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

<u>T. Moragues</u>¹, G. Giannakakis¹, C. Borca², T. Huthwelker², A. Bugaev², A. Clark², A. deMello¹, J. Pérez-Ramírez¹*, S. Mitchell¹*

¹Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Switzerland, ²Swiss 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, insitu 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 L₃-edge and Kedge 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.

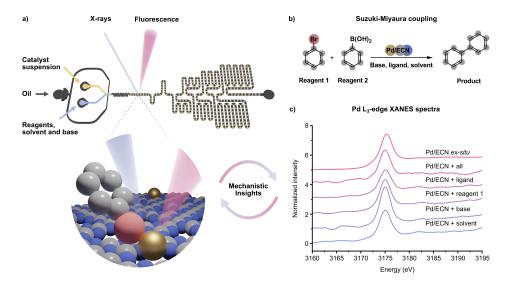


Fig. 1a Schematic of the channel pattern and operation principle in the droplet-based microfluidic device. Time-resolved XAS measurements can be acquired for increasing residence times. **b** Schematic of the studied Suzuki-Miyaura coupling catalyzed by Pd/ECN heterogeneous SAC. **c** Pd L_3 -edge XANES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