

## Experiment Report Form

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- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



**Modulation Excitation XAS studies to Illuminate photothermocatalytic CO oxidation mechanisms over Pt-TiO<sub>2</sub> with different facets**

**Experiment number:**  
CH-5115

<b>Beamline:</b> ID24	<b>Date of experiment:</b> from: 5 Jul 2017 to: 11 Jul 2017	<b>Date of report:</b> 21.03.2018
<b>Shifts:</b> 18	<b>Local contact(s):</b> Dr. Manuel Monte Caballero	<i>Received at ESRF:</i>

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## Report:

### Introduction

Pt-based catalysts are extensively used in many different applications, e.g. as oxidation catalysts for environmental applications or in “hydrogen economy” acting in both production of hydrogen via e.g. catalytic partial oxidation and its utilization in fuel cells. Recently it was found that Pt nanoparticle-based catalysts can utilize both thermal energy and visible light irradiation to drive catalytic reactions under lower temperature or with altered selectivity compared to purely thermal excitation. Previously it was found that a DRIFTS cell is a suitable reactor for photocatalytic experiments and HERFD-XANES could be used to describe changes in the electronic structure of Pt species while catalysing CO oxidation under light and thermal excitation (see report CH-4576). Since recording HERFD-XANES spectra took time on the order of tens of minutes we now performed analogous experiments recording fast Energy Dispersive XAS spectra at the ID24 beamline using the catalysis infrastructure available at ID24 (primarily, the ID24 DRIFTS-XAS catalytic cell, gas dosing and mass spectrometer). The aim of the measurements was to confirm changes in the electronic structure of Pt species during photothermal oxidation of CO, to reveal changes in the electronic structure of Pt during photothermal conversion of CO<sub>2</sub> to CO / CH<sub>4</sub>, to obtain kinetics of photoassisted CO oxidation and CO<sub>2</sub> hydrogenation over Pt catalysts, and, if possible, to obtain structural information via ED EXAFS.

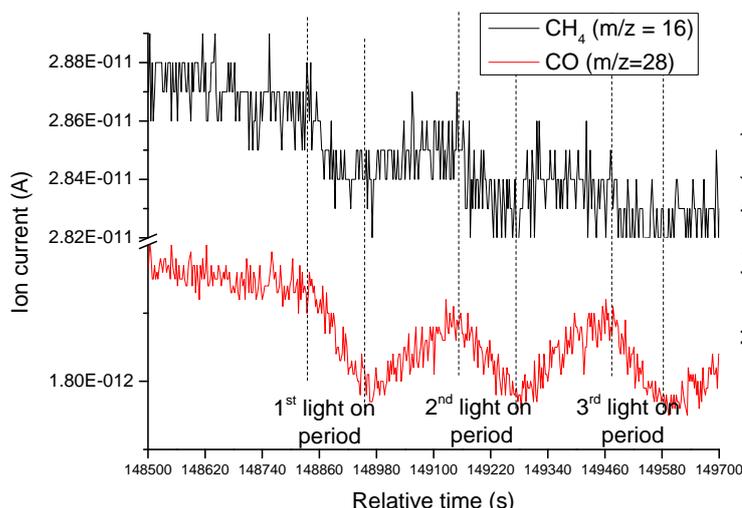
### Experimental Section

2.2 wt.% Pt/Al<sub>2</sub>O<sub>3</sub> was synthesized by incipient-wetness impregnation of SCFa-230 (Sasol)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with hexachloroplatinic acid [1]. Pt/TiO<sub>2</sub> with (101) exposed facets was made by wet impregnation of hydrothermally-made TiO<sub>2</sub> [2] with hexachloroplatinic acid. *Operando* ED XAS measurements at Pt L<sub>3</sub> absorption edge were performed at the ID24 beamline (ESRF, Grenoble, France). X-ray beam generated by 3 undulators was focused on the sample by a Si (311) polychromator. The catalyst sample in form of an approx. 0.5 mm thick wafer pressed without binder (2 tons) was placed in the ID24 home-made *in situ* DRIFTS-XAS cell. The transmitted X-rays were detected by a position sensitive detector (Hamamatsu).

