Oxygen dissociation on iron phthalocyanine: tuning the catalytic activity by the supramolecular order

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Fine control of the interfacial structure between organic molecular layers and the underlying support is critical for the reproducibility of the organic component functional properties in surface-supported devices. Even slight modifications of the interface can, in fact, drastically change the behavior of the overlayer both at the supramolecular and the single-molecule level.
In this scenario Iron Phthalocyanine (FePc) are studied as catalysts for the oxygen reduction reaction (ORR) in fuel cells as alternatives to precious metals. The precise role and the molecular-scale mechanisms of action of these catalysts are still partly unclear and it is recognized that a detailed knowledge of the active site structure and its evolution when oxygen coordination occurs is required to improve their efficiency.
In this report we shown as the local absorption geometry of FePc molecules, controlled by changing the surface coverage around the monolayer regime, both on Ag(110) and Ag(100) open the possibility to sharply switching the reactivity of FePc with respect the molecular oxygen in reproducible way.
A comprehensive and detailed picture built on diverse experimental evidence from scanning tunnelling microscopy, X-ray photoelectron spectroscopy and X-ray absorption spectroscopy, coupled with density functional theory calculations, sheds new light on the nature of the catalytically active molecule–surface coordination and on the boundary conditions for its occurrence.

References:

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