

Advanced characterization of palladium catalysts by *in situ*, *operando* and time-resolved X-ray absorption and scattering

A.L. Bugaev,^{1,2} A.A. Guda,¹ K.A. Lomachenko,³ O.A. Usoltsev,¹ A.A. Skorynina,¹ E. Kamyshova,¹ A.A. Tereshchenko,¹ A. Lazzarini,^{2,4} M. Zabilskiy,⁵ E. Groppo,³ R. Pellegrini,⁶ L.A. Bugaev,¹ A.V. Soldatov,¹ J.A. van Bokhoven⁵ and C. Lamberti^{2,7}

- 1) *The Smart Materials Research Center, Southern Federal University, Rostov-on-Don, Russia*
- 2) *Department of Chemistry, University of Turin, Turin, Italy*
- 3) *European Synchrotron Radiation Facility, Grenoble, France*
- 4) *Department of Chemistry, University of Oslo, Oslo, Norway*
- 5) *Institute for Chemical and Bioengineering, ETH Zurich, Zurich, Switzerland and Laboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institute, Villigen, Switzerland*
- 6) *Chimet SpA - Catalyst Division, Arezzo, Italy*
- 7) *Department of Physics, University of Turin, Turin, Italy*

abugaev@sfnu.ru

Palladium is found to be one of the most versatile materials for catalysis having a wide variety of industrially relevant application. Numerous studies have shown that formation of palladium hydride, carbide and oxide phases is of critical importance for the selectivity and activity of material in a number of catalytic reactions. In case of palladium nanoparticles (NPs), these phases may be formed both in the surface and in the bulk, which have different effect on the catalytic properties. This contribution is aimed to report recent advances in characterization of metallic Pd, PdH, PdC and PdO phases in real industrial nanocatalysts by *in situ*, *operando* and time-resolved X-ray absorption and scattering techniques.

In situ and *operando* XANES, EXAFS and time-resolved XRD measurements were performed at BM01b/BM31 beamlines of ESRF. Time-resolved XANES and EXAFS were collected at ID24 beamline of ESRF and SuperXAS beamline of SLS. Fourier analysis of EXAFS, including higher shell analysis, was performed in Demeter package. XANES region was analyzed via two independent routs: 1) principle component analysis (PCA) and 2) theoretical simulations employing multiple scattering (FEFF) and finite difference (FDMNES) approaches for atomic structures optimized by DFT and Monte-Carlo methods. Rietveld refinement was used to analyze XRD data.

The comprehensive analysis of X-ray absorption and scattering data allowed obtaining a number of new structural results. We provided the first experimental evidence that formation of palladium hydride leads to different interatomic distances in the subsurface and bulk regions of the NPs, resulting in the “core-shell” structures [Bugaev et al., *J. Phys. Chem. C*, **121** (cover page), 18202 (2017)]. Then, we highlighted the unique role of XANES in distinguishing between Pd-H and Pd-C phases under reaction conditions, which was not possible via standard EXAFS and XRD analysis [Bugaev et al., *Catal. Today*, **283**, 119 (2017)]. In addition, we demonstrated the possibility to discriminate bulk carbide from surface Pd-C bonds [Bugaev et al., *Faraday Discuss.* (2018)], which is described in detail in the contribution of Usoltsev et al. Time-resolved and *operando* measurements allowed correlating the structural changes and rapid phase transitions of between PdH and PdC phases with the catalytic performance of materials during hydrogenation of acetylene and ethylene. Finally, we observed surface and bulk Pd-O phases formed upon exposure

to oxygen and during catalytic oxidation of hydrogen. These two phases had different stability and required different treatment for their decomposure.

Based on a series of experiments, we have developed a comprehensive scheme for *in situ* and *operando* investigation of palladium-based catalysts. This scheme included application of advanced EXAFS and XANES analysis, complemented by XRD, laboratory characterization and computer modeling, and allowed us to obtain detailed atomic and electronic structure of palladium hydride, carbide and oxide species formed on the surface and in the bulk of the palladium nanocatalysts.