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Electronic support information: Parallel structural screening of solid materials

J.-D. Grunwaldt[1,*], B. Kimmerle[1], S. Hannemann[1], A. Baiker[1], P. Boye[2], C.G. Schroer[2]
[1]Department of Chemistry and Applied Biosciences, ETH Zurich, Hönggerberg – HCI, CH-8093 Zürich, Switzerland, grunwaldt@chem.ethz.ch
[2] Institute of Structural Physics, TU Dresden, D-01062 Dresden, Germany

This electronic support information gives more detail on the preparation of the samples, the detailed experimental procedure and the entire spectroscopic datasets recorded on the two case studies presented in the communication.

1. Preparation of the samples

1.1. Pd samples:

The preparation of the palladium catalysts is given in Table S1, which corresponds to Table 1 given in the communication. Several commercial catalysts were used for comparison. Some more specific information on the preparation procedures is given below.

Table S1. Preparation of the palladium catalysts of the present study (No. corresponds to the compartment number given in the communication).

Cat. No.	Composition	Preparation Method	More detailed description
1	5%Pd/Al_2O_3	Impregnation	5 wt% Pd/Al_2O_3, Engelhard 40692 (pre-reduced in commercial process, stored in air)
2	Pd black	Commercial	Pure palladium, partly oxidized, as-received
3	5%Pd/Al_2O_3	Impregnation, pre-reduced	5 wt% Pd/Al_2O_3, Engelhard 40692, freshly pre-reduced in hydrogen at 100 °C
4	5%Pd/Al_2O_3	Flame made (Route 1)	Flame spray pyrolysis, using xylene mixtures [1,2]
5	5%Pd/Al_2O_3	Impregnation	5 wt% Pd/Al_2O_3, Engelhard 40692 (pre-reduced in commercial process, stored in air)
6	0.5%Pd/Al_2O_3	Shell-impregnation	Shell-impregnated catalyst, Engelhard 4586 (pre-reduced in commercial process, stored in air)
7	5%Pd/Al_2O_3	Flame made (Route 2)	Flame spray pyrolysis, using methanol/acetic acid mixtures [1,2]
8	33%Pd/ZrO_2	Oxidation of glassy alloy, afterwards reduced	$Pd_{33}Zr_{67}$ alloy oxidized in air and reduced in 5%H_2/He [3,4]
9	33%Pd/ZrO_2	Oxidation of glassy alloy	$Pd_{33}Zr_{67}$ alloy oxidized in air [3,4]
10	0.5%Pd/Al_2O_3	Shell-impregnation	Shell-impregnated catalyst, Engelhard 4586

Flame made catalysts were prepared by flame spray pyrolysis [1,2] using two different solvents (Route 1 and 2). In both cases aluminium *sec*-butoxide (75% in butanol, Acros) as precursor for the support and Pd acetylacetonate (ABCR) for the noble metal particles were used, once dissolved in xylene (Route 1) and once in methanol/acetic acid (Route 2). The liquid mixtures were sprayed with an oxygen stream into a methane-oxygen flame. The as-formed particles were collected on a glass-fiber filter placed on a cylinder mounted above the flame by the aid of a vacuum pump (Vaccubrand).

For preparation of the 33%PdO/ZrO_2 sample from amorphous alloys, a glassy $Pd_{33}Zr_{67}$ alloy [3] was exposed to air at 400 °C until full oxidation was accomplished, in the same way as reported in ref. [4]. The reduced sample was prepared by exposure to 10%H_2/He in hydrogen. The reduction of the samples was performed at the corresponding temperature of the samples for 1 hour.

1.2 Cu samples:

The preparation of the copper catalysts of the present study is given in Table S2, which corresponds to Table 2 given in the communication. Both the preparation method and the support were varied. Additional information is therefore given below.

Table S2. Preparation of the copper catalysts of the present study (No. corresponds to the compartment number given in the communication).

