STRUCTURAL DYNAMICS AS A KEY ELEMENT OF CATALYSTS FUNCTIONALITY

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Present status and objectives

Efficient catalysts, ideally made from earth-abundant materials are a corner stone for a sustainable chemical industry, fuel production and environment-friendly energy schemes. However, further development of such catalysts both for electrochemical and thermally driven processes requires in-depth understanding of their working mechanisms and the link between their catalytic properties and their evolving composition and structure. The progress in addressing these issues remains slow, despite breakthrough advances in operando characterization techniques. The difficulty stems, in part, from the transformations of the catalytically relevant structural motives under harsh reactive environments. Such dynamic processes commonly result in an increased structural complexity of the catalysts due to the coexistence of different species, and, ultimately, in the situations where the structures of working catalysts have little resemblance to the structure of the as-synthesized (pre-catalyst) material. Moreover, in many cases such dynamic transformations play a key role in the catalytic mechanisms themselves, and their in-depth understanding could not only help to rationalize the trends in the catalytic properties, but also to provide pathways for steering the evolution of the catalyst in the desired direction, resulting in new functionalities and new exciting possibilities for the rational design of catalytic systems.

The transiently present bulk and surface species that co-evolve under the catalyst's working conditions all need to be identified, tracked with atomic resolution within the heterogeneous multicomponent systems, and assigned to a particular step in a catalytic mechanism. Furthermore, different length scales might play a role, such that mesoscopic phenomena cannot be ignored. This is a significant challenge for the experimental investigation as well as modelling of catalytic systems. To achieve these objectives, a further development of theoretical methods, data analysis approaches and experimental tools is needed. The latter include *in situ* and *operando* spectroscopic and microscopy mesurements under increasingly more realistic reaction conditions. On the other hand, the complexity of working catalysts also requires a careful selection and design of relevant model systems, and care in bridging the “materials gap”, namely, the correlation of the results obtained in studies of simpler model materials with those of the actual industrially relevant catalysts.

Recent contributions

Our research program specifically focusses on the operando spectroscopic and microscopic investigations of catalytic materials, aiming to shed light into the dynamic processes taking place at the active interfaces. Here the necessity to move beyond the static picture of catalytic materials constitutes a central theme across our recent works. This is exemplified by our recent articles on the electrocatalytic reduction of CO_2 (CO_2RR) and nitrate reduction (NO_xRR), where even well-ordered ultrahigh vacuum-prepared Cu single crystal surfaces experience drastic restructuring into stepped structures, making the surface much more active for CO_2 conversion into valuable multicarbon products [1,2]. These results, obtained by scanning probe microscopy tools and supported by fruitful collaborative work with theory groups, have challenged prior beliefs in the literature that the selectivity could be directly correlated to the structure and specific facet orientation of the precatalyst surface. Furthermore, the transformations of active interfaces are also significantly affected by electrolyte species and reaction intermediates, such as surface hydroxyls, CO or alkali metal cations in CO_2RR that alone, or combined can induce the nanoscale reconstruction of Cu surfaces. Similarly, we have found that the transient formation of surface (hydr-)oxides kinetically stabilizes oxides phase in Cu catalysts during NO_xRR, contrary to thermodynamic expectations. Here, our spectroscopic investigations correlated with electrochemical cell electron microscopy experiments revealed a complex picture of Cu catalyst evolution under NO_xRR conditions (Figure 1), suggesting a tandem reaction mechanism, where co-exisiting, spatially separated Cu_2O particles, and *in situ* formed metallic Cu species are responsible for different steps in the electrocatalytic nitrate reduction, with Cu(I) species first converting nitrate species into NO_2^-, while the latter is transformed into NH_3 on metallic Cu [3].

