Supplementary Information

Augusta Bianca Ene Matthias Bauer Tanja Archipov

Emil Roduner*

May 25, 2010

1 EXAFS Experimental Details and Data Evaluation Procedure

XAS measurements were performed at beamline E4 at the Hamburger Synchrotron Strahlungslabor (HASYLAB) under ambient conditions at 293 K. A Si(111) double crystal monochromator was used for measurements at the Cu K-edge (8.979 keV). The second monochromator crystal was tilted for optimal harmonic rejection. The energy resolution for the Cu K-edge energy is estimated to be 3.0 eV. The spectra were recorded in transmission mode with ionisation chambers filled with nitrogen. The individual pressures were adjusted to optimize the signal to noise ratio. Energy calibration was performed with a copper metal foil, which was measured simultaneously with the samples between the second and third ionisation chamber. To avoid errors in the XANES region due to small changes in the energy calibration between two measurements, all spectra were calibrated to the edge position of the copper foil. The solid samples were embedded in an oxygen-free cellulose matrix and pressed into pellets. Since the copper loading of the liquid ion exchanged samples was an order of magnitude lower than that of the solid state ion exchanged samples, only solid state ion exchanged Cu/HZSM5 samples were analyzed (ZSM500 and ZSM700).

Data evaluation started with background absorption removal from the experimental absorption spectrum by subtracting a Victoreen-type polynomial. Due to several inflection points in the absorption edge, the threshold energy E_0 was determined consistently by taking the energy at half the edge jump [1,2]. For copper metal, this procedure causes a shift of the energy scale in comparison with most published data by around 5 eV. Since all spectra were corrected in a consistent way, this shift does not lead to misinterpretations. To determine the smooth part of the spectrum, corrected for pre-edge absorption, a piecewise polynomial was used. It was adjusted in such a way that the low-R components of the resulting Fourier transform were minimal. After division of

*Institute of Physical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany. e.roduner@ipc.uni-stuttgart.de

the background-subtracted spectrum by its smooth part, the photon energy was converted to photoelectron wave numbers k. The resulting χ(k)-function was weighted with k^3 and Fourier transformed using a Hanning window function. Data analysis was performed in k-space with Fourier filtered data. The filtered range was chosen according to the range of significant data and is given in table 1 together with the results of the fitting procedure. Adjustment of the common theoretical EXAFS expression

$$\chi(k) = \sum_j \frac{N_j}{kr_j^2} S_0^2(k) F_j(k) e^{-2k^2\sigma_j^2} e^{-2r_j/\lambda} sin\left[2kr_j + \delta_j(k)\right] \tag{1}$$

(N_j: one type of neighbor atoms j in a shell, r_j: distance of atoms j from the X-ray absorbing atom, S_0^2: amplitude reduction factor, F_j: backscattering amplitude, σ^2: Debye-Waller like factor, δ_j: overall phaseshift) according to the curved wave formalism of the EXCURV98 program with XALPHA phase and amplitude functions[3]. The mean free path of the scattered electrons was calculated from the imaginary part of the potential (VPI set to -4.00 eV). Since XALPHA phases and amplitudes were used, an amplitude reduction factor S_0^2 was necessary to account for inelastic processes[4]. It was determined experimentally from the reference compounds Cu_2O, CuO and $Cu(OH)_2$ to be 0.8±0.1 by setting the coordination numbers to the crystallographic values[5–7]. S_0^2= 0.8 was used for all samples, but the transfer of the reference S_0^2-value to unknown samples can result in rather large uncertainties of the coordination numbers and Debye-Waller-like factors σ. An inner potential correction E_f was introduced that accounts for an overall phase shift between the experimental and calculated spectra. In the fitting procedure, it was taken into account that the number of fitted parameters (N_{pars}) did not exceed the degrees of freedom (N_{ind}) which are calculated according to $N_{ind} = (2\Delta k \Delta R/\pi)$[8]. The quality of fit is given in terms of the R-factor according to[9]

$$R = \sum \frac{k^3 \left|\chi^{exp}(k_i) - \chi^{theo}(k_i)\right|}{k^3 \left|\chi^{exp}(k_i)\right|} \cdot 100\% \tag{2}$$

Deconvolution of the XANES region was carried out by a least square fit of the spectra using the WINXAS program package[10]. To obtain a good fit, an arctan step function representing the transition of the ejected photoelectron to the continuum in combination with Gaussian functions to model defined transitions were used. All XANES spectra were analyzed in the range of 8.96 - 9.01 keV. No constraints were used, and the fits were repeated several times in order to check the reproducibility of the results.