Cat. No.	Composition	Preparation Method	More detailed description
1	33%Cu/ZnO	Co-precipitation (CP)	Co-precipitation using $Cu(NO_3)_2$ and $Zn(NO_3)_2$ according to ref. [5]
2	6%Cu/SiO_2	Chemisorption-hydrolysis (CH)	Chemisorption-hydrolysis according to ref. [6]
3	1%Au/ $Cu_3Mg_3Al_2O_{11}$	Deposition-precipitation (DP)	Deposition-precipitation according to ref. [7]
4	5%Cu/Al_2O_3	Chemisorption-hydrolysis (CH)	Chemisorption-hydrolysis according to ref. [6]
5	$Cu(OH)_2$	Commercial	As-received (Fluka)
6	33%Cu/ZnO	Co-precipitation (CP)	Co-precipitation (same as catalyst 1)
7	5%Cu/ZrO_2	Flame made	Flame spray pyrolysis according to ref. [2]
8	6%Cu/Al_2O_3	Impregnation	Impregnation of alumina pellets according to ref. [8]
9	6%Cu/SiO_2	Chemisorption-hydrolysis (CH)	Chemisorption-hydrolysis according to ref. [6]

The 33%CuO/ZnO catalyst was prepared by controlled co-precipitation of $Cu(NO_3)_2$ and $Zn(NO_3)_2$ (precipitation pH=9.2) followed by filtration through a 0.45 µm cellulose acetate membrane filter [5]. After drying at 90 °C and grinding, 1.0 g of the precursor powder was calcined in an oven with a temperature ramp of 3 °C/min and a final temperature of 250 °C for 10 hours. Chemisorption-hydrolysis was applied to the catalysts 2, 4, and 9 (the latter being the same as sample 2) using an aqueous solution of $[Cu(NH_3)_4]^{2+}$ and as reported in detail in ref. [6]. The support material of the $Au/Cu_5Mg_1Al_2O_X$ catalyst was prepared by means of flame spray pyrolysis (FSP), gold was deposited by utilizing the deposition precipitation method. The detailed description about the preparation parameters will be described in ref. [7]. The impregnation of the $6\%Cu/Al_2O_3$ catalyst (cat. no. 8) was achieved by impregnation with a $CuCl_2$-solution in the same way as described in ref. [8].

2. Experimental procedures for recording X-ray absorption spectra with a 0.5 x 1.0 mm beam and a CCD-based position sensitive X-ray detector

Spectra were recorded in a conventional manner using a 0.5 mm wide x 1mm high beam and ionization chambers as well as with a new approach using a charged coupled device (CCD) camera. The experiments were performed at beamline X1 at HASYLAB (DESY, Hamburg). The typical beam current of the storage ring was 80 – 120 mA (operating positron energy at 4.5 GeV). In both cases, a Si(311) and Si(111) double crystal monochromator for step-by-step scanning of the energy around the Pd K-edge and Cu K-edge was used. Higher harmonics were effectively removed by detuning of the crystals to 70% of the maximum intensity.

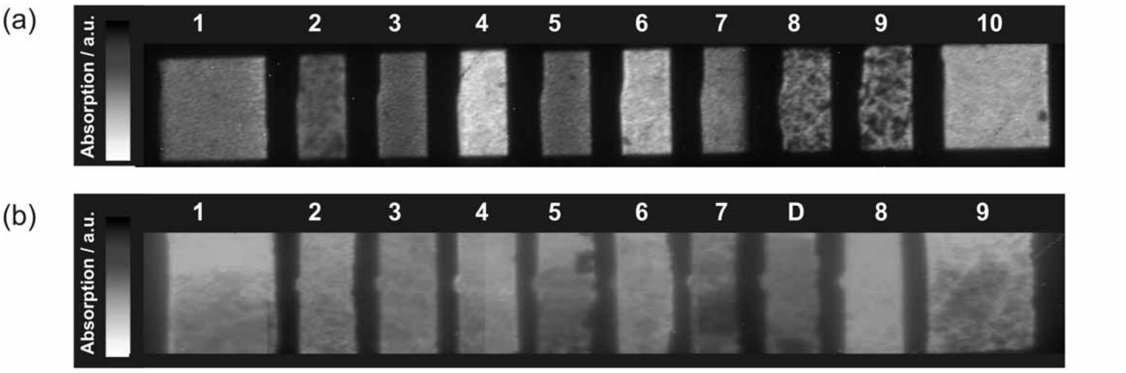

Figure S1: X-ray transmission in the different compartments loaded with (a) Pd-catalysts (according to Table 1) and (b) Cu-catalysts (according to Table 2; compartment D was not considered since the X-ray absorption was too high; transmission images taken above the respective edges).

Prior to the studies the different solid materials were sieved and placed in a specially designed cell with 10 compartments (see Figure 1 in the communication and Fig. S1 in the electronic support information).

