Linking Redox-Driven Structural Reorganisations in a 2D conjugated MOF to its Catalytic Activity

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Two-dimensional conjugated metal–organic frameworks (2D c-MOFs) have recently attracted growing attention for their potential in electrocatalysis. Their inherent tuneability allows tailoring of structural and electronic properties towards specific applications. In addition, the conjugated nature of these frameworks facilitates charge transport, while the two-dimensional morphology provides improved accessibility of catalytically active centres. Despite these advantages, the exact nature of the catalytically active species in 2D c-MOFs under operating conditions remains insufficiently understood.
In this study, we investigate the 2D c-MOF Cu_2[ZnPc–O_8], a well-established catalyst for the hydrogen evolution reaction (HER), under reducing conditions.[1] Using in situ spectro-electrochemical Raman spectroscopy, we find that the catalytically active species resembles a reduced Zn-phthalocyanine linker unit. Insights from chemical reduction of the MOF complement the spectro-electrochemical results. Importantly, the framework is not destroyed under reducing conditions. Instead, our observations suggest that reduction of both Cu and Pc moieties induces a structural transformation of the extended conjugated network into a new framework state, which constitutes the catalytically active form.
These findings provide new insights into the dynamic structural changes of 2D c-MOFs under electrocatalytic operation. Understanding such redox-induced transformations will be key for the rational design of MOF-based catalysts with improved stability and activity.

References

[1] H. Zhong, M. Ghorbani-Asl, K. H. Ly, J. Zhang, J. Ge, M. Wang, Z. Liao, D. Makarov, E. Zschech, E. Brunner, I. M. Weidinger, J. Zhang, A. V. Krasheninnikov, S. Kaskel, R. Dong, X. Feng, Nat. comm. (2020), 11, 1409.