Droplet-based microfluidic platform for operando X-ray absorption spectroscopy of single-atom heterogeneous catalysts in organic synthesis

T. Moragues[1], G. Giannakakis[1], C. Borca[2], T. Huthwelker[2], A. Bugaev[2], A. Clark[2], A. deMello[1], J. Pérez-Ramírez[1]*, S. Mitchell[1]*

[1]Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Switzerland, [2]Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland

Single-atom heterogeneous catalysts (SACs), bridging the gap between the homogeneous and heterogeneous approaches, have recently emerged as a promising alternative for catalyzing organic reactions.[1] That said, very little knowledge exists about the catalytic cycle of reactions on supported catalysts. This is because unlike organometallic catalysts, for which a plethora of characterization techniques is employed to gain a better understanding of the catalytic cycle, *in-situ* and operando tools for heterogeneous catalysts, including SACs, are limited. As such, mechanistic insights largely rely on density functional theory (DFT) calculations and still lack experimental validation.[2] This study introduces a droplet-based microfluidic platform suitable for operando X-ray absorption spectroscopy (XAS) of SACs. The strategy relies on safely flowing catalyst suspensions of precisely tuned size in droplet-based microfluidic systems (**Fig. 1a**).[3] The encapsulation of the particles within the droplets, which act as isolated reactor vessels, prevents clogging and enables time-resolved operando measurements. In this study, the Pd L_3-edge and K-edge of palladium on carbon nitride (Pd/ECN) SACs are investigated under Suzuki-Miyaura reaction conditions (**Fig. 1b**). Notably, we demonstrate the importance of performing *in-situ* XAS by evidencing the differences in Pd L_3-edge X-ray absorption spectroscopy near edge structure (XANES) obtained during operando and ex-situ measurements (**Fig. 1c**). Most importantly, we lay a vital foundation for advancing the mechanistical understanding of liquid-phase organic syntheses catalyzed by SACs.

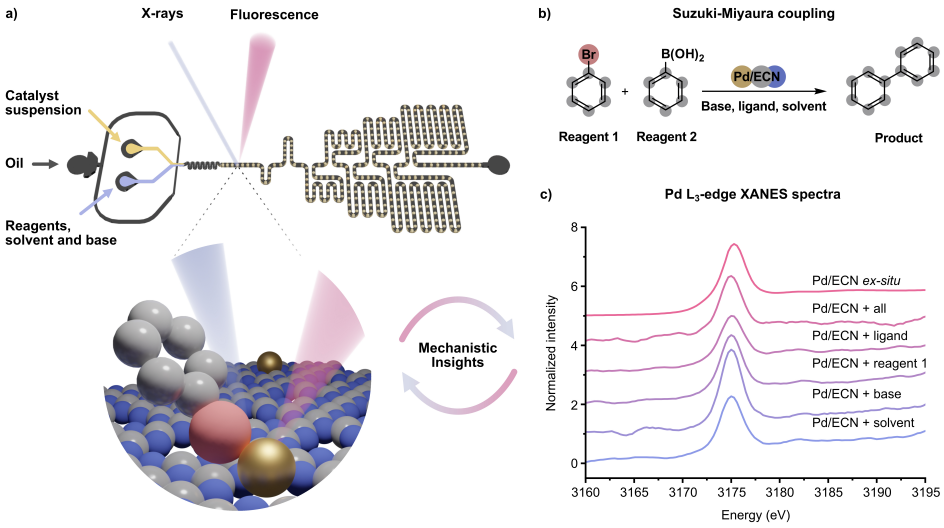

Fig. 1a Schematic of the channel pattern and operation principle in the droplet-based microfluidic device. Time-resolved XAS measurements can be acquired for increasing residence times. **b** Schematic of the studied Suzuki-Miyaura coupling catalyzed by Pd/ECN heterogeneous SAC. **c** Pd L_3-edge XANES spectra acquired in the microfluidic device for various reaction conditions.

[1] Georgios Giannakakis, Sharon Mitchell, Javier Pérez-Ramírez, *Trends Chem.* 2022, 4, 264-276.
[2] Zupeng Chen *et al.*, *Nat. Nanotechnol.* 2018, 13, 702-707.
[3] Thomas Moragues, Sharon Mitchell, Dario Faust Akl, Javier Pérez-Ramírez, Andrew deMello, *Small Structures* 2023, 4, 2200284.