

KN04 | METAL-ORGANIC FRAMEWORKS AS CHEMICAL REACTORS: X-RAY

CRYSTALLOGRAPHIC SNAPSHOTS OF THE CONFINED STATE

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Ultrasmall metal nanoclusters (NCs), consisting of aggregations of less than 10 atoms with a high percentage of them exposed to the external environment, have emerged as formidable catalysts capable to surpass the state-of-the-art catalysts in organic reactions of industrial interest, being thus capable to make feasible certain reactions which are currently financially prohibitive.[1] Such small NCs, that may give rise to a technological leap in a similar way as the irruption of metal nanoparticles (NPs) did, still show important weaknesses regarding the synthetic control of their shape and nuclearity as well as their lack of stability.[2] Metal-Organic Frameworks (MOFs) [3] show unique features to act as chemical nanoreactors for the in-situ synthesis and stabilization of otherwise not accessible functional species and to use single crystal X-ray crystallography as a definitive characterization tool, which offers the unique possibility –among porous materials– to contrast the success of synthetic methodologies, and even more important, to follow/understand what is actually happening within MOFs channels. Supporting these clusters within MOFs is a very promising strategy. MOFs own regular and well-defined channels and exhibit fascinating host-guest chemistry. [3] In principle, they are suitable platforms to synthesize, in a controlled manner, metal clusters below the nanometre allowing to gain information about their nature by means of X-ray crystallography, to shed light on every single step during their synthetic route.[4] Even Supramolecular Coordination Compounds (SCCs) with targeted properties can be self-assembled and stabilized within a MOF.

Here we report on the MOF-mediated chemical synthesis of structurally and electronically well-defined ultrasmall Pt₂, Pt₁₊₁, Fe^{III}, Ru^{III} and [Pd₄]²⁺ catalysts, together with PdII SCCs built within the confined space of preformed MOFs (SCCs@MOF) and their post-assembly metalation to give a Pd^{II}-Au^{III} supramolecular assembly, all crystallographically underpinned. [5] These results open new avenues in both the synthesis of novel NCs and SCCs and their use on heterogeneous metal-based Supramolecular Catalysis. Reactions in which the resulting hybrid materials outperform state-of-the-art metal catalysts will be illustrated.

References:

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