ESRF	**Experiment title:** Enhanced photocatalytic hydrogen production on $CuPt/TiO_2$: understanding the promotion effect of Cu by modulated excitation X-ray absorption spectroscopy	**Experiment number**: CH-4579
Beamline: ID24	**Date of experiment**: from: 17/02/2016 to: 23/02/2016	**Date of report**: 22/02/2018
Shifts: 18	**Local contact(s)**: Giovanni Agostini	*Received at ESRF:*

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Report:

The set up of the experimental equipment into the hatch and correct alignment of the beamline lasted *ca.* 2 days. The data acquisition on the first sample started February 19th at 9:30 a.m. We have tested five samples: three samples of $2wt\%Cu/2wt\%Pt/TiO_2$ prepared by three different methods, *i.e.* flame spray pyrolysis (FSP), reverse micelle (RM), and Cu grafting + Pt deposition-precipitation (GDP), and $2wt\%Cu/TiO_2$ and $2wt\%Pt/TiO_2$ prepared by FSP. Each sample was tested in four different modulation experiments and measured at both the Cu K-edge (8979 eV) and at the Pt L3-edge (11564 eV), using a quartz capillary:
Exp1: 0.5% methanol/He, *vs.* 5% O_2/He in dark, RT
Exp2: 0.5% methanol/He in dark, *vs.* 5% O_2/He + UV-vis irradiation, RT
Exp3: 0.5% methanol/He in dark, *vs.* 1% H_2O/He + UV-vis irradiation, RT
Exp4: 5% H_2, *vs.* 5% O_2/He in dark, 200°C
The aim of this experiments was to simulate the aerobic (Exp2) or anaerobic (Exp3) photocatalytic methanol oxidation under dynamic conditions in order to reveal the redox dynamics of Cu and Pt.
In each experiment we acquired 15 consecutive cycles with a period of 240 s while recording 40 XAS spectra per period (*e.g.* in exp1 20 spectra recorded under 0.5% MeOH/He and 20 spectra recorded under 5% O_2/He). Each XAS spectrum was therefore measured in 6 sec and a whole experiment consisted of 600 XAS spectra. Because of the fast acquisition and low metal loading the obtained time resolved spectra where extremely noisy (Fig 1-A). However, because the phenomenon we were observing was fully reversible, it is possible to merge the 15 consecutive cycles in a single average cycle that leads to a considerable attenuation of the noise (Fig. 1-B). Finally, it is possible to apply the phase sensitive demodulation (PSD) algorithm [1] to the average time resolved spectra in order to convert the domain from the time to the phase resolved (Fig. 1-C). This latter step allows to extract the spectra variations due to the external stimulation (in this case the periodic variation of the gas phase composition and of the UV-vis irradiation). This spectroscopic approach is called Modulated Excitation X-ray Absorption Spectroscopy (ME-XAS) [1].

In-situ ME-XAS proved to be a valuable tool to elucidate the redox dynamics of the metal co-catalysts under photocatalytic conditions. In particular, the application of the PSD functions to the XANES spectra at both the Cu K- and the Pt L3-edges allowed us to reveal even small changes in the oxidation state of the metals when the photocatalysts underwent periodical variation of the gas phase composition. Under H_2O+UV-vis *vs* CH_3OH modulation both Pt and Cu irreversibly reduced in all samples. On the other hand, under O_2+UV-vis *vs* CH_3OH modulation, both Cu or Pt NPs alone were periodically partially oxidised in O_2+UV-vis and reduced in CH_3OH at RT. In contrast, no variation of the oxidation state was observed on the flame made Cu/Pt sample even under O_2 atmosphere. The different behaviour of the Cu/Pt system with respect to the single-metal NPs, *i.e.* an increased stability of the oxidation states during the different modulation experiments, is very likely due to the formation of a Pt-Cu alloy. Thus, the lower photocatalytic activity of the co-modified sample might be due to a decreased work function of the alloy with respect to the pure Pt and therefore to a reduced photopromoted electron trapping capability of the metals NPs. Finally, this results help to explain the different role of Cu and Pt co-catalysts under aerobic and anaerobic conditions. In particular, this work suggests that the switching between Cu^{+} and Cu^{2+} oxidation states for high Cu loading occurs only in presence of O_2 (left panels of Fig.1) but not of H_2O (right panels of Fig.1).