For *in situ* studies a flow of 20 ml/min was fed over the catalysts using mass flow controllers (Brooks). For this purpose pre-mixed gasses (reduction in 5%H_2/He, oxidation in 21%O_2/He) were utilized. The catalysts were heated to the respective reaction temperatures using an oven. The temperature was measured by a thermocouple directly in the stainless steel body. The whole *in situ* cell was mounted on an x,z,θ-table, which allowed to align the cell both in horizontal and vertical translation using step motors.

In case of the conventional XAS experiment, ionization chambers (length 10 cm) served to detect the incoming X-ray intensity I_0 and the intensity of the transmitted X-rays (*in situ* cell located between the first and second ionization chamber, a Pd or Cu-reference foil for energy calibration between the second and third ionization chamber). The gas and its pressure were adjusted so that 15 % of the X-ray intensity was absorbed in the first and 40 % in the second and third ionization chamber. The setup has been reported for example in ref. [9].

For parallel acquisition of the XAS spectra a larger X-ray beam of 8 mm width x 1 mm height was used. Instead of the ionization chamber, the CCD-area detector was used. In the detector, the X-rays are converted into visible light in a thin single crystal scintillator (thickness of the sensitive layer ca. 10 μm) that is imaged onto a CCD-camera by a microscope optic [10]. The spatial resolution of the detector is approximately 10 μm [11], but here resolution was only required on the 100 μm scale. The incoming intensity $I_0(E, x, y)$ was measured by taking an X-ray image without the cell and the transmitted intensity $I(E, x, y)$ by imaging the cell in the beam. The X-ray energy was scanned in the XANES region around the Pd K- ($E = 24320 – 24450$ eV) and Cu K-edge ($E = 8960 – 9040$ eV) in steps of one eV. The exposure time for each image was 10 s.

From these data, the absorption at each point can be obtained for each pixel and by integration over the corresponding compartment area also for each sample. For this purpose, the data were first dark-field corrected, i.e., the influence of the CCD-dark current and read-out noise was removed by subtracting an averaged dark image (without

X-rays) from each of the images. After this correction, each pixel value (or that of the compartment) is proportional to the intensity.

The values for I(E, compartment i) and I_0(E, compartment i) for images taken with and without sample then allow one to give the integral absorption for each compartment i and energy by

$$\int \mu(E, compartment(i), z) \cdot dz = -\ln \frac{I(E, compartment(i))}{I_0(E, compartment(i))}$$

Thus the absorption spectrum for each compartment i can be determined in parallel using this technique.

The raw data were energy-calibrated, background corrected, and normalized using the WINXAS 3.0 software [12]. In order to quantify the relative ratio of oxidized Cu with respect to metallic Cu, linear combination analysis (LCA) of the XANES region around the edge was performed, using the spectra of the reduced and the oxidized (as prepared) materials as spectra for reconstruction.

3. X-ray absorption spectra

In Figures S2 - S9, additional spectroscopic data are given that were used within the present study, but were not reported in detail in the main publication. They give a more profound view on the comparison of the conventional and the new approach as well as the complete set of data that were used for the determination of the oxidation state in Figure 3 and 5 in teh communication.

In detail, Figure S2 and S3 compare spectra at the Pd K-edge recorded in a conventional way using ionization chambers with those recorded with the CCD-camera under different environmental conditions. They correspond to Figure 1, where only the spectra of the samples without a gaseous treatment is given. Figure S4 compares spectra in the same way at the Cu K-edge during reduction 5% H_2/He at an elevated temperature (200 °C). All spectra taken at the Cu K-edge with the CCD-camera at the different conditions in the compartments 1 - 9 are summarized in Figures S5 - S13. These spectra served as a basis for the determination of Cu^0-species in Figure 5 of the publication (analogously Figs. S2 and S3 as well as Fig. 2 in the communication were used for LCA-analysis shown in Fig. 3).

