

Watching Catalysts at Work: Multi-Nuclear High Resolution FlowNMR Spectroscopy for Investigating Dynamic Reaction Networks in Real Time

The development and optimization of homogeneous catalysts is often hampered by limited insight into the kinetics of the reaction and the transformation of the catalyst, enforcing empirical optimization. Rational catalyst and reaction development are only possible through thorough understanding of catalyst activation and de-activation mechanisms, potential resting or dormant states, and the kinetics of the productive cycle (i.e. rate-limiting steps). While rather laborious techniques are available to investigate the afore-mentioned aspects separately, there is no readily applicable technique that may be used universally in early stages of catalyst development. We have built a reaction setup in which a reaction vessel is coupled to a NMR flow tube via small diameter HPLC tubing. With this we can continuously circulate a reaction mixture through the spectrometer, thereby follow the reaction progresses and catalyst transformation under catalytically relevant conditions in real time. We have characterised the hydrodynamic flow characteristics of the setup and measured flow effects on continuous NMR acquisition to quantify changes in T1, T2 and signal intensity as function of volumetric flow velocity. Application in real-time reaction and catalyst monitoring under strictly inert conditions has been demonstrated, and multiple solvent suppression and selective excitation techniques allow the detection of minor intermediates even in non-deuterated solvents. Application to the investigation of several catalytic systems will be discussed.



Uli received a dual education in Chemistry and Chemical Engineering from the University of Würzburg and the École Supérieure de Chimie, Physique et Électronique de Lyon. After finishing a master thesis with Prof. David Cole-Hamilton at the University of St Andrews in 2007, he did his PhD with Prof. Walter Leitner at the RWTH Aachen on continuous-flow asymmetric catalysis using supercritical fluids. He graduated summa cum laude and won the Silver Medal of the European Young Chemist Awards in 2010. As a Humboldt Postdoctoral Fellow, he worked on water- and CH-oxidation catalysis with Prof. Bob Crabtree at Yale

University before starting his independent career at the CSCT in 2013. In 2016 he established the Dynamic Reaction Monitoring (DreaM) Facility at Bath, won the Willi Keim Prize of DECHEMA and the Sir John Meurig Thomas Catalysis Medal. Since 2017 he holds a Royal Society University Research Fellowship, and currently leads a group of 8 enthusiastic PhD students working on a range of topics in applied molecular catalysis with metal complexes, with a particular focus on new methods and technique development