Table S1: Details of the XANES deconvolution.

Parameter	Cu_{metal} Cu(0)	Cu_2O	CuO	ZSM500	ZSM700
Function	Gaussian	Gaussian	Gaussian	Gauss	Gauss
Height (a.u.)	0.38	0.48	0.44	0.634	0.558
Position (keV)	8.976	8.976	8.980	8.978	8.978
FWHM (keV)	0.00596	0.00458	0.00612	0.0054	0.0053
Area (a.u.)	0.00243	0.00234	0.00286	0.00368	0.00314
Function	Gaussian	Gaussian	Gaussian	Gauss	Gauss
Height (a.u.)	0.21	0.29	0.03	0.077	0.08
Position (keV)	8.987	8.989	8.987	8.988	8.988
FWHM (keV)	0.00494	0.00706	0.00224	0.0097	0.0071
Area (a.u.)	0.00107	0.00214	0.00007	0.00079	0.00061
Function	Gaussian	Gaussian	Gaussian	Gauss	Gauss
Height (a.u.)	0.17	0.16	0.26	0.116	0.159
Position (keV)	8.997	9.006	8.991	8.995	8.994
FWHM (keV)	0.00853	0.02059	0.00979	0.0092	0.0093
Area (a.u.)	0.00156	0.00345	0.00266	0.001133	0.00157
Function	Arctan	Arctan	Arctan	Arctan	Arctan
Height (a.u.)	0.90	0.90	1.00	0.97	0.96
Position (keV)	8.980	8.979	8.983	8.980	8.980
FWHM (keV)	0.00573	0.00505	0.00478	0.0048	0.0046
Area (a.u.)	0.02300	0.04109	0.02281	0.02868	0.02841