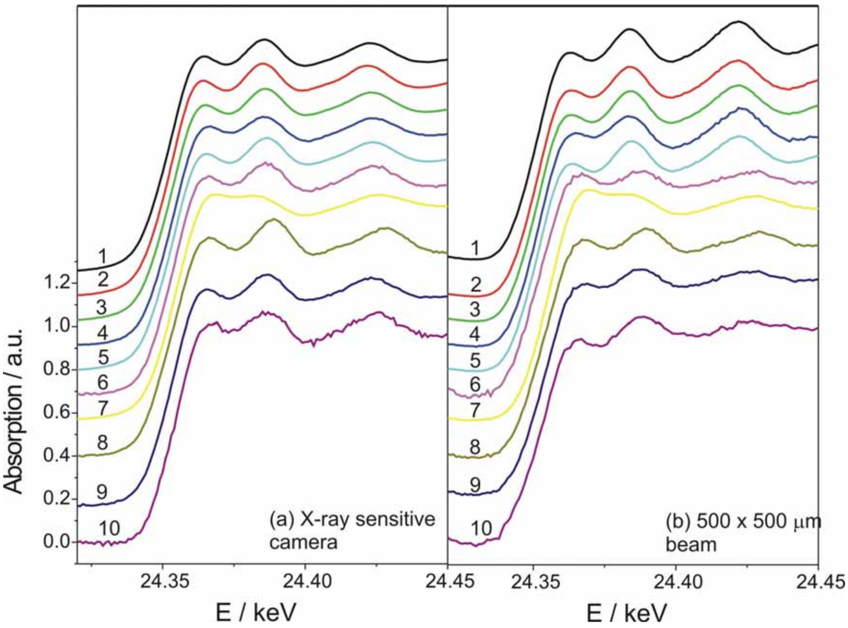

Figure S2: X-ray absorption spectra of the Pd catalysts taken with the X-ray camera (left side) and with a 0.5 x 0.5 mm large beam (right) after reduction in 5%H_2/He; catalysts 1 to 10 are from top to bottom as listed in Table 1.

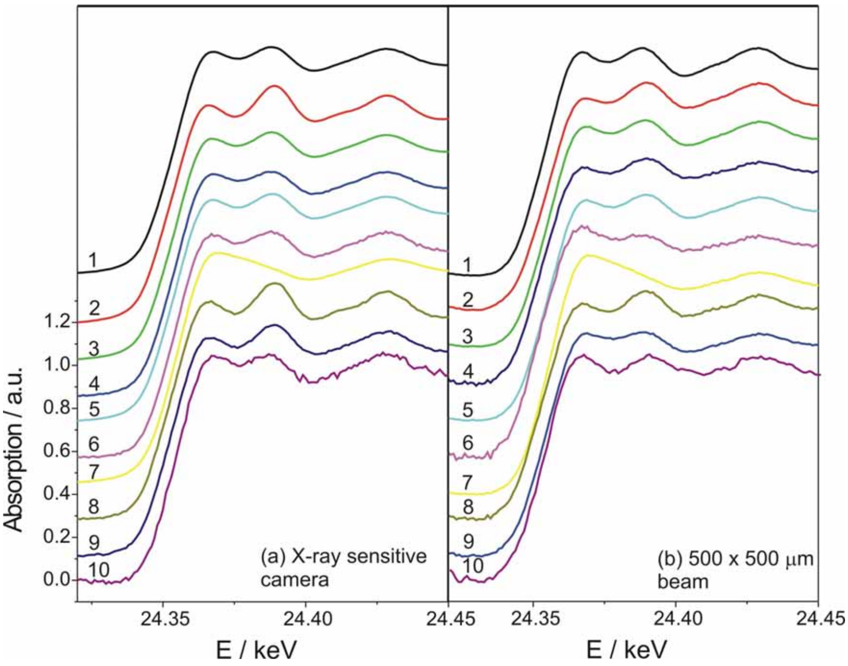

Figure S3: X-ray absorption spectra of the Pd catalysts taken with the X-ray camera (left side) and with a 0.5 x 0.5 mm large beam (right) after reduction in 5%H_2/He and re-oxidation in 21%O_2/He; catalysts 1 to 10 are from top to bottom as listed in Table 1.

