

Theoretical water splitting mechanisms on manganese oxide clusters

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Understanding the factors that affect efficiency of manganese oxides as water oxidation catalysts is an essential step towards developing commercially viable electrocatalysts. It is important to understand the performance of the smallest versions of these catalysts, which will in return be advantageous with bottom up catalytic design. Density functional theory calculations have been employed to investigate water oxidation processes on manganese dimer, trimer, and cubane complexes. The effect of different oxidation states of manganese is considered in this study. Processes such as nucleophilic attack by solvent water molecules are implicated in many of the mechanisms. For all systems studied, the highest energy step in the mechanism, which is responsible for the overpotential in the water splitting process, is found to be the formation of a manganese oxo group. The formation of these manganese oxo groups can be used as a descriptor for selecting a manganese-based water splitting catalyst due to the high electrochemical potentials required for their generation.