ESRF	**Experiment title:** *In Situ* GISAXS Study of the Sintering Behavior of Pt Nanoparticles Synthesized and Stabilized by Atomic Layer Deposition	**Experiment number**: 26-02-726
Beamline: BM26B	**Date of experiment**: from: 17/06/2015 to: 22/06/2015	**Date of report**: 03/08/2015
Shifts: 15	**Local contact(s)**: PORTALE Giuseppe	*Received at ESRF:*

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Report:

Introduction - *In situ* GISAXS and XRF measurements were performed at the DUBBLE BM26B beamline with the aim to investigate the thermal sintering of supported Pt nanoclusters. The nucleation and growth of the Pt nanoparticles by Atomic Layer Deposition (ALD) were previously studied at the same beamline (26-02-672 Jan 2014, 26-02-709 Feb 2015). The first goal of the above-mentioned experiment (26-02-726 Jun 2015) was to study the influence of different conditions on the nanoparticle coarsening, i.e. the substrate nature, initial nanoparticle size and density, and heat treatment atmosphere. Secondly, we evaluated the use of ALD-grown oxide overcoats to prevent nanoparticle sintering.

Experimental – In the beginning of the campaign, we encountered some problems with the monochromator cooling system and had a power outage in the experimental hutch. After solving these problems with the adequate help of the beamline staff, we performed 23 different experiments. These experiments consisted of the controlled heating of Pt nanoparticles supported on three different substrates (SiO_2, Al_2O_3 and MgO) under two different atmospheres (20% O_2 in He and 20% H_2 in He) and with three different starting nuclei densities (obtained by applying a different number of ALD deposition cycles). In addition, a set of supported Pt samples with different thicknesses of Al_2O_3 overcoats was annealed to elucidate the optimal thickness for preventing particle migration and sintering. All samples were heated to 1000^{o}C using a fixed ramp of 1^{o}C/s until 400^{o}C, 5^{o}C/min until 800^{o}C and 10^{o}C/min until 1000^{o}C. *In situ* GISAXS and XRF measurements were continuously recorded during the anneals to monitor the evolution in particle density and dimensions (acquisition time 20 s).

Results - Figure 1 shows the GISAXS patterns measured at 50, 550, 700, 850 and 1000^{o}C during the annealing of Pt nanoparticles grown by 50 ALD cycles on a SiO_2 substrate. The top row (a) shows the images obtained during annealing in O_2 atmosphere. The bottom row (c) was recorded during annealing in H_2. Finally, the middle row (b) shows the effect of a 0.5nm Al_2O_3 overcoat on the coarsening behavior of the Pt nanoparticles in O_2. In all cases, there is hardly any change in particle morphology for annealing temperatures up to 550 ^{o}C. For higher temperatures, particle sintering can be observed in the GISAXS patterns as a shift of the scattering lobes towards smaller q_y-values. This indicates a decrease in center-to-center particle distance and an increase in lateral particle size. Moreover, the second order lobes along q_z shift towards smaller q_z values, meaning that also the particle height increases. Comparison of the top (a) and bottom (c) row shows that particle sintering starts at lower temperatures in O_2 than in H_2. In an O_2 rich atmosphere, PtO_x species are likely formed that can migrate over the surface and cause the larger Pt particles to grow at the cost of smaller particles.