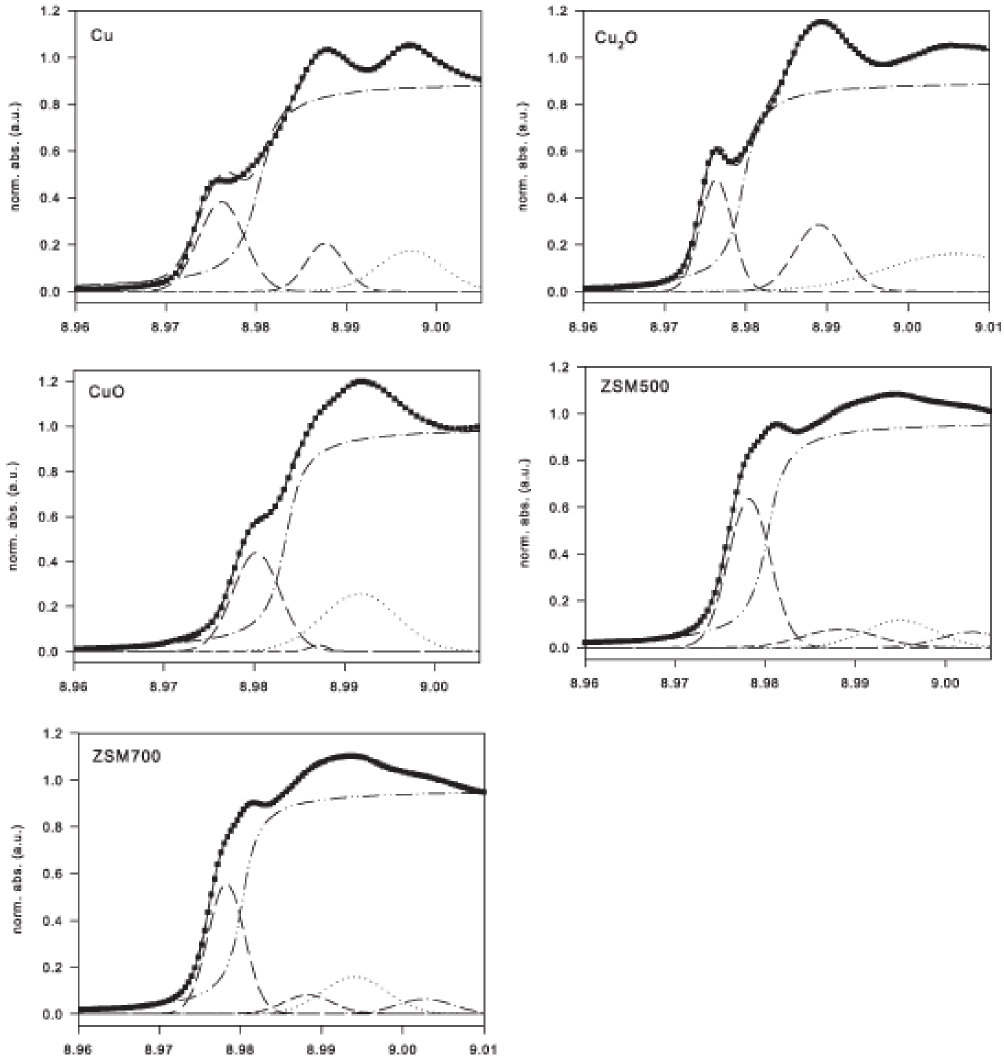

Figure S1: Deconvoluted XANES spectra of the refences Cu0, Cu_2O and CuO, and the samples ZSM500, ZSM700

