ESRF	**Experiment title:** In Situ GISAXS during Dual Atomic Layer Deposition of Pt and In_2O_3 - Towards the Controlled Formation of Nanostructured Bimetallic Pt-In Catalysts	**Experiment number**: 26-02-743
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Introduction – Our work explores the potential of ALD for the controlled synthesis of In_xPt_y bimetallic nanoparticles (BMNPs) for catalytic applications. Our approach starts with the ALD of an In_2O_3 layer with a defined thickness onto a silica support, followed by the deposition of a controlled amount of Pt. The as-deposited Pt/In_2O_3 bilayer is then subjected to a temperature-programmed reduction (TPR) in hydrogen to induce the formation of a pure In_xPt_y phase. By proper tuning of the deposited Pt/In ratio, the synthesis of a well-defined phase ($InPt_3$, In_9Pt_{13}, In_2Pt, In_7Pt_3) is accomplished, as confirmed by XRD. After reduction up to 700 °C, all alloyed phases present bimetallic particles on the support surface, with sizes ranging from microscale down to the nanoscale depending on the total amount of deposited material. In this campaign, we performed an *in situ* GISAXS study during the TPR of a series of Pt/In_2O_3 bilayers with different Pt/In ratios and different total film thicknesses to get **insights in the particle formation mechanism** during TPR.

Methods – Three series of Pt/In_2O_3 bilayers with respective Pt/In ratios of 75 %, 60 % and 45 % were prepared by ALD in our home-lab. Each sample series consisted of three samples with different total bilayer thicknesses in the range 1 to 4 nm. At the DUBBLE beamline, all samples were reduced by heating in 20% H_2/He to 700 °C using a ramp rate of 0.2 °C/s, while *in situ* GISAXS patterns were continuously recorded using 30 s measurements (E = 12keV, $\alpha_i = 0.5°$, sample-detector distance = 4.1 m). Simulations were done in IsGISAXS assuming truncated spheres arranged on a regular 2D lattice [1]. For form factor calculation, the distorted-wave Born approximation (DWBA) was used, including the model of the graded interface [2]. The interference function was based on the 2D paracrystal model. The distance distribution was described by a Gaussian function, while a log-normal distribution function was assumed for the particle dimensions.

Results – In this experimental report, we discuss the data and analysis for one particular sample, while similar results have been obtained for the other samples. The considered as-deposited sample consists of a bilayer with equivalent thicknesses of 1.0 nm Pt and 0.7 nm In_2O_3, yielding a Pt/In ratio of 76%, as confirmed by compositional analysis. *In situ* XRD characterization during TPR of the sample (performed in our home-lab) shows a shift of the Pt (111) peak towards lower 2θ around 330 °C (Fig. 1(a)), implying expansion of the Pt fcc lattice due to insertion of In (atomic radius of 167 pm) into the Pt (atomic radius of 139 pm) structure. This incorporation of In facilitates the alloying and the stabilization of the diffraction peak at 39° suggests the formation of an $InPt_3$ fcc structure. Comparison of the GISAXS lobe observed for the as-deposited sample with simulations (Fig. 1(b)) shows that the Pt ALD process resulted in particles with an average size of 3-4 nm and center-to-center distance of 5.5 nm, as expected due the initial nucleation-controlled growth mode for Pt ALD [see e.g. experimental report 26-02-709]. After TPR up to 700˚C, the scattering in the GISAXS pattern arised from the $InPt_3$ BMNPs as indicated by XRD. The appearance of the

scattering lobe at a lower q_y-value and the presence of a secondary lobe in the q_z-direction indicate that the BMNPs are larger than the as-deposited Pt nanoparticles (Fig. 1(c)). Based on simulations, we estimate the average BMNP size and center-to-center distance to be 7.1 nm and 21 nm, respectively. The temporal evolution of the above-mentioned scattering features is clearly visible in the 2D color plots representing horizontal and vertical intensity line profiles (Fig. 1(d), left). A stable scattering pattern is observed up to a temperature of ca. 300 °C. The horizontal cuts reveal that the onset of alloying observed in *in situ* XRD is accompanied by a gradual shift to lower q_y-values and intensification of the main scattering lobe, followed by a stabilization of the scattering at ca. 450 °C. In the vertical cuts, we observe a clear shift of the scattering minimum to lower q_z-values between 300 and 450 °C. These results indicate that the insertion of In in the Pt fcc lattice goes together with a redistribution of the Pt atoms on the surface causing on average 9 as-deposited Pt nanoparticles to coalesce into a larger BMNP. Above 450 °C, the lateral morphology remains stable, while the increase in $InPt_3$ crystallinity as indicated by *in situ* XRD is accompanied by a gradual increase in particle height (ca. 1 nm from 450 to 700 °C) as concluded from the slow continuous decrease of the $q_{z,min}$-value. In conclusion, the *in situ* GISAXS and XRD studies allow us to conclude that the alloyed phase and particle morphology are formed simultaneously during the TPR.

