CYSS
CataLight Young Scientist Symposium
synthesis • theory • characterization • application

Unraveling the Reactivity of a Tetramanganese-Polyoxovanadate Water Oxidation Catalyst

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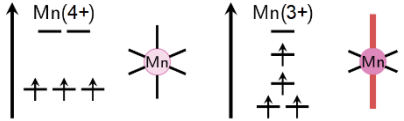
$[Mn_4V_4O_{17}(OAc)_3]^{3-}$
TON > 12 000; TOF > 200 min^{-1} [1]
Model system for MnO catalysts
Water oxidation in ACN:H_2O 9:1
with $[Ru(bpy)_3]^{2+}$, $Na_2S_2O_8$ [2]

Methods

Manual analysis of water ligand conformers; automated generation of Jahn-Teller conformers [3]
77 out of 203 conformers for 21/24 intermediates along 32/64 pathways optimized; remainder is unstable



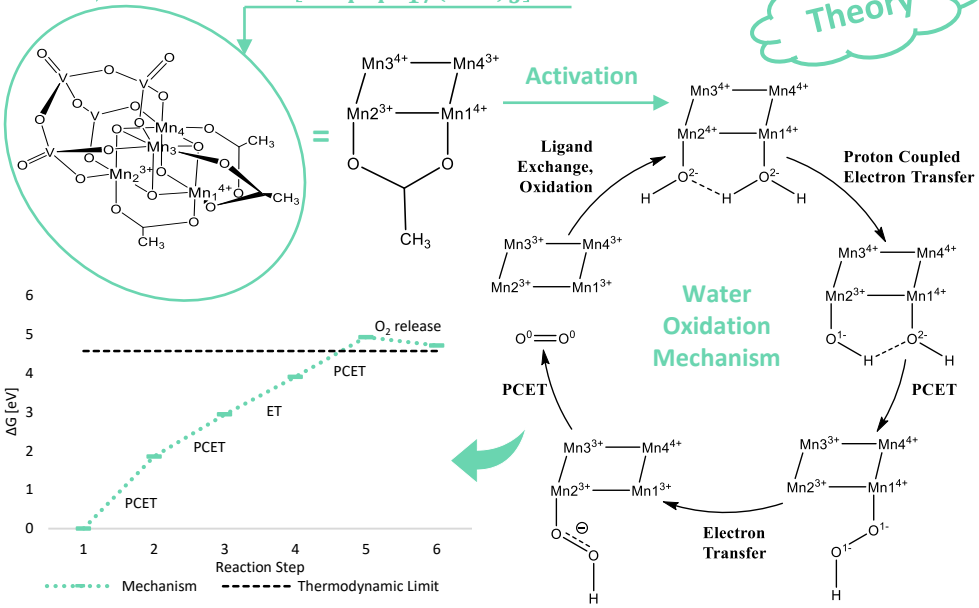
Preopt with constraints: ORCA/ BP86/ZORA-SVP-D3/PCM (ACN)
Final opt: Gaussian16/UB3LYP/ def2svp-D3/PCM (H2O/ACN)

References
[1] F. L. Huber et al., *Sustain. Energy Fuels*, **2018**, 2, 1974.
[2] B. Schwarz et al., *Angew. Chemie Int. Ed.*, **2016**, 55, 6329.
[3] S. Mai et al., *in preparation*, **2020**.
[4] G. Cardenas et al., *submitted*, **2020**.

Start here!

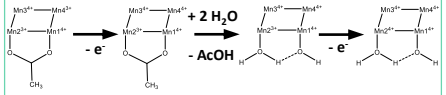
$$2\,H_2O \xrightarrow[\text{cat. } [Mn_4V_4O_{17}(OAc)_3]^{3-}]{} O_2 + 4H^+ + 4e^-$$

Theory



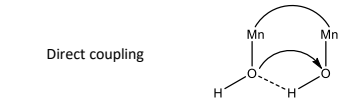
- **Water oxidation** mechanism proposed based on **theory**
- **Direct coupling** via (proton-coupled) electron transfers
- Intramolecular oxidation: **electrocatalysis** possible?

3-step **activation** mechanism (theory + experiment) [4]:



Activated species:
$[Mn^{4+}{}_4V_4O_{17}(OAc)_2(H_2O)(OH)]^{1-}$

Proximity of ligands determines **water oxidation mechanism**:



To release O_2, water ligands must shed 3 H^+ and be oxidized 4 times
Assume proton-coupled electron transfers (PCETs): 3 PCET, 1 ET steps
Proton acceptors in solution
Oxidation can be intramolecular or intermolecular