



Experiment title: Homogeneous goes to heterogeneous catalysts: EXAFS investigations at active Cu species for the photocatalytic water splitting

Experiment number:
CH-4235

Beamline: ID24	Date of experiment: from: 22/01/2015 to: 27/01/2015	Date of report: 27/02/2015
Shifts: 15	Local contact(s): Dr. Suresh Gatla	<i>Received at ESRF:</i>

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Report:

Proposal summary

A reduction of copper containing water reduction catalysts (Cu WRC`s) to metallic Cu occurs during the first minutes under illumination of UV-Vis light in presence of Ir photosensitizers (Ir-PS`s). Crucial for this reduction step are copper species stabilized on mesoporous silica (e.g. MCM-41) or intermediates obtained from homogeneous copper iodide (CuI). The main goal of the proposed experiments was to obtain deeper insights into the changes of active Cu and Ir species during photocatalytic water splitting. Consequently, time resolved in situ investigations would allow mechanistic investigations of the formation of intermediates, the reduction process and the interaction between the Cu nanoparticles and the Ir photosensitizer. Therefore, the main focus of the planned experiments was to identify the active structures during photocatalytic water splitting. Primarily, we intended to investigate the structural aspects of the Cu species, under illumination of UV-Vis light, with EXAFS at Cu K-edge (≈ 8.9 keV) at ID24 with 0.1 second time resolution. Secondly, it was planned to perform Ir L_{III}-edge (11.2 keV) EXAFS measurements in the same time range, seeking for possible interaction with the Cu species.

Experiment description

General

Our idea was to perform EXAFS measurements at Cu K and Ir L_{III}-edges under light on and off conditions for the two catalytic systems, namely homogeneous (CuI) and heterogeneous (CuO_x/MCM-41) samples. Since the kinetics of formation of active Cu species is in the timescale of seconds time resolved XAS measurements with time resolution of 0.1 s were needed to explore the appearing structures.

Experimental setup

The experimental setup was based on i) a reaction cell with two movable Kapton windows to set the distance between both and ii) a UV shutter where the solution can be illuminated with UV light to run the reaction (open modus) and to measure XAS in the dark (closed modus). This set up enabled XAS measurements without being perturbed by the hydrogen gas bubbles produced under UV irradiation (Fig. 1).

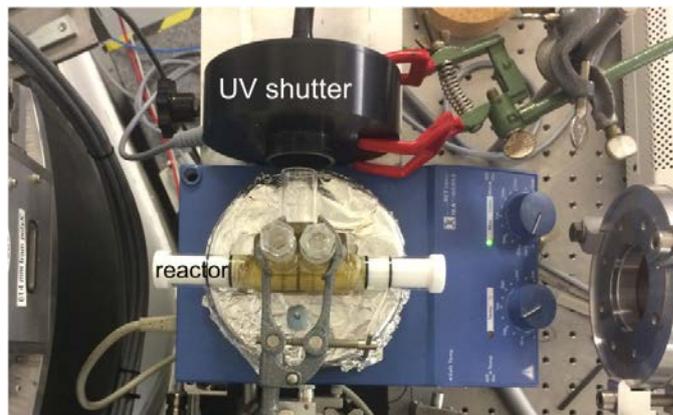
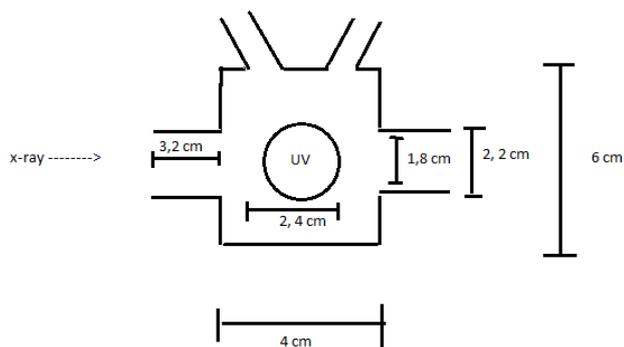


Fig. 1: Scheme of the reaction cell and its implementation in the experimental setup.

To conduct the in situ experiments the catalyst (40-160 $\mu\text{mol Cu}$) and the Iridium photosensitizer ($\text{Ir(ppy)}_2(\text{bpy})$, 60 μmol), were added to the reactor. Then a solution of THF/TEA/ H_2O (3:2:1, 10 ml) was added to the vessel. Afterwards, the reaction was started by opening the shutter while the UV-light source was permanent on (Lumatec, 1,5 W Xe lamp). Spectra were collected in the dark by closing the shutter by accumulating 100 - 7500 spectra (1 accumulation \sim 1 ms). The time resolution was achieved by sequential measurements. Each sequence is defined by a certain time period with UV light on and a subsequent spectra recording period in the dark.

