

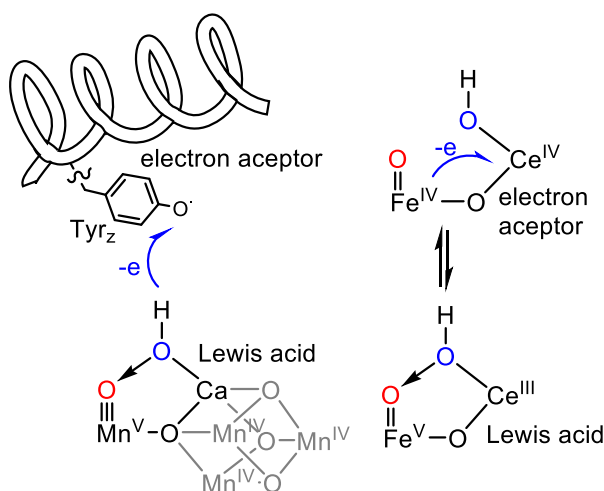
Evidence for an Oxygen Evolving Fe–O–Ce Intermediate in Iron-Catalysed Water Oxidation

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Water oxidation (WO) catalysis constitutes the bottleneck for the development of energy conversion schemes based on sunlight. State of the art of homogeneous WO catalysis is so far efficiently performed with earth-scarce transition metals. For instance, we recently showed that iridium organometallic pre-catalysts are able to catalyze WO with impressive turnover numbers (TON, up to 400,000).^[1] Although abundant and less toxic 3d metal-based complexes are much less established,^[2] we have discovered that readily available iron coordination complexes are highly efficient homogeneous WO catalysts. TON > 350 and >1000 were obtained when using cerium ammonium nitrate (CAN), and NaIO₄, respectively.^[3-4]

Herein, the most active example of homogeneous WO catalysts based on iron will be analyzed. To gain insight into the mechanism of the Fe-catalyzed WO catalysis, we carried out a detailed mechanistic study through kinetics and spectroscopic monitoring of intermediates. The detection and characterization by UV-Vis, ESI-MS and rRaman spectroscopy of a crucial intermediate responsible for carrying out the O–O bond forming step represents the first functional model for the oxygen evolving complex (OEC) of the photosystem II.



Selected bibliography

[1] Z. Codolà; J. M. S. Cardoso; B. Royo; M. Costas; Julio Lloret-Fillol *Chem. Eur. J.* **2013**, 19, 7203.

[2] V. Artero and M. Fontecave *Chem. Soc. Rev.* **2013**, 42, 2338.

[3] J. Lloret Fillol, Z. Codolà, I. Gracia-Bosch, L. Gómez, J. Pla, M. Costas *Nat. Chem.* **2011**, 3, 807.

[4] Z. Codolà, I. Gracia-Bosch, F. Acuña, J. M. Lluís, M. Costas, J. Lloret Fillol *Chem. Eur. J.* **2013**, 19, 8042.