

Abstract Submitted
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Role of oxometallic complex on OH dissociation during water oxidation: A microscopic insight from DFT study MUKUL KABIR, Indian Institute of Science Education and Research, Pune, SOUMYAJIT SARKAR, S.N.Bose National Centre for Basic Sciences, MARTHA GREENBLATT, Department of Chemistry and Chemical Biology, Rutgers University, TANUSRI SAHA-DASGUPTA, S.N.Bose National Centre for Basic Sciences — The uncatalyzed atomic dissociation of water requires breaking strong O–H bond with enthalpy 494 KJ/mol, which necessitates understanding and designing appropriate catalysts. Here we employ transition state theory within quantum chemical density functional theory to understand the role of metal-oxide inorganic complexes to the $\text{OH} \rightarrow \text{O} + \text{H}$ process, the most important reaction in water oxidation. We study the effect of (a) chemical bonding in different M_4O_4 ($\text{M} = \text{Mn}, \text{Co}$) cubane complexes, (b) heterocubane geometry containing Ca, in addition to transition metal ion, (c) dimensionality by considering both three dimensional and two dimensional geometry of the oxometallic unit, and (d) connectivity between two oxometallic cubane units, corner shared versus edge shared geometry. Analysis of our density function theory based calculations singles out a robust microscopic quantity among various plausible and competing factors, which elucidates the important role of metal-oxygen covalency at the oxidized site. The M–O bonding strength inversely determines the strength of the O–H bond, and thus the energy required for OH dissociation. This provides one with an important microscopic design principle for metal-oxide complex catalyst responsible for water oxidation.

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