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Extending Droplet-Based Microfluidic Tools to Single-Atom Heterogeneous Catalysis

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Abstract: From energy-related transformations to organic syntheses, single-atom heterogeneous catalysts (SACs) are offering new prospects to tackle sustainability challenges. However, scarce design guidelines and poor mechanistic understanding due to a lack of discovery and *operando* characterization tools impede their broader development. This perspective offers a glimpse into how droplet-based microfluidic technologies may help solve both of these issues, and provides technical considerations for platform design to systematically fabricate SACs and study them under operational conditions during liquid-phase organic syntheses.

Keywords: Droplet-based microfluidics · High-throughput synthesis · *Operando* characterization · Single-atom heterogeneous catalyst · X-ray absorption spectroscopy

Thomas Moragues received an MEng in Chemistry and an MSc in Microfluidics from Paris Sciences and Letters (PSL) University in 2020. The same year, he joined ETH Zurich to carry out his doctoral studies under the joint supervision of Prof. Andrew deMello and Prof. Javier Pérez-Ramírez. Within the NCCR Catalysis initiative (SNSF), his research focuses on the development of novel microfluidic tools for synthesizing and characterizing single-atom heterogeneous catalysts under operational conditions.

1. Introduction

1.1 *Single-atom Heterogeneous Catalysts*

Better catalysts are needed to address the sustainability challenges of the 21st century. Stability, separability, and recyclability are key parameters in ensuring that they can be reused as many times as possible.[1] Atom efficiency and selectivity towards the product of interest should also be maximized by design. Surprisingly, few catalysts currently used in the industry fit all criteria. Homogeneous catalysts possess excellent selectivity but are typically difficult to recover from the reaction media, while solid heterogeneous catalysts comprising supported metal nanoparticles often suffer from low selectivity and atom efficiency due to poor active-site definition. Single-atom heterogeneous catalysts (SACs) retain the best of both worlds, thanks to well-defined active sites formed by isolated metal atoms stabilized at the surface of suitable carrier materials (Fig. 1).[2] SACs structurally resemble molecular catalysts (typically, metal complexes), with the carrier material playing the role of ligand, whilst contributing to the reactivity through essential electronic metal-support interactions.[3]

The pioneering work of Flytzani-Stephanopoulos and coworkers in 2003 provided the first evidence of the activity of isolated metal species (gold and platinum) stabilized on a carrier (ceria), towards the water-gas shift reaction.[4] Subsequently, Bashyam and Zelenay proposed using cobalt and iron coordinated to nitrogen-functionalized carbons as efficient catalysts for the electrochemical oxygen reduction reaction.[5] However, it was only in 2011, thanks to considerable advances in characterization techniques, that Zhang and coworkers definitively established the isolated nature of platinum species on iron oxide and their role in carbon monoxide oxidation.[6] The following decade has seen many advances with respect to chemical elements,[7] activation (including thermo-, electro-, and photochemical) modes, and applications ranging from small molecule activation to fine chemical production and energy-related transformations. Still, to this day, the majority of SAC synthetic routes and their subsequent applications remain *ad hoc* in nature, offering few clear design guidelines for extension to new metal/carrier combinations. Furthermore, mechanistic elucidations are challenging due to the scarcity of suitable *operando* (*i.e.* under operational conditions) characterization tools and the unique reactivity patterns exhibited by SACs, particularly in liquid-phase organic syntheses.[8,9] As such, they often rely on density functional theory calculations, which lack experimental validation.[10]

Accordingly, to advance the field, there is an urgent need for (i) tools to fabricate these catalysts in a systematic and high-

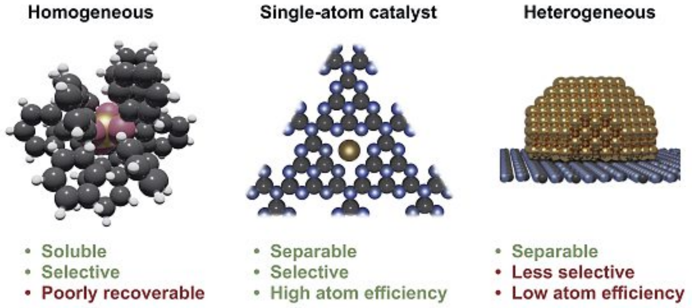

Fig. 1. Molecular models illustrating the typical structures found in homogeneous (left), heterogeneous (right), and single atom heterogeneous catalysts (center), along with their distinctive features.