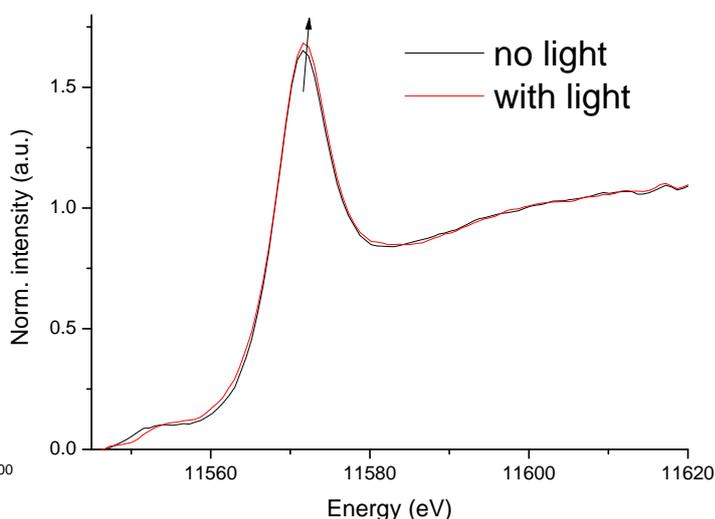
Schott KL 2500 lamp was used as a light source for photocatalysis in the light-assisted experiments. The catalysts were first pretreated (reduced) for 15 min at 400 °C in 5% H<sub>2</sub>/He and cooled to room temperature. Then the gas feed was changed to a mixture of 1000 ppm CO<sub>2</sub> and 2000 – 6000 ppm H<sub>2</sub> in He (total flow 100 ml/min) and the *in situ* cell was heated 200 and 300 °C. After CO<sub>2</sub> hydrogenation experiments the samples were again reductively pretreated for 15 min at 200 °C in 5% H<sub>2</sub>/He and exposed to CO oxidation feed (1000 ppm CO, 10% O<sub>2</sub> in He). During CO oxidation stepwise heating was performed from 30 °C to 70 °C and 130 °C. ED XAS spectra were recorded with a time resolution of 1 spectrum/sec. After 15 min stabilization time at each temperature the XAS spectra were recorded in repeating sequences which contained two groups each, a group with light on (2 min) and a group without light (another 2 min). A minimum of 10 such sequences were recorded in one experiment. I<sub>0</sub> reference signal for transmission data was obtained by recording intensity of X-rays transmitted through air before and after each sequence. Gas composition was monitored online using a Balzers Prisma quadrupole mass spectrometer.

## Results and Discussion

The photothermocatalytic and ED XAS measurements were performed using the *in situ* cell / catalyst configuration (self-supporting wafer) optimized for spectroscopy. In this configuration the feed gas was flowing around the catalyst wafer and the resulting conversions of the reacting species and product yields were negligible. Nevertheless, in certain experiments it was possible to observe changes in the product concentrations when light was turned on and off (Fig. 1). Therefore, we assume that the catalyst was working during the measurements.



**Figure 1.** Ion currents from CH<sub>4</sub> (m/z=16) and CO (m/z=28) observed during photothermally activated hydrogenation of CO<sub>2</sub> over Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (1000 ppm CO<sub>2</sub> and 6000 ppm H<sub>2</sub> in He, 300 °C).



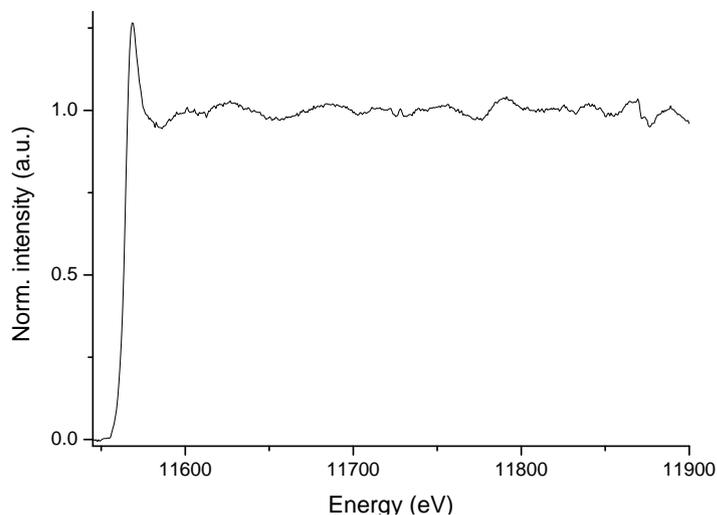
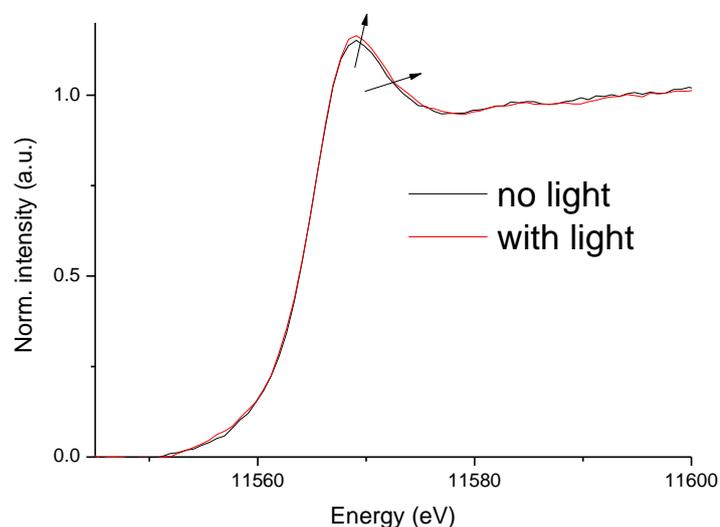
**Figure 2.** Changes in the ED XANES spectra of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst during oxidation of CO with and without light (1000 ppm CO and 10% O<sub>2</sub> in He, 130 °C).

