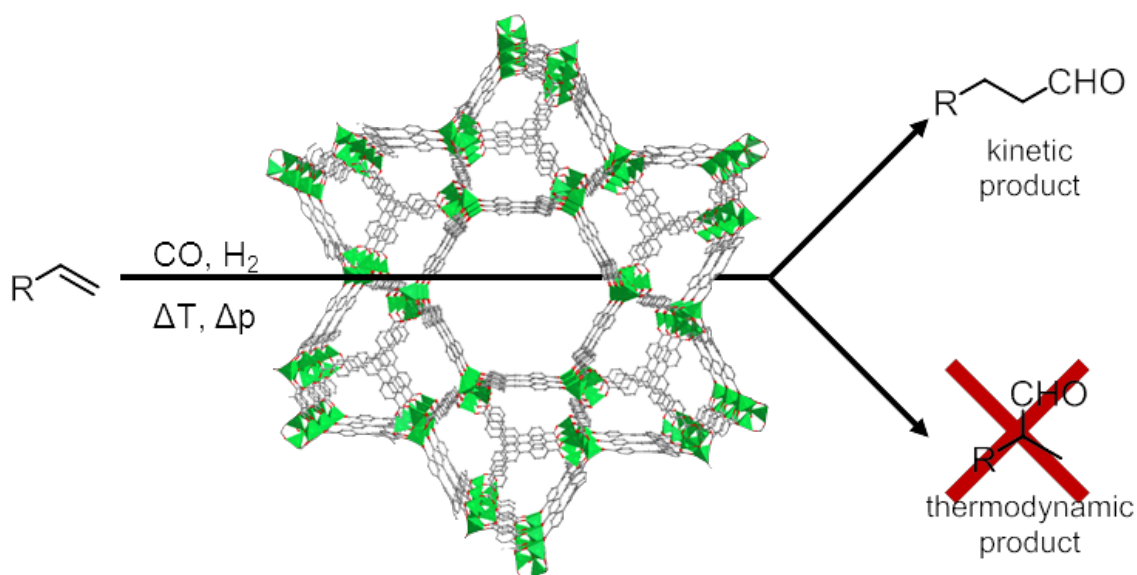


Cobalt-Functionalised Metalorganic Frameworks as Hydroformylation Catalysts: A new Approach for an Old Problem.

G. Bauer¹, G. Capano², B. Smit², M. Ranocchiari^{1*}

¹PSI (Villigen), ²EPFL (Sion)

An interesting research field emerged in the last decade: the investigation of metal-organic frameworks (MOFs) as catalysts.[1],[2] Their structural versatility, tuneable pore size and modularity give a plethora of structures and possibilities to optimise the catalytic performance. The porous framework structures are not just used to “heterogenise” homogenous catalysts; their specific pore size and cavity shape can be thought of as to provide host-guest properties similar to enzymes.[3] Therefore MOFs are ideal candidates to force the hydroformylation reaction from a preferentially thermodynamic regime into the desired kinetic regime to selectively afford *n*-aliphatic aldehydes.[4] With the MOF providing the structural rigidity the focus can be drawn on fine-tuning of the electronic properties of the metal complex to achieve both, high reactivity *and* high selectivity.



The synthesis of different functionalised MOF structures is described using phosphines as anchoring groups. The MOFs are post-synthetically modified with cobalt, the active site for the hydroformylation. The catalytic performance is then tested *in vitro* on a range of different *n*-aliphatic olefines. In parallel *in silico* studies describe the steric and electronic properties of the active centre, in order to map and predict reactivity and selectivity of MOFs. Subsequently this information is fed into the design of new MOF materials to improve and fine tune the catalytic performance.

[1] M. Ranocchiari, J.A. van Bokhoven, *Phys Chem Chem Phys* 2011, 13, 6388-6396. [2] J. Gascon, A. Corma, F. Kapteijn, F.X. Llabrés i Xamena, *ACS Catal* 2014, 4, 361-378. [3] I. Nath, J. Chakraborty, F. Verpoort, *Chem Soc Rev* 2016, 45, 4127-4170. [4] A.L. Tarasova, V.I. Isaeva, I.P. Beletskaya, L.M. Kustov, *Russ J Org Chem*, 2016, 52, 1728-1732.