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Iron Phthalocyanine Electrocatalysis in Aqueous Media: Is Water Simply a Solvent?

Iron Phthalocyanine Electrocatalysis in Aqueous Media: Is Water Simply a Solvent? Alessandro Bonardia, Shuai Xub, Giovanni Di Libertoa, Gianfranco Pacchionia aUniversità degli Studi di Milano-Bicocca, Dipartimento di Scienza dei Materiali, Via Roberto Cozzi 55, 20125 Milan, Italy bSchool of Water and Environment, Chang'an University, 710064, Xi'an, P.R. China alessandro.bonardi@unimib.it The accurate modeling of redox processes in single-atom catalysts (SACs) remains a major challenge in computational electrocatalysis, particularly when dealing with transition metals like iron[1]. Iron phthalocyanine (FePc) is widely employed as a molecular analogue for Fe-based SACs supported on carbon- based materials, such as nitrogen-doped graphene[2]. While experimental studies clearly indicate a Fe(II)/Fe(III) redox transition occurring under oxidative conditions, standard density functional theory (DFT) calculations often fail to reproduce this behavior, incorrectly localizing the oxidation on the ligand rather than the metal center[3,4]. In this work, we investigate the origin of this discrepancy through a systematic series of DFT calculations, employing hybrid functionals and explicit solvation models. Our results show that the root cause of the divergence between theoretical and experimental results does not lie in the functional choice but in the representation of the iron coordination environment. By introducing one or two water molecules as axial ligands, we observe a significant shift in the relative energies of the Fe-centered and ligand-centered orbitals, leading to the correct prediction of an Fe oxidation. This modification not only recovers the correct qualitative interpretation of the oxidation process, but also leads to calculated redox potentials that match experimental values within 0.1–0.2 V. These findings underline the essential role of water, not merely as a bulk solvent, but as a direct ligand capable of modulating the electronic structure and, thus, reactivity of the active site. Beyond FePc, the implications extend to a broad class of Fe-based SACs, suggesting that any reliable computational study must explicitly account for solvent coordination effects. This work offers a practical guideline for improving the predictive power of quantum chemical models in electrocatalysis, highlighting that: 1) redox properties of transition metal complexes and graphene-based SACs are strongly influenced by the coordination environment, including solvent molecules; and 2) modelling of those systems requires the inclusion of water to correctly describe their redox behavior. [1] B. Chang, S. Wu, Y. Wang, T. Sun, Z. Cheng, Nanoscale Horiz., 2022, 7 (11), 1340-1387. [2] S. Ye, F. Liu, F. She, J. Chen, D. Zhang, A. Kumatani, H. Shiku, L. Wei, H. Li, Angewandte Chemie, 2025, 137 (23). [3] M. S. Liao, J. D. Watts, M. J. Huang, Journal of Physical Chemistry A, 2005, 109 (35), 7988-8000. [4] C. J. Ziegler, V. N. Nemykin, Dalton Transactions, 2023, 52 (43), 15647-15655.

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