DXAS study of Pt-Sn supported catalysts during in-situ reduction treatments

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INTRODUCTION

X-ray absorption spectroscopy (XAS) can probe the local structure of very diluted and dispersed species, as occurs for active ones in catalysts. These studies can be performed even during catalytic reactions, by using in situ spectroscopic cells with realistic and well-defined hydrodynamics. The experimental cell reported here was previously employed in conventional X-ray absorption beamlines [1]. We endeavored to combine the specific characteristic of our cell with those of the DXAS beamline at the LNLS. The aim is to obtain a suitable experimental set up for time solved XAS catalysts characterizations. Although these first experiments do not provide any relevant information from the catalytic point of view due to experimental inconveniences at the beamline, from the instrumentation aspect it represents an attractive methodology for studies in catalysis. In this work we present preliminary EXAFS results obtained for Pt and PtSn catalyst supported on SiO_2 at the Pt L_3 edge at the DXAS beamline during reduction treatment in H_2 flux in function of temperature.

EXPERIMENT

An in situ X-ray absorption reaction cell [2] was replicated from a model used by the group of E. Iglesia at UCB, Berkeley, CA (USA), which was a modified version of a previously reported reaction cell [3]. The details are reported elsewhere [1]. The cell consists of a quartz capillary (0.8 or 1.6 mm inner diameter, 0.1 or 0.2 mm wall thickness, 100 mm length) mounted horizontally into a stainless steel base using metal fittings and graphite ferrules (Figure 1).

Samples with 180-250 μm particles formed a dense bed through which gas flows with negligible pressure drop and plug-flow hydrodynamics. Heat is supplied by four cartridge heaters (600 W of maximum power in total) mounted into a finned copper block. The copper block is insulated using a ceramic foam casing. A 20 x 4 mm beam path was cut into the finned copper block and the ceramic insulation in order to provide a clear path for the X-ray beam (10 x 0.2 mm) at a 45° angle through the middle section of the capillary. This configuration was modified after the first tests and a 90° setup was adopted. This change made it easier to align the sample and to move it to perform experiments at a point where a uniform absorption was observed.

Gases were introduced into the cell from lecture bottles mounted in a portable gas manifold unit with built-in gas purifiers (O_2 and H_2O remover) mass flow valves. Features of this XAS cell include small sample loadings (1-10 mg), low flow rates (1.3-13.4 mmol/h), and plug-flow hydrodynamics.

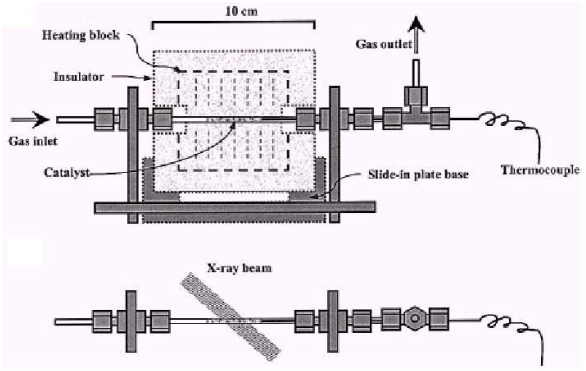

FIG. 1: In-situ experimental cell. Lateral (top figure) and top view (lower figure). Taken form reference 1.

For the preparation of the platinum monometallic catalysts a solution of $[Pt(NH_3)_4]^{2+}$ was added on functionalized silica. The solution had a concentration so as to obtain 1 wt % of Pt exchanged on the support. Then, the solids were repeatedly washed, dried at 105 °C, calcined in air at 500 °C and reduced in flowing H_2 at the same temperature. The bimetallic systems have been prepared by reaction between the monometallic catalyst and different quantities of $SnBu_4$ dissolved in n heptane, maintaining a H_2 flow of 30 cm^3 min^{-1} and a temperature of 90 °C during the reaction time. Powder samples were introduced in the capillary cell and placed in the DXAS beamline for the absorption experiments at the Pt L_3 edge. Temperature was raised between ambient temperature to 500 °C at a rate of 5°C/min. One frame every second was acquired at the DXAS beamline and 100 frames were summed in every spectrum.

RESULTS AND DISCUSSION

Figure 2 show the absorption spectra obtained for the monometallic Pt/SiO_2 catalyst during the reduction treatment in H_2 flux . The reduction of Pt atoms is clearly evidenced in the decrease of the white line intensity as temperature is raised; however, the poor resolution of the experiment makes it difficult to compare the results with those obtained previously at the XAS beamline for the same sample. The low content of Pt in the samples is another problem which makes the spectra very noisy, and no feature from the EXAFS oscil-

lation can be observed.

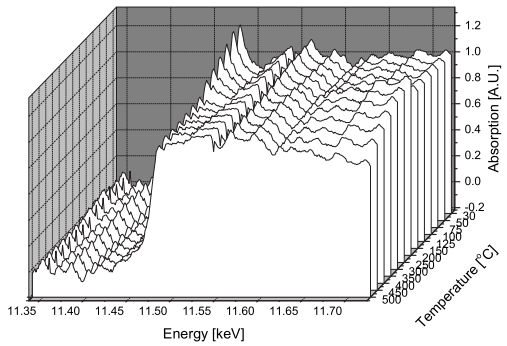

FIG. 2: Pt-L_3 EXAFS spectra of Pt/SiO_2 catalyst during reduction treatment

Figure 3 shows the absorption spectra taken during the reduction treatment of a PtSn organometallic catalyst. In this case, no visible changes can be seen during the experiment. As we have already seen [4], differences in the XANES spectra before and after reduction are very small and can not be detected in these experiments.

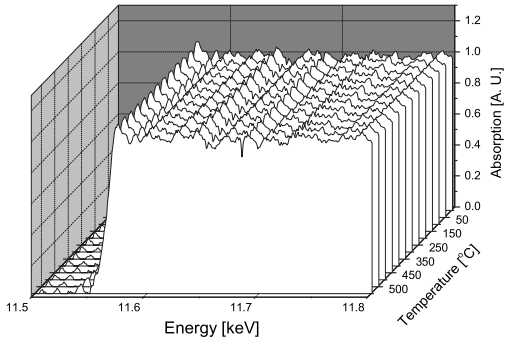

FIG. 3: Pt-L_3 EXAFS spectra of $PtSn/SiO_2$ organometallic catalyst during reduction treatment

CONCLUSION

For the monometallic sample the only feature from which some information can be taken in the Pt L_3 absorption spectra is the intensity of the white line. The reduction of the Pt atoms is clearly seen during the treatment through the decrease of the white line intensity, but a lost of resolution is observed. Because of the low statistic of the experiment, the EXAFS part of the spectra does not give any useful information. In the case of the bimetallic sample, no evidence of the formation of the alloy can be observed, even from the XANES part of the spectra.

ACKNOWLEDGEMENTS

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