



	<b>Experiment title:</b> Kinetic study of a copper catalyzed homogeneous model reaction by combined DEXAFS/UV-Vis measurements	<b>Experiment number:</b> CH-2655
<b>Beamline:</b> ID24	<b>Date of experiment:</b> from: 1 July 2009 to: 7 July 2009	<b>Date of report:</b> 17.02.2010
<b>Shifts:</b> 15	<b>Local contact(s):</b> Mark Newton	<i>Received at ESRF:</i>

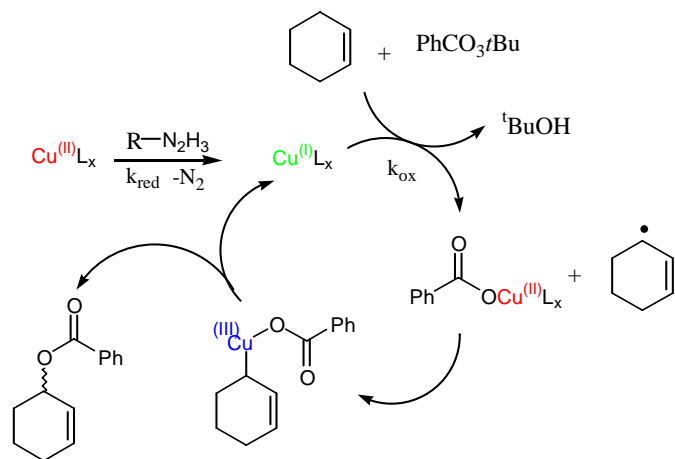
**Names and affiliations of applicants (\* indicates experimentalists):**

**Benjamin Marchetti\***: Institute for physical chemistry, University of Stuttgart, Germany

**Matthias Bauer\***: Institute for physical chemistry, University of Stuttgart, Germany

**Helmut Bertagnolli**: Institute for physical chemistry, University of Stuttgart, Germany

Most of the fine chemicals are produced by reactions that generate stoichiometric amounts of waste and have been nearly unchanged during the last hundred years. Due to the increasing application of fine chemicals a strong demand for catalytic methods exists. In order to improve the efficiency of a catalyst, a sound knowledge of the elementary steps of the catalytic reaction is required. Conventional spectroscopic methods such as NMR have the disadvantage, that metal centre is only probed indirectly and changes in the local structure are often unrevealed. EXAFS spectroscopy in combination with other spectroscopic methods like UV/Vis offers the possibility to study the geometric and electronic structure of the metal catalyst center and the reacting species in course of the catalytic reaction solely in one experiment. The combination of EXAFS with other methods has the advantage, that each spectroscopic method has its “own point of view” and many



**Scheme 1** Proposed reaction mechanism

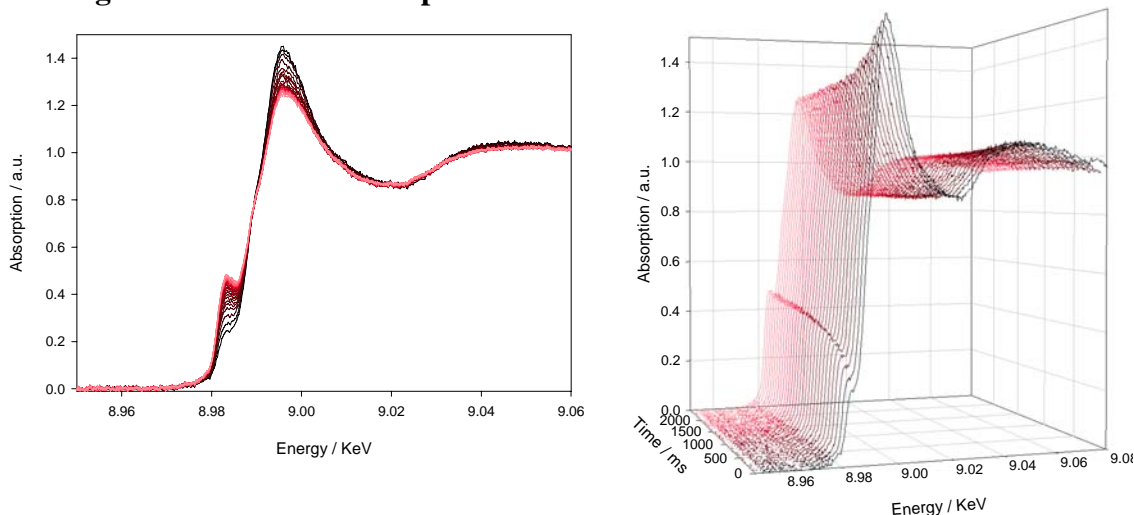
methods deliver complementary information. X-Ray absorption spectroscopy is sensitive for changes of the oxidation state or the local structure around an absorber, while UV-Vis probes mostly the electronic structure of the metal center and its coordinating ligands and for example Raman can be used to monitor educt consumption or product formation. The combination of all information can provide a deeper understanding of the mechanism of the investigated reaction of interest.

