

	Experiment title: Evolution of Pt-Sn alloys under redox environment studied by in-situ XAS	Experiment number: 26-01-1141
Beamline: BM26A	Date(s) of experiment : 31/05/2018 – 05/06/2018	Date of report: 28-06-2018
Shifts: 15	Local contact(s): Alessandro Longo	
Names and affiliations of applicants: Dr. POELMAN Hilde (+32 (0)9 331 17 22, Hilde.Poelman@UGent.be) Dr. GALVITA Vladimir (Vladimir.Galvita@UGent.be) Ir. Nadadur Veeraraghavan Srinath (N.V.Srinath@UGent.be) Prof. dr. ir. MARIN Guy B., (Guy.Marin@UGent.be) All from Ghent University, Laboratory for Chemical Technology, Technologiepark 914, B-9052 Ghent, Belgium		

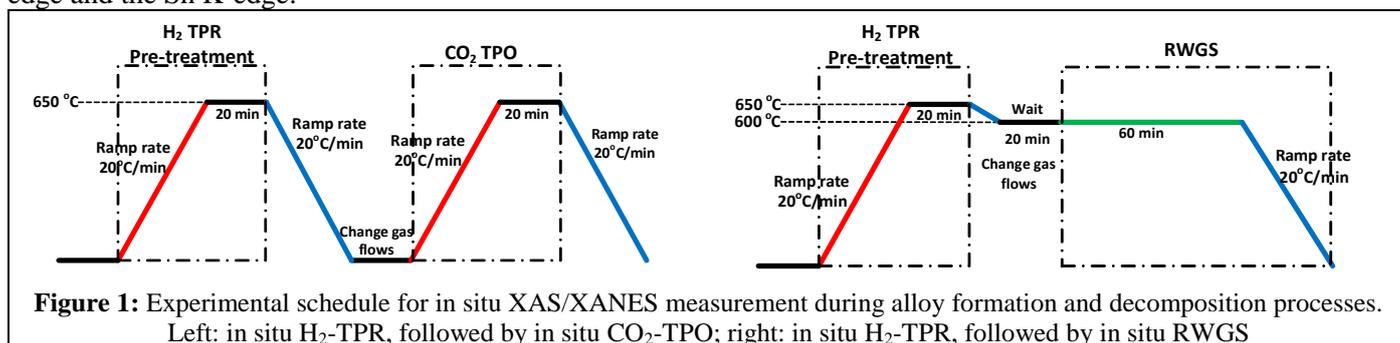
Summary

The effect of the gas environment upon the structure and behaviour of Pt-Sn bimetallic catalysts supported on $MgAl_2O_4$ was studied. Pt-Sn catalysts are widely used for non-oxidative propane dehydrogenation reaction. The behaviour of these catalysts under oxidative conditions is not widely examined and is interesting to explore in view of understanding deactivation. Reduction usually leads to alloy formation, while an oxidising gas can cause atomic rearrangement like dealloying or segregation.

The bimetallic catalysts were prepared by wet-incipient impregnation (WI) on high or low surface area $MgAl_2O_4$ support (HSA – $97m^2/g$ and LSA – $5m^2/g$) and by atomic layer deposition (ALD) (on LSA support). These catalysts were tested for redox activity and the reverse water gas shift (RWGS) reaction. The active phase is a PtSn alloy that is formed upon reduction of the catalysts at 873K. This was followed by TPO with CO_2 at 873K and then reduction again under H_2 atmosphere before performing RWGS. Structural differences based on preparation method (WI vs. ALD) were investigated by XAS as well as the effect of a redox environment on the catalyst. Further, different ratios of Pt:Sn (1:1, 3:1, 5:1) were used to see the effect of the respective metal compositions on structure, reduction, phase etc.