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throughput fashion and (ii) *operando* approaches to characterize them under operational conditions.[11] As I will now discuss, the specific set of capabilities displayed by droplet-based microfluidic systems may offer a solution to both these needs.

1.2 *Droplet-based Microfluidics*

Microfluidics is the science and technology associated with the manipulation of fluids on the micron scale.[12] Here, capillary forces and surface tension dominate over inertia, and viscosity dominates over momentum. The resulting laminar flow regime is essential for precisely controlling mass transport within microfluidic channels. Other desirable features of microfluidic systems include small instrumental footprints, the ability to process minuscule sample volumes, and efficient heat transfer. Droplet-based microfluidic systems retain these advantages. Their purpose is to generate, manipulate, and control sub-microliter droplets surrounded by an immiscible carrier fluid.[13] Droplets are produced at rates of several kHz, which leads to enormous improvements in analytical throughput when compared to traditional batch assays, provided that the chosen detection technique is able to operate at the rate of droplet generation.[14] A plethora of functional components may be integrated within the fluidic workflow to perform various manipulations, such as droplet sorting, splitting, merging, dilution, and incubation. Owing to the presence of a fluidic interface, interactions between the droplet contents and the channel walls are suppressed, preventing cross-contamination and fouling. Additionally, enhanced fluidic mixing, obtained by leveraging chaotic advection, provides the user with very high control over the contact time between species of interest within droplets. This is particularly attractive in synthetic applications, and unsurprisingly droplet-based microfluidic reactors have been extensively used to fabricate materials with bespoke properties,[15–18] such as monodisperse catalytic metal nanoparticles.[19,20] However, perhaps the most notable feature of these platforms is their remarkable ability to conduct thousands of distinct reactions in a high throughput fashion,[21] enabling efficient exploration of parameter space and reaction discovery.[22] All the aforementioned features have driven the rapid development of droplet-based microfluidics over the past two decades in the fields of chemistry and biology, where they are now ubiquitous.[23]

In the following sections, I elaborate on how droplet-based microfluidic reactors can be used for systematic synthesis and