For a complete understanding of reaction mechanisms, kinetic data play an important role. With QEXAFS (Quickscanning-EXAFS) the recording time of few seconds is sufficient to follow most reactions. However, in few cases, oxidation or reduction processes proceed on a much shorter timescale. In order to study such reactions

dispersive EXAFS (DEXAFS) with simultaneous UV-Vis measurements in stopped-flow set-up on ID24 [1]

need to be applied, where acquisition times of 50-100 ms are achieved. In detail we studied the Karash-Sosnovsky-Reaction[2] which as a copper catalyzed oxidation of saturated and unsaturated hydrocarbons with *tert*-Butoxyperbenzoic ester. The products can be used as precursors for fine chemicals. The mechanism of the reaction is so far not clarified but the most probable proposed mechanism[3] is shown in the scheme 1. The reaction offers the possibility to study the reduction on oxidation step individually. When cyclohexen is added, the reaction passes through the full cycle, and the copper(II) species is transformed via the proposed copper(III) intermediate back to copper(I). If copper(III) is present over the detection limit a change in the oxidation kinetics in comparison to the oxidation without cyclohexen should be visible.

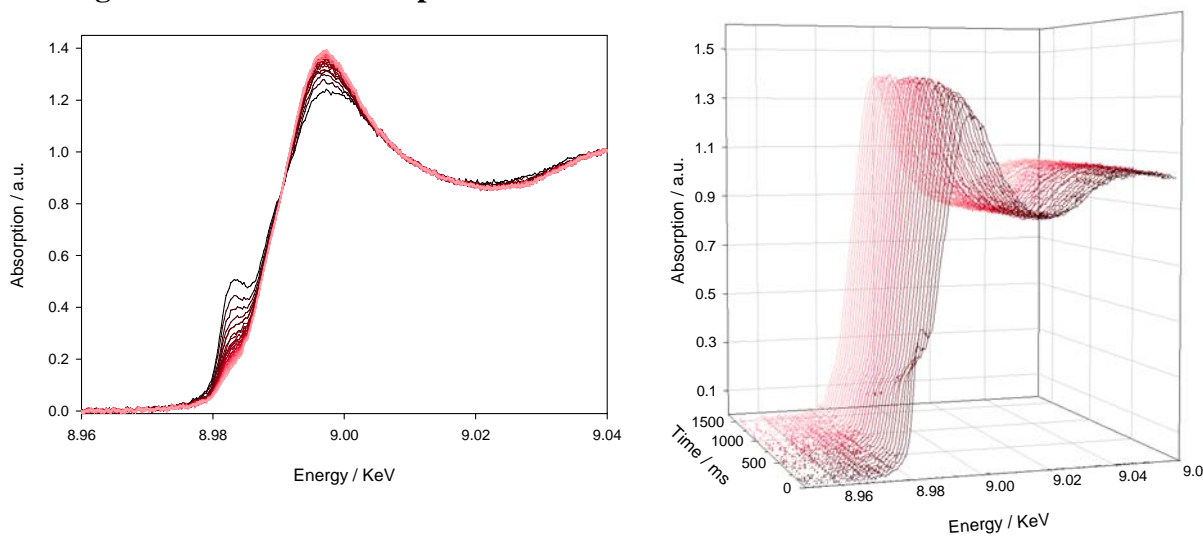
### Investigation on the reduction process:



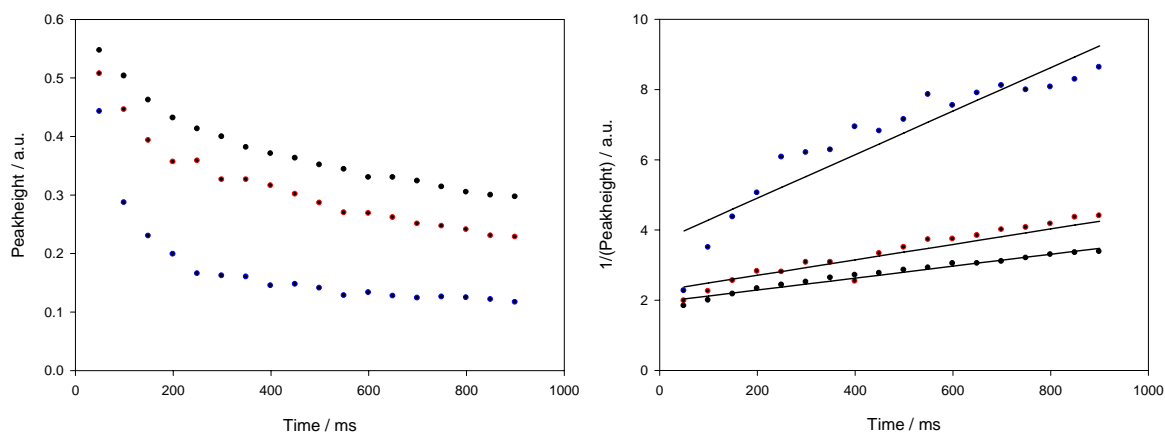
**Figure 1** Two and Three dimensional plot of the XANES during the reduction process going from black to light red.

