

**Experiment title:**

ED-XAFS study of the oxygen activation properties of novel enzyme mimicking iron(II) complexes

Experiment number:

CH-1785

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| Beamline: ID 24 | Date of experiment: from: 8.9.2004 to: 14.9.2004 | Date of report: 18.11.2004 <i>Received at ESRF:</i> |
| Shifts: 18 | Local contact(s): Dr. Gemma Guilera | |

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Report:

During this experiment, simultaneous time-resolved *in-situ* ED XAFS and *in-situ* UV-Vis spectroscopy were used to study homogeneous oxidation catalyst systems. These experiments were performed on a stopped-flow ED XAFS/UV-Vis set-up, which was developed by our group as part of the experiment CH 1275 in cooperation with the beamline ID 24. In addition to a new iron system, a copper-catalyzed oxidation reaction was also studied as a continuation of measurements performed as part of the experiment CH 1275 in November 2003.

Investigation into the oxidation state and geometry of Cu(II)(bipy)₂ complex in the catalytic cycle of benzyl alcohol oxidation

The oxidation of benzyl alcohol to benzaldehyde using a copper bipyridine (1:1) complex as catalyst and TEMPO and base as co-catalysts (all in water/NMP (1:1) as solvent) was studied in the combined UV-Vis/ED-XAFS set-up (Figure 1).

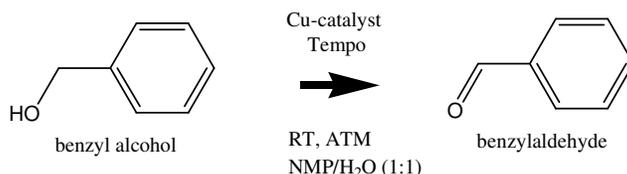


Figure 1. The schematic overview of the Cu-catalyzed oxidation of benzyl alcohol.

Four different 60 mM solutions were prepared and mixed in various ways in the cuvette in order to study the mechanism of the reaction (60 mM TEAOH, 60 mM benzyl alcohol, 60 mM TEMPO and 60 mM CuBr₂ and 60 mM bipyridine). Analysis of the XANES in the X-ray absorption data of the complete reaction mixture shows that reduction of the copper is occurring as soon as the solutions are mixed. A pre-edge feature is coming up in time and the intensity of the white line is going down (Figure 2). The UV-Vis spectra recorded at the same time showed the upcoming of a band at 420 nm (Figure 3), which is indicative for the formation of a binuclear copper complex. Further (EXAFS) analysis of the data has to be done to confirm the assignments.

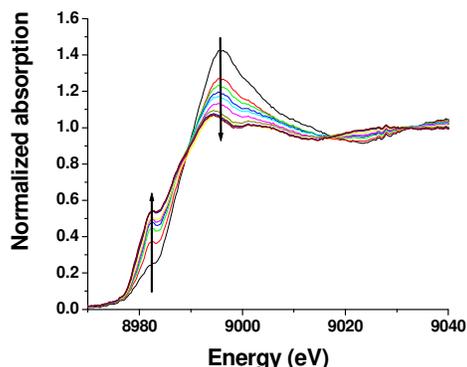


Figure 2: Normalized X-ray absorption spectra of the reaction mixture as function of time. A pre edge feature is coming up and the white line is decreasing in time.

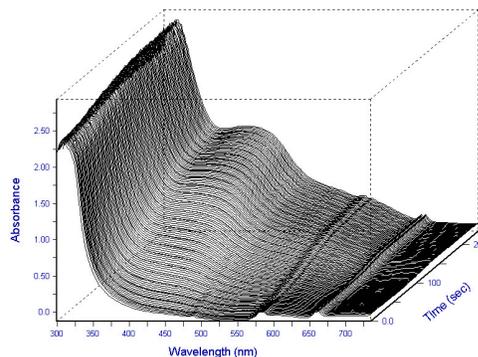


Figure 3: UV-Vis spectra of the reaction mixture as function of time. A band at 420 nm is coming up, which is indicative for the formation of a binuclear copper complex.

Besides that, a number of stability and concentration tests for a number of aqueous copper solutions were performed (Cu(NO₃)₂·3H₂O, CuSO₄·5H₂O, CuBr₂, CuCl₂ and Cu(acetate)₂·H₂O). It was found that the stability of the aqueous copper solution is dependent on the copper precursor salt used to make the copper solution.