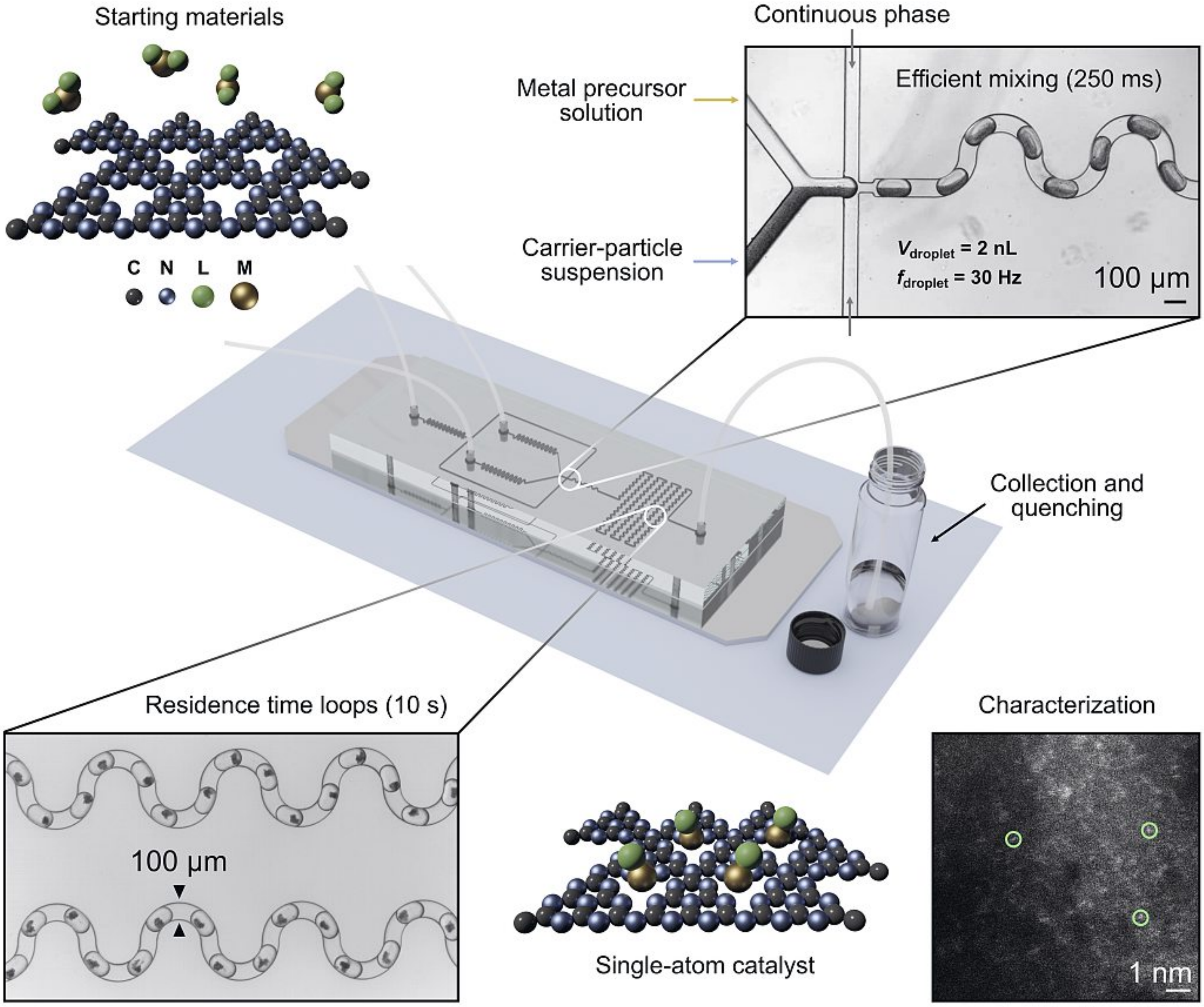

Fig. 2. Droplet-based microfluidic strategy for the synthesis of SACs. An elastomeric device (central image) generates droplets containing metal precursor solution and carrier-particle suspension (top right). After efficient mixing, adsorption occurs over 10 s within residence time loops (bottom left). Following collection and quenching, a palladium SAC based on exfoliated carbon nitride (Pd/C_3N_4) is characterized using AC-ADF-STEM (bottom right). Green circles mark single Pd atoms. C: carbon; N: nitrogen; L: ligand, M: metal. Figure adapted from ref. [25].

operando characterization of SACs, and attempt to predict some exciting future prospects for the field.

2. Systematic SAC Synthesis

Wet chemical approaches to SAC synthesis are versatile and scalable, but also inherently challenging due to the high surface energy of ill-stabilized isolated metal atoms, which leads to their rapid sintering into nanoparticles.[24] One common cause for this is the poor control over the contact time between reactive species, *i.e.* mixing efficiency, in typical batch reactors. In addition and because of the limited attention previously given to the effect of different systematic parameters (*e.g.* time, temperature, concentration, pH, *etc.*) on the stabilization of metal species, the understanding of syntheses is lacking, hindering SACs discovery and design. The following discussion is largely adapted from ref. [25].

