

Formation of metal nanoparticles inside UiO-67 metal-organic framework by *in situ* and *operando* X-ray absorption and diffraction

A.L. Bugaev,^{1,2} K.A. Lomachenko,³ A.A. Guda,¹ E.G. Kamyshova,¹ Alina A. Skorynina, A. Lazzarini,⁴ S. Bordiga,^{2,4} U. Olsbye,⁴ K.P. Lillerud,⁴ A.V. Soldatov,¹ C. Lamberti,^{1,5}

- 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, Norway
- 5) Department of Physics, University of Turin, Turin, Italy

abugaev@sfedu.ru

In the last twenty years, the number of new types of metal organic framework (MOFs) raised exponentially. Functionalization of metal-organic frameworks with metal nanoparticles (NPs) give an additional degree of freedom in synthesis of MOFs with specific properties for practical applications, combining the extremely high porosity of MOFs with chemical activity of metals. We present synthesis and *in situ* characterization of palladium NPs encapsulated inside functionalized UiO-67 metal-organic framework by simultaneous XANES, EXAFS and X-ray powder diffraction (XRPD), as well as several catalytic tests under *operando* conditions.

The initial structure was synthesized with 10% of PdCl₂bpydc moieties with grafted Pd ions replacing standard 4,4'-biphenyldicarboxylate linkers. The material was activated in the flow of 6% H₂/He and pure He. Simultaneous *in situ* XANES, EXAFS and XRPD measurements during material activation were carried out at BM31 beamline of ESRF. The final activated material was tested in the reaction of catalytic hydrogenation of ethylene. Additional *ex situ* EXAFS data for as synthesized material were collected at BM23 beamline of ESRF. The synchrotron data were complemented by laboratory thermogravimetric analysis (TGA), IR spectroscopy, and high-resolution transmission electron microscopy (HR-TEM) and by DFT modeling.

Reduction of UiO-67-Pd material in the flow of hydrogen was monitored *in situ* by XANES, EXAFS and XRPD. Formation of metal Pd NPs starting from T = 200 °C was accompanied by characteristic changes in the near-edge structure. Analysis of EXAFS data indicated the Pd-N₂Cl₂ configuration in the as synthesized material and a gradual growth of Pd-Pd contribution during the reduction. Simultaneously with Pd-Pd bonds formation, the cell parameter of UiO-67 decreased from 26.7986(2) to 26.730(2) Å preserving good crystallinity of material, as determined by XRPD. The resulting material contained 2.1 nm Pd NPs with preferential location inside the pores of UiO-67. This material was tested for the catalytic reaction of ethylene hydrogenation monitored by *operando* EXAFS and XANES, which confirmed the accessibility of the Pd NPs and revealed changes in their structure caused by formation of hydrides and carbides.

We have performed a successful synthesis of UiO-67-Pd material with 10% of PdCl₂bpydc, linkers hosting Pd^{II} ions. Reduction of Pd^{II} to Pd⁰ was monitored by simultaneous *in situ* XAS and XRPD and indicated the detachment of Pd^{II} ions from the linkers, removal of Cl⁻ ligands and growth of Pd NPs accompanied by the decrease of UiO-67 lattice parameter. The resulting material contained homogeneously distributed Pd particles with an average size of 2.1 nm. These Pd NPs in UiO-67 showed high activity towards ethylene hydrogenation, which was monitored by *operando* EXAFS, XANES and laboratory IR spectroscopies.