Experimental conditions

For all samples, the experiments as in **Error! Reference source not found.** have been conducted, at both the Pt L_{III} -edge and the Sn K-edge:



XANES was measured during temperature programmed treatments, while EXAFS was recorded at low temperature after cool down. Some in-situ XRD (fast XRD) measurements were also performed in combination with XAS to see the phases that are present/forming in the reduction/oxidation steps.

Experiments performed and results

- Comparison between Pt:Sn/ $MgAl_2O_4$ HSA-WI and LSA-ALD as prepared and after RWGS at the Sn K edge**
Figure 2 shows the EXAFS R-space spectra at the Sn edge. While the as prepared spectra are quite similar, a clear difference can be seen between the 2 samples after the RWGS. This means that after RWGS different contributions are observed for the 2 samples.
- Comparison between as prepared Pt:Sn/ $MgAl_2O_4$ (HSA & LSA, WI and ALD) at the Pt L_{III} -edge**

Figure 3 shows the R-space signal of the as prepared samples. There is a clear difference in the intensity of the peaks of the fresh samples. This is because for the ALD sample the Pt is deposited as Pt while in the wet-impregnated samples upon calcination Pt is present as PtO₂. The Pt:Sn LSA and HSA samples have an oxide peak due to their calcination in air. The figure suggests that the LSA sample has less O and more Pt-Pt as compared to the HSA sample.

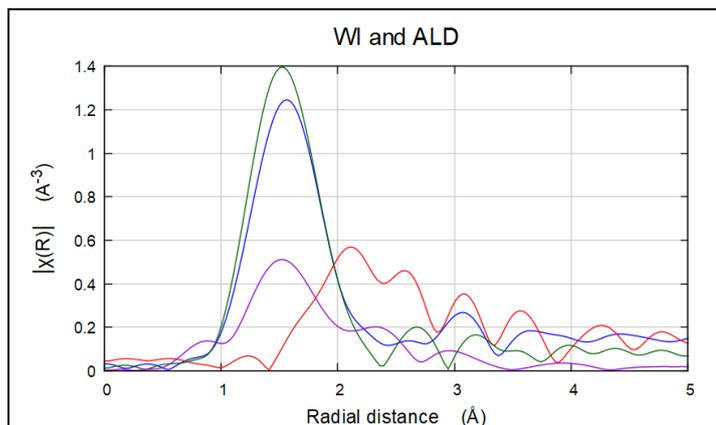


Figure 2: Sn-edge, for 5:1 Pt:Sn/MgAl₂O₄ (HSA-WI) and (LSA-ALD), fresh and after RWGS. Blue- as prepared LSA-ALD sample, red- idem after RWGS; green- as prepared HSA-WI sample, purple- idem after RWGS.

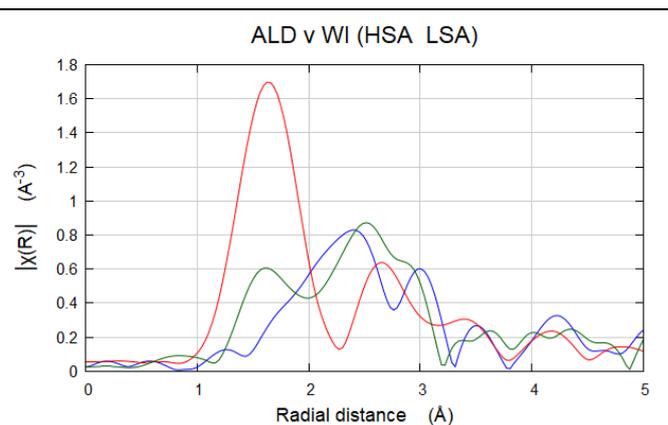


Figure 3: Pt-edge, for 3:1 Pt:Sn/MgAl₂O₄ (HSA-WI and LSA-WI) and for LSA-ALD. Blue- as prepared LSA-ALD, red- as prepared HSA-WI, green- as prepared LSA-WI.

