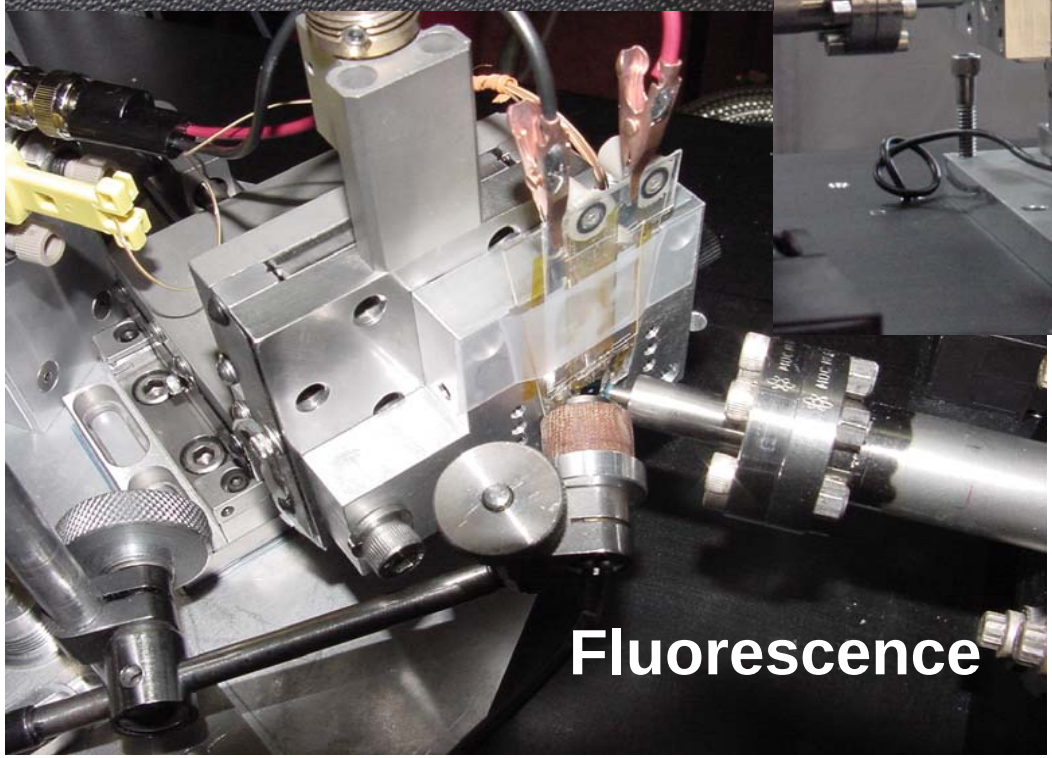


- XANES shows Cu(0) exclusively
- EXAFS matches that of Cu metal
  - $CN_{Cu\text{-}Cu1}$ = 7.8, $R_{Cu\text{-}Cu1}$ =2.52 Å
  - $CN_{Cu\text{-}Cu2}$ = 4.6, $R_{Cu\text{-}Cu2}$ = 3.58 Å
- Average CN correlates to particle size
- Detailed analysis suggests small Cu clusters of 55 atoms

Set Up for In-Situ Al K-edge XANES and EXAFS





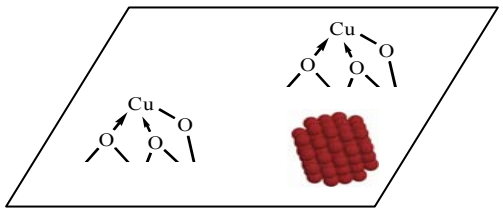


In situ Al K-edge XANES and EXAFS data can be acquired in either transmission or fluorescence mode at BL 9.3.1

