

## **New framework forming chemistry and heterogeneous catalysis – control of molecular organometallic catalysts by cation exchange into a metal-organic framework**

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Crystalline porous materials have had a strong impact on catalysis because of their regular and well-defined chemical environments, which can offer new pathways to the control of reactivity and selectivity. The development of new classes of porous materials is thus of potential relevance for heterogeneous catalysis. This presentation will discuss new synthetic chemistry that allows the direct assembly of crystalline porous organic materials from strong covalent bonds. Previously, the formation of such bonds has been thought of as irreversible, with attempts to form porous frameworks leading to amorphous systems. The new approach is exemplified by two- and three-dimensional crystalline amide frameworks which are stable thermally and under both strong acidic and basic hydrolytic conditions (1).

Metal-organic frameworks are an example of a new class of crystalline open frameworks under-exploited in catalysis. In a project supported by the UK Catalysis Hub, we (collaboration with Weller (Oxford), Brammer, Haynes (Sheffield), Davies (Imperial) Xiao (Liverpool)) have demonstrated the encapsulation of molecular organometallic catalysts in metal-organic frameworks by exploiting the electrostatic field of an anionic host. The synthesis and characterisation protocols were developed using a simple Diels-Alder catalyst as an example (2), where the resulting spatial isolation suppressed deactivation of the molecular catalyst. Recently, we have enhanced the stability and selectivity of Crabtree's catalyst for a set of challenging substrates by similar electrostatic encapsulation in a larger pore system. In this case, the host chemical environment directs the reactivity along one of two competing reaction pathways. (3)

(1) Stewart *Nature Communications* **8**, 1102, 2017

(2) Grigoropoulos *Chem. Sci.*, **7**, 2037, 2016

(3) Grigoropoulos *Angew. Chem. Int. Ed.* 10.1002/anie.201710091, 2018