Discrimination of surface and bulk carbide by combined EXAFS and XANES analysis

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X-ray absorption spectroscopy is an effective tool for material characterization widely recognized by the catalytic community. The method does not require long-range order in the atomic structure and can be applied to the characterization of amorphous samples, surfaces and nanostructured materials. We have shown, that the experimental spectra of palladium nanoparticles (NPs) are sensitive to changes in the atomic and electronic structure, both in the bulk and at the surface of NPs. Combination of XANES and EXAFS analysis complemented by theoretical calculations allowed obtaining qualitative and quantitative information about the local atomic structure and the chemical state of surface and bulk Pd atoms in the NPs.

Experimental spectra were collected *in situ* during exposure of 2.6 nm supported Pd NPs to acetylene, hydrogen and their mixtures at 100 °C at BM01 beamline of ESRF. First shell Fourier-analysis of EXAFS spectra was applied to determine the average Pd-Pd bond distance in the NPs. In addition, theoretical XANES spectra were calculated using finite difference method [Guda, et al., *J. Chem. Theory Comput.*, **11,**4512 (2015)]. The geometrical models used for XANES calculations represented supercells of 32 Pd atoms, where part of the octahedral interstitial sites were occupied by carbon atoms. The structures were optimized using VASP code prior to XANES calculations. The fitting of experimental spectra by theoretical ones using multidimensional interpolation approach [Smolentsev, et al. *Comput. Mater. Sci.*, **39**, 569 (2007)] and allowed us to determine the C/Pd stoichiometry,*y*, of PdC_y particles.

Analyzing the difference between the increase in Pd-Pd distances and the increase of C/Pd concentration, we concluded that upon exposure to pure acetylene immediate formation of surface Pd-C bonds occurs, while only small part of acetylene is decomposed to atomic carbon and form palladium carbide phase with slightly increased Pd-Pd distances. Vacuum conditions do not affect both surface and bulk carbide, while treatment in hydrogen with subsequent evacuation significantly decreases C/Pd stoichiometry but does not affect Pd-Pd distances. This is explained by the fact that hydrogen removes only surface adsorbed acetylene and its derivatives but do not remove bulk carbide.

We demonstrated how simultaneous analysis of *in situ* EXAFS and XANES complemented by theoretical simulations provides information on the structure of both bulk and surface regions of the palladium nanoparticles. The present work, highlight how XANES spectroscopy has become a mature technique that, if properly supported by advanced simulations, can provide quantitative structural and stoichiometric analysis of complex systems.

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