Universiteit
Leiden
The Netherlands

In silico study of reaction mechanisms and design principles for water oxidation catalysts

Vallés Pardo, J.L.

Citation
Vallés Pardo, J. L. (2012, December 19). *In silico study of reaction mechanisms and design principles for water oxidation catalysts*. Retrieved from https://hdl.handle.net/1887/20311

Version:	Corrected Publisher's Version
License:	Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden
Downloaded from:	https://hdl.handle.net/1887/20311

Note: To cite this publication please use the final published version (if applicable).

Cover Page

Universiteit Leiden

The handle http://hdl.handle.net/1887/20311 holds various files of this Leiden University dissertation.

Author: Vallés Pardo, José Luis
Title: In *silico* study of reaction mechanisms and design principles for water oxidation catalysts
Date: 2012-12-19

Chapter 6:

General Discussion and Outlook

Chapter 6

General Discussion and Outlook

In this thesis different catalysts for the water oxidation reaction have been studied. In chapter **5** a thermodynamic study for single-metal catalysts with similar coordinating ligands was performed, obtaining a free energy profile along the whole PCET catalytic cycle. This study allows to evaluate *in silico* the overpotential for each catalyst and to identify structural and/or electronic features that minimize the overpotential, thus providing guiding principles in selecting a promising candidate as WOC.

In chapter **3** and **4** a mechanistic study of the oxygen-oxygen bond formation in the S_2-S_3 step of the catalytic cycle has been performed for

a di-Mn complex and for a mono-nuclear ruthenium catalyst, respectively. From this dynamical study useful information about the reaction mechanism, kinetics and activation barriers can be obtained. Moreover these AIMD simulations can be performed in the presence of an explicit water environment.

Ideally one would like to combine the thermodynamic study with the dynamical simulation of the different reaction steps in the catalytic cycle. This is still challenging for several reasons: Due to the nature of the PCET reaction, in which half hydrogen molecule is released in each step, the number of electrons in the metal complex and therefore its multiplicity is changing along the reaction path. Moreover, one should include in the simulation box also a chemical agent (e.g. Ce^{IV}) able to change its oxidation state to facilitate the electron transfer coupled to the proton transfer.

The possibility of simulating the reaction pathways from the dynamical studies taking into account the proper electronic structure changes along the catalytic cycle will be a very important step in the complete understanding of the whole water oxidation reaction.

The first steps in this direction have been already undertaken during the last months of this thesis project and should constitute a natural follow-up of this research. By performing constrained molecular dynamics (CMD) simulations for different fixed values of the reaction coordinate, one can monitor more extensively each stage of the reaction, checking for example also the ground state multiplicity at

each value of the constraint. Then, the average lagrangian multiplier obtained for each simulation, which represents the constraint force, can be used to derive the free-energy profile through thermodynamic integration. In this way it is also possible to better characterize the transition state and to establish the onset of the PCET step.

Another important question to address in future research is what happens when the catalyst is coupled to a charge separator module in an artificial photosynthesis device. In particular, it is crucial to assess how the electronic structure of the catalyst is affected by different charge separator complexes.