Understanding Homogeneous Catalysis with high-resolution operando FlowNMR Spectroscopy

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Martes, 29 abril 2025
12:00h
Sala de grados del Edif. Físicas (Facultad Ciencias)

CICLO CONFERENCIAS **ISQCH** 2025

Instituto de Síntesis Química y Catálisis Homogénea

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Biography:

Ulrich Hintermair studied Chemistry and Chemical Engineering in Würzburg and Lyon, completing his final year project with David Cole-Hamilton at St Andrews. After a PhD on continuous flow homogeneous catalysis with Walter Leitner at RWTH Aachen he was a Humboldt Fellow with Bob Crabtree at Yale working on chemical energy conversion and C-H oxidation. In 2013 he began his independent career as Whorrod Fellow at the University of Bath where he is currently a Royal Society URF at the Institute for Sustainability. In 2016 he founded Bath's Dynamic Reaction Monitoring Facility which he leads as Scientific Director. Research in the Hintermair lab focuses on homogeneous catalysis including the design and synthesis of novel organometallics as well as operando methods for mechanistic investigations. His work has been distinguished with the 2016 Willi Keim Prize (DECHEMA), the 2016 Sir John Meurig Thomas Medal (UK Catalysis Hub), the 2018 Inorganic Reaction Mechanisms Young Academic Award (RSC), and the 2021 Jochen Block Prize (GECATS).

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Abstract:

The development of efficient catalytic processes is often hampered by limited insights into the mechanism of the reaction and the transformation of the catalyst during turnover, typically requiring empirical optimisation. Rational catalyst development based on a thorough understanding of activation and de-activation mechanisms, potential resting or dormant states, and the kinetics of the productive cycle can be tedious and potentially inaccurate by traditional ex-situ analytical approaches.

We have built a setup in which a reaction vessel is coupled to an NMR flow tube via small diameter air-tight HPLC tubing. With this we can continuously circulate a reaction mixture through a high-resolution spectrometer to simultaneously follow the reaction progresses and catalyst transformation under realistic conditions in real time.[1] We have characterised flow effects on continuous NMR acquisition[2] and optimised mass and heat transport aspects of such setups[3] to ensure accurate and relevant data is collected. Multiple solvent suppression and selective excitation techniques allow the detection of minor intermediates even in non-deuterated solvents,[4] and the use of paramagnetic relaxation agents can greatly improve heteronuclear NMR sensitivity and quantification.[5] Complementary techniques such as UV-vis, HPLC, MS and GPC can be added to the sample flow path which has allowed the comprehensive analysis of asymmetric hydrogen transfer catalysis[6] and dynamic organometallic catalysis under gas pressure.[7, 8] This setup is also useful for interrogating photocatalysis,[9] carrying out chemical shift titrations in complex mixtures,[10] and special FlowDOSY techniques[11] allow following molecular weight evolution during polymerization reactions.[12]

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