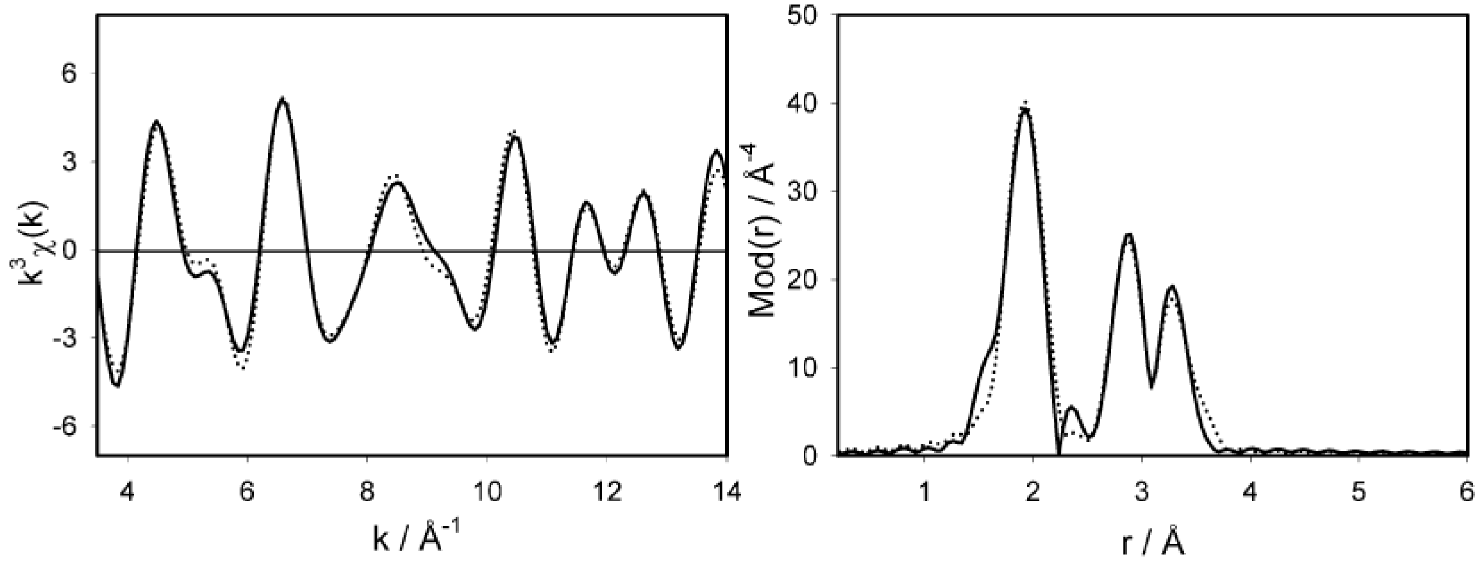

Figure S2: Fitting curves in oscillation and FT for CuO

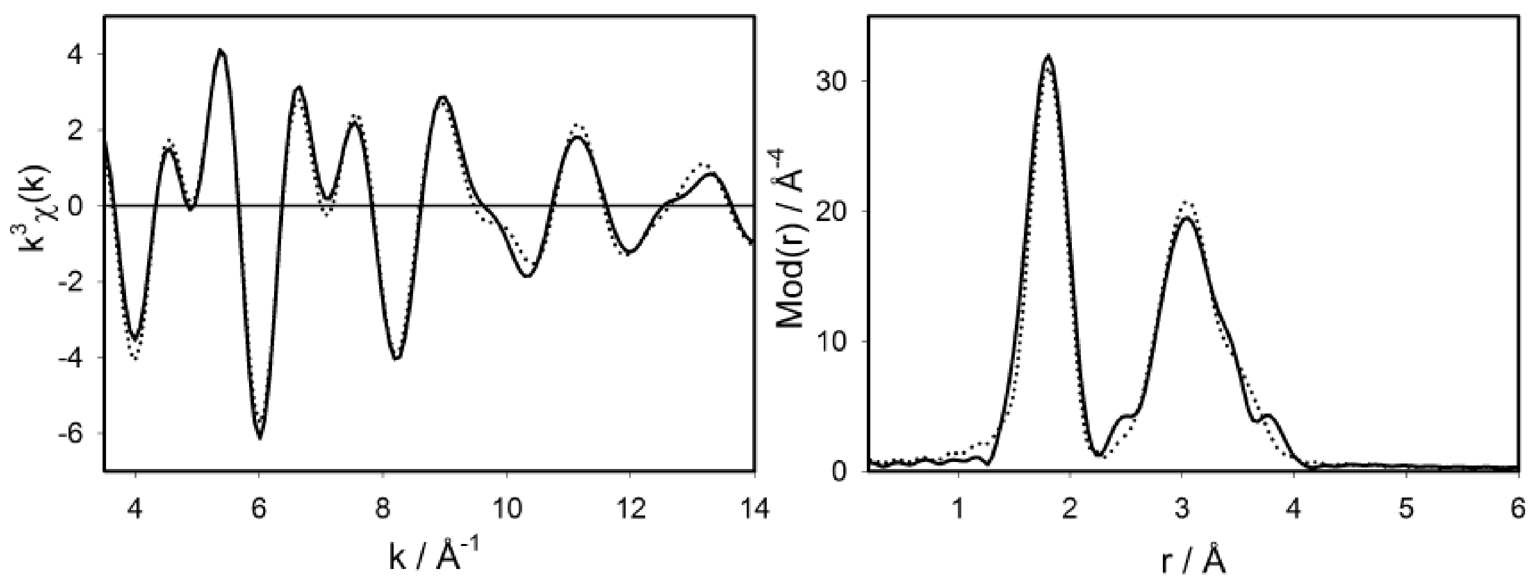

Figure S3: Fitting curves in oscillation and FT for Cu_2O

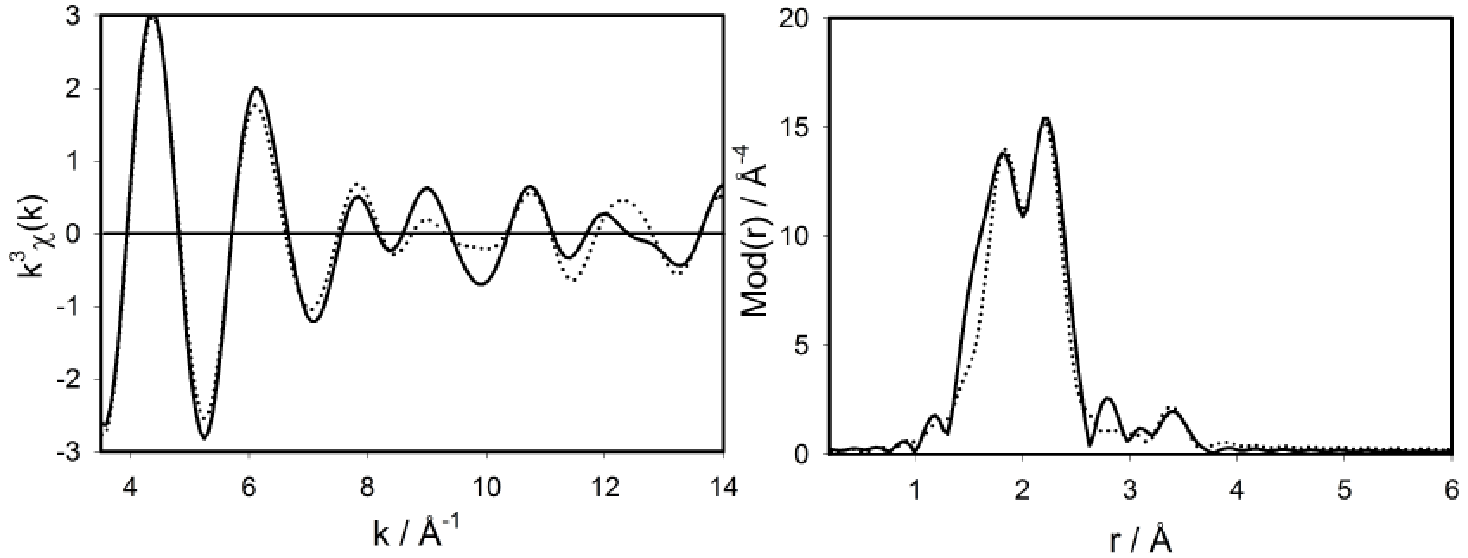

Figure S4: Fitting curves in oscillation and FT for ZSM700

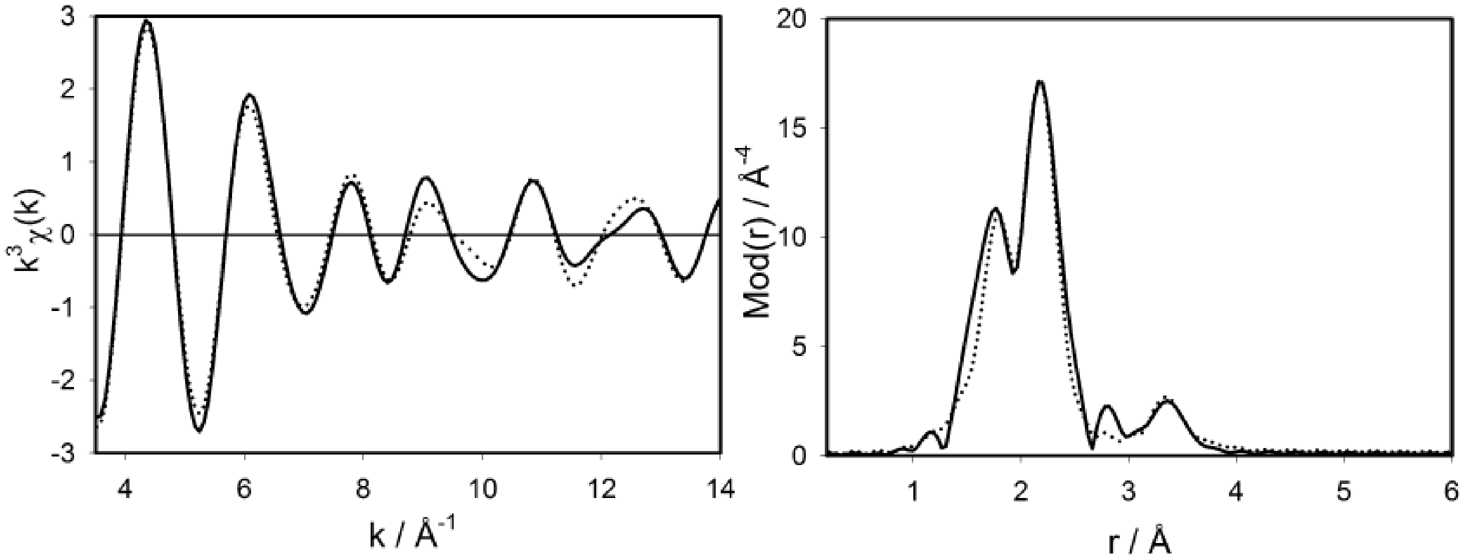

Figure S5: Fitting curves in oscillation and FT for ZSM500

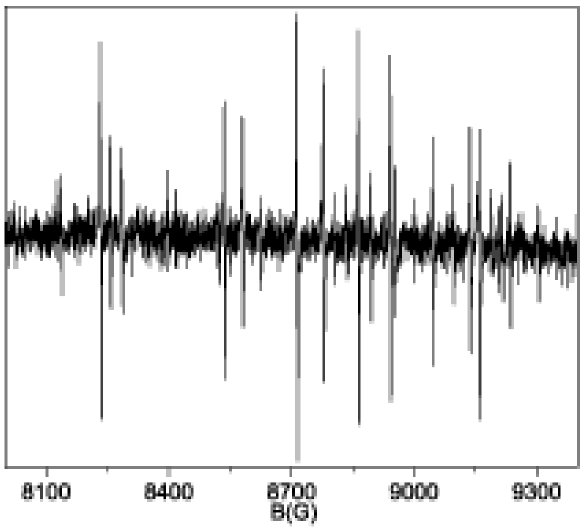

Figure S6: EPR lines of 10^{-8} mol·g^{-1} of gas phase molecular oxygen in Cu/HZSM5.

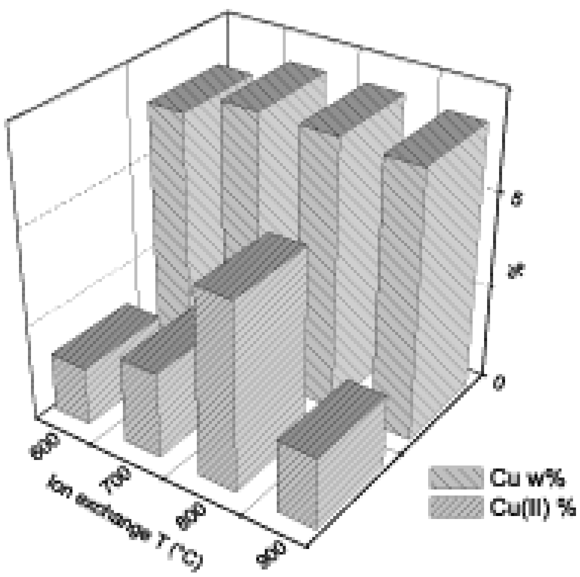

