Machine learning applied to operando XANES spectroscopy for Pd nanocatalysts

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Palladium nanocatalysts play significant role in wide range of reactions such as selective hydrogenation of alkynes. The information extracted during *operando* experiments on working catalysts allows us to consider various processes from a new point of view. X-ray absorption near edge structure (XANES) spectroscopy is a powerful tool widely applied for determining atomic and electronic properties of working catalysts [1]. In many cases, analysis of XANES data requires construction of theoretical models with a huge number of variable parameters. In this case, application of machine learning (ML) to *in situ* and *operando* XANES offers new horizons for structural characterization [2].

In this work, we discuss the construction of the theoretical models of palladium nanoparticles covering a big number of structural parameters. We investigate how the particle size, concentration of carbon impurities, which can be formed during hydrogenation of alkynes, and their distribution in the bulk and at the surface of palladium particles affect the Pd *K*-edge XANES features. We demonstrate step-by-step increasing similarity between the experimental difference spectra and theoretical model by increasing the complexity of the theoretical model, e.g. taking into account only interatomic distances (Fig. 1 dashed red), interatomic distances and carbon concentration (Fig. 1 dashed blue) and interatomic distances, carbon concentrations and particle size effects (Fig. 1 green line). Finally, we suggest a set of formal descriptors relevant to possible structural diversity and construct a library of theoretical spectra for ML-based analysis realized in PyFitit software [3].

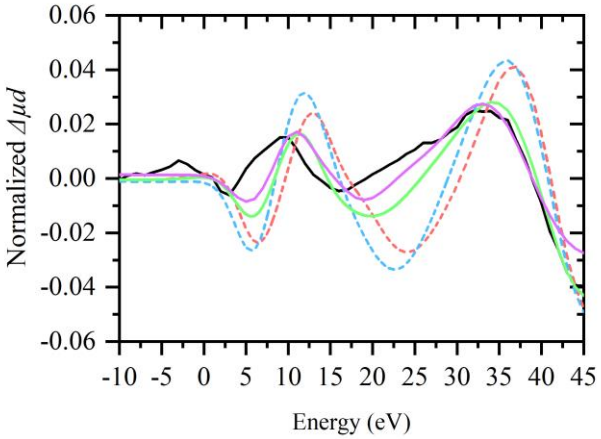

Figure 1. Experimental difference Pd *K*-edge XANES for 2.8 nm Pd NPs in acetylene (solid black) and best fit results using theoretical spectra with interatomic distances only (dashed red), interatomic distances and carbon impurities in the bulk (dashed blue), and interatomic distances, carbon impurities in the bulk and surface (solid green) contribution as variable parameters. The best fit made by ML algorithm is represented by purple line [4].

[1] Bordiga, S., Groppo, E., Agostini, G., Bokhoven, J.A. & Carlo Lamberti, C. (2013). *Chem. Rev.* **113**, 1736.

[2] Guda, A.A., Guda, S.A., Lomachenko, K.A., Soldatov, M.A., Pankin, I.A., Soldatov, A.V., Braglia, L., Bugaev A.L., Martini, A., Signorile, M., Groppo, E., Piovano, A., Borfecchia, E. & Lamberti, C. (2019). *Catal. Today*. **336**, 3.

[3] Martini, A., Guda, S.A., Guda, A.A., Smolentsev, G., Algasov, A., Usoltsev, O., Soldatov, M.A., Bugaev, A., Rusalev, Yu., Lamberti, C. & Soldatov, A.V. (2019). *Comput. Phys. Commun*, **23**, 107064.

[4] Usoltsev, O.A., Bugaev, A.L., Guda, A.A., Guda, S.A. & Soldatov, A.V. (2020) *Top. Catal.*, in press.

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