Exemplary ED XAS spectra obtained during photothermal oxidation of CO are shown in Fig. 2. As observed earlier with HERFD-XANES (experiment CH-4576), under light irradiation the “whiteline” intensity in the Pt L<sub>3</sub> XANES spectra was higher than without light confirming lower electronic density (i.e. partial oxidation) on Pt sites. During continuous light-on/light-off switching Pt sites were slowly but constantly oxidizing. Hence, the observed partial oxidation of Pt is a slow process on the order of minutes. This allows suggesting that the observed decrease on electronic density on Pt is not primarily caused by light irradiation but is due to adsorption of oxygen on bare Pt sites left after light-induced desorption of CO in form of CO<sub>2</sub> (publication in preparation).

Under strongly reducing CO<sub>2</sub> hydrogenation conditions Pt sites stayed in nearly fully reduced state (Fig. 3) and almost to no difference was observed under conditions with and without light irradiation. Small changes in the Pt L<sub>3</sub> XANES spectra included mainly slightly broader “whiteline” typical of Pt sites covered with CO [2]. Whether the observed CO is a reaction product or an intermediate which is hydrogenated further is currently unclear. Background (I<sub>0</sub>) spectra for the hydrogenation datasets were stable resulting also in stable energy scale and shape of the spectra, therefore, treating the datasets as modulation-excitation data to improve signal-to-noise ratio and obtain kinetic information is possible. Unfortunately, even in the phase-resolved

spectra the signal due to light is below the noise level. Hence, irradiation with light was not found to affect structure of Pt species during photothermocatalytic CO<sub>2</sub> hydrogenation in the current study.

Regarding analysis of the extended X-ray absorption fine structure (EXAFS) in spite of low noise level oscillations due to sample inhomogeneity (Fig. 4) prevent extraction and analysis of the EXAFS signal. Further complication for the data analysis were shifts in the energy scale (on the order of several eVs) and changes in the I<sub>0</sub> (background) spectra occurring spontaneously during the some experiments.



**Figure 3.** ED XANES spectra of Pt/TiO<sub>2</sub> catalyst during hydrogenation of CO with and without light (1000 ppm CO<sub>2</sub> and 6000 ppm H<sub>2</sub> in He, 300 °C).

**Figure 4.** X-ray absorption spectrum of the Pt/TiO<sub>2</sub> catalyst showing EXAFS region.

## Conclusions

ED XAS using the DRIFTS-XAS *in situ* cell and catalysis infrastructure available at ESRF ID24 was used to monitor electronic structure of Pt species in Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/TiO<sub>2</sub> catalysts during photothermocatalytic oxidation of CO and hydrogenation of CO<sub>2</sub>. It was found that light irradiation and the catalytic process induced by it changed electronic structure of Pt sites. In the case of CO oxidation partial oxidation of Pt observed previously (see report CH-4576) was confirmed and ascribed to a secondary process (adsorption of oxygen species after the catalytic effort). In the case of CO<sub>2</sub> hydrogenation a signature of CO adsorbed Pt sites was found as a result of light irradiation. To determine whether this is a primary result of light irradiation or the spectral changes are simply caused by the fact that CO is one of the products of CO<sub>2</sub> hydrogenation will require further analysis.

## Acknowledgements

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## References

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2. Y. Zhou, D. E. Doronkin, M. Chen, S. Wei, J.-D. Grunwaldt, *ACS Catal.* 6 (2016) 7799–7809.