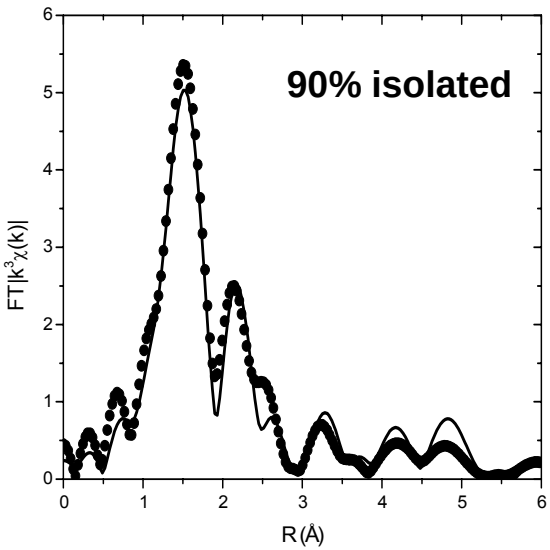
“Proof-of-Concept” Confirmed: In Situ Reduction of Cu(II)

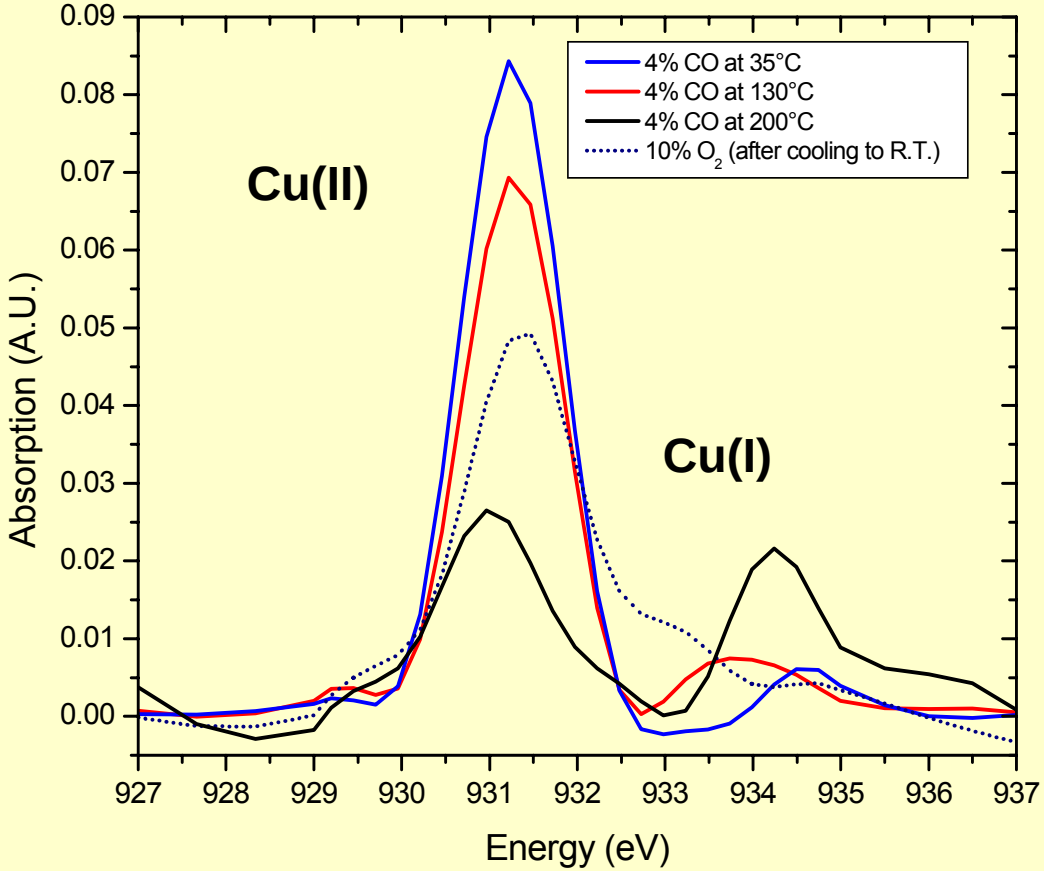
CuCl/SBA-15

Structural Cartoon



EXAFS evidence





In situ L_3 edge XANES of Cu/SiO_2 taken during CO reduction and O_2 oxidation: P = 1 atm; T = 35-200°C