For ultradispersed catalysts, in turn, the transformations of the catalyst are greatly affected by particle-support interactions, which sometimes result in intriguing structural dynamics. In a series of recent works [4,5], we investigated ultradispersed Cu species that are anchored to carbon supports via nitrogen dopants, forming Cu-N-C structures. Under CO_2RR and NO_xRR conditions, the originally singly-disperesed Cu sites were found to sinter into metallic particles. Surprisingly, this process is completely reversible, and interactions with the support, after Cu ion dissolution and redeposition, drive the redispersion of these particles back to singly dispersed sites, once the applied negative potential is lifted (Figure 2). This fascinating behavior makes this system a prime illustration of the importance of operando investigations for understanding the true active states of catalysts at work, since the active species are not present in the prenatal and post-mortem catalyst. Benefitting from this reversible structural dynamics, and guided by the insight from *operando* sub-second X-ray absorption spectroscopy (XAS) measurements, we were also able to design pulsed reaction protocols where the state of the ultradispersed catalyst (predominantly metallic or cationic) and the sizes of metallic catalyst particles could be tuned on demand by changing the durations of the applied potential pulses and/or the values of applied pulsed potentials. This allowed us to explore structure-property relationships in electrocatalysis for the poorly understood regimes of subnanometer particle sizes. In addition, we were also able to employ such potentio-dynamic operation to active model single crystal Cu surfaces through their controlled restructuring and tunability of their chemical state [6].

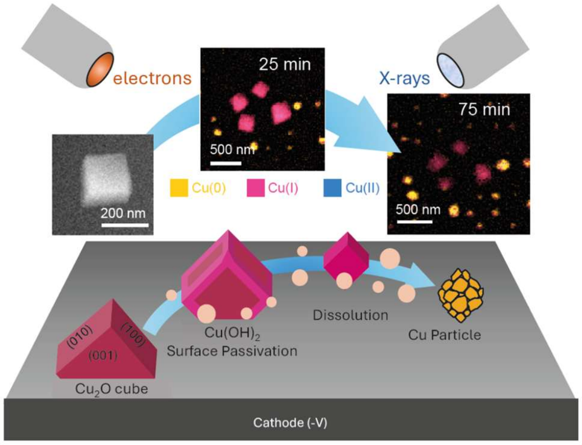

Fig. 1. Schematic describing the use of correlated electron- and X-ray microscopy to follow the structural and chemical state changes of Cu_2O cubes during NO_XRR [4].

Future developments

The realization of the importance of the dynamic nature of working catalysts has called for the reexamination of our current picture of catalytic systems, moving away from old concepts of static “active sites/structures” to that of a dynamic “active state”, a transient high energy feature on a dynamic surface, which can be created, manipulated and consumed in the course of a chemical reaction. This also re-defines the collaboration between experiment and theory, both having to cope now with non-constant atomic positions in various scales of time and space.

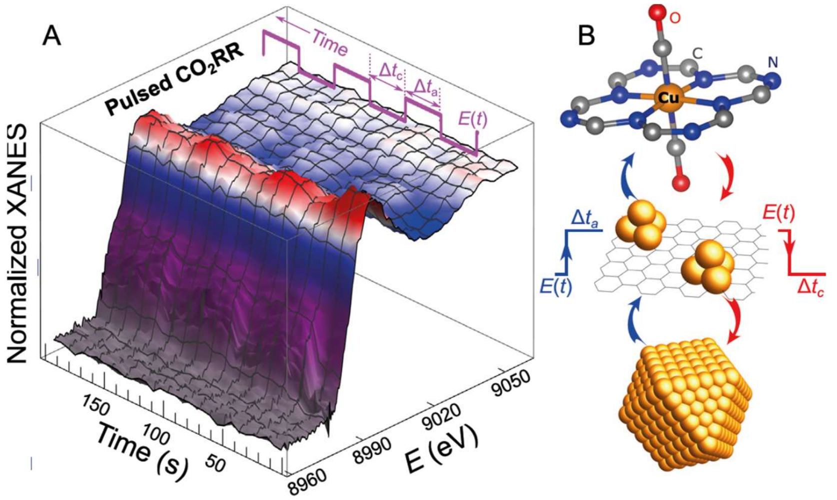

Fig. 2. *Operando* XAS for Cu-N-C catalysts during CO$_2$RR. A. Periodic changes in the time-dependent Cu K-edge XANES spectra under pulsed CO$_2$RR. The pulse of cathodic potential converts the singly dispersed cationic Cu species into metallic ultradispersed clusters, and then to increasingly large Cu particles. The process is fully reversed upon applying an anodict potential pulse (B) [5].