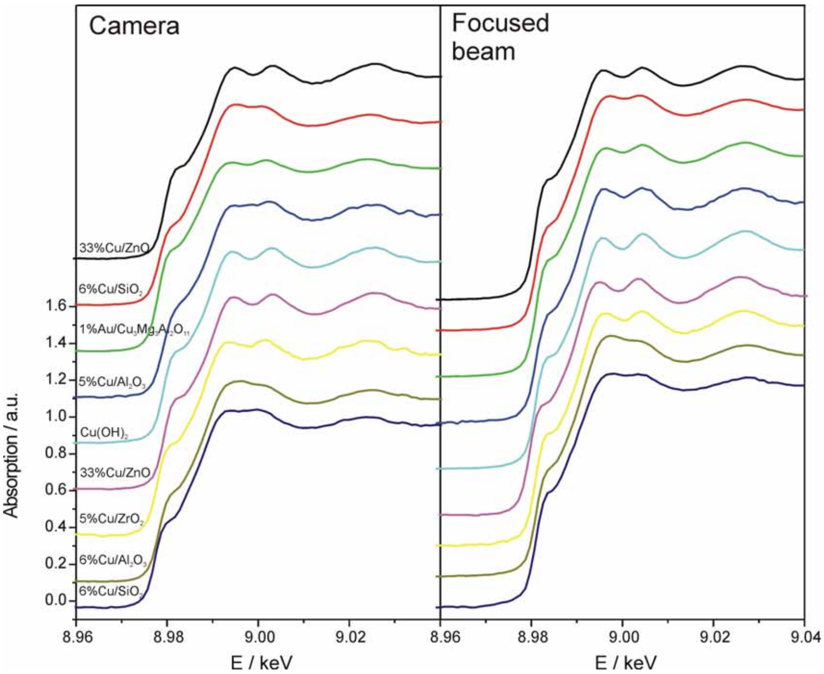

Figure S4: Comparison of X-ray absorption spectra of the Cu catalysts taken during reduction in 5%H_2/He at 220 °C once with the camera (simultaneous scanning) and once with the focused beam (sequential scanning).

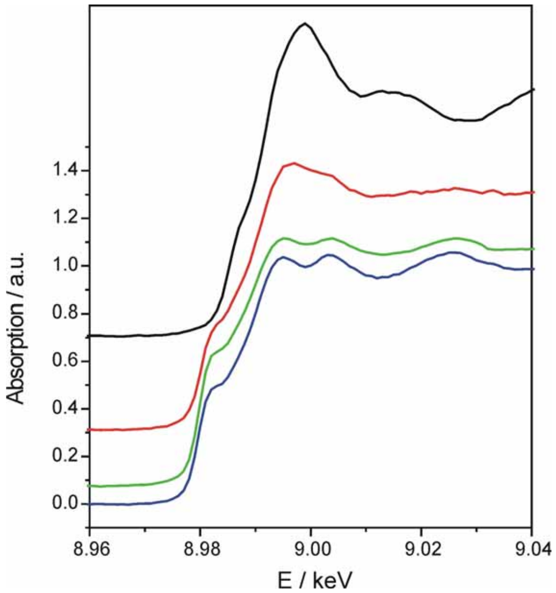

Figure S5: XANES spectra of Cu sample 1 taken with the camera at room temperature, 175 °C, 200 °C, and 220 °C (top to bottom, like in Fig. S4)

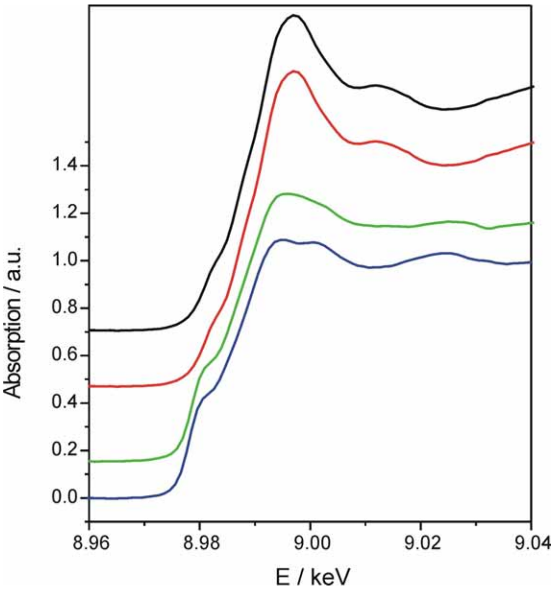

Figure S6: XANES spectra of Cu sample 2 taken with the camera at room temperature, 175 °C, 200 °C, and 220 °C (top to bottom, like in Fig. S4)