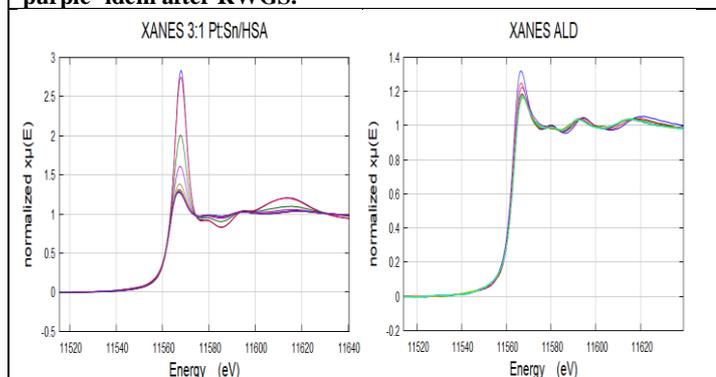


Figure 4: XANES spectra during H₂-TPR for left: 3:1 Pt:Sn/MgAl₂O₄ (HSA-WI) and right: LSA-ALD sample at Pt-edge.

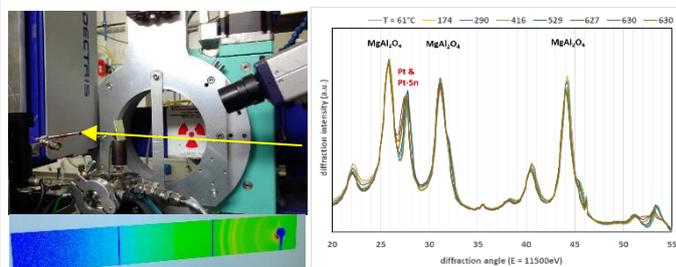


Figure 5: left: setup for simultaneous XAS (photodiode) and XRD (Dectris - Pilatus) with collected 2D pattern below; right: integrated XRD pattern collected in situ during H₂-TPR and simultaneous XAS-XRD measurement.

3. Comparison of XANES during reduction for 3:1 Pt:Sn/MgAl₂O₄ (HSA-WI) and LSA-ALD at the Pt L_{III} edge

Figure 4 shows the XANES spectra at the Pt-edge for the WI and ALD samples. A clear reduction is observed for the WI sample (left - 96% reduction), while the white line intensity for the ALD sample is initially almost at the level of the Pt-foil, which is expected due to it being deposited as Pt (right).

4. XRD measurements during the 4 treatments for the Pt:Sn catalyst (HSA-WI)

On the last beam time day, the setup was changed to allow for simultaneous in situ XAS-XRD recording. XAS was now recorded using a photodiode, while a Pilatus detector measured the diffracted X-ray intensity. The sample was now mounted in a modified microtomo reactor cell, allowing X-ray detection above the horizontal plane. Figure 5 shows a picture of the setup and an in-situ XRD measurement recorded during in-situ treatment of the catalyst. This in-situ XRD measurement was synchronized with the in-situ XANES measurements and both of them were measured together up to a temperature of 773K. While in-situ XAS gives information about the chemical state and short range order, the XRD probes the long range order. The XRD data were collected in order to determine which Pt:Sn phase was present/formed during the experimental process and various such images have been collected.

Concluding, a nice set of XAS data has been collected on several Pt:Sn/MgAl₂O₄ samples both at Pt and Sn edge under different conditions (reduction, CO₂-oxidation and RWGS). This will allow for several comparisons to be made, e.g. synthesis method (ALD vs. WI), support (HSA vs. LSA), ratio Pt:Sn, and their respective influence on the structure and behavior of the bimetallic catalyst. Some differences already appear from a first comparison of XANES and R-space spectra. This will be further examined by modelling of these data. In addition, a first use of combined in situ XAS-XRD was made and evaluated in collaboration with the beam line scientist.

The results of this campaign will be used in a publication with a working title 'Nature of Pt:Sn sites under reducing/oxidizing environment studied by in-situ XAS'.