In view of catalytic applications, the coarsening behavior of the BMNPs was studied during oxidation-reduction cycling. During oxidation in 20% O_2/He, no distinct changes were observed in the scattering pattern (Fig. 1(d), middle), indicating a stable sample morphology. Also during the subsequent reductive treatment a stable lateral scattering was observed, while the vertical scattering revealed a slow increase in particle height above 400 °C (Fig. 1(d), right). Complementary *in situ* XRD showed the repetitive segregation of $InPt_3$ into Pt and In_2O_3 under oxidative environment and realloying under reducing environment. During a previous campaign, we studied the oxidation/reduction of monometallic ALD-grown Pt nanoparticles on a planar silica surface and concluded that the morphology remains stable during reduction, while the oxidative environment caused the Pt particles to sinter at temperatures exceeding 550 °C [experimental report 26-02-726]. Moreover, we showed that an ultrathin Al_2O_3 overcoat could delay the particle coarsening to 800-900 °C. Based on these observations, we believe that under O_2 environment the In in the BMNPs oxidizes and forms a protective In_2O_3 shell surrounding a Pt core, thus preventing the Pt to sinter.

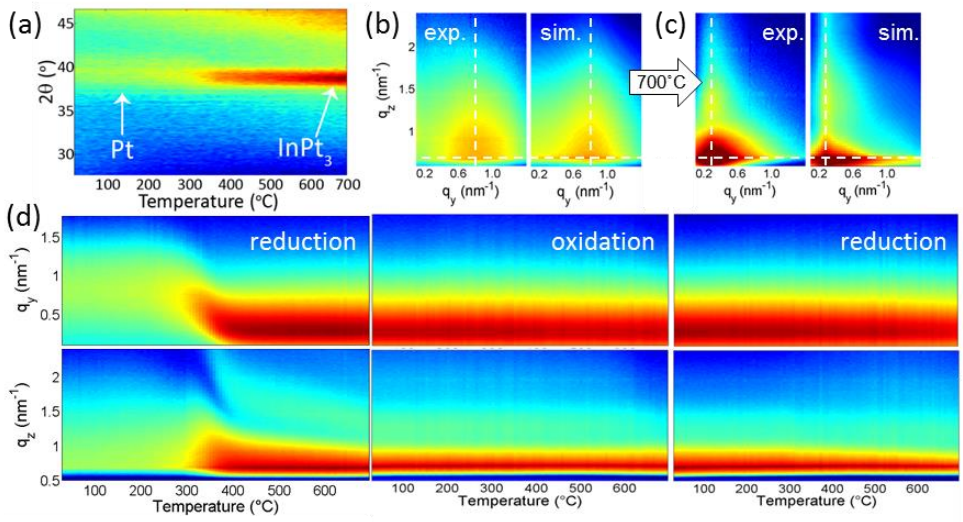

Figure 1. (a) *In situ* XRD patterns measured during TPR in 10 % H_2/N_2. **(b,c)** Experimental and simulated GISAXS pattern of the as-deposited Pt/In_2O_3 bilayer **(b)** and the BMNPs obtained after TPR in 20 % H_2/He up to 700˚C **(c)**. **(d)** 2D color maps showing the intensity evolution of the horizontal line profile at q_z = 0.69 nm^{-1} (top) and the vertical line profile at $q_{y,max}$ (bottom) during TPR in 20 % H_2/He (left), oxidation in 20 % O_2/He (middle), and TPR in 20 % H_2/He (right).

Conclusions – From the *in situ* GISAXS study, it is concluded that the morphology of the In-Pt BMNPs obtained after TPR up to 700 °C is driven by the alloy formation, as shown here in Fig. 1 for the $InPt_3$ phase. Two more trends were observed: (i) in general the average particle size decreases with decreasing amount of deposited material, and (ii) for the same amount of material deposited, larger BMNPs are obtained for the most Pt-rich phase, $InPt_3$, than for the other phases. A manuscript "Tailoring size and composition of bimetallic nanoparticles through atomic layer deposition" is in preparation and will soon be submitted.

[1] Lazzari, R. *J. Appl. Cryst.***2002**, *35*, 406-421. [2] Lazzari, R. et al. *Phys. Rev. B* **2007**, *76*, 125411.