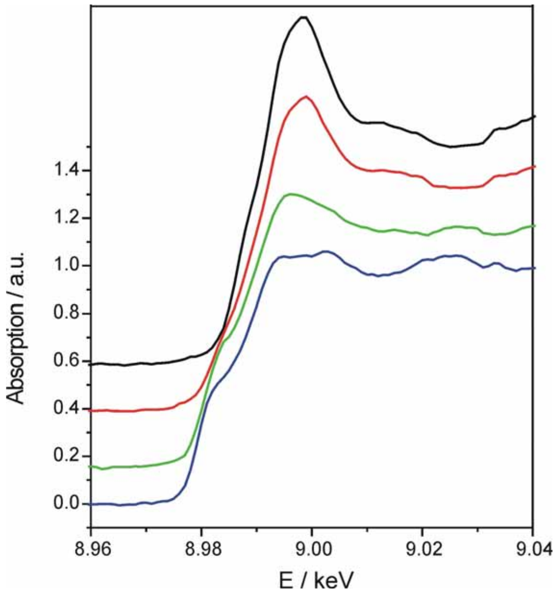

Figure S7: XANES spectra of Cu sample 3 taken with the camera at room temperature, 175 °C, 200 °C, and 220 °C (top to bottom, like in Fig. S4)

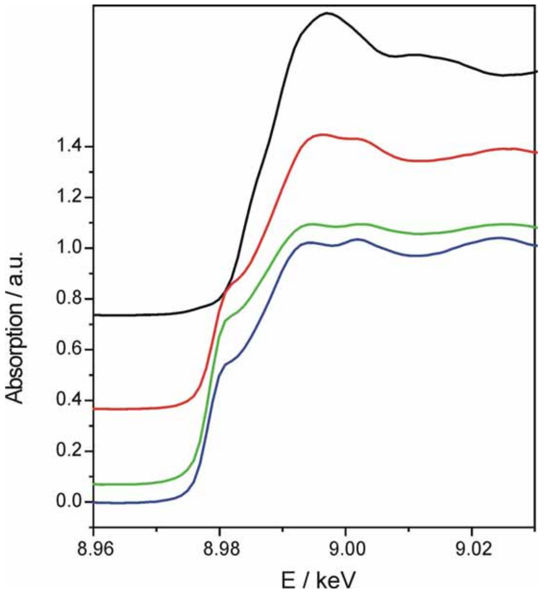

Figure S8: XANES spectra of Cu sample 4 taken with the camera at room temperature, 175 °C, 200 °C, and 220 °C (top to bottom, like in Fig. S4)

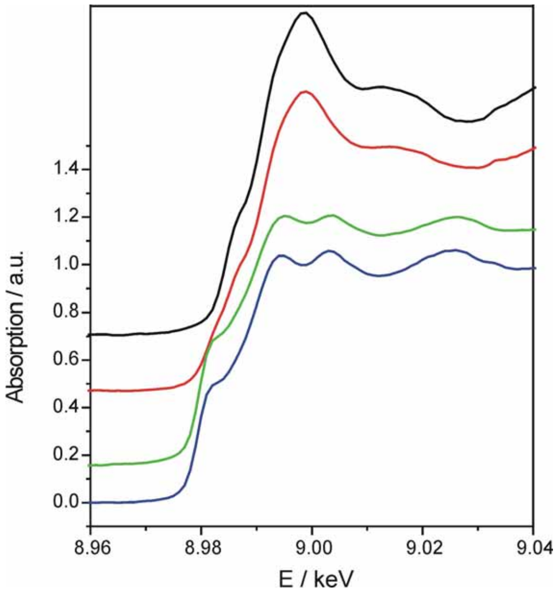

Figure S9: XANES spectra of Cu sample 5 taken with the camera at room temperature, 175 °C, 200 °C, and 220 °C (top to bottom, like in Fig. S4)

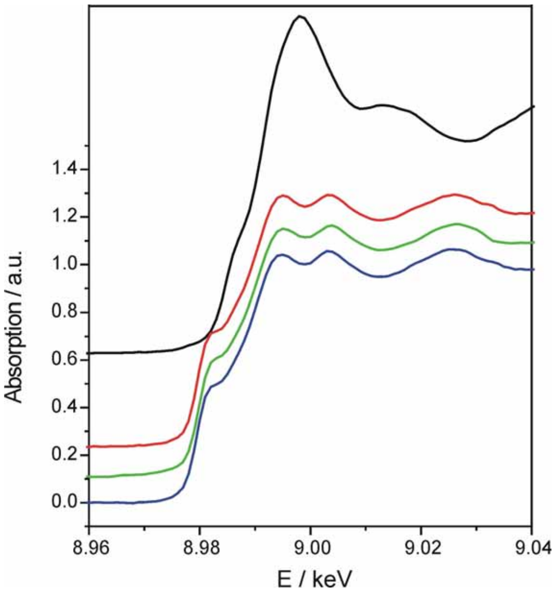

Figure S10: XANES spectra of Cu sample 6 taken with the camera at room temperature, 175 °C, 200 °C, and 220 °C (top to bottom, like in Fig. S4)

