Centre for Sustainable & Circular Technologies

Centre for Sustainable and Circular Technologies; University of Bath

Project Title:	A mechanism-guided approach to improving catalytic amine formation based on multi-nuclear *operando* FlowNMR
Lead Supervisor and co-supervisors:	Dr Ulrich Hintermair (lead), Dr Catherine Lyall, Dr John Lowe
Industrial Partner:	Syngenta

Project Summary

In this project we will use the *operando* FlowNMR spectroscopic capabilities of Bath's DReaM Facility to gain fundamental insights into the mechanisms of homogeneously catalysed amine formation reactions including imine reduction, reductive amination, and H2-borrowing amination mediated by chiral organometallic complexes of Ru, Rh and Ir. All of these are highly relevant to the synthesis of amine functionalities in the fine chemical industry, but often suffer from limited efficiency due to insufficient mechanistic understanding.

The core of our approach will be to correlate product formation kinetics (analysed over the course of the reaction via RPKA methods) with catalyst speciation profiles acquired via advanced 1D and 2D heteronuclear NMR techniques under the same conditions. As the steady-state distribution of catalytic intermediates reflects the individual rate constants within the cycle, a wholistic mechanistic picture may thus be obtained. Polarisation and saturation exchange techniques will be used to probe interconversion dynamics that serve to position each observed intermediate in the cycle, distinguishing productive in-cycle intermediates from dormant off-cycle species. Another focus will lie on detecting and characterising novel transient species in-situ and quantifying the amount of dissolved H2 and NH3 in solution. All this information together with insights into activation and inhibition/deactivation pathways will allow the rational development of improved protocols and precursors with increased efficiency. Our industrial partner Syngenta will be supplying industrial background knowledge and research materials, and offer research placements and training opportunities for the student at their R&D site in Jealotts Hill.

This will be a multidisciplinary project where the student will gain experience in a variety of areas including analytical chemistry, physical-organic chemistry, kinetics, and synthetic organometallic chemistry. Our Centre for Sustainable and Circular Technologies will provide additional support and training opportunities, including public engagement and outreach activities.

References

A. M. R. Hall, J. C. Chouler, A. Codina, P. T. Gierth, J. P. Lowe, U. Hintermair, *Catalysis Science & Technology* **2016**, *6*, 8406-8417.

A. M. R. Hall, P. Dong, A. Codina, J. P. Lowe, U. Hintermair, *ACS Catalysis* **2019**, *9*, 2079-2090.

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Sustainability issues addressed

Flow NMR investigations can provide insights into the reaction pathway. This knowledge is key to optimising product yields whilst reducing energy consumption and minimising waste.