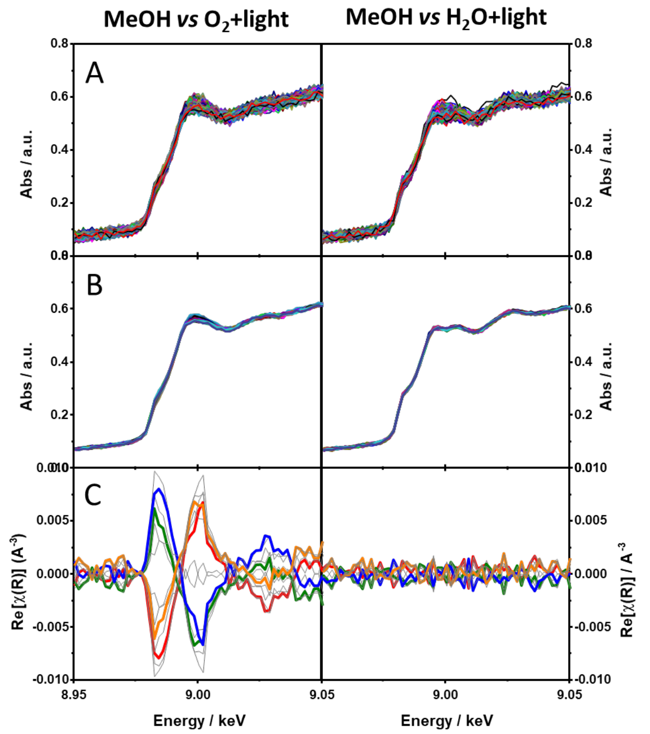

Figure 1: XANES spectra at the Cu K edge recorded under periodic variation of the gas phase composition. (A) the 600 time resolved spectra recorded during 15 consecutive cycles; (B) averaged time-resolved spectra; (C) phase-resolved spectra

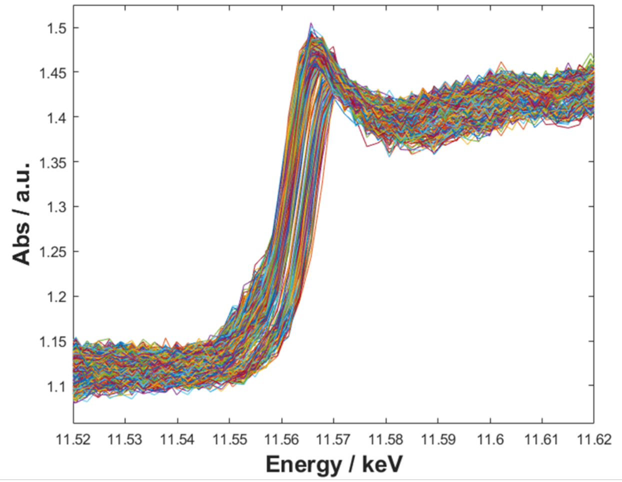

Figure 2: 600 time resolved XANES spectra at the Pt L3 edge showing that the energy was shifting randomly back and forward during the experiment.

The allocated beamtime was therefore successful, despite we had a great problem during the experiments recorded at the Pt L3-edge. In this case the energy was continuously randomly shifting back and forward (Fig. 2). The local contact himself was not able to fix this problem. Thus, it took us a big effort to post-align the thousands of recorded spectra. However, post processing of the spectra is a delicate task because of the risk to lose information or to introduce artifact. This spectra post treatment was extremely time consuming.

The results of this work was presented in an invited talk at the "AdvPhotoCat-E 2017 workshop, 16-18 July, Crete, Greece" and a paper will be soon submitted to *Catalysis Today*.

Reference

[1] G.L. Chiarello, D. Ferri, "Modulated excitation extended X-ray absorption fine structure spectroscopy", *Phys. Chem. Chem. Phys.*, 17 (**2015**) 10579–10591