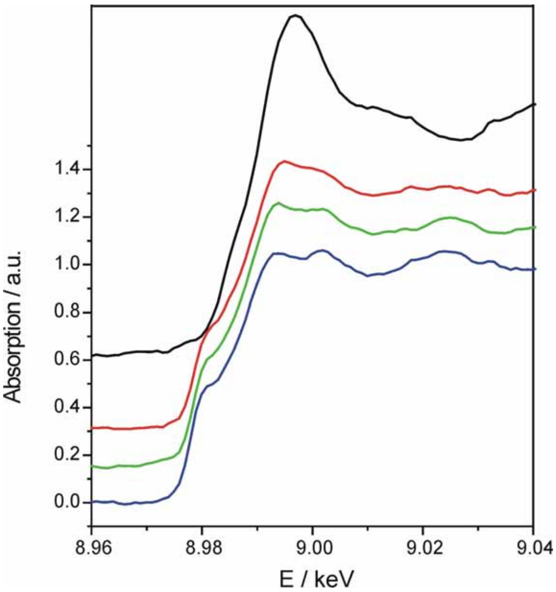

Figure S11: XANES spectra of Cu sample 7 taken with the camera at room temperature, 175 °C, 200 °C, and 220 °C (top to bottom, like in Fig. S4)

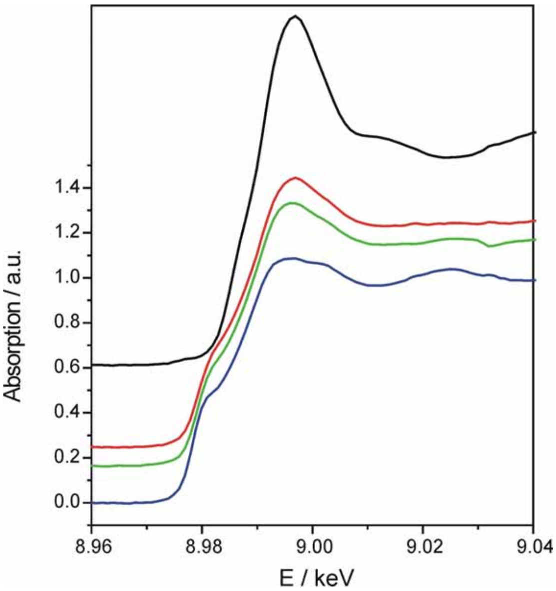

Figure S12: XANES spectra of Cu sample 8 taken with the camera at room temperature, 175 °C, 200 °C, and 220 °C (top to bottom, like in Fig. S4)

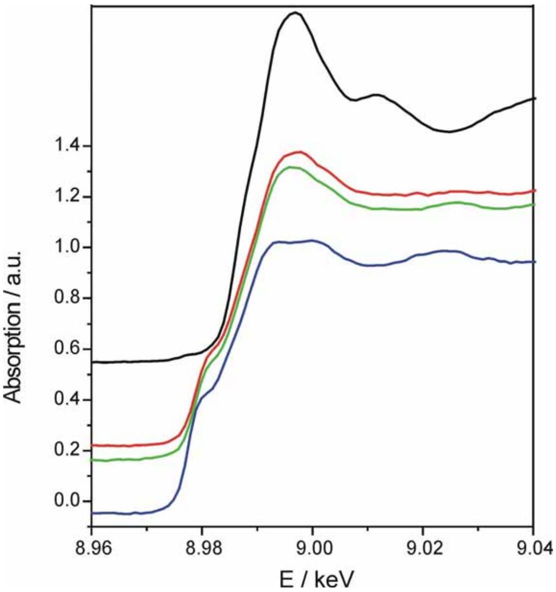

Figure S13: XANES spectra of Cu sample 9 taken with the camera at room temperature, 175 °C, 200 °C, and 220 °C (top to bottom, like in Fig. S4)

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