

The Heck coupling is an important reaction that can create new C-C bonds between aryl halides and olefins. Palladium species embedded on metal organic frameworks (Pd@MOFs) have been recently developed as effective catalysts for this reaction. However, detailed investigations into the catalyst activation, nature of active species and possible deactivation of such heterogeneous system are difficult to perform. These situations raised the demand of using operando methods for a deeper understanding of the catalytic process, especially the methods that can directly probe the structure of the catalytic centers. With our custom-made batch reactor where liquid-solid reactions can be performed, operando X-ray absorption spectroscopy (XAS) was used as a major tool to investigate the mechanism of Pd@MOFs catalyzed Heck reaction. By analyzing the XAS data and other investigations, such as operando powder X-ray diffraction (PXRD) following the crystallinity of the MOFs, nuclear magnetic resonance (^1H NMR) kinetic studies and transmission electron microscopy (TEM) analysis, Pd species at different stages of the reaction were identified and their evolutions were followed. It was found that the Pd(II) complexes in the as-synthesized catalyst transformed into another form by losing Cl^- ligands right after they were added into the reaction mixture. The newly formed mononuclear Pd complexes became the dominant active species at the beginning of the reaction at $60\text{ }^\circ\text{C}$. After one turnover, these complexes detached from the linkers of the MOFs and the free Pd(II) complexes gradually transformed into Pd nanoclusters with 13-20 Pd atoms on average in later catalytic turnovers at $90\text{ }^\circ\text{C}$. The rate of such transformation was determined by linear combination fit of XANES spectra. The mixture of Pd complexes and nanoclusters became the dominant active species at this stage. When the reaction approached to the end, the Cl^- ions started to coordinate to the surface of the Pd nanoclusters, which caused the poisoning of the active sites. The recycled catalyst consisted of 100% Pd nanoclusters with their surfaces overwhelmed by Cl^- . By understanding the reaction and deactivation mechanisms, lifetime prolongation of the catalyst was achieved. Moreover, the method is applicable for different reaction systems, such as homogenous catalysis.