

## PAPER

# Operando study of palladium nanoparticles inside UiO-67 MOF for catalytic hydrogenation of hydrocarbons†

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Functionalization of metal–organic frameworks with metal nanoparticles (NPs) is a promising way for producing advanced materials for catalytic applications. We present the synthesis and *in situ* characterization of palladium NPs encapsulated inside a functionalized UiO-67 metal–organic framework. The initial structure was synthesized with 10% of PdCl<sub>2</sub>bpydc moieties with grafted Pd ions replacing standard 4,4'-biphenyldicarboxylate linkers. This material exhibits the same high crystallinity and thermal stability of standard UiO-67. Formation of palladium NPs was initiated by sample activation in hydrogen and monitored by *in situ* X-ray powder diffraction and X-ray absorption spectroscopy (XAS). The reduction of Pd<sup>II</sup> ions to Pd<sup>0</sup> occurs above 200 °C in 6% H<sub>2</sub>/He flow. The formed palladium NPs have an average size of 2.1 nm as limited by the cavities of UiO-67 structure. The resulting material showed high activity towards ethylene hydrogenation. Under reaction conditions, palladium was found to form a carbide structure indicated by *operando* XAS, while formation of ethane was monitored by mass spectroscopy and infra-red spectroscopy.

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