Thermodynamic and kinetic origins of efficient water oxidation by multi-redox catalysts

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We present a computational study addressing the catalytic cycle of a recently-synthesized inorganic catalyst capable to promote water oxidation with low overpotential and high turnover frequency [Sartorel et al., J. Am. Chem. Soc., 2008, 130, 5006; Geletii et al., Angew. Chem., Int. Ed., 2008, 47, 3896]. This homogeneous catalyst consists of a tetraruthenium-oxo core [Ru4O4(OH)2(H2O)4]6+ capped by two polyoxometalate [SiW10O36]8- units and is one of the best catalysts for water oxidation reported to date. The reaction mechanism and thermodynamics underpinning its efficiency are currently under debate. The energetics of the relevant intermediates of the catalytic cycle is studied here with density functional theory calculations. This ab-initio thermodynamics identifies the energetically most demanding step, thus establishing the origin of the catalyst overpotential. The reaction mechanism for water oxidation and O2 evolution is then addressed with the metadynamics technique. We demonstrate that the catalyst is activated by the formation of a Ru-oxo moiety, which undergoes a nucleophilic attack from a water molecule. The origins of the high efficiency of this metal-oxo catalytic core will be discussed in the context of heterogeneous metal-oxide surfaces and homogeneous metal-organic complexes.