Reference spectra and stability of several iron salts in water, methanol and acetonitrile

Iron complexes have not been studied with the in-situ ED-XAFS/UV-Vis set-up before, and therefore the stability and concentration tests were performed with several iron salts in three different solvents. Reference spectra were measured of 80 mM Fe(NO₃)₃·9 H₂O, FeCl₃·6 H₂O, FeBr₂ and Fe(acac)₃ solutions in methanol and the samples were exposed to the beam for longer periods (10 minutes) to check for their stability in the high energy x-ray beam. 25 mM FeCl₃·6 H₂O and 25 mM Fe(acac)₃ were also measured in acetonitrile, whereas other salts did not dissolve well enough in this solvent. FeCl₃·6 H₂O, FeBr₂ and Fe(acetate)₂ were measured in water in a mylar cell, as no signal could be detected if using the quartz cell of the ED XAFS/UV-Vis set-up. This is due to the silica windows together with water absorbing too much of the low energy X-ray beam. No changes were observed in the samples during exposure to the beam, except perhaps in the sample of FeCl₃·6 H₂O in water (Figure 4). Further analysis of the data must still take place before confirmation.

Investigation into the geometry and oxidation state of iron in an enzyme-mimicking complex

The complex **1** [(*NNN*)Fe(OTf)₂] was synthesized by reaction of a new tridentate *NNN*-ligand with iron(II) triflate salt. Upon addition of tBuOOH to complex **1**, a purple species is formed, which is characterized with UV-Vis and Raman spectroscopy as an iron(III)-alkyl peroxy complex. The presence of water plays a significant role in the stability of this iron alkyl peroxy species. To find out why water decreases

the stability of the alkyl peroxy complex and what is the product after decomposition, simultaneous ED XAFS/UV-Vis experiments were performed during this beamtime. Measurements were performed with varying complex **1** to tBuOOH ratios, with tBuOOH dissolved in water or in decane and with just water and complex **1** in solution.

The complex **1** with tBuOOH catalyzes the oxidation of cyclohexene to cyclohexanone, cyclohexanol and epoxide and the oxidation of phenyl methyl sulfide to sulfoxide. To improve the selectivity of these reactions and to elucidate the reaction mechanism, it is important to know what is the active catalytic species, does the substrate coordinate to the metal center and what is the deactivation mechanism of the catalyst. Thus time-resolved ED XAFS/UV-Vis measurements were performed with complex **1** and cyclohexene (Figure 5) or phenyl methyl sulfide in the absence and presence of tBuOOH in acetonitrile. With these experiments we hope to see if $\text{Fe}^{\text{IV}}=\text{O}$ species is involved in the reaction, if substrate coordination occurs and if the substrate and the alkyl peroxy-group are coordinated simultaneously to the iron center. The analysis of the data is presently taking place.

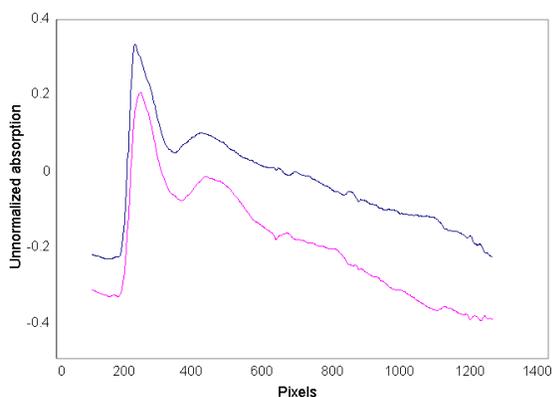


Figure 4. Sample spectra of 50 mM $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ in water measured in a mylar cell. These spectra are unnormalized raw data before energy calibration.

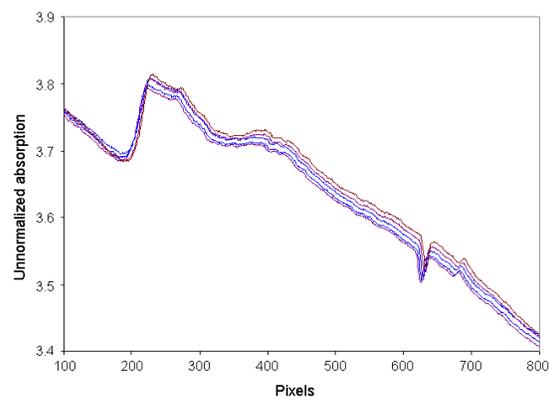


Figure 5. Sample spectra of a time-resolved measurement of 25 mM complex **1**, 75 mM TBuOOH/decane and 75 mM cyclohexene in dry acetonitrile. These spectra are unnormalized raw data before energy calibration.

New developments for studying heterogeneous catalyst systems

During this beamtime we were also able to carry out the first stage of testing of our new *in situ* setup for studying heterogeneous catalysts using ED XAFS in combination with UV-Vis and Raman spectroscopy. These initial tests focused on determining both the total X-ray transmission and overall data quality, through a typical sample mounted in an especially designed reactor for simultaneous spectroscopic measurements. The results obtained were useful in determining the quality and consistency of the X-ray transmission through the newly designed cell and also gave us an indication of the various types of sample (i.e. various K-edge energies in which suitable transmission would occur) that could be studied using such a setup. With this information we would now be able to further optimize the design of the cell to enable better data quality ready for further testing during our beamtime later this year.