The accurate tracking of the genesis of active species in the sequence of processes from the pre-catalyst activation over “steady state” operation to de-activation remains a major challenge, and calls for further development in experimental tools, such as high-speed time-resolved operando microscopy, correlative multiprobe methods and spectroscopic tools with enhanced sensitivity to different time- and length-scales relevant for catalysts. The analysis and interpretation of the vast amounts of experimental data generated for such complex systems is expected to be well outside the applicability of conventional approaches. Thus, hand-in-hand development of advanced computation methods to model dynamic catalysts must take place, including the incorporation of data science and machine learning tools.

Considering the dynamic nature of catalysts, their future rational design cannot be based solely on the design of their initial static structure, but they should be rather desiged for a specific function, such as enhanced selectivity and long-term stability, which involves controlling the active, transient states. This calls for the adoption of automated experimentation and the adaptation of the reaction conditions through realtime ("on the fly") analysis, enabling thus the experiment to self-optimize its operation. This involves a combined catalyst-reactor-process design, including fully-automated feedback control of all process variables. Here a “smart” (AI-guided) feedback loop could be based on the observed catalytic performance, but also on the outcome of multi-method *operando* experimentation. This would allow to steer the material’s performance by automatically selecting operation conditions that facilitate the appearance and kinetic statbilization of the active structural motifs or chemical states. We have demonstrated the feasibility of such closed-loop experiments, by coupling an automated electrochemical setup to a lab-based operando XAS spectrometer [7]. Furthermore, very recently we were able to implement a first example of a spectroscopy-guided “self-driving laboratory”, where the reaction conditions during pulsed-CO_2 electroreduction were are automatically selected in a dynamic reaction protocol that autonomously adapted to the changes in the catalyst structure and chemical state. Such approaches could ensure a constant regeneration of the active states, which might be unstable under static reaction conditions, and thus counter the catalyst deactivation and degradation. Ultimately, these developments could pave the road for novel catalytic systems, where the superior catalytic performance is ensured not (only) by the presence of new structural moieties in the increasingly more complex as-synthesized pre-catalyst materials, but rather through the rational control of catalyst dynamics and the material’s self-rejuvination under operation conditions.

References

1. K. C. Nguyen, J.P. Bruce, A. Yoon, J.J. Navarro, F. Scholten *et al.*, *ACS Energy Lett*. **9**, 644 (2024).
2. D. Cheng, K. C. Nguyen, V. Sumaria, Z. Wei, Z. Zhang, *et al*. *Nature Comm.* **16**, 4064 (2025).
3. A. Yoon, L. Bai, F. Yang, F. Franco, C. Zhan *et al.*, *Nature Mater.* **24**, 762 (2025).
4. J. Timoshenko, C. Rettenmaier, D. Hursan, M. Rüscher, E. Ortega *et al.*, *Nature Comm.* **15,** 6111(2024)
5. D. Hursán, J. Timoshenko, A. Martini, H. S. Jeon, E. Ortega *et al.*, *Adv. Func. Mater.* e10827 (2025)
6. L. Tanase, M. J. Prieto, L. de Souza Caldas, A. Tiwari, F. Scholten, P. Grosse, A. Martini, J. Timoshenko, T. Schmidt, B. Roldan Cuenya Nature Catalysis **8**, 881 (2025).
7. M. Rüscher, J. B. Jang, A. Martini, P. Bischoff, W. Frandsen *et al. Chemistry-Methods* 2500016 (2025).

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