2.1 *Droplet-based Syntheses*

The general synthetic approach relies on encapsulating aqueous metal precursor solutions and carrier-particle suspensions within nanoliter-volume droplets produced inside a polydimethylsiloxane (PDMS) device (Fig. 2).[25] To this end, flow dispensing systems (*e.g.* syringe pumps) permitting precise tuning of the concentration of each payload component and of the reaction time, are employed. Serpentine structures positioned directly after the cross-flow droplet generation junction allow for fast and efficient mixing (within 250 ms) of droplet contents. In comparison, this is at least two orders of magnitude faster than in typical batch systems, depending on the reactor volume, mixing technology, temperature, and initial reagent concentrations. The remaining flow path comprises residence time loops (total length *ca.* 1 m), after which the supported metal catalysts may be isolated by collecting droplets and quenching through dilution. Subsequent off-line characterization is performed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) and aberration-corrected annular dark field scanning transmission electron microscopy (AC-ADF-STEM), allowing measurement of the metal content in the catalyst and control of the nuclearity of surface species, respectively.

Carbon carriers, including activated carbon (AC), N-doped carbon (N–C), and carbon nitride (C_3N_4, structure presented in Fig. 1 and Fig. 2) have gained considerable attention owing to their ability to stabilize metal centers by coordination to heteroatom-containing surface moieties.[26,27] Accordingly, the droplet-based synthesis of *ca.* 1 wt.% palladium and platinum single-atom catalysts supported on exfoliated carbon nitride (Pd/C_3N_4 and Pt/C_3N_4) was completed within 10 seconds, when previously reported batch syntheses are typically carried out over several hours or days.[10,26] Remarkably, the metal uptake showed a strong dependence on pH, indicating the role of electrostatic interactions in stabilizing the metal species. This phenomenon is broadly accepted for oxide carriers,[28,29] but had not been previously reported for carbon-based hosts. Thorough investigations evidenced the importance of opposite charges between the host surface and the ionic metal precursor for optimal uptake. This can be achieved by carefully adjusting the pH to the metal precursor/host combination and constitutes a new design guideline for fabricating SACs by wet impregnation, further showcasing the potential of droplet-based microfluidic platforms for systematic parametric studies. Extension to other relevant metals (Ni) and carriers (N–C, γ-Al_2O_3) also confirmed the generality of the method.[25]

2.2 *Challenges and Outlook*

The ability to make solids flow is a well-known challenge for the flow chemistry community. Fouling eventually turns to clogging, leading to pressure build-ups, flow instabilities, and ultimately reactor rupture. The compartmentalization of solid inside droplets addresses this issue by negating fouling. However, the realization of consistent solid dosing is not trivial, since settling of carrier materials can occur in the syringe prior to the reaction. To avoid this, particle size distributions (PSD) are carefully optimized using ultrasonication. For carbon nitride, the optimal PSD was found to be between 0.2 and 10 µm. Nevertheless, this may differ between carriers, with the suspension stability depending on numerous parameters such as particle surface area, concentration, chemical composition, and carrier fluid.

Currently, the analytical throughput is limited by the reliance on off-line characterization. Although adapting the fluidic design to include acoustophoretic or centrifugal separation followed by droplet splitting would allow the removal of solid and measurement of the metal content in-line using fluorescent molecular probes, this is far from straightforward. Instead, pico-injection[30] of reagents inside the droplet would enable direct spectroscopic catalyst testing and provide selection criteria for further off-line testing. Here, the reactor material could be adapted for enhanced chemical compatibility. Finally, integrating such an improved platform within a machine learning (ML)-assisted closed-loop experimentation workflow would undoubtedly be valuable in accelerating catalyst optimization or discovery.[31,32]

3. *Operando* SAC Characterization in the Liquid Phase

One of the most attractive applications of SACs lies in their potential to replace state-of-the-art homogeneous catalysts for organic synthesis. That said, most reported reactivity patterns over SACs cannot be directly extrapolated from either homogeneous or heterogeneous pathways.[10] Their unraveling is also hindered by the limitations of current *operando* characterization approaches for tracking the state of metal centers under operational conditions in the liquid phase. Notably, packed-bed reactors lack operational flexibility in switching between experimental conditions, while batch cells typically display poor control over the catalyst-reagent contact time.[33] As such, detailed comprehension of structures and functions of active sites under reaction environment, although key to advancing SACs design principle, remains limited.

