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In situ and operando X-ray spectroscopy studies of the carbon dioxide electro-reduction

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In the last decades, the electrochemical CO₂ reduction reaction (CO₂RR) to high value-added compounds has attracted much attention because it could bring significant benefits to society, not only for the storage of renewable energy in excess, but also as CO₂ emission control strategy. Despite the intense research on the subject, little progress has been made on the design of active and stable materials, especially those enabling the C-C coupling. The aim of this study is to provide mechanistic insights into the CO₂RR as a strategy of catalyst design by applying a multi-techniques characterization approach, using synchrotron based in situ spectroscopy. The catalysts of interest are ferrihydrite on O and N functionalized carbon materials, which show promising activity to acetic acid.

Operando X-ray absorption experiments were performed at the B18 Core EXAFS beam line of Diamond Light Source in the UK to investigate oxidation state and coordination geometry of the catalysts upon polarization.¹

The chemical bonding state of CO₂ chemisorbed on the catalysts and the catalysts surface electronic structure are investigated by means of ambient pressure X-ray photoelectron spectroscopy at the synchrotron facility BESSY II in Germany, using an in situ electrochemical

cell previously developed.² State of the art electron microscopy with atomic resolution capability is performed at the ePSIC facility in the UK to identify the nuclearity of the Fe species. This study has enabled us to shed light into the chemical effects induced by the N-functionalization of the carbon support, the nature of the sites responsible for the C-C coupling and the structural transformation leading to unselective catalyst.

We show here that small ferrihydrite clusters or single Fe atoms at the edge of the graphitic layers are the most relevant species, where potential induced Fe²⁺ species adsorb and reduce HCO₃⁻ species. We also show that N-functionalization of the carbon support has a direct effect on the formation of these Fe²⁺ species. Moreover, N species act concertedly to chemisorb CO₂-related species enabling the C-C coupling to acetic acid. When the cathodic potential is decreased further; the hydrogen evolution reaction (HER) is the favored reaction path. The HER is concomitant with the formation of Fe⁰.

References

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[2] R. Arrigo *et al.*, *Angew. Chem. Int. Ed.* **2013**, 52, 11660.