Figure S7: Amount of ion exchanged copper in weight percent and percentage of Cu(II) of the total amount of exchanged copper vs. the ion exchange temperature of the samples

References

[1] T. S. Ertel, H. Bertagnolli, S. Huckmann, U. Kolb and D. Peter, *Appl. Spectrosc.*, 1992, **46**, 690–698.

[2] M. Newville, P. Livins, Y. Yacoby, J. J. Rehr and E. A. Stern, *Physical Review B*, 1993, **47**, 14126–14131.

[3] S. J. Gurman, N. Binsted and I. Ross, *J. Phys. C: Sol. State Phys.*, 1984, **17**, 143–151.

[4] M. Roy and S. J. Gurman, *J. Sync. Rad.*, 1999, **6**, 228–230.

[5] A. Kirfel and K. Eichhorn, *Acta Crystallographica Section A*, 1990, **46**, 271–284.

[6] H. Yamada, Y. Soejima, X. G. Zheng and M. Kawaminami, *Trans. Mater. Res. Soc. Jap.*, 2000, **25**, 1199–1202.

[7] H. R. Oswald, A. Reller, H. W. Schmalle and E. Dubler, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1990, **46**, 2279–2284.

[8] E. A. Stern, *Phys. Rev. B*, 1993, **48**, 9825–9827.

[9] N. Binsted, *EXCURV98: CCLRC Daresbury Laboratory computer program, Manual*, F. Mosselman, 1998.

[10] T. Ressler, *Journal De Physique*, 1997, **7**, 269–270.