

Electrochemical and spectroelectrochemical approaches for the characterization of transient copper-oxygen models of oxygenases

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The development of energy-efficient, environmentally benign and cost-effective catalysts which can selectively oxidize C-H bond of alkanes, such as methane, from clean oxidant (O₂) remains a formidable social challenge. For that purpose, many molecular Cu-based complexes inspired from the active site of copper oxygenases have been designed over the past decades.^{1,2} Recent works have particularly emphasized that H-Atom Abstraction (HAA) from strong C-H bonds of hydrogenated substrates could be obtained with [Cu^{II}O₂*], [Cu^{II}O*] and [Cu^{III}(OH)] cores,³ as well as dinuclear mixed-valent [Cu^{III}(μ-O(H))Cu^{II}] species.^{4,5,6} Nevertheless, one main issue to address is to better clarify the relationships between the structural features of these active copper-oxygen adducts and their thermodynamic/kinetic/reactivity properties towards alkanes. In particular, it is necessary to determine how the ligand field affects thermochemical properties of the Cu catalysts and orientates towards stepwise or concerted proton-coupled electron transfers. So far, this understanding is mainly impaired by the lack of thermodynamic data (redox, pKa) for copper-oxygen adducts, because of their high instability. In this context, we have developed an original cryo-spectroelectrochemical approach which allows the *in-situ* generation and time-resolved characterization of these transient copper-oxygen species. This set-up also affords the determination of redox properties in terms of thermodynamics and electron-transfer kinetics.^{7,8}

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