



	Experiment title: In situ EXAFS investigations at active Cu and Ir species during the photocatalytic splitting of water	Experiment number: CH-4582
Beamline: ID 24	Date of experiment: from: 07.10.2015 to: 13.10.2015	Date of report: 01.03.2016
Shifts: 18	Local contact(s): Manuel Monte Caballero	<i>Received at ESRF:</i>
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Report:

Summary

A reduction of copper containing water reduction catalysts (Cu WRC's) to metallic Cu occurs during the illumination of UV-Vis light in presence of Ir photosensitizers (IR-PS's). Aim of these experiments was to correlate the redox properties of the catalysts with their activity in water splitting. Three different systems were investigated in a systematic manner: CuI which showed the highest activity, copper(II) species supported on mesoporous silica (MCM-41) with a medium activity and the nearly inactive CuO. A clear relationship between the reducibility of the copper species and the activity can be established with the XAFS measurements performed at this beamtime.

Experimental description

Experiments on both edges, Cu K (8.9 keV) and Ir L_{III} (11.2 keV) edges under light on and off conditions were performed. Our experiments were focussed on the Cu K edge due to the technical problems at the beamtime at January 2015 (CH-4235).

The experimental setup was based on a reaction cell with two movable glassy carbon (HTW Hochtemperatur-Werkstoffe GmbH, Thierhaupten) to optimize the X-ray path through the sample. For the illumination a movable UV-Vis light source (Lumatec, 1.5 W Xe lamp) were used. It was possible to perform the XAS

investigation with or without light using a UV shutter. Spectra were collected in both modi, with and without light. An advantage of the used setup was that it allows measurements without any perturbation by the hydrogen gas bubbles produced under UV irradiation (Fig. 1)

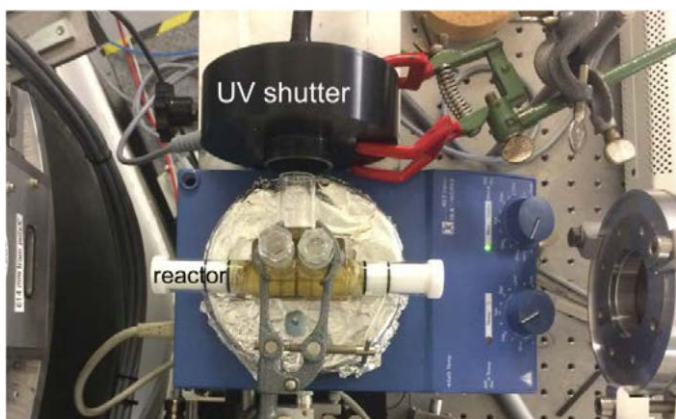


Fig. 1: The reaction cell with the movable glassy carbon window, UV shutter and its implementation at ID 24.

For the *in situ* experiments the catalysts (160 μmol Cu for CuI and Cu/MCM-41; 120 μmol for CuO) and the Iridium photosensitizer ($\text{Ir}(\text{ppy})_2(\text{bpy})$, 60 μmol) were added to the reactor. Then a solution of tetrahydrofuran (THF), triethylamine (TEA) and water (3:2:1, 30 ml) was added to the vessel. Afterwards, the reaction was started. In each sequence of 60 s eight spectra with and one spectrum without illumination were collected.

Results and discussion

The XANES results are presented in Fig. 2. CuI was measured for in total 70 min, $\text{Cu}^{2+}/\text{MCM-41}$ and CuO for more than 200 min. Not all measured spectra are shown, the measurement time of one spectra is 10 s.

A clear correlation between the reducibility of the Cu compound and the catalytic activity could be established. At CuI at the beginning a mixture between Cu^+ and Cu^{2+} were found confirming the former results obtained at BM 23¹, for both other samples at the begin only Cu^{2+} was observed as expected. During the illumination CuI is significantly reduced to Cu^0 , whereas for $\text{Cu}^{2+}/\text{MCM-41}$ only a slight reduction and for CuO no reduction was observed. It can be stated clearly from these observation, that the more reducible the Cu is, the more active the sample is.

Surprisingly, for CuI the reduction of the Cu was not finished after 20 min and slower as we observed in former investigations.¹ In contrast to these investigations, the amount of reduced Cu is much higher at this recent investigations. The most probable reason for these differences are the different reaction cell design we used for the different studies. At BM 23 we used a capillary, for this recent measurements we used the reaction cell described above which allows measurements under conditions which are more realistic with the conditions in a “usual” chemistry lab or for further applications.

