

## Operando studies of nanoparticulate palladium catalysts

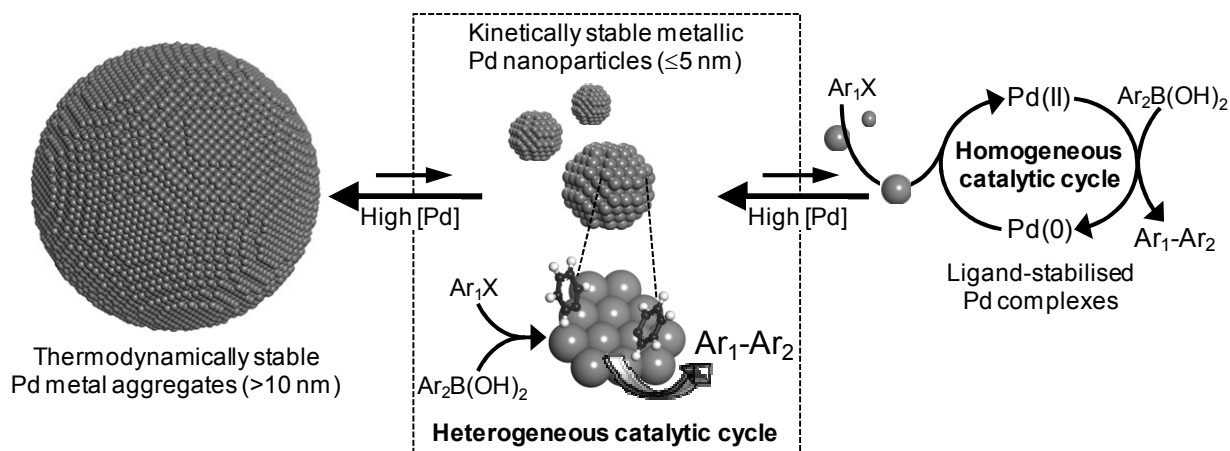
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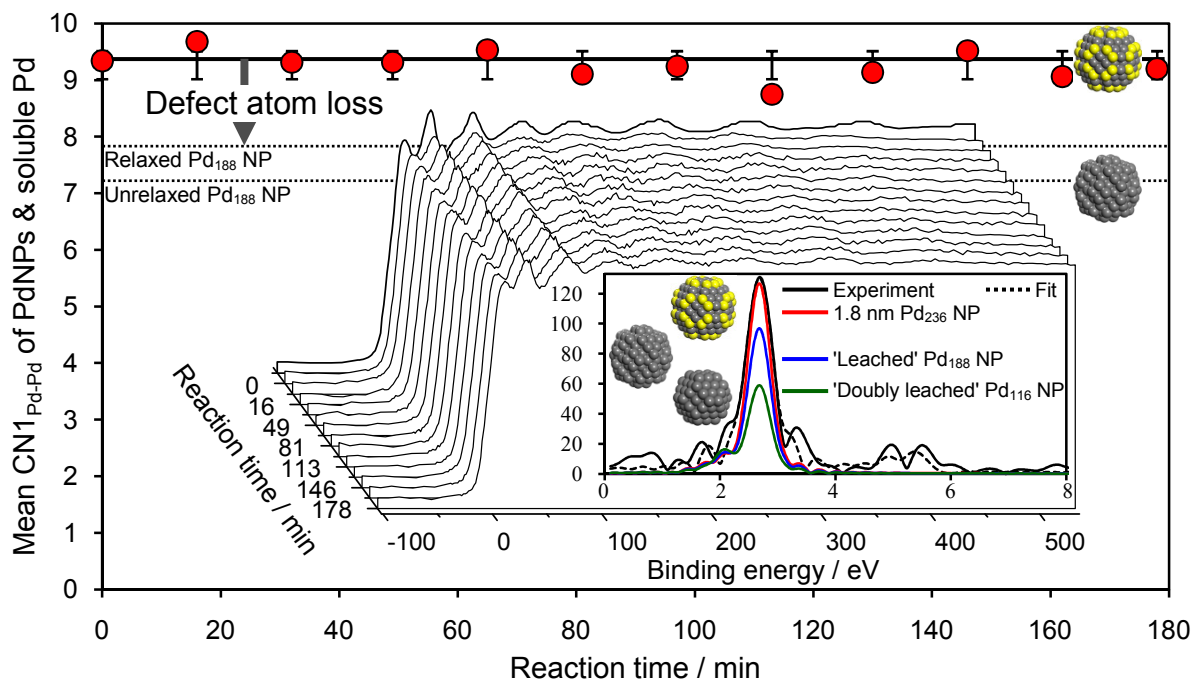
One of the most important processes in modern chemistry is the carbon-carbon bond-forming reaction, which represents key steps in the construction of complex molecules from simple precursors. However, not until the discovery and development in the 1970s of metal-catalysed cross-coupling reactions was there a simple and direct catalytic method for carbon-carbon bond formation. A wide variety of these reactions now exist and have become powerful tools, finding application in the synthesis of biological molecules, liquid crystals, macromolecules and also in supramolecular chemistry, i.e. across a spectrum of important scientific activities.

The active catalytic species responsible for palladium-mediated cross-couplings such as Heck arylation and Suzuki-Miyaura reactions, has been hotly debated in recent years, specifically whether heterogeneous catalysis occurs directly at the surface of Pd nanoparticles, or these simply act as inert reservoirs of soluble Pd for homogeneous catalysis (**Figure 1**). In this beamtime we utilised BM26A to perform operando liquid phase XAS measurements on a series of size-selected Pd nanoparticles to investigate whether particle sintering or dissolution occurred during reaction (the latter would indicate a homogeneous catalytic cycle).



**Figure 1.** Possible reaction pathways operating in Pd nanoparticle catalysed Suzuki cross-couplings

Fluorescence XAS revealed our Pd nanoparticles were extremely stable during the liquid phase cross-coupling of iodoanisole and phenylboronic acid (**Figure 2**), enabling us to eliminate the possibility of significant particle sintering, and place an upper limit on the fraction of soluble Pd that could be present due to leaching. This dissolved Pd represents <5 atom% of the total palladium present within our nanoparticles, and careful spiking tests using Pd(OAc)<sub>2</sub> showed this concentration of dissolved Pd was insufficient to account for the observed catalysis. This XAS study provides the first direct evidence for surface-mediated cross-coupling over Pd nanoparticles, and has been published as a communication in *Angew. Chemie Int. Ed.* **2010**, *49*, 1820, accepted as a full article in *Dalton Transactions* (July 2010) and presented at the 240th ACS National Meeting in Boston.



**Figure 2.** Operando Pd K-edge XAS fits for 1.8 nm PdNPs during the Suzuki coupling of iodoanisole and phenylboronic acid. Inset shows normalised, time-dependent EXAFS spectra, and actual/simulated radial distribution functions for as-prepared (236-atom) and leached (188 or 116-atom) Pd cubeoctahedra