Results and discussion

In our recent beamline CH4235 on ID24 serious problems with the beam (ring breakdown, no fast orbit correction, from 23/01/2015 to 25/01/2015) during the measurements at the Cu K-edge (\approx 8.9 keV) led to very noisy spectra which cannot be used for EXAFS analyses (e.g. Fig. 2, left). However, during the first few minutes of irradiation a clear shift of the absorption edge to lower energies was detected. This indicates a reduction of the oxidic Cu to a stable metallic copper which was already observed in capillary experiments¹ and could now be transferred at ID 24 in the new cell. With the high time resolution of ID24 it was now possible to monitor this reduction during the first minutes which was not possible with the acquisition time of 20 min, necessary for the investigation at BM 23. It must be noted, that the reduction was only observed under UV-Vis illumination. In contrast, using a stable beam (with fast orbit correction i.e. when machine operators got the control over the feedback system), the spectra at the Ir L_{III} -edge (11.2 keV) appear sharp (measured on 26/01/2015). To obtain sharp XANES spectra a time resolution of 100 ms is enough. Spectra with quality to investigate EXAFS was got with a time resolution of 0.3 s at the investigated low catalyst concentrations. These observation showed clearly that the setup (Fig 2. right) is appropriate for the planned photocatalytic investigations.

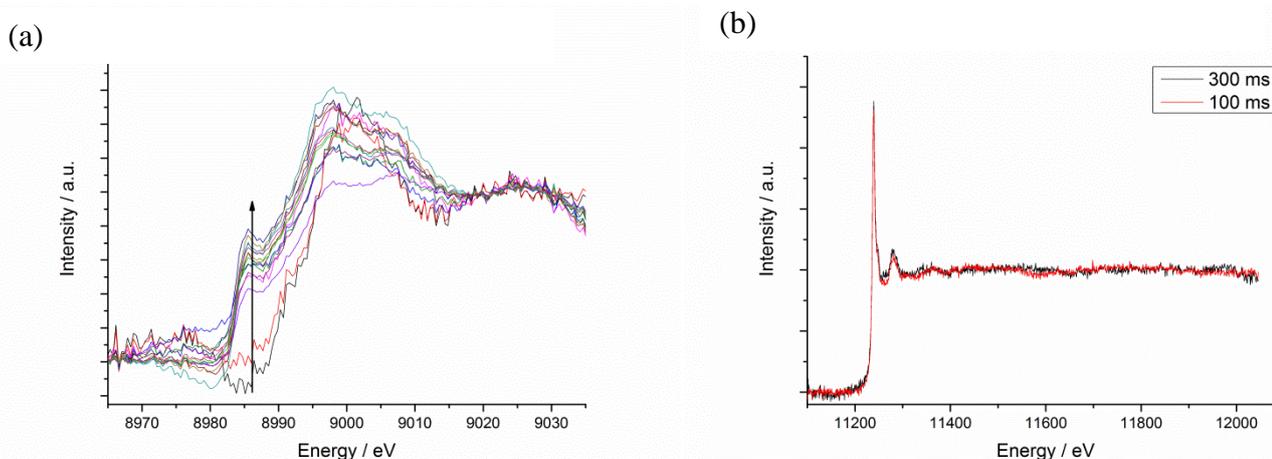


Fig. 2: Measured spectra from a starting solution containing 40 $\mu\text{mol CuI}$ and 60 $\mu\text{mol Ir-PS}$; a) no fast orbit correction, spectra at the Cu K-edge (\sim 8.9 keV) measured from 2-15 min under UV light illumination (13 sequences, UV shutter open: 60 seconds, UV shutter closed: 7500 spectra accumulations (1 ms each)); b) fast orbit correction, spectra at the Ir L_{III} -edge (11.2 keV) measured at 100, 200 and 300 accumulations $\hat{=}$ 100, 200, 300 ms.

New insights were obtained regarding the role of the Ir species. With the Cu-WRC the Ir-PS was already present in the oxidized active form, and then, reduced slowly to metallic Ir. Without Cu-WRC an initial oxidation of the Ir-PS was observed in the first minutes (Fig. 3), afterwards, the Ir-PS was also reduced. We assume underlying activation and deactivation of the Ir-PS depends on Cu-species present in the reaction solution.