3.1 The Space-to-time Conversion

Droplet-based microfluidic systems possess an enormous advantage over packed-bed reactors for *operando* characterization of heterogeneous catalysts. Since droplets are consistently generated at the same point and continuously move along a fixed flow path at constant velocity, their position at any given time is directly related to the residence time τ. In other words, space may be converted into time (Fig. 3).

This deconvolution of τ from the experiment time t enables prolongated acquisitions at defined positions, which overcomes problems associated with low signal-to-noise ratios that stem from the limited amount of material studied. In turn, the user is

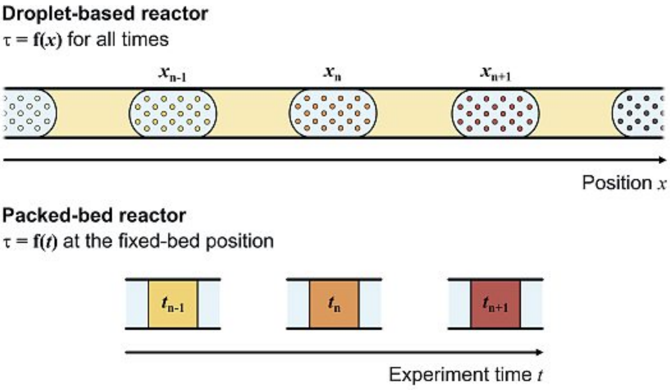

Fig. 3. Schematic of a droplet-based reactor (top), for which the residence time τ is governed by the droplet position x, and of a packed-bed reactor (bottom), for which τ only depends on the experiment time t.

granted unparalleled operational flexibility in studying phenomena occurring on short timescales, such as the first catalytic turnovers of chemical reactions. In the case of high-energy radiation-based techniques, the constant renewal of droplets illuminated also avoids sample damage during measurement.

3.2 Droplet-based XAS

X-ray absorption spectroscopy (XAS) is a characterization technique performed at synchrotron beamlines, and one which is sensitive to both the oxidation state and coordination environment of the analyzed atomic center. In the field of catalysis, it is broadly employed to track the state of the metal active site under operational conditions.[34] Previous studies have demonstrated the capabilities of droplet-based XAS microfluidic platforms to investigate the kinetics of calcium carbonate precipitation, laying the foundations for other applications, including those in heterogeneous catalysis.[35] Following a similar strategy to that presented in the previous section, droplets may be loaded with SAC suspensions and reagents dissolved in solvent. XAS can then be performed at defined positions along the flow path, providing snapshots of the state of the metal center at various time points.[35-37]

Taking palladium as an example, there are a few points to consider when developing droplet-based platforms for use at synchrotron beamlines. Palladium XAS can be carried out at the L_3-edge (3.17 keV) or the K-edge (24.35 keV). Combining insights from both edges is particularly interesting as they exhibit different sensitivities towards oxidation state and coordination environment (*i.e.* the type and number of neighbors and geometry around the metal center). At the L_3-edge, a vacuum chamber is needed to mitigate the absorption of low-energy photons by light gases. In addition, the fluidic channels must be enclosed with an ultrathin, X-ray permeable, silicon nitride (Si_3N_4) membrane, as a glass slide or PDMS layer would absorb most photons (Fig. 4a-b). As such, only fluorescence detection, with both incident and emitted beams traversing the Si_3N_4 membrane, is feasible, the time resolution of the measurement being governed by the size of the beam and the flow rates used (typically, a few hundred milliseconds).

In contrast, the high X-ray energy at the K-edge allows thin glass slides (or PDMS) to be used with minimum loss of signal, opening the possibility to measure in transmission and fluorescence modes simultaneously. However, the loss of sensitivity at high energies, as a result of the lower absorption cross-section, warrants a change of strategy, since more droplets now need to be exposed to obtain a signal of comparable quality. Besides prolongated exposure, one option is to target the X-rays directly through the fluidic channels from the side of the device (Fig. 4c).[38] This however comes at the expense of spatial, and thus temporal resolution (now *ca.* a few seconds), which should be taken into account depending on the timescale of the phenomena studied.

