

Homogeneous Water Oxidation Catalysis with Iron Coordination Complexes

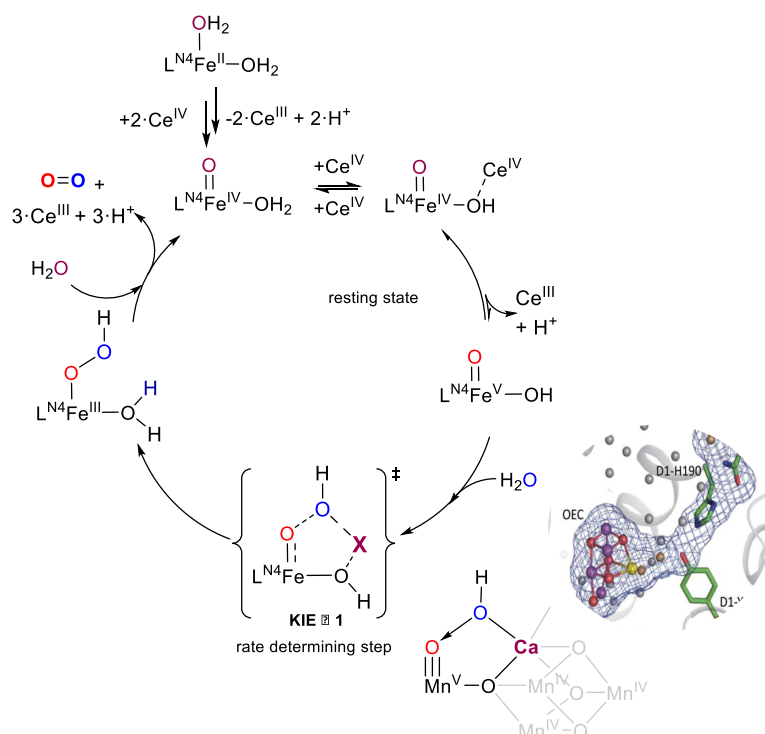
Julio Lloret-Fillol

*Institut de Química Comptacional i Catalisi, Departament de Química,
Universitat de Girona, Campus de Montilivi, 17071 Girona (Spain)*

Julio.lloret@udg.edu

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.^[3-5]

We present here one of the few examples of homogeneous WO catalysts based on 1st row transition metals. To gain insight into the mechanism of the Fe-catalyzed WO catalysis, we carried out a detailed mechanistic^[3-5] study through kinetics, spectroscopic monitoring of intermediates, isotopic effects, isotopic labeling, electronic effects and DFT calculations.^[5] The roles of the high oxidation state oxo-iron (IV) and (V) and new Fe-O-Ce species in the O-O forming event as well as possible intermediates in the oxidation of organic substrates^[6] will be discussed.



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.
- [5] F. Acuña, Z. Codolà, M. Costas, J. M. Lluís, J. Lloret Fillol* *submitted*.
- [6] I. García, Z. Codolà, I. Prat, X. Ribas, J. Lloret-Fillol, M. Costas* *Chem. Eur. J.* **2012**, *18*, 13269.