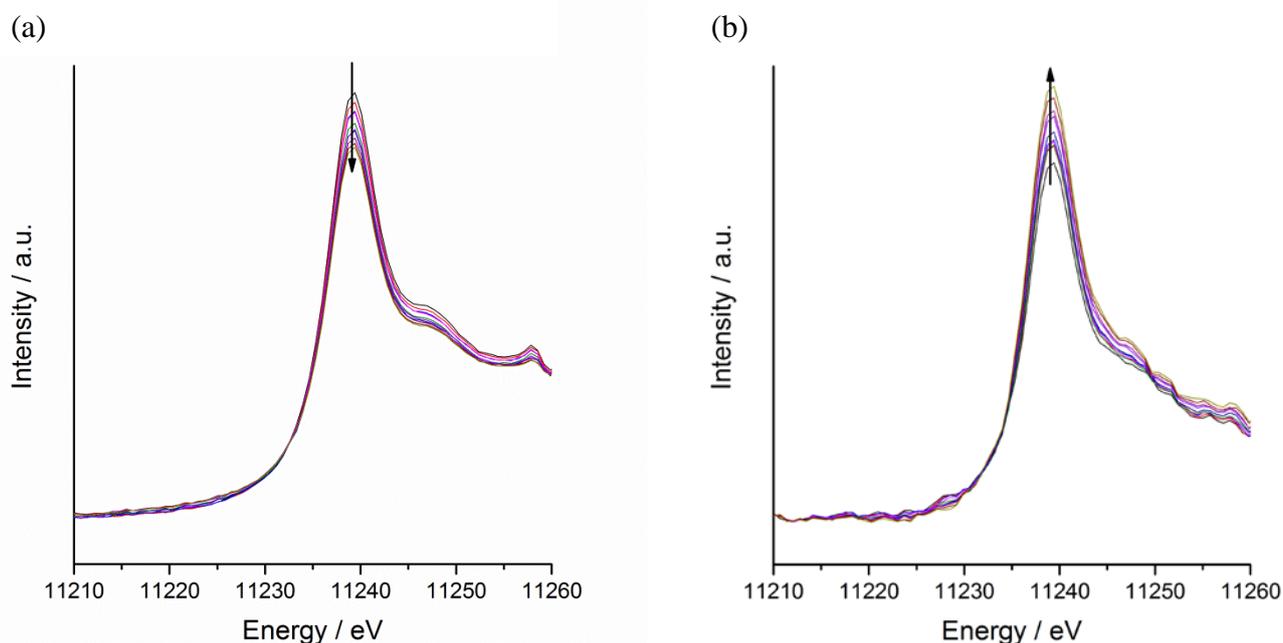


Fig. 3: Measured spectra at the Ir L_{III}-edge (11.2 keV) from a starting solution containing 60 μmol Ir-PS measured from 0 to 10 min under UV light illumination (10 sequences, UV shutter open: 60 seconds, UV shutter closed: 7500 spectra accumulations (1 ms each), a) in the presence of 40 μmol CuI and b) without Cu WRC.

Conclusions

It could be shown that measurements in ms time resolution are possible on this system. Additionally, further insights into the the formation and activation of Cu catalysts (time scale) and of the interaction between these species with the Ir photosensitizer were achieved. However, the comparison between the nanoparticles obtained from a homogeneous catalyst and the ones stabilized by mesoporous silica was not possible since measurement suffered from an unstable beam or even no beam. Systematic investigations on the IR-PS in dependence on the Cu-WRC could also not been executed.

In fact a deeper understanding in the underlying processes is necessary. This could help to lower the cost of preparation and would lead to better practicable catalysts. Since we principally showed the feasibility of such experiments, an effort from the LIKAT and ESRF, a systematic investigation would represent the first study of this kind with a comprehensive insight into homogeneous and analogous heterogeneous systems under reaction conditions.

Used shifts

Shifts 1-3,7: Setup, macros, tests

Shifts 4-6, parts of 9 and 10: no beam (no fast orbit feedback – no fast orbit correction)

Shifts 8, parts of 9 and 10: Kinetic measurements on the homogeneous CuI_Ir-PS system (Cu K-edge)

Shift 11: Orienting tests to measure heterogeneous Cu catalysts on MCM-41, change to Ir L_{III}-edge

Shifts 12-15: Kinetic measurements on the homogeneous CuI_Ir-PS system (Ir L_{III}-edge)

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.