4. Conclusion and Future

Single-atom heterogeneous catalysts have tremendous potential to address sustainability challenges. Thanks to well-defined active site architectures, they are also perfect candidates for demonstrating the high levels of control and precision displayed by droplet-based microfluidic platforms. In this perspective, I have reviewed two novel applications of such platforms, geared towards SACs synthesis and *operando* characterization, and aiming at taking them to the next level.

First, the short-timescale, systematic synthesis of palladium and platinum SACs based on carbon nitride was demonstrated through in-droplet wet-impregnation. By leveraging the presented platform, the influence of pH on the adsorption of metal species over porous carbon-based carriers was uncovered. Nevertheless, the substantial potential for enhanced discovery by greatly increasing throughput *via* direct catalyst testing and subsequent ML integration remains to be taped in.

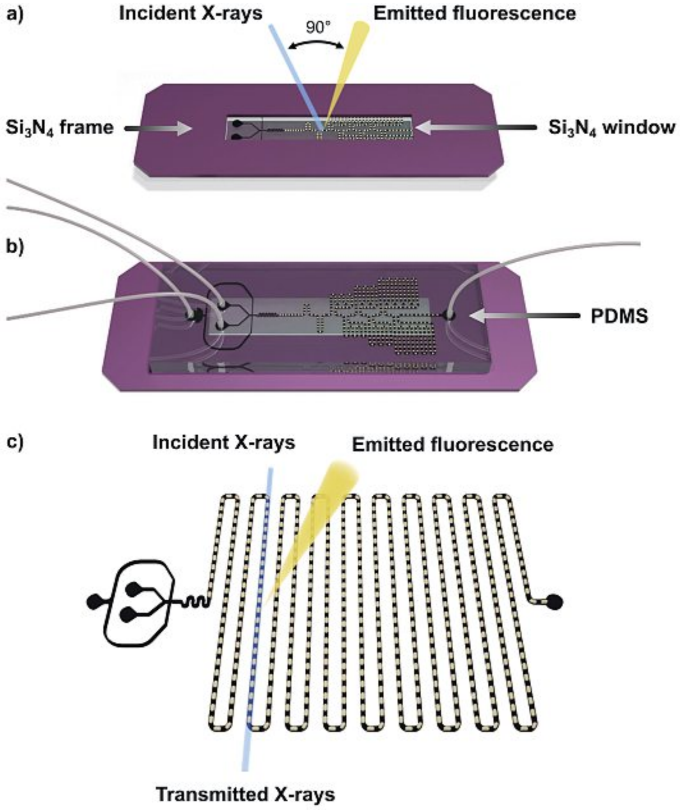

Fig. 4. Conceptual images of a droplet-based platform for palladium L_3-edge XAS, in a) top and b) bottom views. c) strategy to maximize the number of droplets illuminated, exposing the channels from the side.

Second, a strategy for droplet-based X-ray absorption spectroscopy applied to heterogeneous catalysis was described, with a particular emphasis on technical platform development over various energy ranges. In the near future, I foresee that similar approaches may be transposed to, or combined with other characterization techniques such as electron paramagnetic resonance or infrared spectroscopy, which would undoubtedly contribute to enhancing our understanding of SACs' active site structures and reaction pathways. That said, I believe that the greatest advantage of said platforms pertains to their direct applicability to both homogeneously and heterogeneously catalyzed systems in the liquid phase. As a result, they effectively constitute ideal characterization tools for comparing behaviors under operational environments.

Finally, it should be remembered that SACs, however promising, cannot be considered drop-in solutions to all reactions. To advance sustainable chemistry, we will need all types of catalysts available to us. That includes (but is not limited to) enzymes, metal complexes, metal-organic frameworks, supported single atoms, and metal nanoparticles, all of which can now be efficiently studied within droplet-based microfluidics platforms.

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