



	Experiment title: Probing the State of Pd in a Metal Organic Framework (MOF) during Catalysis and the Phase Transition of a La-MOF by In Situ X-ray Diffraction and X-ray Absorption Spectroscopy	Experiment number: 01-01-996
Beamline: SNBL-BM01B	Date of experiment: from: 03-Dec-2015 to: 09-Dec-2015	Date of report: 12-Aug-2016
Shifts: 18	Local contact(s): Michela Brunelli	<i>Received at ESRF:</i>
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Report:

Probing the state of Pd in a Metal Organic Framework during catalysis by *in situ* X-ray diffraction and absorption spectroscopy

A custom-made *in situ* reactor (Figure 1) was developed to perform *in situ* X-ray absorption spectroscopy (XAS) and X-ray powder diffraction (XPD) measurements during liquid phase reactions. In this experiment, a palladium (II) catalyst supported on a metal organic framework (8 wt% Pd(II)@MIL-101-NH₂) was used to catalyze the Heck reaction.¹⁻²

The *in situ* XPD patterns confirmed that the catalyst maintained its crystallinity during the reaction. Palladium species were identified and their structural changes were followed by *in situ* XAS. From the EXAFS data analysis of the as-prepared, dry catalyst, it could be confirmed that the Pd (II) in the catalyst binds to one -NH₂ group of the linker, one cyano group from the Pd(II)

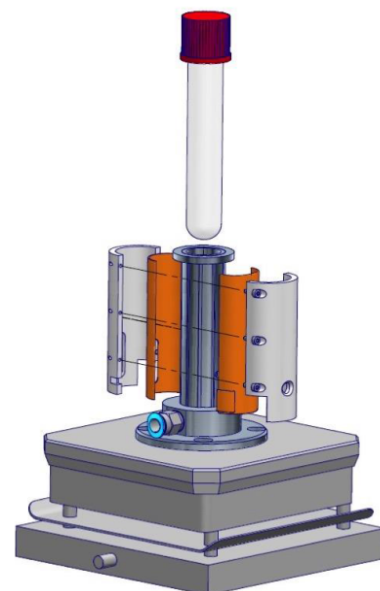


Figure 1. Schematic image of the *in situ* reactor. It consists of a 6 mL pyrex glass tube with heating wires, aluminum windows for the beam and a stirring device.

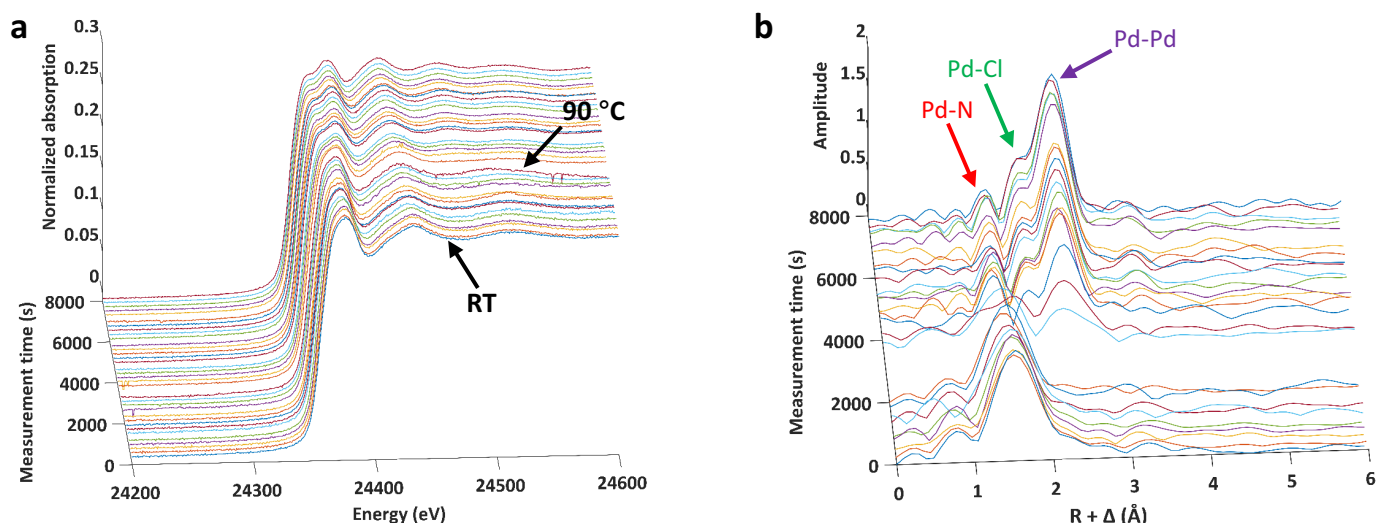


Figure 2. (a) Normalized XANES and (b) Fourier transformed EXAFS spectra of the Pd(II)@MIL-101-NH₂ catalyst as a function of time.

precursor and two Cl ions.

From the XANES spectra (Figure 2a) and Fourier transformed EXAFS spectra (Figure 2b), it was observed that the Pd-Cl bonds were replaced by *p*-iodobenzonitrile as ligands bonded to Pd(II). Both spectra indicated that the local structures of Pd were similar up to scan 17 (the first scan after the blank gap, where EXAFS data were too poor for analysis) when the temperature was increased from room temperature to 90 °C. Interestingly, the catalytic reaction had already commenced at this stage. Together with TEM and NMR results acquired after the beamtime, it was determined that the Pd(II) complex was reduced to a Pd(0) complex, that this species could catalyze the Heck reaction at 60 °C, and that the local structure of Pd in the main intermediate during the Heck reaction was very similar to that at the beginning of the reaction. From scan 17 onwards, a Pd-Pd peak started to appear in the Fourier transformed EXAFS spectra. This indicates that the Pd(0) complex started to aggregate into palladium clusters. These palladium clusters continued to catalyze the Heck reaction. As the catalytic reaction continued at 90 °C, the palladium clusters grew larger with reaction time. From the coordination numbers of the Pd-Pd shells derived from the EXAFS spectra, these clusters grew from 2 to 6 atoms on average.³ At the same time, an increasing proportion of the Pd atoms in the palladium clusters were re-oxidized and started to bond to Cl⁻ ions and solvent ligands. When a significant number of Pd(II) were bound to Cl⁻ near the end of the catalytic reaction, the growth of the palladium clusters was effectively hindered and catalytic activity began to decrease. Once the catalyst was recycled by washing and filtration, the size of the palladium clusters became even larger (17 Pd atoms on average) and a large number of palladiums atoms were bonded to Cl⁻. By understanding the structural changes and thereby the deactivation mechanism, the catalytic activity of the catalyst could be prolonged.

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