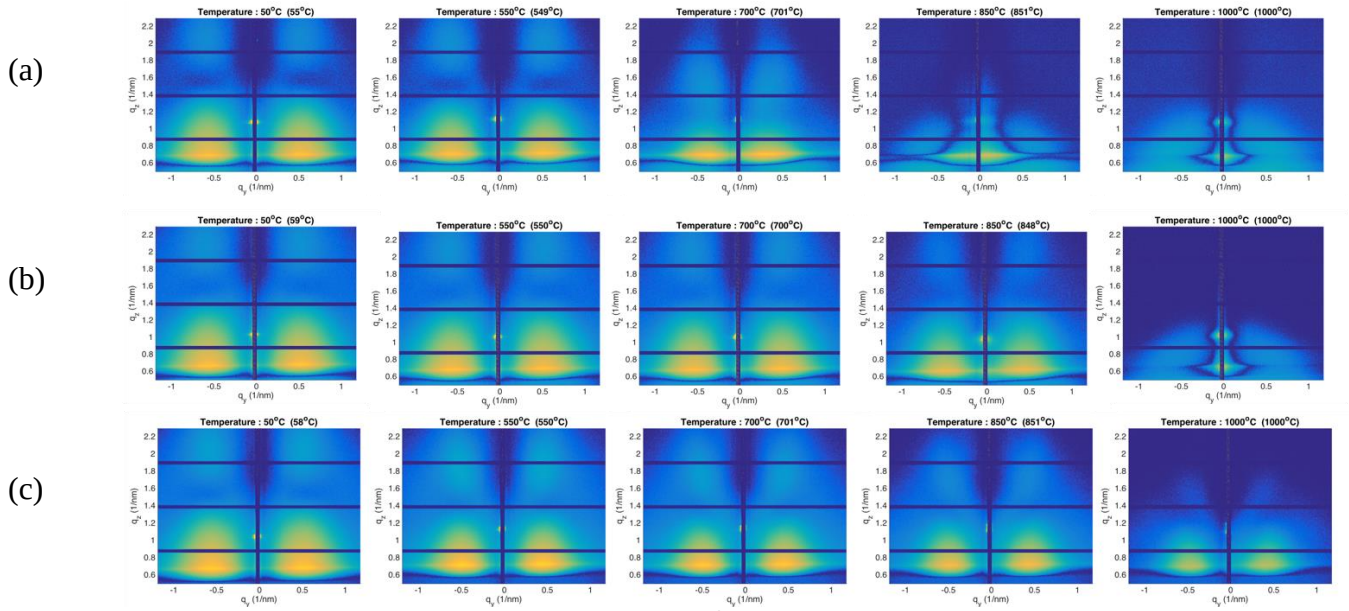

Figure 1. GISAXS patterns recorded at 50, 550, 700, 850 and 1000°C of supported Pt nanoparticles deposited by 50 ALD cycles on SiO_2 annealed in O_2 atmosphere (a) and H_2 atmosphere (c). In (b), the Pt nanoparticles were overcoated with 0.5 nm of Al_2O_3 and annealed in O_2 atmosphere.

Because the particle sintering was more clear for annealing in O_2, this atmosphere was further used to study the effect of substrate nature and initial particle size and density on the particle sintering. Figure 2 (a) shows the average center-to-center distance between the Pt particles as a function of the annealing temperature. This value was estimated from the q_y-position of the main scattering lobe as $2\pi/q_{y,Lobe}$. Curves are displayed for Pt nanoparticles grown by 50 ALD cycles on different substrates (SiO_2, Al_2O_3 and MgO) with and without 0.5 nm Al_2O_3 overcoat. Without overcoat, particle coarsening starts on all substrates in the temperature range 600-700°C. 5 ALD cycles of Al_2O_3 overcoating, corresponding to an expected layer thickness of only 0.5 nm, significantly delay the particle coarsening to a temperature range of 800-900°C.

For smaller Pt nanoparticles grown by 30 ALD cycles, 5 ALD cycles of Al_2O_3 overcoating did not prevent particle sintering (Figure 2 b). Therefore, we systematically increased the number of Al_2O_3 ALD cycles to determine the required overcoat thickness to "pin" the Pt nanoparticles and prevent migration and sintering. The effect of the overcoating was most clear for 20 and 30 Al_2O_3 ALD cycles, i.e. for layer thicknesses of ca. 2 and 3 nm.

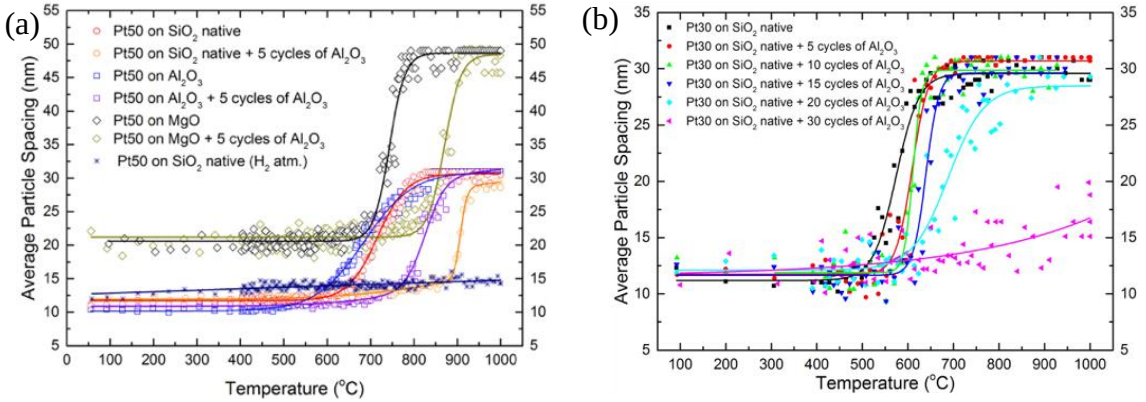

Figure 2. (a) Evolution of the center-to-center particle distance during annealing in O_2 of Pt nanoparticles deposited by 50 ALD cycles on different substrates with and without Al_2O_3 overcoat. (b) Effect of different overcoat thicknesses on the evolution in center-to-center particle distance during annealing in O_2 of Pt nanoparticles deposited by 30 ALD cycles on SiO_2.

Conclusions – The beamtime at BM26B allowed us to systematically investigate the thermal sintering of supported Pt nanoparticles with interesting applications in catalysis. Current preliminary analysis of the measurements proves that ALD is an adequate technique to produce and stabilize Pt nanoparticles onto different substrates. Further analysis is ongoing to determine the evolution in particle dimensions. Moreover, additional experiments are performed in our home lab to study the remaining accessibility of the overcoated Pt nanoparticles for reactants in catalytic processes. This work will be of high interest for applications of ALD-synthesized Pt nanocatalysts.