Atomic structure of Pd nanoparticles on graphene / Ir(111) under H₂ and CO exposure

D. Franz¹, V. Vonk¹, B. Arndt¹, H. Noei¹, J. Strempfer² and A. Stierle¹

¹Universität Hamburg / DESY Nanolab (FS-NL), Notkestr. 85, 22607 Hamburg, Germany
²DESY, Petra III / Photon Science, Notkestr. 85, 22607 Hamburg, Germany

Palladium nanoparticles are important ingredients of catalysts used for hydrogenation reactions during which chemical energy is stored in form of hydrogen in hydrocarbon molecules [2]. This represents an essential step for hydrogen storage in future regenerative energy cycles [3]. During hydrogenation reactions, interstitial hydrogen is formed as well as interstitial carbon [4,5]; both processes are assumed to play an important role for catalytic activity and selectivity. Recent hydrogen molecular beam experiments on a Pd/Al₂O₃ model catalyst system indicated that the incorporation of hydrogen is promoted by the presence of deposited carbon [6,7]. On the other hand, carbon incorporation during CO oxidation over a supported Pd catalyst is an unwanted process since it leads to a deactivation of the catalyst [10,8]. Further on, Pd nanoparticles are found to incorporate pure hydrogen easier as a bulk single crystals, resulting in a shift of concentration – pressure isotherms to lower pressures [9]. It is unclear if the bulk miscibility gap between the low H concentration α phase and the high H concentration α’ phase observed in Pd bulk below 298 °C also persists for small nanoparticles.

To pinpoint structure-functionality relationship for systems containing small nano-objects an atomic scale understanding of their structure is mandatory. We have recently demonstrated that surface x-ray diffraction (SXRD) combined with templated growth using the 2.5 nm x 2.5 nm graphene moiré on Ir(111) is a possible route for detailed structure determination of metal clusters with 1-2 nm size [1,11,12]. Additional information on cluster height and surface coverage can be gained with x-ray reflectivity measurements (XRR).

In the UHV laboratory of DESY/NanoLab a closed graphene layer has been prepared on top of a Ir(111) single crystal surface via chemical vapor deposition (CVD) and temperature programmed growth (TPG) of ethylene which has established as a standard preparation method for high quality graphene [6]. Using the graphene / Ir(111) surface as a template for metal cluster lattice growth SXRD experiments has been carried out at P09 (Resonant Scattering and Diffraction Beamline at Petra III/DESY in Hamburg/Germany). An e-beam triple evaporator was used to grow an Ir seeded Pd cluster lattice in which all clusters contain 0.15 ML Ir and 0.6 ML Pd. The cluster have been grown in ultra-high vacuum conditions (10⁻¹⁰ mbar - 10⁻⁹ mbar) using a mobile x-ray diffraction chamber equipped with an e-beam evaporator and the opportunity for gas dosing.

Fig. 1 displays a linescan in K direction using Ir(111) surface coordinates and screens the formation of the 2d cluster lattice after deposition of Ir (blue line) and Pd (red line) in UHV. After deposition of Pd a broad signal originating from uncorrelated particles appears, which reflects an increasing disorder of the cluster lattice.

Fig. 2 shows a reciprocal space map of the Pd/Ir cluster lattice in 10 mbar H₂ environment. The sharp surface rods conclude that the cluster lattice remains intact although there is a broad signal from disordered clusters visible.

In summary we could grow an Ir seeded Pd cluster lattice and measure a complete SXRD data set of this cluster lattice in UHV and in 10 mbar H₂ environment. Data analysis will shed light on H₂ induced structural changes of the clusters. Also the lattice parameter of particles which are not in registry with the cluster lattice will be extracted from the measurements and possibly reveal support induced differences in the behaviour of the particles during gas exposure.
0.8 0.9 1.0 1.1 1.2 1.3

Figure 1: linescan crossing (0 1) CTR and surrounding cluster lattice rods (black) graphene on Ir(111) (blue) 0.15 ML Ir on C/Ir(111) (red) 0.6 ML Pd/0.15 ML Ir on C/Ir(111)

Figure 2: H-L mesh of Pd/Ir on graphene / Ir(111) in 10 mbar H2 environment, visible: surface rods of cluster lattice, diffuse scattering of uncorrelated clusters

References