In figure 1, the DEXAFS spectra recorded in course of the first step of the reaction, namely the reduction of a 0.05M Cu(II)Triflate solution in acetone with 0.1 mmol of phenylhydrazin are shown. Since Cu(I) shows a characteristic prepeak at  $\sim 8.983$  keV, this signal was used to follow the kinetic oxidation state changes. The kinetics were evaluated according to the method of integrated rate laws by plotting the peakheight,  $\ln(\text{peakheight})$ ,  $1/(\text{peakheight})$  against the reaction time. Linear regression analysis revealed a reaction order of zero with a rate constant of  $k_{\text{red}} = 0.002$  [1/(mol·ms)]

### Investigation on the oxidation process:



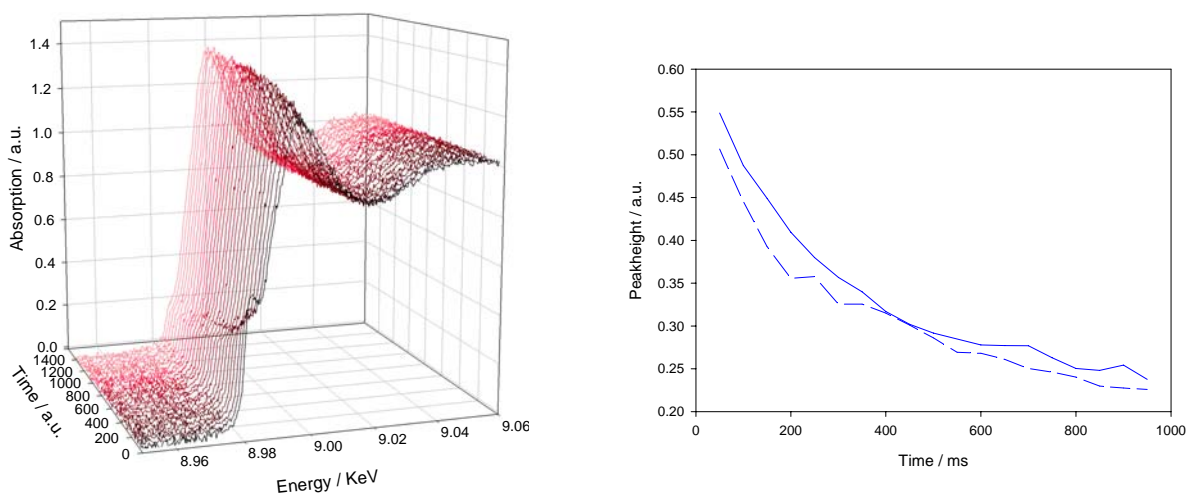
**Figure 2** Two and Three dimensional plot of the XANES during the oxidation process going from black to light red



**Figure 3** The evaluation of the prepeak-height with time for a ratio of Cu/<sup>tert</sup>Butoxyperbenzoic ester of 1:20(red), 1:10(black) and 1:40(blue) and linear regression according to a integrated second-order rate law (right)

In figure 2 the DEXAFS spectra in course of the second step of the reaction, namely the oxidation of a 0.05M Cu(I)Triflate solution in acetone with 0.5, 1 and 2 mmol of <sup>tert</sup>Butoxyperbenzoic ester, are shown. The Cu(I)Triflate solution was prepared according to first reaction step. In the plots in figure 3 the evaluation of the prepeak-height was plotted against time. The best linear regression could be achieved with a plot of 1/(prepeakheight) against time which means that the oxidation has a reaction order of two, which is in agreement with the half-life method. With the three different rate constants, obtained from the linear regression in figure 3, the rate constant of the oxidation step  $k_{ox}$  and the reaction order with respect of <sup>tert</sup>Butoxyperbenzoic ester was determined by plotting the rate constants against the concentration of <sup>tert</sup>Butoxyperbenzoic ester. This lead to a rate constant of  $k_{ox} = 0.003 [l^2/(mol^2 \cdot ms)]$  and a reaction order of one, which was also confirmed by the method of the initial reaction rate.

#### Investigation of the full cycle.



**Figure 4** The oxidation with the inclusion of cyclohexen (start of the reaction) and comparison of the oxidation kinetics with(long dash) and without cyclohexen

In figure four the oxidation of Cu(I)Triflate with the inclusion of 1mmol cyclohexene is shown. The reaction rates with and without cyclohexene are very similar and follow both a second order kinetic. The results are unfortunately not comparable without doubt. Due to problems with the stopped-flow setup (damage of the only appropriate cuvette) a new cuvette that was not appropriate for ED-EXFAS measurements of copper had to be used, which lead to a low signal to noise ratio. This made an unambiguous determination of a shift of the egde or prominent prepeak features impossible.

#### Literature

- [3] A.J.Dent , J. Evans , S.G. Fiddy, B. Jyoti, M. A. Newton, M. Tromp, *Ang. Chem. Int. Ed.* **2008**, 46 , 5356
- [2] M. S. Kharash, G. Sosnovsky, *J. Am Chem Soc.*, **1958**, 80, 756
- [3] J. Eames, M. Watkinson, *Angew. Chem. Int. Ed.* **2001**, 113, 19