¹ H. Junge, Z. Codolà, A. Kammer, N. Rockstroh, M. Karnahl, S.-P. Luo, M.M. Pohl, J. Radnik, S. Gatla, S. Wohlrab, L. Lloret, M. Costas, M. Beller, *J.Mol.Catal.A: Chem.*, 2014, **395**, 449-456

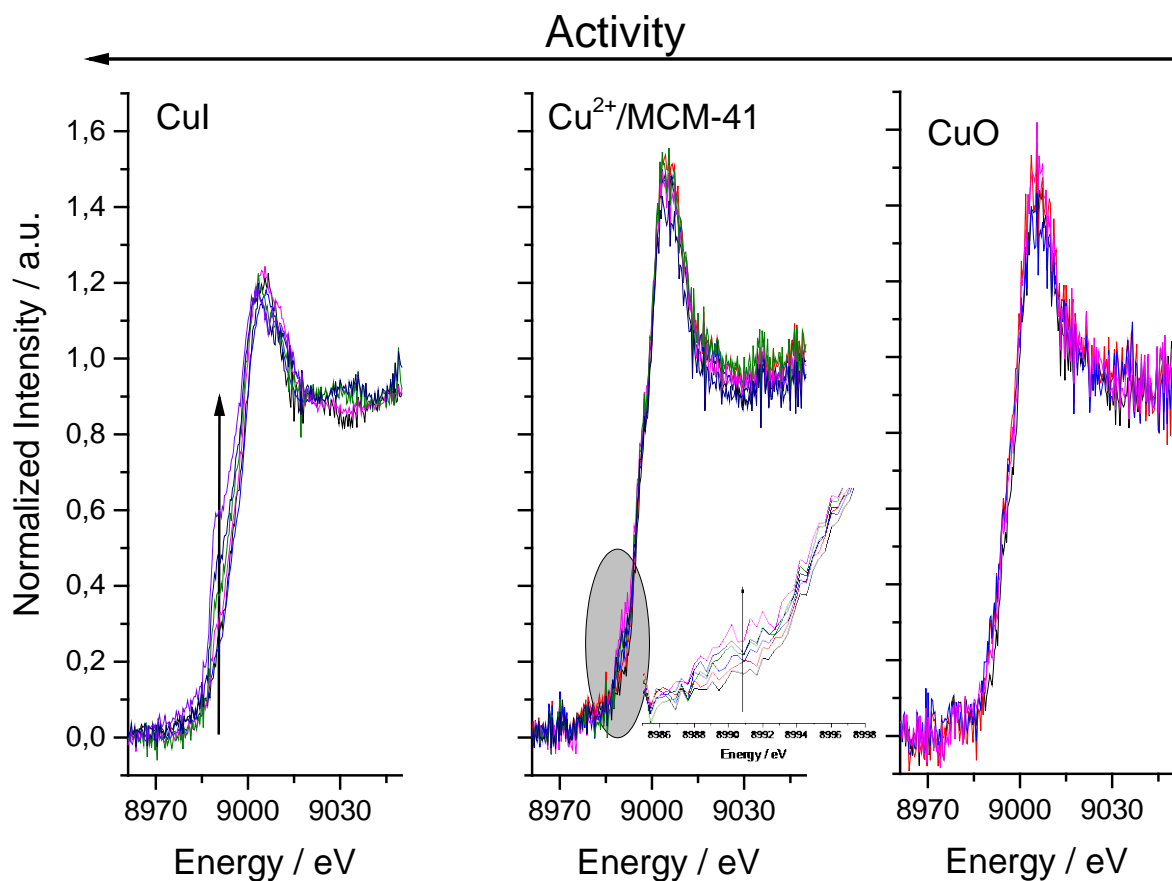


Fig. 2: Normalized XANES spectra of CuI, Cu²⁺/MCM-41 and CuO. The activity of the catalysts decreases from left to right. The inset shows the increase of the reduced species for Cu²⁺/MCM-41 (marked by the circle).

Conclusions

It could be shown that XAFS measurements are possible at ID 24 with a time resolution less than 1 sec or for low-concentrated samples with a time resolution in the second range. A clear relationship between reducibility of the Cu species and their activity in water splitting could be established. The new reaction cell design allows measurements under realistic conditions for homogeneous and for heterogeneous systems with liquid/solid phases. One still existing problem is the data reduction and evaluation for the high amount of spectra measured at such beamtime. It would be very helpful for the user, if the ESRF (or other members of the community) will find a good solution for this problem.