ESRF	**Experiment title:** XAS study of the metal (Pd and Au) nanoparticles electronic structure evolution during the growth and self-organization processes	**Experiment number**: CH-3911
Beamline: ID26	**Date of experiment**: from: 25.09.2013 to: 01.10.2013	**Date of report**: 19.02.2014
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Report:

The main goal of the study was the insight into the metal clusters (Pd and Au) growth process in solution. A number of palladium and gold compounds were studied in solution as well as in the solid state.

Au L_3-edge XAS spectroscopy was utilized for the characterization of electronic structure and local environment of the gold atoms. For the model gold (I) compound – PPh_3AuCl it was shown that dissolution in chloroform did not lead to the observable structural changes. For both solid in liquid samples XAS spectra were almost identical. The addition of silver salt (AgOTf) did not facilitate the formation of bimetallic Au/Ag clusters. Only the formation of PPh_3AuOTf was detected in this case. Therefore, all studied gold compounds appeared to be stable in solution. The formation of gold clusters was not detected.

Both *K*-edge and L_3-edge XAS spectroscopy were employed for the characterization of Pd samples. On the firs step we focused on the soluble Pd complex with dibenzylideneacetone – Pd_2dba_3. Although Pd_2dba_3 is considered to be zero-valent Pd compound, its XANES spectrum is different from that of metal foil (Figure 1). So, the formation of metal clusters in this system can be easily detected.

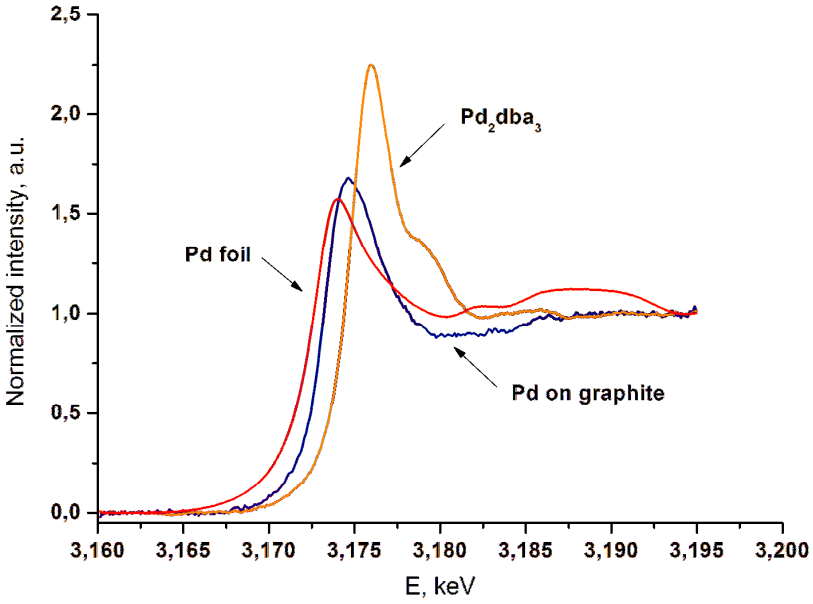

Figure 1. Pd L3-edge XANES spectra of Pd foil, Pd_2dba_3 and Pd on graphite support.

We failed to perform XAS measurements for Pd_2dba_3 in chloroform solution because of very high sensitivity of the solution to X-ray beam. Complete decomposition of the metal complex was observed after 2-3 seconds of irradiation. To overcome these difficulties we tried to use the carbon support. XAS analysis of the palladium species disposed onto the graphite surface from Pd_2dba_3 chloroform solution showed the formation of small Pd metal clusters (Figure 1).

On the next step, Pd L_3-edge XANES and Pd *K*-edge EXAFS measurements were performed for the several catalytic systems relevant to Pd-catalyzed coupling reactions. Both methods proved the formation of small soluble metal clusters that were considered to be an actual catalyst in the number of Pd-mediated chemical transformations.

Publications:

1. Evgeniy O. Pentsak, Alexey S. Kashin, Kristina O. Kvashnina, Pieter Glatzel, and Valentine P. Ananikov, “Spatial Imaging of the Reactivity of Graphene”, **2014**, *submitted*.
2. Alexey S. Kashin, Kristina O. Kvashnina, Pieter Glatzel, and Valentine P. Ananikov, “Pd L_3-edge XANES spectroscopy: a powerful tool for the detection of catalyst active form in Pd-mediated C-C bond formation reactions”, **2014**, *in preparation*.